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# Supercollision Energy Transfer Studies in Single Collisions between Vibrationally Hot

Benzene-like Molecules and Ground-state Bath Molecules: the Effect of Physical

Properties of Donor and Bath Molecules on Supercollision Energy Transfer

Kilyoung Kim

A dissertation submitted to the faculty of Brigham Young University in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

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Brigham Young University

April 2011

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Abstract

# Supercollision Energy Transfer Studies in Single Collisions between Vibrationally Hot

Benzene-like Molecules and Ground-state Bath Molecules: the Effect of Physical

Properties of Donor and Bath Molecules on Supercollision Energy Transfer

Kilyoung Kim

Department of Chemistry and Biochemistry, BYU

Doctor of Philosophy

This research is focused on single-collision energy transfer events between highly vibrationally excited benzene-like donor molecules and small bath molecules, CO2 and N2O in the vibrational ground level. Measuring how much energy is transferred from donors to bath molecules was accomplished by probing bath molecules scattered into specific-rotational states using a tunable  $\Delta v=0.0003$  cm<sup>-1</sup> solid state diode laser. The normalized energy transfer probability distribution function, P(E,E'), determined from energy gain information, is very useful in comparing collisional energy transfer efficiency between various collision systems. P(E,E') is also used to investigate the effects of donor and bath physical properties on collisional energy transfer. The first chapter details the C<sub>6</sub>H<sub>5</sub>F–CO<sub>2</sub> system, which is the basis of a study on the effect of donor fluorination on strong collision energy transfer. The second chapter is about all fluorobenzene-CO<sub>2</sub> systems, which investigates the effect of excess vibrational excitation energy of donors on supercollision energy transfer efficiency as well as donor fluorination effect. The third chapter focuses on how the physical properties of bath molecules affect supercollision energy transfer by measuring state-specific energy gain of N<sub>2</sub>O scattered into  $00^{0}0$ , J=59-75. Instead of CO<sub>2</sub>, N<sub>2</sub>O was used as a bath molecule with a pyrazine donor to compare energy gain results of bath molecules with somewhat different physical properties. N<sub>2</sub>O and CO<sub>2</sub> are isoelectronic and have similar mass, but  $N_2O$  has a small dipole moment. Comparison of P(E,E')obtained from pyrazine-CO<sub>2</sub>, -N<sub>2</sub>O, -DCl, and -H<sub>2</sub>O systems helps to elucidate the effect of the bath physical properties on supercollision energy transfer efficiency. The last chapter is dedicated to the extension of the measurement range of N<sub>2</sub>O energy gain to the mid J states (J=37-75). In this chapter I discuss reliability of P(E,E') obtained from only high J tail as well as the correction of overall energy transfer rate constant.

**Keywords**: Collision energy transfer, Energy gain, Fluorination, Energy transfer probability, Nitrous oxide, Pyrazine, Fluorobenzene, Carbon dioxide, Energy transfer efficiency, and Energy dependence

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# **INTRODUCTION**

To understand the nature's phenomena occurring through a variety of chemical reactions, it is necessary to investigate chemical reaction mechanisms, which typically consist of a number of elementary reactions.<sup>1-3</sup> It is well known that overall chemical reactions can be strongly affected by only a few unimolecular or recombination reactions rather than all elementary reactions.<sup>4</sup> That is, enhancing or limiting the rate-determining unimolecular reactions, one can control the overall chemical reaction. On the other hand, unimolecular reactions compete with collisional relaxation processes and the fate of reactant molecules, whether they undergo chemical reactions or not, is determined by collisional energy transfer processes. Therefore, collisions between highly vibrationally excited donors and small bath molecules at room temperature have been studied as a means to gain insight into and fully understand the nature of unimolecular reactions. Experiments to measure energy loss of activated molecules by collisions with bath molecules have been performed using a variety of spectroscopic methods, such as time-resolved IR fluorescence (IRF),<sup>5, 6</sup> UV absorption (UVA),<sup>7</sup> and kinetically controlled selective ionization (KCSI).<sup>8-10</sup> These studies have measured the average energy transferred from donor to acceptor molecules. KCSI studies further allow for the calculation of the energy transfer probability distribution for collision complexes. In contrast, an approach to measure state-specific vibrational, rotational, and translational energy gain of bath molecules in collisions with activated donors was developed by Flynn and coworkers.<sup>11-15</sup> Since the time that Flynn group developed the high-resolution (0.0003 cm<sup>-1</sup>) IR laser probing approach to obtain statespecific bath energy gain information in single collision energy transfer events, the Mullin<sup>16-33</sup> and Sevy groups<sup>34-42</sup> have used this approach to understand the dynamics and kinetics of collisional energy transfer by investigating the effect of donor and bath physical properties on

collision energy transfer. In this study, we show that state-specific energy gain information obtained from experiments can be converted to the average energy gain amount and the pattern of energy gain results is correlated not only with donor but also with bath physical properties. Furthermore, we can calculate the energy transfer probability distribution function, P(E,E'), by resorting state-specific energy gain results to total energy transfer ( $\Delta E$ )-indexed values.

The energy transfer probability distribution function, P(E,E'),<sup>15, 33</sup> which describes the probability that a donor molecule with the initial energy E' undergoes a collision process with a bath molecule and ends up with the final energy  $E (= E' - \Delta E)$  after transferring an amount of energy  $\Delta E$  to the bath molecule is a key tool in comparing collision energy transfer efficiency between various collision systems. P(E,E') can also be applied to master equation calculations to obtain accurate unimolecular reaction rates.<sup>43</sup> This study uses P(E,E') to study the effect of donor (the first and second chapters) and bath physical properties (the third and fourth chapters) on collisional energy transfer efficiency.

The strength of the bath-probing technique to obtain state-specific bath energy gain information originates from using a IR diode laser with high-resolution (0.0003 cm<sup>-1</sup>) capable of measuring state-specific rotational and translational energy gain of bath molecules in collisions with hot donors. Details of V $\rightarrow$ RT energy transfer (energy transfer from vibration in donors to rotation and translation in bath molecules) are explored by obtaining state-specific bath energy gain information and measuring the energy transfer probability distribution function, P(E,E'). In the first chapter, experiments of collision energy transfer between highly-vibrationally excited monofluorobenzene (MFB) and CO<sub>2</sub> are described. The experimental P(E,E') obtained from state-specific bath energy gain results was fit to a bi-exponential function to extract weak and strong collision parameters for simple comparison. The bi-exponential fit parameters are plotted

as the energy dependence of donor state density and discussed with the relationship with the shape of P(E,E'). Finally, the donor fluorination effect on supercollision energy transfer efficiency is discussed by assigning motions of low frequency vibrational modes of MFB and calculating low frequency mode efficiency in the strong collision energy transfer region,  $\Delta E = 2,000-8,000$  cm<sup>-1</sup>.

The second chapter is focused on all fluorobenzene–CO<sub>2</sub> collision systems, which investigates the excess excitation vibrational energy dependence of donors on supercollision energy transfer efficiency as well as completes the study of the donor fluorination effect on supercollision energy transfer. Fluorinated benzenes ( $C_6H_{6-n}F_n$ ), in this chapter, are used to elucidate how the fluorination of donor molecules affects collision energy transfer. UV absorption spectroscopy<sup>44, 45</sup> and photophysical<sup>46, 47</sup> studies have been performed for fluorobenzenes and showed that  $C_6H_{6-n}F_n$  with n=1–4 have a different spectroscopic absorption pattern from  $C_6H_{6-n}F_n$  with n=5–6. Zgierski et al.<sup>48</sup> also observed two different fluorescence features for  $C_6H_{6-n}F_n$  with n=1–4 and n=5–6. In this chapter, we observed that supercollision energy transfer efficiency is shown with two different patterns,  $C_6H_{6-n}F_n$  with n=1–4 and n=5–6. The similarity between energy transfer efficiency and spectroscopic absorption features for fluorobenzenes provided the motivation to investigate the nature of the excited electronic states of the fluorobenzenes as well as the relationship between supercollision energy transfer efficiency and the electronic excited state features of the fluorobenzene donors. Furthermore, the vibrational mode assignment for all fluorobenzenes provides insight into how the donor fluorination affects supercollision energy transfer efficiency.

The third chapter is dedicated to how physical properties of bath molecules affect supercollision energy transfer. There are a number of studies previously performed measuring

energy loss of donors or energy gain of bath molecules to investigate the physical property effects of bath molecules on collision energy transfer. Through comparison with previous studies, we discuss which bath physical properties play a significant role in governing collision energy transfer. In this chapter, we measured state-specific energy gain amounts of N<sub>2</sub>O bath in collisions with hot pyrazine and could elucidate the effect of bath physical properties on supercollision energy transfer by comparing N<sub>2</sub>O energy gain results with H<sub>2</sub>O,<sup>49</sup> DCl,<sup>24</sup> and  $CO_2^{13}$  energy gain results obtained in previous studies.

The last chapter presents the results of extending the measurement range of energy gain by bath molecules to lower J states of ground vibrational level. Recently, Mullin group have shown that the energy transfer probability distribution function obtained by extrapolating the energy gain results of only the high J states is improved by measuring energy gain of bath molecules for the whole J range.<sup>28, 31, 33</sup> They reported fully measured energy transfer probability distribution without any extrapolation of energy gain data. This chapter is aimed at extending the energy gain measurements of N<sub>2</sub>O molecules scattered by single collisions with highly vibrationally excited pyrazine ( $E' = \sim 41,000 \text{ cm}^{-1}$ ) to the mid J range (J = 37–57) by employing short (200 and 100 cm) collision cells. We found that the energy transfer probability distribution obtained from J = 37-75 data for collisions between pyrazine and N<sub>2</sub>O is not very different from that obtained using only J = 59-75 data; that is, P(E,E') obtained from only the high J data is reliable even though the results of lower J states are an extrapolation of the high J data. However, we suggest that the energy gain measurements for the low J states must be performed to obtain an accurate collision rate constant as well as measure complete P(E,E') without any extrapolation.

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# Chapter 1

High Resolution IR Diode Laser Study of Collisional Energy Transfer between Highly Vibrationally Excited Monofluorobenzene and CO<sub>2</sub>: the Effect of Donor Fluorination on Strong Collision Energy Transfer

# I. Introduction

To obtain better efficiency in combustion, reduce pollutants released into the environment, and understand nature's phenomena occurring through a variety of chemical reactions, it is necessary to investigate chemical reaction mechanisms, which may consist of a number of elementary reactions.<sup>1,2</sup> Overall chemical reaction rates are often affected by only a few unimolecular or recombination reactions rather than all elementary reactions.<sup>3</sup> That is, enhancing or limiting rate-determining reactions can alter overall performance of chemical reactions. On the other hand, unimolecular reactions compete with collisional relaxation processes and the fate of reactant molecules poised to undergo chemical reactions is determined by collisional energy transfer processes. For several decades collisional energy transfer studies have been performed as an indirect way to understand unimolecular reactions, in contrast to a direct detection of unimolecular reactions.<sup>4</sup> As a result, a number of collisional energy transfer studies have given insight into the kinetics and dynamics of chemical reaction mechanisms. Of greater interest has been the understanding of gas phase collisional energy transfer processes as rate-limiting steps in the overall unimolecuar reaction, since controlling gas pressure provides an easy way to vary the rate of collisions that decide the fate of unimolecular reactions. For example at 20 mTorr and 300 K, the mean gas kinetic collision time is about ~4  $\mu$ s.

Recently, collision energy transfer studies have been focused on obtaining the energy transfer probability distribution function, P(E,E'),<sup>5, 6</sup> which describes the probability that a molecule with initial energy E' undergoes a collision process with a bath molecule and ends up with the final energy  $E (= E' - \Delta E)$  after transferring an amount of energy  $\Delta E$  to the bath molecule. The function, P(E,E'), is a key tool in comparing collision energy transfer efficiencies between

various collision systems. P(E,E') is also critical in master equation calculations to obtain accurate unimolecular reaction rates.<sup>7</sup>

Energy loss measurement techniques, such as UV absorption (UVA),<sup>8</sup> IR fluorescence (IRF),<sup>9-12</sup> and Kinetically Controlled Selective Ionization (KCSI),<sup>13-16</sup> have been used to measure average energy transfer amounts and in some limited cases information about P(E,E'). Alternatively a diode laser probe technique, to obtain state-specific information for energy gain of bath molecules developed by Flynn and coworkers,<sup>4, 5, 17-19</sup> has focused on understanding collision energy transfer processes by calculating P(E,E') from state-specific information. The probe technique has been used in both the Mullin group<sup>20-25</sup> and our lab.<sup>26-28</sup> The strength of the probe technique to obtain accurate bath energy gain information originates from using a narrow frequency (0.0003 cm<sup>-1</sup>) IR diode laser capable of state-specific probing of rotationally and translationally excited bath molecules following collisions with hot donor molecules. Details of V $\rightarrow$ RT energy transfer (energy transfer from vibration in donors to rotation and translation in bath molecules) can be revealed by obtaining state-specific bath energy gain information and measuring the energy transfer probability distribution function, P(E,E'), in the  $\Delta E = 2,000-7,000$  cm<sup>-1</sup> region.

Our previous studies on collisions of pyrimidine,<sup>26</sup> pyridine,<sup>27</sup> and difluorobenzene (DFB) isomers<sup>28</sup> with CO<sub>2</sub> indicate that the type and frequency of donor vibrational modes correlate with the shape of P(E,E'). Those studies concluded that low frequency, out-of-plane vibrational modes (less than 500 cm<sup>-1</sup>) are primarily responsible for strong collision energy transfer and determine the shape of P(E,E') in the high  $\Delta E$  tail region, which is represented by the bi-exponential fit parameters ( $1/\gamma$  and  $1/\alpha$ ). This conclusion is in good agreement with Fermi's Golden Rule<sup>5</sup> given that the shape of P(E,E') is linearly proportional to the shape of the

donor state density (the energy dependence of donor state density). Studies of Clary and coworkers<sup>29, 30</sup> using Vibrational Close-Coupling and Infinite-Order-Sudden Approximation (VCC-IOSA) Calculations and Classical Trajectory Calculations (CTC) were performed to understand the strong collision mechanism between highly vibrationally excited benzene-like molecules and atoms. They suggested that low frequency donor vibrational modes with out-ofplane motion govern strong collision energy transfer events because the low frequency out-ofplane modes have larger cross sections in vibrational excitation and relaxation than do high frequency modes with in-plane motion. Lendvay<sup>31</sup> investigated CS<sub>2</sub>–CO collisions using CTC and noticed that the efficiency of collisional energy transfer is strongly influenced by these donor vibrational mode properties: low frequency, bending, and out-of-plane motions. That is, out-ofplane bending modes with lower frequency are most effective on collisional energy transfer in comparison with in-plane, stretching, and higher frequency modes. This study displays that low frequency donor vibratoinal modes with bending motion play a dominant role in governing strong collision energy transfer. Thus, this work is in good agreement with previous studies in our lab<sup>26-28</sup> as well as the studies of Clary et al.<sup>29, 30</sup> and Lendvay.<sup>31</sup>

In this study, collision energy transfer experiments between highly-vibrationally excited monofluorobenzene (MFB) and CO<sub>2</sub> in the vibrational ground level have been performed to measure the energy transfer probability distribution function, P(E,E'). MFB as a donor has been chosen to compare with the previous studies on collisions of DFB isomers<sup>28</sup> and C<sub>6</sub>F<sub>6</sub><sup>19</sup> with CO<sub>2</sub>. Results are used to distinguish correct donor fluorination effect from other physical properties. Additionally these studies allow us to investigate the connection between the density of states, low frequency bending modes, and the increase of fluorine atoms in the donor, as well as the effect of donor fluorination on P(E,E') in the high  $\Delta E$  tail ( $\Delta E = 2,000-7,000$  cm<sup>-1</sup>).

Experimentally obtained P(E,E') is fit to a bi-exponential function to clarify the relationship between the physical properties of donor molecules and the nature of P(E,E'); bi-exponential fit parameters are composed of three characteristic parameters that describe a strong collision energy transfer magnitude ( $\gamma$ ), a weak collision energy transfer magnitude ( $\alpha$ ), and the relative contribution between strong and weak collisions (x). Previous studies using pyrimidine,<sup>26</sup> pyridine,<sup>27</sup> and DFB isomers<sup>28</sup> in collisions with CO<sub>2</sub> performed in our lab suggested that the biexponential parameters  $(1/\gamma \text{ and } 1/\alpha)$  is correlated with the final state density of donor molecules and showed that  $1/\gamma$  and  $1/\alpha$  have linear proportionality to the energy dependence of donor's final state density. The bi-exponential fit parameters obtained from this work and previous studies on DFB isomers– $CO_2^{28}$  and hexafluorobenzene– $CO_2^{19}$  systems are plotted versus the energy dependence of donor state density. The relationship between P(E,E') shape and the donor state density energy dependence is explained using Fermi's Golden Rule. Finally, the effect of the donor fluorination is discussed by assigning the motions of low frequency vibrational modes in MFB and calculating low frequency mode efficiencies in strong collision energy transfer region,  $\Delta E = 2,000-8,000$  cm<sup>-1</sup>. Energy transfer efficiency of fluorobenzenes according to the increase of donor initial energy E' is also discussed in this study.

In short, the purpose of this work is to elucidate how P(E,E') is different in various fluorobenzenes– $CO_2$  collision systems, how the increase of fluorine atoms in the donor is related with the shape and magnitude of P(E,E'), and which vibrational modes in MFB play the most effective role in the strong collision energy transfer.

# **II. Experimental**

The present experiment using a UV pump/IR probe technique to study collision energy transfer processes of a MFB–CO<sub>2</sub> system has been presented in detail elsewhere;<sup>27</sup> thus, only a brief description is given here. 10.0 mTorr of gas phase MFB and 10.0 mTorr of CO<sub>2</sub> flow simultaneously through a 300 cm long Pyrex collision cell with a total pressure of 20.0 mTorr. Pulsed 248 nm UV light generated from a KrF excimer laser (Lamda Physik Complex 201) is passed into the cell to excite MFB molecules via the S<sub>1</sub> $\leftarrow$ S<sub>0</sub> electronic transition, followed by rapid radiationless internal conversion (IC) to the electronic ground state, S<sub>0</sub>\* $\leftarrow$ S<sub>1</sub>.<sup>32-34</sup> UV intensity is maintained at ~40 mJ/cm<sup>2</sup> to ensure no multi-photon absorption.

Rotationally and translationally excited CO<sub>2</sub> molecules produced by collisions with highly-vibrationally excited MFB were probed using a tunable high-resolution (0.0003 cm<sup>-1</sup>) IR diode laser (Laser Components). The IR diode laser light (~4.3  $\mu$ m) is collinearly propagated with 248 nm UV light through the collision cell. The IR beam is then passed into a single grating monochromator (Acton Spectra pro 500i) to select a single diode laser mode and focused onto a 77 K-cooled InSb detector (Judson Technologies). The rise time of the detector and the pre-amplifier (Perry Amplifier) is about 400 ns, shorter than mean single gas kinetic collision time at 20.0 mTorr, 4  $\mu$ s. The signal is recorded with two channels (AC and DC) using a digital oscilloscope (Lecroy LT364 Waverunner, 500 MHz). This dual channel technique is used to collect the transient absorption signals while reducing the fluctuation in the incident IR diode laser intensity,  $I_0$ .<sup>18</sup> The IR transient absorption signal is obtained by dividing the AC signal ( $\Delta I$ ) by the DC signal ( $I_0$ - $\Delta I$ ). The transient signals are then averaged over 100 UV shots by the oscilloscope and transferred to a computer for further analysis.

Approximately 4% of the IR laser light is split off and transmitted through a 100 cm reference cell filled with CO<sub>2</sub>. This reference beam passes through a monochromator (Acton Spectra pro 300i) and is focused onto a second liquid-nitrogen-cooled InSb detector. This reference signal is then transferred to a lock-in amplifier (Stanford Research Systems), which corrects for drifts of the IR diode laser frequency by locking the laser frequency to the peak of a  $CO_2 (00^00; J \rightarrow 00^01; J \pm 1)$  transition.

Doppler-broadened full widths at half maximum (FWHM) for the individual rotational states of  $CO_2(00^00;J)$  were obtained by locking the diode laser frequency to a fringe peak of a scanning Fabry-Perot etalon (Free spectral range = 289 MHz) used in place of the reference cell. IR transient absorption signals of  $CO_2(00^00;J)$  were collected at a series of 40 distinct frequencies evenly distributed over the absorption line and averaged over 100 excimer laser shots at each frequency. Doppler-broadened linewidths were then calibrated by scanning the etalon distance between two well-known  $CO_2$  rovibrational transition peaks.

To correct for the underestimation of energy transfer rate constants due to UV divergence over the 300 cm long collision cell, additional 8 cm short-cell measurement using a MFB–CO<sub>2</sub> pair and long-cell reference measurements using a pyrazine–CO<sub>2</sub> pair were performed in this study and described in detail elsewhere.<sup>26</sup> These additional reference measurements allow us to determine the corrected absolute energy transfer rate constants and scattering probabilities as well as compare with different donor–CO<sub>2</sub> collision energy transfer studies.

MFB (Aldrich, 99% purity) was degassed using 3 freeze(77 K)-pump-thaw cycles prior to use. Carbon dioxide (Intermountain Airgas Inc, 99.999% purity) was used without further purification.

# **III. Results**

# A. IR transient absorption measurements for the $CO_2(00^01;J\pm1\leftarrow00^00;J)$ transition

IR transient absorption signals for CO<sub>2</sub> scattered into the J = 58–80 states of the 00<sup>0</sup>0 vibrational level, averaged over 100 excimer laser pulses, were measured as a function of time ( $\mu$ s scale) to determine the nascent CO<sub>2</sub> rotational and translational energy distribution. IR transient absorption signals measured at 1  $\mu$ s following 248 nm UV laser pulse were employed to calculate the population density of post-collision CO<sub>2</sub> excited into the 00<sup>0</sup>0;J = 58–80 states by a single collision with hot MFB. At 20 mTorr and 300 K, the mean gas kinetic collision time is ~4  $\mu$ s.<sup>5, 19, 35</sup> Thus measurements at 1  $\mu$ s consist of almost entirely single collision events. Statespecific population density of CO<sub>2</sub> (00<sup>0</sup>0;J = 58–80) in single collisions with hot MFB is obtained using the absorption line strengths obtained from the HITRAN<sup>36</sup> spectroscopic database, along with the measured IR transient absorption signals and Doppler broadened linewidths.

#### B. Rotational energy gain of CO<sub>2</sub> by single collisions with MFB

The nascent rotational Boltzmann distribution for CO<sub>2</sub> scattered into  $00^{0}0$ ; J = 58–80 by single collisions with highly vibrationally excited MFB is plotted in Figure 1-1 as a function of final CO<sub>2</sub> rotational energy ( $E_{rot} = BJ(J+1)$ ), where *B* is the rotational constant for CO<sub>2</sub>. A single rotational temperature, representing the Boltzmann distribution for the scattered CO<sub>2</sub> in single collisions with hot MFB, is obtained from the slope of the Boltzmann plot. The use of a rotational temperature provides a convenient way to compare average rotational energy gain of CO<sub>2</sub> in single collisions with different donors because rotational temperature can describe the



Final CO<sub>2</sub> Rotational Energy, BJ(J+1) (cm<sup>-1</sup>)

Figure 1-1. The nascent rotational Boltzmann distribution for CO<sub>2</sub> (00<sup>0</sup>0;J = 58–80) scattered by single collisions with various fluorobenzene molecules, measured at 1  $\mu$ s following UV excitation of fluorobenzene donors. Symbols represent the Boltzmann population measured over J = 58–80 of the final CO<sub>2</sub> (00<sup>0</sup>0); circles, squares, diamonds, and triangles represent post-collision CO<sub>2</sub> populations following single collisions with MFB, 12-DFB, 13-DFB, and 14-DFB, respectively. Data for collisions with DFB isomers with CO<sub>2</sub> were obtained from Ref. <sup>28</sup>. The lines indicate the best linear least squares fit to the measured data. The rotational temperature of post-collision CO<sub>2</sub> molecules, *T<sub>rot</sub>*, was obtained from the slope (-1/*k*<sub>B</sub>*T<sub>rot</sub>)* of these linear fits, where *k*<sub>B</sub> is the Boltzmann constant and *T<sub>rot</sub>* is the rotational temperature. *T<sub>rot</sub>* for CO<sub>2</sub> scattered by single collisions with MFB is 1030 ± 60 K. *T<sub>rot</sub>* for CO<sub>2</sub> scattered

by single collisions with DFB isomers was obtained from Ref. <sup>28</sup> ( $T_{rot}$  for 12-, 13-, and 14-DFB are 1020 ± 80 K, 970 ± 80 K, and 930 ± 80 K, respectively). The population of post-collision CO<sub>2</sub> following collisions with MFB is smaller than the post-collision CO<sub>2</sub> population for the DFB isomers, while the rotational temperature of the scattered CO<sub>2</sub> in collisions with MFB is larger than the rotational temperatures for the DFB isomer–CO<sub>2</sub> systems.

average rotational energy of molecules,  $\langle E_{rot} \rangle_f = k_B T_{rot}$ , where  $k_B$  is the Boltzmann constant and  $T_{rot}$  is the rotational temperature. The rotational temperature of vibrational ground state CO<sub>2</sub> scattered into the high J states (J = 58–80) by single collisions with vibrationally hot MFB is  $T_{rot}$  = 1030 ± 60 K. This indicates that a significant amount of vibrational energy in hot MFB is transferred to cold CO<sub>2</sub> during the collisions. Rotational temperatures obtained from the previous study of the DFB isomer–CO<sub>2</sub> systems<sup>28</sup> are also plotted in Figure 1-1 for comparison;  $T_{rot}$  of post-collision CO<sub>2</sub> following collisions with 12-DFB, 13-DFB, and 14-DFB are 930 ± 80 K, 970 ± 80 K, and 1020 ± 80 K, respectively. Figure 1-1 shows that the population of the scattered CO<sub>2</sub> in collisions with MFB is smaller than the scattered CO<sub>2</sub> population following collisions with DFB isomers, while  $T_{rot}$  for the MFB–CO<sub>2</sub> system is larger than  $T_{rot}$  for the DFB isomer–CO<sub>2</sub> systems. For, The rotational temperature for HFB–CO<sub>2</sub> system,<sup>19</sup> another fluorobenzene–CO<sub>2</sub> collision system, is  $T_{rot} = 795$  K.

### C. Translational energy gain of CO<sub>2</sub> by single collisions with MFB

The distribution of relative recoil velocities for the scattered CO<sub>2</sub> can be measured from Doppler-broadened line profiles obtained by probing anti-symmetric ro-vibrational transitions  $(00^{0}1;J\pm1 \leftarrow 00^{0}0;J)$  of post-collision CO<sub>2</sub>. The measured Doppler-broadened IR absorption line profiles were fit to a Gaussian function to determine the full width at half maximum (FWHM),  $\Delta v_{obs}$ , which is related to lab frame translational temperature for the scattered CO<sub>2</sub>. A typical Doppler-broadened line profile for the CO<sub>2</sub> ro-vibrational transition  $(00^{0}1;J=75 \leftarrow 00^{0}0;J=76)$ measured in this work is shown in Figure 1-2, along with a corresponding lab frame translational temperature. The lab frame translational temperature,  $T_{trans}$ , for the final CO<sub>2</sub> was obtained from



Relative Frequency to the center frequency (cm)

Figure 1-2. The nascent Doppler-broadened IR transient absorption line profile for the  $CO_2(00^01;J=75) \leftarrow CO_2(00^00;J=76)$  transition, showing the translational distribution for  $CO_2$  molecules scattered into the  $00^00$ , J=76 state by single collisions with highly vibrationally excited MFB. The Doppler-broadened line profiles were obtained by measuring fractional IR transient absorption signals distributed across the center line of the  $CO_2(00^01;J=75) \leftarrow CO_2(00^00;J=76)$  transition. Circles indicate the fractional IR absorbance of  $CO_2(00^00;J=76)$  measured 1  $\mu$ s after 248 nm UV excitation of MFB, averaged over 100 excimer laser shots. The dash-dotted line is the best non-linear least squares fit to a Gaussian function. The full width at half maximum (FWHM) obtained from the Gaussian fit is  $\Delta v_{obs} = 0.0099 \pm 0.0011$  cm<sup>-1</sup>, which corresponds to a lab frame CO<sub>2</sub> translational temperature of  $T_{trans} = 1630 \pm 380$  K. For comparison, the FWHM for CO<sub>2</sub> at the same pressure as this work (20 mTorr) and 300 K is 0.0042 cm<sup>-1</sup>.

$$T_{trans} = \frac{mc^2}{8k_B \ln 2} \left(\frac{\Delta v_{obs}}{v_0}\right)^2,\tag{1}$$

where *m* is the mass of CO<sub>2</sub>, *c* is the speed of light,  $k_B$  is the Boltzmann constant,  $\Delta v_{obs}$  is the FWHM for the final CO<sub>2</sub> measured by fitting Doppler-broadened line profiles to a Gaussian function, and  $v_0$  is the center frequency of the absorption line. As shown in Figure 1-2, the FWHM for the scattered CO<sub>2</sub> (00<sup>0</sup>0;J=76) in collisions with MFB is  $\Delta v_{obs} = 0.0099 \pm 0.0011$  cm<sup>-1</sup>; the corresponding lab frame translational temperature is  $T_{trans} = 1630 \pm 380$  K. In comparison with the Doppler-broadened linewidth for CO<sub>2</sub> at 300 K ( $\Delta v_{obs} = 0.0042$  cm<sup>-1</sup>),  $\Delta v_{obs}$  for post-collision CO<sub>2</sub> measured in this work indicates that a large amount of vibrational energy in MFB is imparted into translation of CO<sub>2</sub> during collisions with MFB. Relative (Center-Of-Mass: COM) translational temperatures ( $T_{trans}^{COM}$ ), which are a more accurate description for the translational energy gain amount of CO<sub>2</sub>, were obtained from the measured lab frame translational temperatures according to

$$T_{trans}^{COM} = T_{trans} + (T_{trans} - T_{cell}) \left( \frac{m_{CO_2}}{m_{donor}} \right)^{18},$$
(2)

where  $T_{cell}$  is the temperature of the collision cell,  $m_{CO_2}$  is the mass of CO<sub>2</sub>, and  $m_{donor}$  is the mass of donor (MFB in this study). The measured FWHMs for CO<sub>2</sub> (00<sup>0</sup>0;J = 58–80) scattered by collisions with highly vibrationally excited MFB are listed in Table 1-1, along with lab frame and center-of-mass translational temperatures.

Figure 1-3 shows the lab frame and COM translational temperatures of the scattered  $CO_2$  for various fluorobenzenes as a function of the final  $CO_2$  rotational state. As shown in Figure 1-3, we can state that the translational temperature for each collision system increases with the  $CO_2$
Table 1-1. Full width at half maximum (FWHM) for Doppler line broadenings, and lab frame and Center-Of-Mass (COM) translational temperatures for the scattered  $CO_2$  (00<sup>0</sup>0;J = 58–80) following single collisions with highly vibrationally excited MFB<sup>*E*</sup>.

$CO_2 (00^0 0)$	From single collisions with MFB <sup>E'd</sup>				
J <sub>final</sub> state	$\Delta v_{obs}^{a}$ (cm <sup>-1</sup> )	$T_{trans}^{b}$ (K)	$T_{trans}^{COM c}$ (K)		
58	$0.0057 \pm 0.0011$	$540 \pm 210$	$650 \pm 300$		
62	$0.0085 \pm 0.0005$	$1180\pm150$	$1580\pm220$		
66	$0.0093 \pm 0.0006$	$1410\pm180$	$1920\pm260$		
70	$0.0097 \pm 0.0006$	$1570\pm180$	$2150\pm270$		
76	$0.0099 \pm 0.0011$	$1630\pm380$	$2250\pm550$		
80	$0.0112 \pm 0.0010$	$2110\pm370$	$2930\pm540$		

a Full width at half maximum (FWHM) for Doppler line broadenings of the ro-vibrational transitions,  $CO_2(00^01;J-1) \leftarrow CO_2(00^00;J)$ . This FWHM was obtained from the best non-linear least squares fit of the fractional IR transient signals, measured at ~40 different frequencies near the center frequency of the absorption, to a Gaussian function. For comparison, the Doppler broadened linewidth for CO<sub>2</sub> at 300 K is 0.0042 cm<sup>-1</sup>.

**b** Lab frame CO<sub>2</sub> translational temperatures,  $T_{trans}$  calculated using Equation (1).

c Center-Of-Mass (COM) translational temperatures,  $T_{trans}^{COM}$ , calculated using Equation (2).

d The initial energy for MFB excited by 248 nm UV absorption:  $E = 40,843 \text{ cm}^{-1}$ .



Final CO<sub>2</sub> Rotational State, J

Figure 1-3. Lab-frame (left Y axis) and Center-Of-Mass (right Y axis) translational temperatures for CO<sub>2</sub> molecules scattered into  $00^{0}$ ; J = 58–80 by single collisions with highly vibrationally excited fluorobenzenes as a function of the final CO<sub>2</sub> rotational state, J. Data for DFB isomers and HFB were obtained from Ref. <sup>28</sup> and <sup>19</sup>, respectively. Circles, squares, diamonds, up-triangles, and down-triangles represent CO<sub>2</sub> translational temperatures following single collisions with MFB, 12-DFB, 13-DFB, 14-DFB, and HFB, respectively. Lab-frame translational temperatures,  $T_{trans}$ , were directly obtained from the Doppler-broadened linewidths (FWHM) measured 1  $\mu$ s following a 248 nm excimer laser shot using Equation (1). Center-Of-Mass translational temperature,  $T_{trans}^{COM}$ , was obtained using Equation (2) to determine actual translational energy transfer between fluorobenzene donors and CO<sub>2</sub>.

rotational state even though there are odd patterns for 14-DFB ( $T_{trans}$  higher for J = 62 than for J = 66) and HFB (almost invariant  $T_{trans}$  for J = 62–70). This trend suggests that V $\rightarrow$ T (Vibrational to Translational) collision energy transfer events obey classical collision dynamics,  $(h/2\pi)\Delta J = \mu\Delta \upsilon_{rel}b_{eff}$ ; thus, the relative velocity change is proportional to the total rotational angular momentum change in this range.  $(h/2\pi)\Delta J$  is the change of total rotational angular momentum,  $\mu$  is the reduced mass between donor and bath molecules,  $\Delta \upsilon_{rel}$  is the change of relative recoil velocity for the bath to the donor, and  $b_{eff}$  is the effective impact parameter.<sup>5</sup>

# D. Energy transfer rate constants and scattering probabilities for single collisions between hot MFB and CO<sub>2</sub>

The energy transfer process that scatters  $CO_2$  into the  $00^00$ ; J = 58–80 states following collisions with hot MFB is represented according to

$$MFB^{E'} + CO_2 \xrightarrow{k_2^{J'}} MFB^E + CO_2(00^0; J = 58 - 80, V).$$
(3)

In equation (3), E' is the initial donor energy following the absorption of a 248 nm photon,  $E (= E' - \Delta E)$  is the final donor energy following single collisions with CO<sub>2</sub>, and  $k_2^J$  is the statespecific energy transfer rate constant. The state-specific energy transfer rate constant,  $k_2^J$ , for the energy transfer process (3) was calculated from the modified rate expression using

$$k_2^J = \frac{[CO_2(00^00; J, V)]}{[CO_2]_0[MFB^{E'}]_0 t},\tag{4}$$

where  $[CO_2]_0$  is the number density of the initial bulk CO<sub>2</sub> molecules,  $[MFB^{E'}]_0$  is the number density of highly vibrationally excited MFB molecules with the energy E' prior to the collisions with CO<sub>2</sub>, and  $[CO_2(00^00;J,V)]$  is the final state-specific CO<sub>2</sub> number density obtained from the IR transient absorption signal at 1  $\mu$ s (t) following a UV laser pulse. The number density of hot MFB with the energy E' is determined from the number of UV photons absorbed by MFB. UV laser intensity was maintained at ~40 mJ/cm<sup>2</sup> to ensure only single photon absorption. For evidence, UV absorbance of MFB was measured as a function of laser intensity and was found to be constant from 20 to 50 mJ/cm<sup>2</sup>. This indicates that UV absorbance in that range occurs by single photon absorption. Therefore, the number of the absorbed UV photons can be directly transformed into the number density of highly vibrationally excited MFB molecules.

State-specific energy transfer rate constants,  $k_2^J$ , for single collisions between hot MFB with  $E' = 40,843 \text{ cm}^{-1}$  and cold CO<sub>2</sub> are listed in Table 1-2. As described in the Experimental section, to correct for the divergence of UV laser beam through the 300 cm long collision cell, the measured  $k_2^J$  values were calibrated using two reference experiments.<sup>26</sup>  $k_2^J$  values for various fluorobenzene–CO<sub>2</sub> systems are plotted as a function of the final CO<sub>2</sub> rotational state for comparison in Figure 1-4.  $k_2^J$  values for DFB isomers–CO<sub>2</sub> systems in Figure 1-4 were obtained from our previous study<sup>28</sup> and for HFB–CO<sub>2</sub> system were from the report of Michaels et al.<sup>19</sup> Figure 1-4 shows that energy transfer rate constants decrease with the increase in the final CO<sub>2</sub> J state. The magnitude of  $k_2^J$  values are largest for collisions of HFB and smallest for HFB and the smallest for MFB.  $k_2^J$  values are largest for collisions of HFB and smallest for collisions of MFB with CO<sub>2</sub> according to the following order, HFB > 14-DFB > 12-DFB > 13-DFB > MFB.

The probability that  $CO_2$  molecules are scattered into the high J states of the ground vibrational level in collisions with hot MFB are also listed in Table 1-2 and shown in Figure 1-4. The scattering probability,  $P_J$ , is obtained by dividing the state-specific energy transfer rate constant by the Lenard-Jones collision rate constant,

$$P_{J} = \frac{k_{2}^{J}}{k_{LJ}}.$$
(5)

	In single collisions with $MFB^{E}$			
Final CO <sub>2</sub> J state	$k_2^{Ja}$ (10 <sup>-12</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$P_J^{\rm b}$ (10 <sup>-3</sup> /col)		
58	$4.5 \pm 0.4$	$8.3\pm0.7$		
62	$4.1 \pm 0.3$	$7.6\pm0.6$		
66	$2.6 \pm 0.2$	$4.8\pm0.3$		
70	$2.2\pm0.2$	$4.2\pm0.3$		
76	$1.4 \pm 0.1$	$2.5\pm0.1$		
80	$1.3 \pm 0.1$	$2.3 \pm 0.1$		
	$k_2^{\text{intc}} = 31.1$	$P_2^{\text{intd}} = 57.9$		

Table 1-2. State-specific energy transfer rate constants,  $k_2^J$ , and scattering probabilities,  $P_J$ , for the process of MFB<sup>*E*</sup> + CO<sub>2</sub>(00<sup>0</sup>0)  $\rightarrow$  MFB<sup>*E*- $\Delta E$ </sup> + CO<sub>2</sub>(00<sup>0</sup>0;*J*).

a State-specific energy transfer rate constant,  $k_2^J$ , calculated using Equation (4).

b Scattering probability for the energy transfer process of MFB<sup>*E*</sup> + CO<sub>2</sub>(00<sup>0</sup>0)  $\rightarrow$  MFB<sup>*E*-AE</sup> + CO<sub>2</sub>(00<sup>0</sup>0;*J*) obtained from  $k_2^J/k_{LJ}$ .  $k_{LJ}$  is the Lennard-Jones gas kinetic collision rate constant defined as  $k_{LJ} = \pi [(d_{CO_2} + d_{donor})/2]^2 \sqrt{(8k_BT/(\pi\mu)}\Omega_{12}, \text{ where } d_{CO_2} = 4.5 \text{ Å},^{37} d_{MFB} = 5.3 \text{ Å} \text{ for MFB},^{38} k_B \text{ is the}$ Boltzmann constant, and  $\mu$  is the reduced mass.  $\Omega_{12}$  is the Lennard-Jones collisional integral given by the expression  $\Omega_{12} = [0.636 + 0.567 \log(k_BT/\epsilon_{12})]^{-1},^{39}$  where  $\epsilon_{12}$  is the MFB–CO<sub>2</sub> well depth given by  $\epsilon_{12} = \sqrt{\epsilon_{MFB}\epsilon_{CO_2}}$  calculated using  $\epsilon_{MFB}/k_B = 435 \text{ K}^{38}$  and  $\epsilon_{CO_2}/k_B = 195 \text{ K}.^{39}$  The Lennard-Jones collision rate constant,  $k_{LJ}$ , for collisions between MFB and CO<sub>2</sub> at 300 K is  $5.37 \times 10^{-10} \text{ cm}^3$ molecule<sup>-1</sup>s<sup>-1</sup>. c The integrated energy transfer rate constant,  $k_2^{\text{int}}$ , obtained by  $\Sigma k_2^J$  for J = 58–80.  $k_2^J$  values are interpolated based on the measured values.

d The integrated scattering probability,  $P_2^{\text{int}}$ , obtained using  $k_2^{\text{int}}/k_{LJ}$ .



Figure 1-4. State-specific energy transfer rate constants ( $k_2^J$ ; left Y axis) and scattering probabilities ( $P_J$ ; right Y axis) for the process that CO<sub>2</sub> are excited to  $00^00$ ; J = 58–80 states by single collisions with hot fluorobenzenes,  $Donor^{E'} + CO_2 \xrightarrow{k_2^J} Donor^E + CO_2(00^00; J = 58-80)$ , as a function of the final CO<sub>2</sub> rotational state. All  $k_2^J$  values were measured 1  $\mu$ s following UV excitation of donors at 248 nm. Data for DFB isomers and HFB were obtained from Ref. <sup>28</sup> and <sup>19</sup>, respectively.

In Figure 1-4, one can see that scattering probabilities for DFB isomer– $CO_2$  and HFB– $CO_2$  systems are larger than scattering probabilities for the MFB– $CO_2$  system. This indicates that the collisional energy transfer efficiency for large  $\Delta E$  scattering is lowest for the MFB– $CO_2$  collisions in comparison with DFB isomer– $CO_2$  and HFB– $CO_2$  collisions.

## E. Energy transfer probability distribution function, P(E,E')

In addition to the detailed energy transfer dynamic information, kinetic information in terms of the energy transfer probability distribution function, P(E,E'), can be obtained by resorting the state-resolved probabilities to  $\Delta E$ -indexed probabilities. P(E,E') describes the probability that donor molecules with the initial energy E' transfer  $\Delta E$  to CO<sub>2</sub> in single collisions with CO<sub>2</sub> and end up with the energy of  $E (= E' - \Delta E)$ . The procedure to calculate P(E,E') has been described in detail elsewhere.<sup>5, 40</sup> Knowledge of both initial and final  $CO_2$  states is required to obtain P(E,E') by calculating correct total energy transfer amount. The final CO<sub>2</sub> rotational state and recoil velocity distribution are accurately determined in this study; however, the initial CO<sub>2</sub> rotational state and velocity are not determined in this work, but are a distribution of statistical velocities.<sup>26</sup> The average initial velocity,  $\langle v_i \rangle$ , can be obtained from a translational gap law model using the isotropic Boltzmann-Maxwell velocity distribution at room temperature and the initial CO<sub>2</sub> rotational state can be determined from temperature-dependent energy transfer studies and a rotational gap law model.<sup>18</sup> For example, previous pyrazine,<sup>18</sup> HFB,<sup>19</sup> and methylpyrazine<sup>5</sup> studies have obtained  $\langle J_i \rangle = 22, 31$ , and 26.5, respectively, from temperaturedependent experiments. Previous work in our lab<sup>26</sup> considered the effect of deviation in  $\langle J_i \rangle$  on P(E,E') in the large  $\Delta E$  region. We concluded that altering the initial J value in the  $\langle J_i \rangle = 22-32$ 

range has very little effect on P(E,E'); it resulted in altering P(E,E') parameters by at most 5%. This is because  $\Delta E_{rot}$  used to calculate P(E,E') depends on differences in  $J^2$  according to  $\Delta E_{rot} = BJ_f (J_f + 1) - B < J_i > (< J_i > + 1)$ ; thus, exact knowledge of the final state is more important than exact determination of the initial state, as long as final J states are much larger than the average initial J state. As a result, temperature-dependent experiments have not been performed for this MFB-CO<sub>2</sub> study. Instead, P(E,E') for this system was calculated using  $< J_i > =$ 28.7; the average  $< J_i >$  values obtained from the previous pyrazine, HFB, and methylpyrazine studies.<sup>26-28</sup>

P(E,E') profiles resulting from single collisions between various highly vibrationally excited fluorobenzene molecules and CO<sub>2</sub> are displayed in Figure 1-5; the data for HFB–CO<sub>2</sub> and DFB–CO<sub>2</sub> systems were obtained previously.<sup>19, 28</sup> The experimentally obtained P(E,E') for  $\Delta E = 2,000-7,000 \text{ cm}^{-1}$  matches the extrapolated P(E,E') in this range, since we cannot obtain accurate  $\Delta E$  values for small  $\Delta J$  values due to a spread in initial rotational states. Figure 1-5 shows that P(E,E') for the MFB–CO<sub>2</sub> system in  $\Delta E = 2,000-7,000 \text{ cm}^{-1}$  has the lowest probability and the gentlest slope when compared with P(E,E') for DFB isomer–CO<sub>2</sub> and HFB–CO<sub>2</sub> systems. This indicates that MFB is the least efficient fluorobenzene donor for energy transfer to CO<sub>2</sub> when compared with the DFB isomers and HFB in this  $\Delta E$  range. However, even though P(E,E') for MFB–CO<sub>2</sub> collisions is smaller than the other fluorobenzene donor–CO<sub>2</sub> systems in this  $\Delta E$  range, P(E,E') for the MFB–CO<sub>2</sub> system must be greater in other  $\Delta E$  regions because P(E,E') is a normalized function. In other words, the sum of P(E,E') over the entire range of  $\Delta E$  must be 1 for all systems, and P(E,E') curves must cross at some  $\Delta E$  point. This makes it difficult for



Energy Transfer Amount,  $\Delta E$  (cm<sup>-1</sup>)

Figure 1-5. Energy transfer probability distribution function, P(E,E'), for

 $Donor^{E'} + CO_2 \xrightarrow{k_2^J} Donor^E + CO_2(00^00; J = 58 - 80)$  plotted against the amount of energy transfer from 2,000 to 7,000 cm<sup>-1</sup>. The initial energy of all highly vibrationally excited fluorobenzene molecules is ~41,000 cm<sup>-1</sup>. P(E,E') for 12-, 13-, and 14-DFB-CO<sub>2</sub> collision systems were obtained from Ref. 28, while P(E,E') for the HFB-CO<sub>2</sub> collision system was obtained from Ref. 19. P(E,E') between different systems to be directly compared. Relative probability can only be compared at a specific  $\Delta E$  or  $\Delta E$  range.

One way to facilitate direct comparison between P(E,E') of different systems is to fit P(E,E') to a model that allows comparison using only a few parameters for all  $\Delta E$  values. Previously, we used a bi-exponential function to fit the experimentally obtained P(E,E').<sup>26-28</sup> The bi-exponential function includes both weak and strong collision parameters that account for both weak and strong energy transfer events, making it convenient for P(E,E') to be directly compared for different systems. The bi-exponential formula for down collisions, when the donor loses energy, is defined as

$$P(E,E') = \frac{x_1 \exp\{-(E'-E)/\alpha\} + x_2 \exp\{-(E'-E)/\gamma\}}{x_1(\alpha+\beta) + x_2(\gamma+\delta)} \text{ for } E' > E.^{41,42}$$
(6)

In equation (6),  $x_1$  and  $x_2$  are the "fractions" of weak and strong collisions, respectively  $(x_1+x_2=1)$ ; although collisions are not strictly either strong or weak,<sup>5</sup> it is convenient to define the fit parameters as weak and strong terms for comparison.  $\alpha$  is defined as the average energy transfer magnitude for weak collisions and  $\gamma$  as the average energy transfer magnitude for strong collisions when E'>E.  $\beta$  and  $\delta$  are the average energy transfer magnitude for weak and strong collisions, respectively, when E'<E.  $\alpha$  and  $\beta$  as well as  $\gamma$  and  $\delta$  are related to each other and can be described by detailed balance.<sup>41, 42</sup> The experimental P(E,E') curve of the MFB–CO<sub>2</sub> system and the bi-exponential fit line are plotted as a function of energy transfer amount,  $\Delta E (= E - E')$ , in Figure 1-6. The experimental P(E,E') curve for the MFB–CO<sub>2</sub> system are precisely fit to the bi-exponential function in the  $|\Delta E| = 2,000-7,000 \text{ cm}^{-1}$  region. It should be noted that the extrapolated fit of the experimental P(E,E') to other  $\Delta E$  region was uniquely obtained by requiring that P(E,E') be normalized over the entire  $\Delta E$  range and that detailed balance be



Energy Transfer Amount,  $\Delta E (= E - E') (\text{cm}^{-1})$ 

Figure 1-6. The fit of experimentally obtained P(E,E') (noisy line) for single collisions between vibrationally excited MFB and CO<sub>2</sub> to a bi-exponential function. Bi-exponential fit parameters of the experimental P(E,E') related to downward collisions were determined as  $\alpha = 299$  cm<sup>-1</sup> (the magnitude of weak collision energy transfer),  $\gamma = 1,925$  cm<sup>-1</sup> (the magnitude of strong collision energy transfer),  $x_2 =$ 0.031 (the fraction of strong collisions), and  $\langle \Delta E \rangle_d = 575$  cm<sup>-1</sup> (the average amount of energy transfer for downward collisions).

obeyed. The P(E,E') bi-exponential parameters for MFB–CO<sub>2</sub>, DFB–CO<sub>2</sub>, <sup>28</sup> and HFB–CO<sub>2</sub><sup>19</sup> systems are listed in Table 1-3. Table 1-3 also includes the donor initial energy, the donor state density at E', and the number of low frequency vibrational modes < 500 cm<sup>-1</sup> to examine the relationship between donor physical properties and P(E,E').

### **IV. Discussion**

The present work is a benchmark for studying the effect of donor fluorination on strong collision energy transfer between highly vibrationally excited fluorobenzene donors and CO<sub>2</sub> bath molecules; MFB is the fluorobenzene donor possessing the fewest fluorine atoms. Substituting a fluorine atom for a hydrogen atom in benzene lowers local vibrational frequency in comparison with the vibrational frequencies of C–H bonds because vibrational frequency is inversely proportional to the square root of the reduced mass. This study on collision energy transfer of the MFB–CO<sub>2</sub> system establishes a basis to investigate the effect of increasing the number of fluorine atoms in the benzene structure on single collision energy transfer with CO<sub>2</sub>. To monitor the change of rotational energy gain of  $CO_2$  with the increase of fluorine atoms in collisions between fluorobenzene donors and CO<sub>2</sub>, final CO<sub>2</sub> rotational temperature, T<sub>rot</sub>, was obtained using a Boltzmann distribution plot. Using equipartition theory, the average final CO<sub>2</sub> rotational energy for CO<sub>2</sub> molecules scattered into the high J tail can be determined from  $\langle E_{rot} \rangle_f = k_B T_{rot}; \langle E_{rot} \rangle_f$  for MFB ( $T_{rot} = 1030$  K), 12-DFB ( $T_{rot} = 930$  K), 13-DFB ( $T_{rot} = 970$  K), 14-DFB ( $T_{rot} = 1020$  K), and HFB ( $T_{rot} = 795$  K) are 716, 647, 675, 709, and 553 cm<sup>-1</sup>, respectively. The average rotational energy gain of  $CO_2$  in collisions with hot fluorobenzene molecules,  $\langle \Delta E_{rot} \rangle$ , can be obtained by subtracting  $\langle E_{rot} \rangle_i$  from  $\langle E_{rot} \rangle_f$ , where

Table 1-3. Bi-exponential fit parameters ( $\gamma^{a}$ ,  $\alpha^{b}$ ,  $x_{2}^{c}$ , and  $\langle \Delta E \rangle_{d}^{d}$ ) obtained by fitting the energy transfer probability distribution function, P(E,E'), to Equation (6) for various fluorobenzene–CO<sub>2</sub> collision systems, the initial energy (E')<sup>e</sup>, the pre-collision anharmonic state density ( $\rho(E')$ )<sup>f</sup>, and the number of low frequency vibrational modes < 500 cm<sup>-1</sup> (s)<sup>g</sup> for the fluorobenzene donor.

Donor	$\gamma^{a}$ (cm <sup>-1</sup> )	$\alpha^{\rm b}$ (cm <sup>-1</sup> )	$x_2^{c}$ (#/col)	$\left< \Delta E \right>_d^{\mathbf{d}} (\mathrm{cm}^{-1})$	$E'^{e}$ (cm <sup>-1</sup> )	$\rho(E')^{f}$	$s^{g} (< 500 \text{ cm}^{-1})$
				-			
MFB	1925	298	0.03	575	40,843	$2.0 \times 10^{16}$	4
1,2-DFB <sup>h</sup>	1850	343	0.06	739	41,025	$4.3 \times 10^{17}$	5
1,3-DFB <sup>h</sup>	2061	295	0.03	638	41,011	$7.6 \times 10^{17}$	5
1,4-DFB <sup>h</sup>	2408	294	0.03	713	41,019	$8.0 \times 10^{17}$	6
HFB <sup>h</sup>	1411	620	0.15	847	41,822	$3.0 \times 10^{23}$	13

Table 1-3. Continued.

a Average magnitude of strong collision energy transfer determined from the bi-exponential fit of the experimental P(E,E') data.

b Average magnitude of weak collision energy transfer determined from the bi-exponential fit of the experimental P(E,E') data.

c Fraction of strong collisions determined from the bi-exponential fit of the experimental P(E,E') data. d Average energy transfer amount determined according to  $\langle \Delta E \rangle_d = (\alpha^2 x_1 + \gamma^2 x_2)/(\alpha x_1 + \gamma x_2)$ , where  $x_1 + x_2 = 1$ .  $x_1$  and  $x_2$  are weak collision and strong collision fractions, respectively.

e The initial energy E' of fluorobenzene donor molecules following absorption of 248 nm UV light.

f The anharmonic state density for fluorobenzenes with the initial energy *E'* following the absorption of a 248 nm laser photon, obtained from Wang-Landau Random Walk Algorithm.<sup>43-45</sup> The anharmonic density of vibrational states for molecules with more than 4 atoms is calculated using ADENSUM code, MultiWell-2010 program.<sup>46</sup> The anharmonicity for various fluorobenzenes were calculated at the DFT (B3-LYP) level of theory using a cc-pvqz basis set in Gaussian03 program.<sup>47</sup> Geometry optimization were performed using NWChem at the B3-LYP level of theory and a cc-pvqz basis set.

g The number of low frequency vibratonal modes with < 500 cm<sup>-1</sup> for fluorobenzene donor molecules. Vibrational mode frequencies are obtained from Refs. 48-52 for MFB, 30, 48, 53-56 for DFB isomers, and 48, 57-60 for HFB.

h DFB parameters are obtained from Ref. 28 while HFB parameters are obtained from Ref. 19.

 $\langle E_{rot} \rangle_i = k_B T_{cell} \approx 209 \text{ cm}^{-1}$  ( $T_{cell}$  is 300 K). Therefore,  $\langle \Delta E_{rot} \rangle$  for CO<sub>2</sub> resulting from collisions with MFB, 12-DFB, 13-DFB, 14-DFB, and HFB are 507, 438, 466, 500, and 344 cm<sup>-1</sup>, respectively. As one can see, an increase in the number of donor fluorine atoms decreases the amount of rotational energy gain of CO<sub>2</sub> in collisions with fluorobenzene donors. This decrease of rotational energy gain for post-collision CO<sub>2</sub> appears to be related to the number of fluorine atoms, which decreases the local vibrational frequencies of fluorobezene donors, as well as the matching effect of the masses of donor and bath molecules. Classically when a donor mass is similar to an acceptor mass, the energy transfer is most efficient. The increase of donor fluorine atoms is oppositely proportional to the mass matching effect and may result in a decrease in the average energy gain.

The pattern for the decrease of average CO<sub>2</sub> rotational energy gain according to the increase in the number of donor fluorine atoms also seems to appear in the average translational energy gain,  $\langle \Delta E_{trans} \rangle$ .  $\langle \Delta E_{trans} \rangle$  for MFB-, 12-DFB-, 13-DFB-, 14-DFB-, and HFB-CO<sub>2</sub> systems are 1450, 1680, 1640, 1670, and 860 cm<sup>-1</sup>, respectively.  $\langle \Delta E_{trans} \rangle$  was obtained from the following equations

$$\Delta E_{trans}^{J} = \frac{3}{2} k_{B} T_{trans}^{COM} - \frac{3}{2} k_{B} T_{cell} \tag{7}$$

$$\left\langle \Delta E_{trans} \right\rangle = \sum_{58}^{80} P_J \Delta E_{trans}^J \bigg/ \sum_{58}^{80} P_J \,, \tag{8}$$

where  $\Delta E_{trans}^{J}$  is the state-specific translational energy gain of CO<sub>2</sub> and  $P_{J}$  is the state-specific scattering probability in the J = 58–80 range. According to classical collision theory, there is a relationship between the angular momentum change and the relative velocity change of bath molecules given by,  $(h/2\pi)\Delta J = \mu \Delta v_{rel} b_{eff}$ .<sup>5</sup> Since rotational angular momentum change of CO<sub>2</sub> in collisions with various fluorobenzenes is the same for each CO<sub>2</sub> final state (because the initial CO<sub>2</sub> state is same for all donors and the measured final CO<sub>2</sub> state is also same for all donors), the relative velocity change  $(\Delta v_{rel})$  for each J state is then inversely proportional to the reduced mass between the donor and CO<sub>2</sub> given that the effective impact parameter is a constant. To simplify the relation between  $\Delta v_{rel}$  and  $\mu$ , we set  $(h/2\pi)\Delta J$  equal to a constant *C* due to its invariance at each final CO<sub>2</sub> J state for different fluorobenzenes. Then, since the reduced mass between donors and CO<sub>2</sub> are different for various fluorobenzene donors, we can use  $\Delta \mu$  between different donors, instead of a constant  $\mu$ . The equation finally becomes as the following formula

$$\frac{C}{\Delta\mu} = \Delta \upsilon_{rel} b_{eff}.$$
(9)

Note that  $\Delta v_{rel}$  is the state-specific relative velocity change and *C* is different for each J state but same for various fluorobenzenes in each J state.  $b_{eff}$  for MFB, 12-DFB, 13-DFB, 14-DFB, and HFB are ~2.13, ~1.60, ~1.65, ~1.72, and ~2.44 Å, respectively, in the J = 58–80 range.

In other words, as the donor–CO<sub>2</sub> reduced mass increases with the number of fluorine atoms, the relative velocity change decreases and hence the translational energy gain of CO<sub>2</sub> decreases. The reason that  $\langle \Delta E_{trans} \rangle_{MFB/CO_2} = 1450 \text{ cm}^{-1} < \langle \Delta E_{trans} \rangle_{DFBs/CO_2} = \sim 1650 \text{ cm}^{-1}$  is because  $b_{eff}$  for MFB is larger than those for DFB isomers. If we assume that  $b_{eff}$  is same for all donors, the relative velocity of CO<sub>2</sub> for MFB is largest and for DFB isomers are second largest while  $\Delta v_{rel}$  for HFB is smallest. That is,  $\langle \Delta E_{trans} \rangle$  for the HFB–CO<sub>2</sub> system with the largest reduced mass is smallest while  $\langle \Delta E_{trans} \rangle$  for the MFB–CO<sub>2</sub> system becomes largest and for DFB isomers–CO<sub>2</sub> systems becomes second largest in this comparison after counting the  $b_{eff}$  factor. Therefore, CO<sub>2</sub> translational velocity decreases with the increase of the reduced mass of a collision complex, as shown in equation (9). To further investigate the relationship between the reduced mass and

 $\langle \Delta E_{trans} \rangle$ , collision energy transfer experiments of trifluorobenzene isomers–, tetrafluorobenzene isomers–, and pentafluorobenzene–CO<sub>2</sub> systems are planned to be performed.

One way to simply compare the energy transfer efficiency of various donors for scattering CO<sub>2</sub> into J=58–80 is to compare the integrated scattering probability,  $P_{I}^{int}$ , defined as

$$P_{J}^{\text{int}} = k_{2}^{\text{int}} / k_{LJ} = \Sigma k_{2}^{J} / k_{LJ}, \qquad (10)$$

which corresponds to the ratio of the summation of all state-specific energy transfer rate constants for the high J tail to the Lennard-Jones collision rate constant  $(k_{LJ})$ .<sup>20, 23</sup> Note that this is only the sum of the rate constants for the J = 58–80 range of the scattered CO<sub>2</sub>; the sum of the rate constants for all J states must be close to  $k_{LJ}$  if V→RT energy transfer collision is predominant and V→V energy transfer collision is negligible in single collisions and if  $k_{LJ}$  is an accurate collision rate constant.  $k_2^{int}$  for MFB–, 12-DFB–, 13-DFB–, 14-DFB–, and HFB–CO<sub>2</sub> systems is  $31.1 \times 10^{-12}$ ,  $38.5 \times 10^{-12}$ ,  $34.0 \times 10^{-12}$ ,  $43.7 \times 10^{-12}$ , and  $64.6 \times 10^{-12}$  cm<sup>3</sup>molecule<sup>-1</sup>sec<sup>-1</sup>, respectively.  $P_J^{int}$  for MFB–, 12-DFB–, 13-DFB–, and HFB–CO<sub>2</sub> systems is obtained with  $57.9 \times 10^{-3}$ ,  $62.3 \times 10^{-3}$ ,  $55.4 \times 10^{-3}$ ,  $71.0 \times 10^{-3}$ , and  $129.1 \times 10^{-3}$  /collision, respectively. According to these values, HFB is the most efficient donor for scattering CO<sub>2</sub> into the high J tail.

The energy transfer probability distribution function, P(E,E'), is a primary measure in evaluating the total collision energy transfer efficiency as well as comparing the energy transfer results obtained from different collision systems. The main purpose of this study using experimentally obtained P(E,E') is to verify (i) how P(E,E') relates to donor physical properties in various fluorobenzene– $CO_2$  collision systems, (ii) how increasing the number of fluorine atoms influences strong energy transfer efficiency, and (iii) which vibrational modes in MFB are the most effective at transferring large amounts of energy corresponding to the large  $\Delta E$  range,  $2,000-7,000 \text{ cm}^{-1}$ . We explore comparison of the experimental P(E,E') between various collision systems to resolve these questions.

To help examine the relationship between P(E,E') and donor physical properties, Table 1-3 lists various donor physical properties (the initial energy E', the anharmonic state density at E', and the number of low frequency vibrational modes) and bi-exponential fit parameters obtained from the experimental P(E,E') for MFB-, the DFB isomer-,  $^{28}$  and HFB-CO<sub>2</sub><sup>19</sup> systems (strong and weak collision energy transfer magnitude:  $\gamma$  and  $\alpha$ , strong collision fraction:  $x_2$ , and average energy transfer amount for downward collision:  $\langle \Delta E \rangle_d$ ). Investigation of donor physical property effect on collision energy transfer can be performed by examining relationships between a variety of bi-exponential fit parameters and donor physical property parameters because the bi-exponential fit parameters can represent P(E,E') over the entire  $\Delta E$  range. For example, downward average energy transfer amount,  $\langle \Delta E \rangle_d$ , is ordered as HFB (847 cm<sup>-1</sup>) > 12-DFB  $(739 \text{ cm}^{-1}) > 14$ -DFB  $(713 \text{ cm}^{-1}) > 13$ -DFB  $(638 \text{ cm}^{-1}) > MFB (575 \text{ cm}^{-1})$ . It is interesting that this order for  $\langle \Delta E \rangle_d$  is consistent with the orders of the initial energy E', the anharmonic state density  $\rho(E')$ , and the number of low frequency vibrational modes; see Table 1-3. A trajectory calculation study of Lenzer et al.<sup>61</sup> on collisions between excited benzene or hexafluorobenzene and helium, argon, or xenon displayed that the increase of donor mass increases average energy transfer amounts,  $-\langle \Delta E \rangle$  and  $\langle \Delta E^2 \rangle^{1/2}$ . They suggested that the fluorination drops the vibrational frequencies and increases the number of low frequencies in donors, resulting in the greater average energy transfer magnitudes. Their suggestion is in good agreement with our results as can be seen in the average energy transfer amount,  $\langle \Delta E \rangle_d$ . The study of Lendvay et al.<sup>62</sup> on the SO<sub>2</sub>–Ar collision system shows that the average amount of

energy transferred,  $\langle \Delta E \rangle$ , relates to the initial energy of the donor, in particular the proximity to the dissociation threshold. They concluded that energy transfer efficiency is much higher near the dissociation threshold of donor than at low energy;  $\langle \Delta E \rangle$  increases linearly at low energies and grows quadratically near the dissociation energy of the donor. Even though  $\langle \Delta E \rangle$  measured in their study is different from  $\langle \Delta E \rangle_d$  in this study ( $\langle \Delta E \rangle$  includes upward and downward collision energy transferred, while  $\langle \Delta E \rangle_d$  does only include downward collision energy transferred), the  $\langle \Delta E \rangle_d$  pattern in this study agree with the study of Lendvay et al.<sup>62</sup> given that  $\langle \Delta E \rangle$  increases with the initial energy of the donor. That is, the donor initial energy plays a positive role in transferring energy to bath molecules. The initial anharmonic state density also shows an increasing pattern with the rise of  $\langle \Delta E \rangle_d$ . Based on these patterns, we conclude that the initial energy *E'* and the pre-collision anharmonic state density of donor molecules directly influence energy transfer efficiency in collisions with CO<sub>2</sub>.

With the other bi-exponential fit parameters ( $\gamma$ ,  $\alpha$ , and  $x_2$ ), it is hard to determine a relationship between donor physical properties due to the irregular pattern of those parameters between MFB and DFB isomers as listed in Table 1-3. To make a simple comparison of biexponential fit parameters based on only the number of donor fluorine atoms, we can use the average of bi-exponential fit parameters for three DFB–CO<sub>2</sub> systems. The average values of  $\alpha$ ,  $\gamma$ ,  $x_2$ , and  $\langle \Delta E \rangle_d$  for DFB isomers are 311 cm<sup>-1</sup>, 2106 cm<sup>-1</sup>, 0.04, and 697 cm<sup>-1</sup>, respectively. The order of weak collision energy transfer magnitude:  $\alpha$  (HFB; 620 > DFB; 311 > MFB; 299 cm<sup>-1</sup>) and strong collision fraction:  $x_2$  (HFB; 0.15 > DFB; 0.04 > MFB; 0.03) exactly have the same order as  $\langle \Delta E \rangle_d$ , initial energy, the initial state density, and the number of low frequency vibrational modes for donors. However, the magnitude of strong collision energy transfer,  $\gamma$ , does not follow this trend.  $\gamma$  for HFB is the smallest. This result seems to be the same as the pattern for  $\langle \Delta E_{trans} \rangle$  and  $\langle \Delta E_{rot} \rangle$  given that  $\langle \Delta E_{trans} \rangle$  and  $\langle \Delta E_{rot} \rangle$  are largest for MFB–CO<sub>2</sub> and smallest for HFB–CO<sub>2</sub> system. Although we are beginning to see small trends in the energy transfer parameters for these fluorobenzene donors, drawing too many mechanisms is difficult without the results of the remaining fluorobenzene donors. Results from the remainders will enable us to make additional observations related to energy transfer and molecular properties.

Using Vibrational Close-Coupling, Infinite-Order-Sudden Approximation computations (VCC-IOSA) and Classical Trajectory Calculations (CTC) of benzene-He collisions, Clary and coworkers<sup>29</sup> reported that low frequency vibrational modes with out-of-plane motion has large cross-section for vibrational relaxation in strong collisions. They suggested that low frequency modes play a significant role in supercollision energy transfer. We believe that the relationship between low frequency modes and strong collision energy transfer is due to multi-quanta relaxation via the low frequency modes during the collision. For example, if benzene is excited into highly vibrational states, a vibrational mode ( $v_{16}$ ) with low frequency (398 cm<sup>-1</sup>) and out-ofplane motion is excited to a higher quantum state (or has larger state density). For a given energy transfer amount, a low frequency mode must undergo a larger change in quantum number. In other words, the  $v_{16}$  mode in benzene is very efficient to transfer large amounts of energy to the acceptor molecule. Therefore, we expect that as a donor has more low frequency modes, the probability of strong collision energy transfer increases. In this study, the number of low frequency vibrational modes  $< 500 \text{ cm}^{-1}$  is 4, 5~6, and 13 for MFB, DFB isomers,<sup>28</sup> and HFB,<sup>19</sup> respectively. This result is in good agreement with the increasing pattern of the fraction of strong collisions ( $x_2 = 0.03$ , 0.04: averaged fraction, and 0.15 per collision for MFB, DFB isomers, and HFB, respectively). This finding is consistent with previous work in our lab,<sup>27</sup>

given that methylpyrazine with more low frequency modes (4) has the largest fraction of strong collisions in comparison with pyrazine (2), pyrimidine (2), and pyridine (2). This comparison between the strong collision fraction and the number of low frequency donor vibrational modes implies that the low frequency modes in donor governs the strong collision energy transfer. Our previous DFB isomer– $CO_2$  study<sup>28</sup> indicates that this relationship between the fraction of strong collisions and the number of low frequency vibrational modes is an over-simplification because although 14-DFB has the largest number of low vibrational modes <500 cm<sup>-1</sup> (6), its strong collision fraction (0.03/collision) is smaller than that of 12-DFB (0.06/collision) and the same as that of 13-DFB (0.03/collision). However, if only the number of fluorine atoms in the donor is concerned, using average values for DFB isomers may give us a simple comparison to better understand the relationship between the strong collision fraction and the number of low frequency with our previous studies as well as the study of Clary et al.<sup>29</sup>

The relationship between the donor anharmonic state density and P(E,E') can be found by plotting the energy dependence of P(E,E') versus the energy dependence of donor final state density. For example, the anharmonic state density in this study is  $3.01 \times 10^{23}$  for HFB at 41,822 cm<sup>-1</sup> which is greater than ~6.62×10<sup>17</sup> for the DFB isomers at ~41,000 cm<sup>-1</sup> which is in turns greater than  $1.97 \times 10^{16}$  for MFB at 40,843 cm<sup>-1</sup>. The energy dependence of the final state density, obtained from the slope of a plot of ln( $\rho(E'-\Delta E)$ ) vs.  $\Delta E$ ,<sup>22, 23, 25-28</sup> is  $6.37 \times 10^{-4}$ /cm<sup>-1</sup> for HFB,<sup>19</sup> ~5.26×10<sup>-4</sup>/cm<sup>-1</sup> for the DFB isomers,<sup>28</sup> and  $5.04 \times 10^{-4}$ /cm<sup>-1</sup> for MFB. As shown in the previous studies,<sup>21-23, 25-28</sup> Fermi's Golden Rule can be used to explain the relationship between P(E,E') and the donor state density according to

$$P(E,E') \propto \left| V_{if} \right|^2 \rho(E) \rho(E'), \tag{11}$$

where  $\rho(E')$  and  $\rho(E)$  are the density of states at the initial energy E' and the final energy E, respectively, and  $V_{ij'}$  is the matrix element,  $\langle i|H|f\rangle$ , that describes the transition between the initial and final states. Note that  $\rho(E')$  is a constant for the donor molecule. This model indicates that the shape of P(E,E') resembles the energy dependence of the donor final state density ( $\rho(E)$ ). Our previous studies have shown that the shape of P(E,E'), representing the energy dependence of P(E,E') on  $\Delta E$ , can be displayed by the reciprocal weak and strong collision magnitude:  $1/\gamma$  and  $1/\alpha$ .<sup>26–28</sup> Figure 1-7 shows that the shape of P(E,E') obtained using  $1/\gamma$  and  $1/\alpha$  mimics the energy dependence of  $\rho(E)$  for MFB, the DFB isomers, and HFB; that is, the shape of P(E,E') is linearly proportional to the energy dependence of  $\rho(E)$ . It is remarkable how accurate this relationship is especially when we consider that  $\alpha$  is obtained entirely by extrapolation of the experimentally measured energy transfer. This linearity indicates that energy transfer in these systems can be characterized by Fermi's Golden Rule.

To investigate how donor fluorination influences strong collision energy transfer efficiency, low frequency vibrational modes with < 500 cm<sup>-1</sup> for MFB,<sup>48-52</sup> 12-DFB,<sup>48,53,54</sup> 13-DFB,<sup>48,53,55</sup> 14-DFB,<sup>30,48,53,56</sup> and HFB<sup>48,57-60</sup> are assigned using Wilson notation<sup>63,64</sup> in Table 1-4 since each mode has the same motion in this assignment. Clary<sup>29,30</sup> reported that the strong collision energy transfer is governed by low frequency donor vibrational modes, which have larger energy transfer cross sections in vibrational relaxation than do high frequency modes. The fact that substituting hydrogen atom with fluorine atom decreases the frequency of local vibrational modes can be explained by a simple Hooke's law model,  $v = (1/2\pi)\sqrt{k/\mu}$ , where v is the local vibrational frequency, k is the force constant, and  $\mu$  is the reduced mass. According to the study of Clary and general knowledge of the effect of fluorine atom substitution, motions of only the low frequency modes are assigned. Low frequency modes are then considered with



Figure 1-7. Relationship between the shape of P(E,E') and the energy dependence of donor final state density. The X axis is the slope obtained from the plot of  $\ln(\rho(E'-\Delta E))$  versus  $\Delta E$  and represents the energy dependence of the state density of donor molecules on  $\Delta E$ , while the Y axis is the shape of P(E,E'), given by the reciprocal strong collision ( $\gamma$ ) and weak collision energy transfer ( $\alpha$ ) magnitudes; see Ref. 26-28. Squares and circles, shown with 10 % error bar, represent  $1/\alpha$  and  $1/\gamma$  values, respectively. The shape of the strong collision P(E,E'),  $1/\gamma$ , is linearly increasing with the energy dependence of donor final state density, while the shape of the weak collision P(E,E'),  $1/\alpha$ , is linearly decreasing with the energy dependence of donor final state density.

Mode <sup>a</sup>	MFB <sup>b</sup>	1,2-DFB <sup>c</sup>	1,3-DFB <sup>c</sup>	1,4-DFB <sup>c</sup>	HFB <sup>d</sup>
4					249 – <mark>ο</mark> , α
6a				451 – γ	264 – <mark>y</mark>
6b					264 – <mark>y</mark>
9a			330 – <mark>β</mark>		443 – <mark>β</mark>
9b		$440 - \beta$		440 <b>-</b> β	443 – <mark>β</mark>
10a		275 – <mark>ο</mark> , β	251 – <mark>ο</mark> , β		370 – <mark>ο, β</mark>
10b		198 – <mark>ο</mark> , β	230 – <mark>ο</mark> , β	375 – <mark>ο</mark> , β	370 – <mark>ο, β</mark>
11	$249^{e} - 0, \beta$			162 – <mark>ο</mark> , β	215 – <mark>ο, β</mark>
15		287 <b>-</b> β	478 – <mark>β</mark>	349 <b>-</b> β	208 – <mark>β</mark>
16a	414 – <mark>ο</mark> , α			422 – <mark>ο</mark> , α	175 – <mark>ο, α</mark>
16b	498 – <mark>ο</mark> , α	450 – <mark>ο</mark> , α	458 – <mark>ο</mark> , α		175 – <mark>ο, α</mark>
18b	$400 - \beta$				
20a					315 <b>-</b> β
20b					315 <b>-</b> β
Tot. #	4	5	5	6	13

Table 1-4. Wilson notation assignment of low frequency vibrational modes  $< 500 \text{ cm}^{-1}$  for various fluorobenzene donors.

o : out-of-plane mode

 $\alpha$  : C–C ring bending (or deformation) mode

 $\beta$ : C–F bending (wagging, boating, or twisting) mode

 $\gamma$  : C–F stretching mode

a Wilson notation expression for fundamental vibrational modes of the benzene molecule obtained from Refs. 63, and 64.

- **b** Frequencies of vibrational modes  $< 500 \text{ cm}^{-1}$  for MFB obtained from Refs. 48-52.
- c Frequencies of vibrational modes < 500 cm<sup>-1</sup> for 12-DFB, 13-DFB, and 14-DFB obtained from Refs. 28,

## 30, 48, 51, 53-56.

- d Frequencies of vibrational modes  $< 500 \text{ cm}^{-1}$  for HFB obtained from Refs. 48, 57-60.
- e The unit of all vibratoinal mode frequencies is cm<sup>-1</sup>.

P(E,E') to investigate the effect of the increase of donor fluorine atoms on strong collision energy transfer, since P(E,E') measured in the high  $\Delta E$  region (2,000–7,000 cm<sup>-1</sup>) represents strong collision energy transfer probability.

For MFB, there are four low frequency modes: two C–F bending modes (249 cm<sup>-1</sup> for  $v_{11}$ out-of-plane and 400 cm<sup>-1</sup> for  $v_{18b}$  in-plane modes) and two ring out-of-plane bending modes  $(414 \text{ cm}^{-1} \text{ for } v_{16a} \text{ and } 498 \text{ cm}^{-1} \text{ for } v_{16b})$ .<sup>49, 50, 59, 60</sup> For HFB, there are thirteen low frequency modes: eight C-F bending (five in-plane and three out-of-plane modes), three ring out-of-plane bending, and two C–F stretching modes.<sup>57-60</sup> For DFB isomers, 12-DFB and 13-DFB have five low frequency modes (two C-F in-plane bending, two out-of-plane C-F bending, and one ring out-of-plane bending modes),<sup>28, 53, 59, 60</sup> while 14-DFB has six low frequency modes (two in-plane C-F bending, two C-F out-of-plane bending, one ring out-of-plane bending, and one C-F stretching modes).<sup>28, 30, 53</sup> It is interesting that one of low frequency modes in 14-DFB ( $v_{6a}$ ) is not a bending, but a C–F stretching mode. The p-DFB–He collision study of Clary<sup>30</sup> displayed that the C–F low frequency stretching mode ( $v_{6a}$ ) in 14-DFB has the smallest cross section in vibrational relaxation, resulting in smallest rate constant, in comparison with the other five low frequency bending modes. As a result, we believe that the  $v_{6a}$  mode in 14-DFB is not effective in strong collision energy transfer processes and conclude that the effective low frequency modes on strong collision energy transfer are only five bending modes in each DFB.

From this mode analysis, we recognize two surprising points as considering with the results of the strong collision fraction,  $x_2$ , obtained from the fit of P(E,E') to a bi-exponential function: 0.15 for HFB > 0.04 for DFB > 0.03 for MFB. The first is that the low frequency vibrational modes with less than 500 cm<sup>-1</sup> are composed mainly of bending modes (wagging, boating, or twisting) except for one C–F stretching mode in 14-DFB ( $v_{6a}$ ) and two C–F stretching

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modes in HFB ( $v_{6a}$  and  $v_{6b}$ ). The second is that the number of bending type, low frequency vibrational modes increases with the number of C–F bonds in the donor. These points allow us to conclude that bending type, low frequency modes play an important role in the strong collision energy transfer and affect the strong collision fraction for P(E,E') of the high  $\Delta E$  region. Lendvay's study on CS<sub>2</sub>–CO energy transfer.<sup>31</sup> reported that large amounts of energy leak out of these low frequency, bending type modes, which have been labeled gateway modes for strong collision energy transfer. He suggested that the lower frequency bending mode has a greater efficiency in energy transfer than the higher frequency stretching mode. As agreed with the study of Lendvay, most low frequency modes in Table 1-4 include C–F bending type motions. In other words, since C–F bonds result in lower vibrational frequency than C–H and C–C bonds, when the donor is vibrationally excited to a specific energy level, low frequency bending modes with C–F bond have a greater value in the minimum vibrational quantum number  $(v_{\min} = \Delta E/hv_i)$  for transferring a given amount of vibrational energy. Therefore, the larger quantum number in C-F vibrational modes results in the larger change of state density, which affects the shape of P(E,E'); this corresponds to Fermi's Golden Rule.

Finally, the mode efficiency on strong collision P(E,E') is evaluated by comparing the fraction of molecules that have at least a certain amount of energy ( $\Delta E = \upsilon h v_i$ ) in different vibrational modes. If an energy transfer event occurs by leaking  $\Delta E$  out through lower frequency modes as suggested by Clary<sup>30</sup> and Lendvay,<sup>31</sup> the fraction of molecules with at least  $\Delta E$  in a given mode,  $f_i$ , can be a useful tool to compare the mode efficiency in energy transfer. This fraction is calculated using

$$f_{i} = G_{i} \frac{\sum_{\nu_{\min}}^{\nu_{\max}} \rho_{s-1}(E' - \nu h \nu_{i})}{\sum \rho_{s}(E')},^{27, 65}$$
(12)

where  $G_i$  is the degeneracy of the mode, and  $\rho_s(E^{*})$  and  $\rho_{s-1}(E^{*}-\omega\hbar v_i)$  are the density of states for all *s* oscillators at the energy E' and for all oscillators except for the mode of interest at an energy  $E^{*}-\omega\hbar v_i$ , respectively.  $v_i$  is the frequency of the mode and  $\upsilon$  is the vibrational quantum number of that mode.  $\upsilon_{min}$  can be obtained by  $\Delta E/\hbar v_i$ , which corresponds to the minimum vibrational quantum number needed to excite the mode of interest with a certain amount of energy,  $\Delta E$ . For  $v_{11}$ , the lowest frequency mode in MFB ( $E' = 40,843 \text{ cm}^{-1}$ ), with a frequency of 249 cm<sup>-1</sup>,  $\upsilon_{min} = \Delta E/\hbar v_i$  is 9 when  $\Delta E$  is 2,000 cm<sup>-1</sup>;  $\upsilon_{min} = 17$  and 33 for  $\Delta E = 4,000 \text{ cm}^{-1}$  and 8,000 cm<sup>-1</sup>, respectively. The maximum  $\upsilon_{max}$  is obtained by  $E'/\hbar v_i$ ;  $\upsilon_{max}$  for  $v_{11}$  in MFB is 164 in this study. Figure 1-8 shows the fractions of MFB molecules that possess low frequency modes ( $v_{11}$ ,  $v_{16a}$ ,  $v_{16b}$ , and  $v_{18b}$ ) with at least (a) 2,000 cm<sup>-1</sup>, (b) 4,000 cm<sup>-1</sup>, or (c) 8,000 cm<sup>-1</sup> for  $E' = 40,843 \text{ cm}^{-1}$ . At any value of  $\Delta E$ , the fraction for  $v_{18b}$  mirrors the trend in the high J tail of P(E,E) relative to other modes.

Based on this mode fraction analysis, we conclude that  $v_{18b}$  (C–F in-plane bending) mode of MFB plays an important role in P(E,E') shape in the high J tail ( $\Delta E = 2,000-8,000 \text{ cm}^{-1}$ ). On the other hand, the fraction for  $v_{11}$  mode relatively increases with the energy transfer amount  $\Delta E$ in comparison with the other two modes except for  $v_{18b}$ , while the fraction for  $v_{16a}$  mode decreases with  $\Delta E$  relative to the other modes. This result allows us to predict that as the amount of energy transfer from MFB increases,  $v_{11}$  (C–F out-of-plane bending) mode becomes more effective, but  $v_{16a}$  (ring out-of-plane bending) mode becomes less effective.  $v_{16b}$  (ring out ofplane bending) mode seems to be play the smallest role in the strong collision energy transfer process. This interpretation is in good agreement with our previous study on DFB isomers–CO<sub>2</sub>



Low Frequency Vibrational Mode < 500 cm<sup>-1</sup> in MFB



Low Frequency Vibrational Mode < 500 cm<sup>-1</sup> in MFB



Low Frequency Vibrational Mode < 500 cm<sup>-1</sup> in MFB

Figure 1-8. Fraction of MFB molecules that have a low frequency mode with at least  $\Delta E$  ( $\Delta E$  = (a) 2,000 cm<sup>-1</sup>, (b) 4,000 cm<sup>-1</sup>, and (c) 8,000 cm<sup>-1</sup>) when MFB molecules are given with energy E' = 40,843 cm<sup>-1</sup>. The fraction for  $v_{18b}$  mode is the highest in any  $\Delta E$  value in comparison with fractions for other low frequency modes. The fraction for  $v_{16a}$  mode decreases relative to the other two modes ( $v_{11}$  and  $v_{16a}$ ) when  $\Delta E$  increases, while the fraction for  $v_{11}$  mode increases relative to the other modes. The fraction for  $v_{16b}$  mode is the lowest in any  $\Delta E$  value.

collision systems<sup>28</sup> that the fraction for C–F bending modes ( $v_{10}$  for 12-DFB and 13-DFB, and  $v_{11}$  for 14-DFB) increase relative to yields of other excited modes with the energy transfer amount  $\Delta E$  and the fraction for ring bending modes ( $v_{16b}$  for 12-DFB and 13-DFB, and  $v_{16a}$  for 14-DFB) decrease with  $\Delta E$ ; see Figure 1-9 in Ref.<sup>28</sup> In other words, C–F bending modes strongly influence the strong collision energy transfer. Thus, we conclude that the number of fluorine atoms (C–F bonds) increases with the number of low frequency, bending modes, which plays a significant role in the shape of P(E,E') in the high J tail.

## V. Conclusion

We have performed experiments to investigate collision energy transfer between highly vibrationally excited MFB and vibrational ground level CO<sub>2</sub> to obtain state-specific kinetic information. An high-resolution (0.0003 cm<sup>-1</sup>) IR diode laser was used to measure the state-specific rotational and translational energy gain by CO<sub>2</sub> in single collisions with hot MFB. The measured state-specific CO<sub>2</sub> energy gain information was compared with the previous investigations on collisional relaxations between the DFB isomers<sup>28</sup> or HFB<sup>19</sup> and CO<sub>2</sub>. This comparison showed that rotational and translational energy gain of CO<sub>2</sub> decreases with an increase in the number of fluorine atoms in the fluorobenzene donors. Collisional energy transfer rate constants and scattering probabilities were calculated using state-specific energy transfer information, then, the energy transfer probability distribution function, P(E,E'), was obtained by rearranging the scattering probabilities for individual rotational states to the probability of a certain amount of energy transfer,  $\Delta E$ . P(E,E') for various fluorobenzene–CO<sub>2</sub> collision systems was compared to understand the relationship between P(E,E') and the physical

properties of donors. Comparison of P(E,E') shows that the shape of P(E,E') are proportional to the initial energy, the anharmonic vibrational state density, the number of low frequency modes < 500 cm<sup>-1</sup>, and the number of fluorine atoms for fluorobenzene donors. To test the correlation between P(E,E'), state density, and the number of low frequency modes, previous studies were reviewed and compared with this present study; low frequency modes in donors have larger vibrational relaxation cross sections and affect the shape and magnitude of strong collision P(E,E').<sup>30,31</sup> In addition, to study the effect of the number of fluorine atoms on P(E,E'), low frequency donor vibrational modes were assigned by characteristic motion using Wilson notation.<sup>63,64</sup> Since most low frequency modes in fluorobenzene donors contain C–F bending modes, it can imply that the fluorination of donor molecules essentially affects P(E,E') in the large energy transfer region. Finally, the calculation of mode fraction with a specific energy amount  $\Delta E$  gives insight into which vibrational mode plays an important role in strong collision energy transfer. We noticed that the low frequency C–F bending motion modes ( $v_{18b}$  and  $v_{11}$  in MFB) are primarily responsible for strong collision energy transfer.

This study provides a benchmark to be compared with further studies of additional fluorinated donor– $CO_2$  systems. The studies on single collisions of trifluorobenzene isomers, tetrafluorobenzene isomers, and pentafluorobenzene with  $CO_2$  will be performed to complete the investigation of donor fluorination effect on strong collisional energy transfer.

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# Chapter 2

Super-collision Energy Transfer Study in Fluorobenzene–CO<sub>2</sub> Systems using a High-Resolution (0.0003 cm<sup>-1</sup>) IR Diode Laser: Excess Excitation Energy Dependence of Super-collision Energy Transfer

## **I. Introduction**

Collisions between highly vibrationally excited benzene-like donors and small bath molecules at room temperature have been studied for many years to understand the nature of collision energy transfer events. Flynn and coworkers<sup>1-5</sup> developed a high-resolution (0.0003 cm<sup>-1</sup>) bath-probing technique to obtain state-specific bath energy gain information in single collision energy transfer events that Mullin and coworkers,<sup>6-22</sup> and our group<sup>23-28</sup> have used to study the dynamics of collision energy transfer. The strength of this probing technique is that it provides state-specific vibrational, rotational, and translational energy gain information of bath molecules in single collisions with highly excited donors. State-resolved data can be resorted to obtain the energy transfer probability distribution function, P(E,E'). In addition, we can measure average energy gain for bath molecules allowing us to compare with the results of donor energy loss measurement studies.

Fluorinated benzenes ( $C_6H_{6-n}F_n$ ) have been studied to elucidate how the fluorination of molecules affects properties such as absorption, emission, photodissociation, and so on. For example, UV absorption spectroscopy<sup>29, 30</sup> and photochemistry<sup>31, 32</sup> studies have been performed for fluorobenzenes and found that  $C_6H_{6-n}F_n$  with n=1–4 have a different spectroscopic absorption pattern than  $C_6H_{6-n}F_n$  with n=5–6. Absorption spectra for  $C_6H_{6-n}F_n$  with n=1–4 are composed of many sharp peaks for  $S_1 \leftarrow S_0$  absorption at ~5 eV, while  $C_6H_{6-n}F_n$  with n=5–6 have smooth structureless absorption spectra. The study of Zgierski et al.<sup>33</sup> on fluorinated benzenes using jet-cooled fluorescence spectroscopy and time-dependent density function theory calculations found that pentafluorobenzene (PFB) and hexafluorobenzene (HFB) have small fluorescence yields and short fluorescence lifetimes, while  $C_6H_{6-n}F_n$  with n=1–4 have strong fluorescence and high fluorescence yields. They suggested that the weak fluorescence for PFB and HFB results from

 $S_1(\sigma^*) \rightarrow S_0(\pi)$  emission while the strong fluorescence for fluorobenzenes with 1–4 fluorine atoms is due to  $S_1(\pi^*) \rightarrow S_0(\pi)$  emission; electron promotion from  $\pi$  to  $\sigma^*$  results from the electronegativity of C–F bond orbitals, while promotion from  $\pi$  to  $\pi^*$  is related to the benzene ring orbitals. That is, they concluded that absorption and emission are strongly dependent on the number of fluorine atoms. Present work shows that super-collision energy transfer efficiency for fluorobenzenes has the same pattern as fluorobenzene spectroscopic features. Based on this result, we discuss how the excited electronic state is related to collisional energy transfer events using experimentally measured P(E,E').

The energy transfer probability distribution function, P(E,E'), represents the probability that a molecule with initial energy E' undergoes a collision process with a bath molecule and ends up with the final energy  $E (= E' - \Delta E)$  after transferring an amount of energy  $\Delta E$  to the bath molecule. P(E,E') measured using the state-specific energy gain information is fit to a biexponential function for simple comparison with other collision systems. The fit parameters of P(E,E') curves can describe both weak and strong collision energy transfer. Our previous studies on pyrimidine,<sup>23</sup> pyridine,<sup>24</sup> the di-fluorobenzene (DFB) isomers,<sup>25</sup> and monofluorobenzene (MFB)<sup>26</sup> with CO<sub>2</sub> showed that the fit parameters ( $1/\gamma$  and  $1/\alpha$ ), which represent the shape of P(E,E') and are defined as the energy dependence of P(E,E'), are linearly proportional to the energy dependence of donor state density. The fit parameters, in this work, are also used to compare super-collision energy transfer efficiency between various fluorobenzene–CO<sub>2</sub> collision systems. From this comparison, we verify that super-collision energy transfer efficiency correlates with donor state density at the initial energy  $E'(\rho(E'))$  through the shape of P(E,E').

This study is aimed at investigating excess excitation energy dependence of supercollision energy transfer as well as donor fluorination effect on collision energy transfer

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efficiency as a continued study of our previous MFB study.<sup>26</sup> Here we present out study of collisional energy transfer between excited PFB and CO<sub>2</sub> and compare with previous studies of collisional relaxation of other fluorobenzene molecules with CO<sub>2</sub> to investigate how fluorination of aromatic molecules influences energy transfer in single collisions with CO<sub>2</sub>. In particular we are interested in how the substitution of fluorine atoms for hydrogen atoms affects the energy transfer probability distribution function, P(E,E'). Our previous studies are in good agreement with the computational studies of Clary et al.<sup>34</sup> and Lendvay<sup>35</sup> suggesting that bending motion modes with low frequency strongly influence collisional energy transfer efficiency. In a continuation of previous studies, we analyze the vibrational mode assignment for all fluorobenzene donors and verify our previous observation that the number of donor fluorine atoms is proportional to the number of bending modes with low frequency. Furthermore, the relationship between excess excitation energy and super-collision energy transfer efficiency for the fluorobenzenes is discussed.

### **II. Experimental**

The experiments presented here to collect data for single collisions between highly vibrationally excited PFB and vibrational ground state CO<sub>2</sub> at 300 K have been described in detail in previous studies;<sup>23-26</sup> therefore, only a brief description is presented here. A 1:1 20.0 mTorr mixture of gas phase PFB and CO<sub>2</sub> flows through a 300 cm collision cell at 300 K. 248 nm UV light generated from a KrF excimer laser (Lamda Physik Complex 201) at a rate of 1 Hz is propagated into the collision cell to excite PFB molecules via the S<sub>1</sub> $\leftarrow$ S<sub>0</sub> electronic transition, S<sub>1</sub>(1B<sub>2u</sub>:  $\pi^*$  with partial  $\sigma^*$ )  $\leftarrow$  S<sub>0</sub>(XA<sub>1g</sub>:  $\pi$ ).<sup>30, 33, 36</sup> Rapid radiationless internal conversion into the vibrationally excited states of the electronic ground level, S<sub>1</sub> $\rightarrow$ S<sub>0</sub>\*, follows the UV excitation

of PFB. UV power density was maintained at  $\sim 40 \text{ mJ/cm}^2$  to ensure single photon absorption. A tunable CW IR diode laser (Laser Components) ( $\Delta \nu = 0.0003 \text{ cm}^{-1}$  and  $\lambda = -4.3 \mu \text{m}$ ), passed through the cell collinearly with the UV beam, was used to probe the rovibrational transition  $(00^{0}1 \leftarrow 00^{0}0)$  of CO<sub>2</sub> rotationally and translationally excited by single collisions with hot PFB. The IR beam is then directed into a single grating monochromator (Acton Research Corporation, SpectraPro 500i) to select a single laser mode and focused onto a liquid-nitrogen-cooled (77 K) InSb diode detector (Judson Technologies). The response time of the detector and a preamplifier (Perry Amplifer, 100 ns rise time) is ~400 ns, shorter than 1 µs when IR transient absorption signals of post-collision  $CO_2$  are measured. This early time ensures that we are measuring results for single collision events given that the mean gas kinetic collision time at 20 mTorr gas pressure and 300 K is ~4  $\mu$ s.<sup>38</sup> Signals converted from the detector are amplified and recorded on a digital oscilloscope (LeCroy LT364, 500 MHz) via two channels (AC and DC). The IR transient absorption signals we collect at 1  $\mu$ s after UV excitation are obtained from the ratio of AC (=  $\Delta I$ ) to DC (=  $I_0$ - $\Delta I$ ) signals,  $\Delta I/(I_0-\Delta I)$ . The measured IR transient absorption signal at early time  $(1 \mu s)$  is used to calculate the post-collision number density; the IR absorption signal corresponds to  $\Delta I/I_0$  (=1-exp( $-\alpha \rho l$ )), where  $\alpha$  is the absorption coefficient,  $\rho$ is the density of the probed molecule, and *l* is the collision cell length. This dual-channel method is also useful to stabilize short-term drifts in overall IR light intensity  $(I_0)$ .<sup>3</sup> Transient absorption signals are averaged over ~100 UV pulses with the oscilloscope and transferred to a computer for further analysis.

About 4 % of the IR diode laser light is directed into a 100 cm reference cell. This reference beam passes through a second monochromator and is focused onto a second liquidnitrogen-cooled (77 K) InSb detector. The reference signal from the second detector is sent to a lock-in amplifier (Standard Research Systems) to correct for long-term drifts of the IR diode laser frequency by locking the laser frequency to the rovibrational transition center peak of the scattered CO<sub>2</sub>, while the transient absorption signal is being measured.

The population of  $CO_2$  scattered by single collisions with PFB is determined using the transient absorption signal and a Doppler-broadened linewidth of each final rotational state of the scattered  $CO_2$ . The Doppler-broadened full width at half maximum (FWHM) is obtained by locking the IR diode laser frequency to a fringe of a scanning Fabry-Perot etalon (Laser Components, free spectral range=289 MHz) in place of the reference cell and measuring transient absorption signals at 40 frequencies evenly distributed over the center of the probed  $CO_2$  rovibrational transition. Each measured absorption signal at the 40 frequencies is also averaged for 100 UV pulses.

Divergence of UV laser light over the 300 cm collision cell produces errors in the measured energy transfer rate constants. Two methods to calibrate for the UV divergence have been discussed in previous studies;<sup>23, 26</sup> the ratio of scattering results obtained from present PFB–CO<sub>2</sub> and pyrazine–CO<sub>2</sub> experiments to the previously published pyrazine–CO<sub>2</sub> scattering<sup>3</sup> values under the same conditions is applied as a scaling factor to calculate absolute energy transfer rate constants for the present PFB–CO<sub>2</sub> system.

Pentafluorobenzene (Aldrich, 99+ % purity) and pyrazine (Aldrich, 99+ % purity) were purified using 3 freeze-pump-thaw cycles prior to use, while  $CO_2$  gas (Intermountain Airgas Inc., 99.999+ % purity) was used without any purification.

## **III. Results and Discussion**

## A. IR transient absorption signal of scattered $CO_2$ (00<sup>0</sup>0;J = 58–80)

The number density of post-collision CO<sub>2</sub> excited into  $00^{0}0$ ; J = 58–80 states by collisions with highly vibrationally excited PFB was obtained from IR transient absorption signals measured at 1 µs following UV excitation of PFB at 248 nm. Frequency of the measured IR transient absorption signals corresponds to the center frequency of ro-vibrational ( $00^{0}1$ ;J-1  $\leftarrow$  $00^{0}$ , 00, 1) transitions for CO<sub>2</sub>. Figure 2-1 displays IR fractional transient absorption signals ( $\Delta I/I_{0}$ ) for post-collision CO<sub>2</sub> transitions of  $00^{0}1$ ; J-1  $\leftarrow 00^{0}0$ ; J = 58–80, which result from the mathematical re-expression of raw IR transient absorption signals,  $\Delta I/(I_0 - \Delta I)$ . The absorption measurement at 1  $\mu$ s after a UV excitation pulse provides information regarding the rotational population increase of CO<sub>2</sub> ( $00^{0}0$ ; J = 58–80) scattered by single collisions with excited PFB. The fractional IR absorption signals in early time, as shown in Figure 2-1, become larger for lower J state. This indicates that CO<sub>2</sub> molecules are more likely scattered into lower J states in single collisions with hot PFB. Doppler-broadened full widths at half maximum (FWHM) were measured for each transition of the high J states and used with IR transient absorption signals to calculate the number density of post-collision CO<sub>2</sub> using absorption line strengths for CO<sub>2</sub> from the HITRAN database.<sup>37</sup>

#### B. Rotational and translational energy gain of CO<sub>2</sub> by single collisions with hot PFB

Nascent rotational distributions of CO<sub>2</sub> ( $00^{0}0$ ) scattered from single collisions with excited PFB were measured for the J=58–80 states using the measured fractional IR transition absorption signals at early time (1  $\mu$ s). Figure 2-2 shows a Boltzmann plot of the nascent



Figure 2-1. Fractional IR transient absorption signals for the CO<sub>2</sub> rovibrational transitions of  $(00^{0}1;J-1) \leftarrow (00^{0}0;J = 58-80)$  as a function of time after a 248 nm UV pulse. The linearity of fractional IR absorption in early time (< 1  $\mu$ s) indicates that population increase of CO<sub>2</sub> at this time results from single collisions between CO<sub>2</sub> and highly vibrationally excited PFB.



Rotational Energy for Scattered CQ,  $E_{rot} = BJ(J+1)$  (cm<sup>-1</sup>)

Figure 2-2. Boltzmann plot of the nascent rotational distribution for the scattered CO<sub>2</sub> at  $00^{0}0$ ; J = 58–80 in collisions with highly vibrationally excited PFB, obtained from fractional IR absorption signals at 1  $\mu$ s following UV excitation of PFB. Squares are the experimentally measured nascent density of the scattered CO<sub>2</sub>. The solid line is the best linear least squares fit line obtained from the plot of  $\ln(N_J/(2J+1))$  versus a function of post-collision CO<sub>2</sub> rotational energy ( $E_{rot} = BJ(J+1)$ ). The slope corresponds to  $-1/k_BT_{rot}$  with  $T_{rot}$  of 860 ± 70 K for CO<sub>2</sub> scattered from a single collision with hot PFB.

rotational distribution for J=58–80 of CO<sub>2</sub> (00<sup>0</sup>0) scattered by single collisions with excited PFB. A single rotational temperature,  $T_{rot} = 860 \pm 70$  K, representing the rotational distribution of postcollision CO<sub>2</sub> (00<sup>0</sup>0;J=58–80) in collisions with hot PFB, was obtained from the slope of the Boltzmann plot as shown in Figure 2-2. As discussed elsewhere,<sup>26</sup> the post-collision rotational temperature represents the average rotational energy of scattered CO<sub>2</sub> in collisions with vibrationally excited donors. Therefore, the average rotational energy gain of CO<sub>2</sub> can be determined according to  $\langle \Delta E_{rot} \rangle = \langle E_{rot} \rangle_f - \langle E_{rot} \rangle_i$ , where  $\langle \Delta E_{rot} \rangle$  is the average rotational energy gain of CO<sub>2</sub> and  $\langle E_{rot} \rangle_f$  and  $\langle E_{rot} \rangle_i$  are the average rotational energy of the scattered and the initial CO<sub>2</sub>, respectively.  $\langle E_{rot} \rangle_f$  is calculated from the post-collision rotational temperature of the scattered CO<sub>2</sub> ( $\langle E_{rot} \rangle_f = k_B T_{rot}$ ) and  $\langle E_{rot} \rangle_i \approx 209$  cm<sup>-1</sup> prior to collisions was obtained from  $k_B T_{cell}$ , where  $k_B$  is the Boltzmann constant and  $T_{cell} = 300$  K.

The average rotational energy gain of CO<sub>2</sub> in collisions with various excited fluorobenzene donors are listed in Table 2-1, along with  $T_{rot}$  and  $\langle E_{rot} \rangle_f$ . Figure 2-3 displays a plot of  $\langle \Delta E_{rot} \rangle$  as a function of the fluorine-atom number in fluorobenzene donors. Note that the rotational temperatures of CO<sub>2</sub> in collisions with DFB isomers,<sup>25</sup> tri-fluorobenzene isomers,<sup>27</sup> and tetra-fluorobenzene isomers<sup>28</sup> are the average value for the isomers with the same number of fluorine atoms. It is worth noting that as the number of fluorine atoms in the fluorobenzene donors increases, the average rotational energy gain of CO<sub>2</sub> decreases, as seen in Figure 2-3. The decrease of  $\langle \Delta E_{rot} \rangle$  with increasing fluorine-atom number may result from the number of low frequency modes. Our previous MFB–CO<sub>2</sub> study<sup>26</sup> explored the relationship between the average CO<sub>2</sub> rotational energy gain and the number of donor fluorine atoms by comparing results of MFB–, DFB isomer–,<sup>25</sup> and HFB–CO<sub>2</sub><sup>4</sup> collision energy transfer and suggested that the

Table 2-1. Rotational temperature  $(T_{rot})$ ,<sup>a</sup> average final rotational energy  $(\langle E_{rot} \rangle_f)$ ,<sup>b</sup> and average rotational energy gain  $(\langle \Delta E_{rot} \rangle)$ <sup>c</sup> of CO<sub>2</sub> scattered into 00<sup>0</sup>0;J = 58–80 by single collisions with various excited fluorobenzene donors with energy E' (= ~41,000 cm<sup>-1</sup>).

Donor	$T_{rot}^{a}$ (K)	$\left\langle E_{rot} \right\rangle_f^{\rm b} (\rm cm^{-1})$	$\left<\Delta E_{rot}\right>^{c}$ (cm <sup>-1</sup> )	
MFB <sup>d</sup>	$1030 \pm 60$	716	509	
12-DFB <sup>d</sup>	$930\pm80$	646	439	
13-DFB <sup>d</sup>	$970\pm80$	674	467	
14-DFB <sup>d</sup>	$1020\pm80$	709	502	
123-TFB <sup>d</sup>	$950 \pm 40$	661	446	
124-TFB <sup>d</sup>	$920 \pm 90$	640	431	
135-TFB <sup>d</sup>	$910 \pm 100$	633	428	
1234-TFB <sup>d</sup>	$940 \pm 110$	654	446	
1235-TFB <sup>d</sup>	$920\pm70$	640	432	
1245-TFB <sup>d</sup>	$870 \pm 110$	605	400	
PFB	$860\pm70$	598	388	
HFB <sup>d</sup>	795	553	345	

a Rotational temperature of CO<sub>2</sub> scattered into 00<sup>0</sup>0;J = 58–80 states in single collisions with various excited fluorobenzene donors, obtained from a Boltzmann distribution plot of ln(N<sub>J</sub>/(2J+1)) as a function of state-specific rotational energy,  $E_{rot} = BJ(J+1)$ , where  $B (= 0.394 \text{ cm}^{-1})$  is the rotational constant of CO<sub>2</sub> and J is the final rotational state of CO<sub>2</sub> scattered by collisions with excited fluorobenzene donors. b Average final rotational energy of CO<sub>2</sub> scattered by collisions with excited fluorobenzene donors, determined using  $\langle E_{rot} \rangle_f = k_B T_{rot}$ , where  $k_B$  is the Boltzmann constant. c Average rotational energy gain of post-collision CO<sub>2</sub> in collisions with excited fluorobenzene donors,

determined from  $\langle \Delta E_{rot} \rangle = \langle E_{rot} \rangle_f - \langle E_{rot} \rangle_i$ .  $\langle E_{rot} \rangle_i$  is average initial rotational energy of CO<sub>2</sub> obtained from  $k_B T_{cell}$  ( $\approx 209 \text{ cm}^{-1}$ ), where  $T_{cell}$  is the collision cell temperature (= 300 K).

d Data for MFB, DFB isomers, Tri-FB isomers, Tetra-FB isomers, and HFB are obtained from Refs. 26, 25, 27, 28, and 4, respectively.



# of Fluorine Atoms in Fluorobenzene Donors

Figure 2-3. Average rotational energy gain,  $\langle \Delta E_{rot} \rangle$ , of the scattered CO<sub>2</sub> in collisions with a variety of vibrationally excited fluorobenzene donors.  $\langle \Delta E_{rot} \rangle$  is calculated from  $\langle \Delta E_{rot} \rangle = \langle E_{rot} \rangle_f - \langle E_{rot} \rangle_i$ , where  $\langle E_{rot} \rangle_f$  and  $\langle E_{rot} \rangle_i$  are average rotational energy of the scattered and the initial CO<sub>2</sub>, respectively. The values of  $\langle \Delta E_{rot} \rangle$  for all fluorobenzene–CO<sub>2</sub> collisions are listed in Table 2-1 and shown here with 10 % error bar. For DFB, Tri-FB, and Tetra-FB isomers,  $\langle \Delta E_{rot} \rangle$  is averaged for each isomer group.  $\langle \Delta E_{rot} \rangle$  decreases with the increase of fluorine-atom number in fluorobenzene donors.

increase of fluorine-atom number results in an increase of low frequency modes, which decreases average  $CO_2$  rotational energy gain, but increases strong collision fraction. In this study, we compare energy gain results for all fluorobenzenev $CO_2$  collision systems versus the fluorineatom number of the donor. The donor fluorination effect on the average  $CO_2$  energy gain change is discussed in detail in section **D**, along with bi-exponential parameters obtained from the energy transfer probability distribution function, P(E,E').

The moment of inertia for a donor-bath complex can be considered as a factor that affects the average rotational energy gain according to the number of donor fluorine atoms. When an excited donor collides with  $CO_2$ , a certain amount of vibrational energy in the donor is imparted into the rotational states of CO<sub>2</sub>. During the moment of the energy conversion from vibration to rotation, the moment of inertia of the donor- $CO_2$  complex is governed by the reduced mass of the complex. That is, the moment of inertia of the complex may affect the rotation of the recoiled  $CO_2$  after the complex splits because the moment of inertia is a main component determining rotational energy. Therefore, average rotational energy gain of CO<sub>2</sub> from vibrationally excited donors may decrease according to the increase of the reduced mass between donors and  $CO_2$ . Alternatively, based on classical collision thought we believe that the match between donor mass and acceptor mass enhances energy transfer. For example, on plane of a billiard one ball transfers most energy into the other ball with similar mass when they collide. In this study, the increase of donor fluorine atoms results in more non-matching of the masses of donor and bath. As a result, the increase of donor fluorine atoms decreases the energy gain of CO<sub>2</sub> in collisions with donors. This suggestion is in good agreement with the results obtained from the study of Park et al.<sup>12</sup> on the methylation effects on donor quenching in collisions with CO<sub>2</sub>. Their results show that as methyl groups are added to pyridine, the average rotational energy gain of CO<sub>2</sub> decreases;  $\langle \Delta E_{rot} \rangle$  of CO<sub>2</sub> for pyrazine, pyridine, 2-methylpyridine, and 2,6-dimethylpyridine are 606, 373, 221, and 160 cm<sup>-1</sup>, respectively.

Doppler broadened linewidths for CO<sub>2</sub> rovibrational transitions ( $00^{0}1$ ;J-1  $\leftarrow 00^{0}0$ ;J), due to collisions with vibrationally excited PFB, were measured for J = 58–80 to obtain state-specific

translational energy gain of CO<sub>2</sub>. The measured linewidths for each J state can be converted to lab-frame translational temperature,  $T_{trans}$ , for the scattered CO<sub>2</sub> using the relationship

$$T_{trans} = \frac{mc^2}{8k_B \ln 2} \left(\frac{\Delta v_{obs}}{v_0}\right)^2,\tag{1}$$

where *m* is the mass of CO<sub>2</sub>, *c* is the speed of light,  $k_B$  is the Boltzmann constant,  $\Delta v_{obs}$  is the full width at half maximum for the final CO<sub>2</sub> measured by fitting a set of transient absorption signals near the center peak to a Gaussian function, and  $v_0$  is the center frequency of the absorption line. Figure 2-4 displays the transient absorption signals distributed over the center of the absorption line fit to a Gaussian function, along with a lab-frame translational temperature,  $T_{trans}$ , for CO<sub>2</sub> scattered into J = 70 ( $\Delta v_{obs}$  = 0.0079 ± 0.0007 cm<sup>-1</sup>:  $T_{trans}$  = 1020 ± 210 K). For comparison, the CO<sub>2</sub> linewidth at 300 K corresponds to  $\Delta v_{obs}$  = 0.0042 cm<sup>-1</sup>. Measured Doppler-broadened full widths at half maximum ( $\Delta v_{obs}$ ) for the ro-vibrational transitions of CO<sub>2</sub> scattered into J=58–80 are listed in Table 2-2, along with equivalent lab-frame translational temperatures, center-ofmass translational temperatures ( $T_{trans}^{COM}$ ), and the amount of J-specific translational energy gain ( $\Delta E_{trans}^J$ ).  $T_{trans}^{COM}$  is used to calculate  $\Delta E_{trans}^J$  for CO<sub>2</sub> following collisions with vibrationally hot PFB and is obtained by

$$T_{trans}^{COM} = T_{trans} \left( 1 + m_{CO_2} / m_{PFB} \right) - T_{cell} \left( m_{CO_2} / m_{PFB} \right), \tag{2}$$

where  $m_{CO_2}$  and  $m_{PFB}$  are the mass of CO<sub>2</sub> and PFB, respectively.  $\Delta E_{trans}^J$  is calculated from  $\Delta E_{trans}^J = 3/2 \times k_B (T_{trans}^{COM} - T_{cell})$  and employed to calculate average CO<sub>2</sub> translational energy gain. In general,  $\Delta v_{obs}$ ,  $T_{trans}$ ,  $T_{trans}^{COM}$ , and  $\Delta E_{trans}^J$  increase with the final CO<sub>2</sub> J state; although J = 62 is off from the trend in this results, the trend works within experimental error. This trend is in good agreement with  $\Delta L = (h/2\pi)\Delta J = \mu\Delta v_{rel} \langle b_{eff} \rangle$ ,<sup>2</sup> which describes the relationship between the



Relative Frequency to the Center Frequency (cm)

Figure 2-4. Doppler-broadened line profile for the ro-vibrational absorption transition ((00<sup>0</sup>1;J=69)  $\leftarrow$  (00<sup>0</sup>0;J=70)) of scattered CO<sub>2</sub>, obtained from fitting fractional IR absorption signals distributed over the center frequency of the absorption line to a Gaussian function. Fractional IR absorption signals (circles) were collected over approximately 100 shots at 1  $\mu$ s following a UV pulse and then averaged. The solid line is the best non-linear least squares fit to a Gaussian function. The full width at half maximum ( $\Delta v_{obs}$ ) obtained from this fit is 0.0079 ± 0.0007 cm<sup>-1</sup> corresponding to a lab-frame translational temperature,  $T_{trans}$ , of 1020 ± 210 K. The dashed line represents  $\Delta v_{obs} = 0.0042$  cm<sup>-1</sup> at 300 K for comparison.

Table 2-2. Full width at half maximum (FWHM) for Doppler-broadened line shapes ( $\Delta v_{obs}$ ), <sup>a</sup> lab-frame translational temperature ( $T_{trans}^{COM}$ ), <sup>c</sup> and translational energy gain ( $\Delta E_{trans}^{J}$ )<sup>d</sup> for the final CO<sub>2</sub> (00<sup>0</sup>0;J = 58–80) following single collisions with vibrationally excited PFB (E'= 41,611 cm<sup>-1</sup>).

$CO_2 (00^0 0)$	Η	$\operatorname{PFB}^{E} + \operatorname{CO}_2(00^00) \to \operatorname{F}$	$PFB^{E-\Delta E} + CO_2 (00^0 0; J)$	
J <sub>final</sub> state	$\Delta v_{obs}^{a}$ (cm <sup>-1</sup> )	$T_{trans}^{b}(\mathbf{K})$	$T_{trans}^{COM c}$ (K)	$\Delta E_{trans}^{J  \mathbf{d}}  (\mathrm{cm}^{-1})$
58	$0.0071 \pm 0.0006$	820 ± 100	960 ± 120	690
62	$0.0063 \pm 0.0006$	$660 \pm 80$	$760 \pm 100$	480
70	$0.0079 \pm 0.0006$	$1020\pm100$	$1210\pm120$	950
76	$0.0085 \pm 0.0006$	$1200\pm110$	$1430\pm140$	1180
80	$0.0098 \pm 0.0006$	$1610\pm120$	$2000\pm160$	1720

a Full width at half maximum (FWHM) for a Doppler-broadened line shape, measured by fitting IR absorption signals for the transition of  $CO_2(00^01;J-1) \leftarrow CO_2(00^00;J)$  at 1  $\mu$ s following 248 nm UV excitation of PFB to a Gaussian function. IR absorption signals, distributed evenly near the center frequency of the absorption, were collected and averaged over 100 shots. For comparison, the Dopplerbroadened full width at half maximum for  $CO_2$  at 300 K is 0.0042 cm<sup>-1</sup>.

b Lab-frame translational temperatures determined using Equation (1).

c Center-of-mass translational temperatures determined according to Equation (2).

d State-specific translational energy gain of the scattered CO<sub>2</sub> calculated from the formula

$$\Delta E_{trans}^{J} = 3/2 \times k_{B} (T_{trans}^{COM} - T_{cell}).$$

recoil velocity change and the total angular momentum change in collisional energy transfer. In this relationship,  $\Delta L$  is the change of total angular momentum,  $\Delta J$  is the change of rotational quantum number,  $\Delta v_{rel}$  is the change of relative velocity between pre- and post-collisions in donor-bath center of mass coordinates, *h* is Plank's constant,  $\mu$  is the reduced mass of donor and bath, and  $\langle b_{eff} \rangle$  is the average effective impact parameter for collisions that populate in J = 58-80. That is to say, as  $\Delta J$  increases,  $\Delta v_{rel}$  increases, which is observed as an increase in  $\Delta v_{obs}$ ,  $T_{wans}^{COM}$ , and  $\Delta E_{trans}^{J}$  as shown in Table 2-2.

## C. State-resolved energy transfer rate constants and scattering probabilities

The collisional energy transfer reaction between vibrationally excited PFB and CO<sub>2</sub> is represented by

$$PFB^{E'} + CO_2 \xrightarrow{k_2^J} PFB^{E' - \Delta E} + CO_2(00^00; J = 58 - 80, V).$$

$$\tag{3}$$

In this reaction, E' and  $\Delta E$  are the initial donor energy following 248 nm UV absorption and the amount of energy transferred to CO<sub>2</sub> in the collision, respectively. *J* is the final CO<sub>2</sub> rotational state, *V* is the final recoil velocity of CO<sub>2</sub>, and  $k_2^J$  is the state-resolved energy transfer rate constant. The state-resolved energy transfer rate constant can be calculated using

$$k_{2}^{J} = \frac{[CO_{2}(00^{0}0; J = 58 - 80, V)]_{t}}{[CO_{2}]_{0}[PFB^{E'}]_{0}t},$$
(4)

where  $[CO_2(00^00; J = 58 - 80, V)]_t$  is the state-specific CO<sub>2</sub> density at 1  $\mu$ s (*t*) following a UV laser pulse,  $[CO_2]_0$  is the initial bulk CO<sub>2</sub> number density, and  $[PFB^{E'}]_0$  is the concentration of vibrationally excited PFB molecules with the energy *E'* prior to the collision, determined by the number of absorbed UV photons.  $[CO_2(00^00; J, V)]_t$  is determined from the fractional IR

transient signal at 1  $\mu$ s (*t*) following a UV laser pulse. Energy transfer rate constants,  $k_2^J$ , have been calculated assuming that collisions between CO<sub>2</sub> (00<sup>0</sup>0) and PFB<sup>E'</sup> are the dominant event at early times. Other processes including diffusion of CO<sub>2</sub> out of the IR laser probe beam axis, self-quenching of vibrationally excited donors, and other collisions processes are negligible under these experimental conditions.<sup>38</sup> The linearity of the early-time IR transient signals further confirms that the effect of these other events can be neglected.<sup>2, 6, 38</sup> State-specific energy transfer rate constants,  $k_2^J$ , for single collisions between vibrationally excited PFB (E' = 41,611cm<sup>-1</sup>) and CO<sub>2</sub> at 300 K are listed in Table 2-3. Figure 2-5 displays  $k_2^J$  values for various fluorobenzene–CO<sub>2</sub> collision systems as a function of the final CO<sub>2</sub> rotational state to explore the dependence of  $k_2^J$  on donor fluorination. Note that in this study  $k_2^J$  values were obtained from the fractional IR transient absorption signals at early times using Equation (4) as described above. As can be seen in Figure 2-5, the increase in donor fluorination leads to larger  $k_2^J$  values with the exception of 135-TFB, which has the smallest  $k_2^J$  values. The exception of 135-TFB will be discussed later.

State-specific scattering probabilities for collisions between PFB<sup>*E*</sup> and CO<sub>2</sub> are obtained from the ratio of the state-specific absolute energy transfer rate constant to the Lennard-Jones rate constant,  $P_J = k_2^J/k_{LJ}$ , and are listed in Table 2-3. The Lennard-Jones collision rate constant,  $k_{LJ}$ , rather than the hard sphere collision rate constant,  $k_{HD}$ , was used in calculating scattering probabilities to compare with all previously obtained data using this technique.  $k_{LJ}$  for collisions between PFB<sup>*E*</sup> and CO<sub>2</sub> at 300 K is  $5.37 \times 10^{-10}$  cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup>. Scattering probabilities can be used to determine the average amount of translational energy gain of all collisions that excite CO<sub>2</sub> into the J = 58–80 range according to

Table 2-3. State-resolved energy transfer rate constants  $(k_2^J)^a$  and scattering probabilities  $(P_J)^b$  for the process of PFB<sup>*E*</sup> + CO<sub>2</sub>(00<sup>0</sup>0)  $\rightarrow$  PFB<sup>*E*-\Delta *E*</sup> + CO<sub>2</sub>(00<sup>0</sup>0;J,V).

$CO_2 (00^0 0)$	$PFB^{E} + CO_2(00^00) \rightarrow PFB^{E \cdot \Delta E} + CO_2(00^00; J, V)$		
J <sub>final</sub> state	$k_2^{Ja}$ (10 <sup>-12</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$P_{J}^{b}(10^{-3})$	
58	$10.4 \pm 1.1$	$20.5\pm2.2$	
62	$6.5\pm0.7$	$12.9\pm1.4$	
66	$5.2\pm0.6$	$10.3 \pm 1.1$	
70	$3.9 \pm 0.5$	$7.7 \pm 0.9$	
76	$2.3 \pm 0.3$	$4.5\pm0.6$	
80	$1.8\pm0.2$	$3.6 \pm 0.4$	
$k_2^{\text{intc}}$ (10 <sup>-12</sup> cm <sup>3</sup> molecules <sup>-1</sup> s <sup>-1</sup> )	56.9		

a State-resolved energy transfer rate constant,  $k_2^J$ , obtained according to Equation (3).

b Scattering probability obtained by  $P_J = k_2^J / k_{LJ}$ .  $k_{LJ}$  is the Lennard-Jones gas kinetic collision rate constant defined as  $k_{LJ} = \pi [(d_{CO_2} + d_{donor})/2]^2 \sqrt{(8k_BT/(\pi\mu)\Omega_{12})}$ , where  $d_{CO_2} = 4.5$  Å,<sup>39</sup>  $d_{donor} = 5.3$  Å for PFB,  $k_B$  is the Boltzmann constant, and  $\mu$  is the reduced mass of CO<sub>2</sub> and PFB.  $\Omega_{12}$  is the Lennard-Jones well depth integral determined from  $\Omega_{12} = [0.636 + 0.567 \log(k_BT/\epsilon_{12})]^{-1}$ ,<sup>40</sup> where the well depth potential,  $\varepsilon_{12}$ , is obtained from  $\varepsilon_{12} = \sqrt{\varepsilon_{PFB}\varepsilon_{CO_2}}$ .  $\varepsilon_{PFB}/k_B = 435$  K is obtained from

 $\varepsilon_{PFB}/k_B = 1.15 \times T_b$ ,<sup>41,42</sup> where  $T_b$  is the boiling temperature of PFB, and  $\varepsilon_{CO_2}/k_B = 195$  K is obtained from Ref. 39. The Lennard-Jones collision rate constant,  $k_{LJ}$ , at 300 K is  $5.37 \times 10^{-10}$  cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup> for a PFB–CO<sub>2</sub> pair.

c The integrated rate constant calculated by  $\Sigma k_2^J$  when J = 58–80.  $k_2^J$  values for J states not measured in this study were obtained from the interpolation.



Figure 2-5. State-specific energy transfer rate constants,  $k_2^J$ , for collisions between various highly vibrationally excited fluorobenzenes and CO<sub>2</sub> as a function of the scattered CO<sub>2</sub> rotational state.  $k_2^J$  for all donor–CO<sub>2</sub> collision systems were obtained according to Equation (3). Rate constants for other fluorobenzene systems were obtained from Refs. 26, 25, 27, 28, and 4 for MFB, DFB isomers, Tri-FB isomers, Tetra-FB isomers, and HFB, respectively.

$$\left\langle \Delta E_{trans} \right\rangle = \sum_{J=58}^{80} P_J \Delta E_{trans}^J \bigg/ \sum_{J=58}^{80} P_J \,. \tag{5}$$

Figure 2-6 shows average translational energy gain of CO<sub>2</sub> in collisions with the various fluorobenzene donors.  $\langle \Delta E_{trans} \rangle$  for MFB, DFB isomers, and 124-TFB is 1,450–1,650 cm<sup>-1</sup> while  $\langle \Delta E_{trans} \rangle$  for the remaining fluorobenzenes, except for 1245-TFB, is ~850 cm<sup>-1</sup>.  $\langle \Delta E_{trans} \rangle$  for 1245-TFB is ~600 cm<sup>-1</sup>. As can be seen in Figure 2-6, we can say that in general the increase in the number of fluorine atoms results in a decrease in the average translational energy gain of CO<sub>2</sub>.

If the change of average translational energy gain is related to the angular momentum change in collision events, the relationship between the reduced mass of donor-CO2 and  $\langle \Delta E_{trans} \rangle$  can be explained. The correlation between rotational angular momentum change and translational energy change in collisions can be described classically according to  $(h/2\pi)\Delta J = \mu \Delta v_{rel} \langle b_{eff} \rangle$ . The rotational angular momentum change for CO<sub>2</sub> following collisions with various fluorobenzenes are the same for the various fluorobenzene-CO2 systems because the same final states are included in each study and the average initial state,  $\langle J_i \rangle$ , is the same; therefore,  $(h/2\pi)\Delta J$  is a constant C for all the fluorobenzenes. However, the reduced mass between fluorobenzene donors and CO<sub>2</sub> changes with the number of donor fluorine atoms. Thus in order to account for the change in  $\mu$ , either  $\langle b_{eff} \rangle$  or  $\Delta v_{rel}$  must change for collisions in the different fluorobenzene-CO<sub>2</sub> systems. We have calculated the impact parameter for various fluorobenzene–CO<sub>2</sub> systems using  $(h/2\pi)\Delta J = \mu \Delta v_{rel} \langle b_{eff} \rangle$ ; the impact parameters from MFB to HFB with CO<sub>2</sub> range from  $1.6 \times 10^{-10}$  to  $2.5 \times 10^{-10}$  m for collisions that result in population of CO<sub>2</sub> in the high J tail. Note for each collision system  $\langle b_{eff} \rangle$  is nearly constant, ~2 × 10<sup>-10</sup> m.



**# of Donor Fluorine Atoms** 

Figure 2-6. Average translational energy gain of CO<sub>2</sub> in single collisions with vibrationally excited fluorobenzene donors.  $\langle \Delta E_{trans} \rangle$  for MFB, DFB isomers, 124-TFB is 1,450 – 1,650 cm<sup>-1</sup> and for the other fluorobenzenes, except for  $\langle \Delta E_{trans} \rangle$  of 1245-TFB, is ~850 cm<sup>-1</sup>. For 1245-TFB  $\langle \Delta E_{trans} \rangle$  is ~600 cm<sup>-1</sup>. The increase of donor fluorine atoms results in a decrease in  $\langle \Delta E_{trans} \rangle$ .

Assuming that the impact parameter is constant, the relationship between the change in the reduced mass of donor–CO<sub>2</sub> and the change of  $\Delta v_{rel}$  can result in

$$\frac{C}{\Delta\mu} = \Delta^2 \upsilon_{rel} \langle b_{eff} \rangle,^{26}$$
(6)

where  $\Delta^2$  represents the difference of difference. According to equation (6), the increase of the donor–CO<sub>2</sub> reduced mass results in a decrease in the relative velocity change ( $\Delta v_{rel}$ ) during energy transfer collisions and hence a decrease of  $\langle \Delta E_{trans} \rangle$ . This consideration is in good agreement with the studies of Park et al.<sup>12</sup> and Liu et al.<sup>17</sup> Park and coworkers<sup>12</sup> showed that methylation of pyridine (considered as an increase of donor–CO<sub>2</sub> reduced mass) decreases total average energy gain of CO<sub>2</sub> in V–RT collision energy transfer events; both rotational and translational energy gain decrease with the methylation of pyridine. The study of Liu et al.<sup>17</sup> on alkylation effect on strong collisions obtained similar results when considering the relationship between donor–CO<sub>2</sub> reduced mass and  $\langle \Delta E_{trans} \rangle$ ;  $T_{trans}^{COM}$  for pyridine is the highest (1,500–3,500 K) and  $T_{trans}^{COM}$  for 2-methylpyridine, 2-ethylpyridine, and 2-propylpyridine are smaller and similar to each other (700–1,100 K).

## **D.** Normalized energy transfer probability distribution function, P(E,E')

The energy transfer probability distribution function, P(E,E'), can be obtained from the state-resolved rotational and translational energy gain information and absolute energy transfer rate constants measured in these experiments, as described elsewhere.<sup>43</sup> To convert experimentally measured state-specific rotational and translational energy gain information to total energy transfer amount ( $\Delta E$ ) employed in P(E,E'), the initial and final rotational states and relative velocities for CO<sub>2</sub> are required. While the final rotational state and velocity distributions

in this study are measured exactly, the initial rotational state and velocity can only be described by a room temperature distribution. In some previous studies, a temperature dependence along with an experimental gap law model was used to determine the average initial state and velocity.<sup>3-5</sup> Because previous studies<sup>23</sup> have shown that the initial state is essentially constant and that the change of that state has little effect on the total energy transfer within a small uncertainty, we have used an average initial rotational state ( $\langle J_i \rangle \approx 28.7$ ) obtained from our previous studies.<sup>23-25</sup> The average initial velocity is still obtained using a velocity gap law model with a  $T_{cell} = 300$  K initial velocity distribution. The energy transfer probability distribution function, P(E,E'), can then be determined by resorting the state-indexed probabilities measured in this experiment to the  $\Delta E$ -indexed probabilities. Figure 2-7 displays P(E,E') curves for various fluorobenzene–CO<sub>2</sub> collision pairs. The areas under P(E,E') curves for  $|\Delta E| =$ 4,000–7,000 cm<sup>-1</sup> are slightly different for each pair, even though the total area is normalized for all  $\Delta E$ . The area for  $|\Delta E| = 2,000-4,000 \text{ cm}^{-1}$  range is greatest for HFB, followed by PFB, while the integrated probability for  $|\Delta E| = 2,000-4,000 \text{ cm}^{-1}$  range is smallest for 135-TFB and second smallest for MFB. This indicates that total energy transfer probability for  $|\Delta E| = 2,000-7,000$ cm<sup>-1</sup> is greatest for collisions with HFB and smallest for 135-TFB. Direct comparison of P(E,E') curves is difficult since we must specify a specific  $\Delta E$  or range of  $\Delta E$  to compare. Hence, the total area for each system must be the same which requires that the probability in other  $\Delta E$ ranges for MFB or 135-TFB must be larger than the probability for HFB or PFB, making direct comparison of P(E,E') for various systems difficult.

To provide a means of direct comparison of P(E,E'), for different fluorobeznene donors P(E,E') curves were fit to a bi-exponential function<sup>44,45</sup>



Total Energy Transfer Amount,  $\Delta E$  (cm<sup>-1</sup>)



Total Energy Transfer Amount,  $\Delta E$  (cm<sup>-1</sup>)

Figure 2-7. (a) Experimentally measured energy transfer probability distribution functions, P(E,E'), for energy transfer between various excited fluorobenzenes<sup>*E'*</sup> (*E'* = ~41,000 cm<sup>-1</sup>) and CO<sub>2</sub>. (b) The fit of the energy transfer probability distribution function, P(E,E'), for collisions between excited PFB<sup>*E'*</sup> and CO<sub>2</sub> to a bi-exponential function. The noisy line is the experimentally measured P(E,E') data and the solid line is the best fit to a bi-exponential function. Experimental data and the best fit line agree over the range of experimentally obtained data,  $\Delta E = -2,000 - -7,000$  cm<sup>-1</sup>.

$$P(E, E) = \frac{1}{N} \left[ (1 - f) \cdot \exp\left(-\frac{(E - E)}{\alpha}\right) + f \cdot \exp\left(-\frac{(E - E)}{\gamma}\right) \right] \text{ for } E' \ge E$$
(7)

where  $\alpha$  and  $\gamma$  is the average "weak" and "strong (super)" energy transfer magnitude for downward collisions, respectively, and *f* is defined as the strong collision fraction, when  $E' \ge E$ . The experimentally obtained P(E,E') curves in this study cannot be accurately fit to a single exponential function while maintaining normalization and detailed balance, as was the case for previous fluorobenzene studies.<sup>4, 25-28</sup> Figure 2-7b shows the evidence that P(E,E') for  $\Delta E = -$ 2,000 - -7,000 cm<sup>-1</sup> obtained from the present PFB-CO<sub>2</sub> experiments is accurately described by a normalized bi-exponential function. The fit of the experimental P(E,E') to a bi-exponential function indicates that collisions between PFB and CO<sub>2</sub> can be described as consisting of two types of collisions, strong (super) collisions, corresponding to large  $\Delta E$ , and weak collisions, corresponding to small energy transfer events. In this study the bi-exponential fitting of P(E,E')is used to (i) extract strong and weak collision energy transfer parameters from P(E,E') data, (ii) directly compare super-collision energy transfer efficiency for various fluorobenzenevCO<sub>2</sub> collision systems, and (iii) understand dynamics of donor fluorination effect on super-collision energy transfer efficiency via the shape of P(E,E'). Parameters obtained from fitting the experimental P(E,E') data to equation (7) for collisions between the fluorobenzene donors and CO<sub>2</sub> are listed in Table 2-4, along with the donor initial anharmonic state density and the number of low frequency vibrational modes  $< 500 \text{ cm}^{-1}$ . Note that the parameters in Table 2-4 are only for downward collisions.

Direct comparison of P(E,E') for different donor molecules can be the performed using the bi-exponential fit parameters for downward collisions ( $\alpha$ ,  $\gamma$ , and f). As seen in Table 2-4, as

Donor	$\gamma^{a}$ (cm <sup>-1</sup> )	$\alpha^{b}$ (cm <sup>-1</sup> )	$f^{c}$	$\gamma \times f^{d}$ (cm <sup>-1</sup> )	$\rho(E')^{e}$	$s^{f} < 500 \text{ cm}^{-1}$
MFB <sup>g</sup>	1924	298	0.03	59.7	$2.0 \times 10^{16}$	4
12-DFB <sup>g</sup>	1850	343	0.06	111.0	$4.3 \times 10^{17}$	5
13-DFB <sup>g</sup>	2061	295	0.03	61.8	$7.6 \times 10^{17}$	5
14-DFB <sup>g</sup>	2408	294	0.03	72.2	$8.0 \times 10^{17}$	6
123-TFB <sup>g</sup>	1821	377	0.051	92.9	$1.3 \times 10^{19}$	7
124-TFB <sup>g</sup>	1727	349	0.047	81.2	$2.6 \times 10^{19}$	7
135-TFB <sup>g</sup>	2056	341	0.014	28.8	$1.4 \times 10^{19}$	7
1234-TFB <sup>g</sup>	1796	391	0.055	98.8	$4.1 \times 10^{20}$	8
1235-TFB <sup>g</sup>	1886	376	0.046	86.8	$1.2 \times 10^{21}$	8
1245-TFB <sup>g</sup>	1617	380	0.047	76.0	$3.5 \times 10^{20}$	10
PFB	1504	487	0.115	173.0	$1.9 \times 10^{22}$	11
HFB <sup>g</sup>	1411	620	0.150	211.7	$3.0 \times 10^{23}$	13

Table 2-4. Downward collision bi-exponential fit parameters ( $\gamma^{a}$ ,  $\alpha^{b}$ ,  $f^{c}$ , and  $\gamma \times f^{d}$ ) for experimental data, the pre-collision anharmonic state density ( $\rho(E')$ ),<sup>e</sup> and the number of low frequency vibrational modes < 500 cm<sup>-1</sup> (s)<sup>f</sup> for various fluorinated benzene donors.

Table 2-4. Continued.

a Average strong energy transfer amount determined from the bi-exponential fit of the experimental P(E,E') data for downward collisions between donors and  $CO_2$ .

b Average weak energy transfer amount determined from the bi- exponential fit of the experimental P(E,E') data for downward collisions between donors and  $CO_2$ .

c Strong collision fraction determined from the bi- exponential fit of the experimental P(E,E') data for downward collisions between donors and  $CO_2$ .

d Super-collision energy transfer efficiency determined from  $\gamma \times f$ .

e The anharmonic vibrational state density for the fluorobenzenes with the initial energy *E'* following 248 nm photon absorption, obtained from Wang-Landau Random Walk Algorithm.<sup>46-48</sup> The anharmonic vibrational state density for molecules with more than 4 atoms was calculated using ADENSUM code, MultiWell-2010 program.<sup>49</sup> The anharmonicity for various fluorobenzenes was calculated using B3-LYP DFT and a cc-pvqz basis set in Gaussian03 program.<sup>50</sup> Geometry optimization was performed prior to the vibrational calculations using NWChem, B3-LYP and a cc-pvqz basis set.

f The number of low frequency vibrational modes  $< 500 \text{ cm}^{-1}$  for fluorobenzenes.

g Data for MFB, DFB isomers, Tri-FB isomers, Tetra-FB isomers, and HFB are obtained from Refs. 26, 25, 27, 28, and 43, respectively.

the number of fluorine atoms in fluorobenzene donors increases,  $\gamma$  decreases while  $\alpha$  and f increase except between MFB and some DFB molecules. The decrease of  $\langle \Delta E_{rot} \rangle$  and  $\langle \Delta E_{trans} \rangle$ , described previously, with the increasing number of fluorine atoms correlates with  $\gamma$ , which can be thought of as strong collision energy transfer amount parameter, because these both  $\gamma$  and average energy transfer changes ( $\langle \Delta E_{rot} \rangle$  and  $\langle \Delta E_{trans} \rangle$ ) are directly obtained from strong collision energy transfer measurements in this work.

The decreasing pattern of strong (super) collision energy transfer amount ( $\gamma$ ) must be considered with strong collision fraction (f) for energy transfer efficiency. As can be seen in Figure 2-7 and Table 2-4, the P(E,E') curves with the largest value of  $\gamma$  do not necessary have the largest value of average energy transfer,  $\langle \Delta E \rangle$ , due to a small probability of strong collisions indicated by f. Thus, a large  $\gamma$  with small f or a large f with small  $\gamma$  does not translate to a large value of super-collision energy transfer or a large super-collision energy transfer efficiency. More fluorine atoms in the fluorobenzene donors generally result in a decrease of vibrational frequency of the molecule's local modes since C-F bond motion has a smaller frequency than C–H motion ( $v = 1/2\pi \cdot \sqrt{k/\mu}$  where v is the vibrational frequency, k is the force constant, and  $\mu$ is the reduced mass). The studies of Clary et al.,<sup>34, 51</sup> Lendvay et al,<sup>35, 52</sup> and our previous studies<sup>24-26</sup> indicated that lower frequency donor modes strongly affect energy transfer efficiency since it appears that energy transferred in collisions leaks out of a few low frequency donor modes in collisions with the bath. These studies also suggested that the increase in the number of low frequency modes leads to an increase of super-collision energy transfer efficiency. In other words, we suggest that the donor fluorination correlates to super-collision energy transfer efficiency.

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As discussed in our previous MFB study,<sup>26</sup> the average energy gain amount,  $\langle \Delta E \rangle$ , can be obtained by summing the product of the state-specific probability ( $P_i$ ) and change in energy ( $\Delta E_i$ ), such as  $\Sigma \Delta E_i P_i$ . Using this concept, average super-collision energy transfer amount can be estimated by multiplying strong collision magnitude ( $\gamma$ ) with strong collision fraction (f) because the measurements of this work were performed in strong collision energy transfer region ( $\Delta E =$ 2,000–7,000 cm<sup>-1</sup>). The previous studies of MFB–CO<sub>2</sub> collisions<sup>26</sup> and Lenzer et al.<sup>53</sup> on benzene– or HFB–atom collisions showed that the donor fluorination increases the average energy transfer amount in collisions and the average energy transfer amount is correlated with energy transfer efficiency. That is, the average super-collision energy transfer amount (=  $\gamma \times f$ ) can be used in this study to represent the super-collision energy transfer efficiency.

Super-collision energy transfer efficiency ( $\gamma \times f$ ) is also listed in Table 2-4. Figure 2-8 shows that as the number of fluorine atoms in the donor increases, the super-collision energy transfer efficiency also increases, except for the 12-DFB and 135-TFB systems. This trend corresponds to the quantum scattering and classical trajectory studies of Clary et al.<sup>34, 51</sup> and Lendvay et al.<sup>35, 52</sup> in that the substitution of hydrogen atoms to fluorine atoms in the donor results in the increase in the number of low frequency modes, which leads to larger energy transfer cross section and thus greater efficiency as a function of the number of fluorine atoms in the donor increasing (MFB to TetraFB) and the other steeply rising (PFB to HFB). The two different growing patterns seem to relate with the electronic excited state (S<sub>1</sub>) characteristics for fluorobenzene group that will be discussed in section **E**.

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Figure 2-8. Super-collision energy transfer efficiency ( $\gamma \times f$ ) plotted as a function of the number of fluorine atoms in the fluorobenzenes. This efficiency, obtained from the average super-collision energy transfer magnitude,  $\gamma$ , and the "fraction" of strong collision, *f*, shows a gradual increase from MFB to the Tetra-FBs and a steep rise from PFB to HFB. Only the results for 12-DFB and 135-TFB data do not lie in the trend line.
The correlation between P(E,E') shape (the energy dependence of P(E,E')) and donor fluorination can also be investigated using the bi-exponential fit parameters. We have investigated the relationship between the shape of P(E,E') and donor physical property parameters in our previous studies.<sup>23-28</sup> We observed that energy dependence of the donor state density is linearly related to the shape of P(E,E'), defined by  $1/\gamma$  and  $1/\alpha$  in our previous studies. This relationship is also shown in this work as displayed in Figure 2-9 and verifies that our fluorobenzene–CO<sub>2</sub> collision energy transfer studies satisfy Fermi's Golden Rule of collisional energy transfer following as

$$P(E,E) \propto \left| \left\langle \psi_f \left| \hat{H} \right| \psi_i \right\rangle \right|^2 \rho(E) \rho(E'),$$
(8)

where  $\rho(E')$  and  $\rho(E)$  are the density of states at the initial energy E' and the final energy E, respectively,  $\hat{H}$  is the perturbation operator governing collisional energy transfer in aspect of donor molecules, and  $\langle \psi_f | \hat{H} | \psi_i \rangle$  is the matrix element that describes the transition between the initial and final states. In other words, the linearity of the data displayed in Figure 2-9 indicates that the change of donor state density with  $\Delta E$  is correlated to the change of P(E,E') with the amount of energy transferred,  $\Delta E$ .

Furthermore, to elucidate the effect of donor fluorination on P(E,E'), Figure 2-10 displays the plots of (a) the number of low frequency modes and (b) the donor state density versus the number of fluorine atoms in the donor. Figure 2-10 shows that the number of fluorine atoms in the fluorobenzenes is linearly proportional to the number of low frequency normal modes and exponentially proportional to the donor state density. In the MFB–CO<sub>2</sub> collision study,<sup>26</sup> we suggested that the low frequency, bending motion modes govern super-collision energy transfer because the increase of fluorine atoms results in an increase of the number of low frequency



The Slope of  $\ln(\rho (E' - \Delta E))$  vs.  $\Delta E$ 

Figure 2-9. Correlation between donor state density and P(E,E') using the energy dependence. Relationship between the shape of P(E,E') (determined as  $1/\alpha$  and  $1/\gamma$ ) and energy dependence of donor state density for fluorobenzene–CO<sub>2</sub> systems is linear. Thus, the energy dependence of P(E,E') on energy transfer amount ( $\Delta E$ ) resembles the energy dependence of the donor state density on  $\Delta E$ , according to Equation (8). Squares and circles represent the reciprocal weak and strong collision energy transfer magnitudes, respectively, obtained from the fit of P(E,E') to a bi-exponential function.



# of Fluorine Atoms in Fluorobenzene Donors



**# of Donor Fluorine Atoms** 

Figure 2-10. The plot of (a) the number of low frequency normal modes (< 500 cm<sup>-1</sup>) in each fluorobenzene donor and (b) the donor initial state density ( $\rho(E')$ ) as a function of the number of fluorine atoms in the fluorobenzene donors. Circles in (a) represent the number of low frequency normal modes with frequency < 500 cm<sup>-1</sup> for each fluorobenzene. Circles and squares in (b) represent the donor initial density of states and the logarithm-scaled initial state density, respectively. In (a) we can see that the number of low frequency modes increases linearly with the number of fluorine atoms, while in (b) we observe that the donor initial density of states at energy *E'* exponentially increases with the number of fluorine atoms.

modes followed by the rise in donor state density, which influences on the shape of P(E,E'). This notion is supported with the results obtained from all the fluorobenzene donors from MFB to HFB in single collisions with CO<sub>2</sub>, as shown in Figure 2-8, 2-9, and 2-10: the increase in the number of fluorine atoms leads to an increase in the number of low frequency normal modes, which in turn leads to the exponential-increase of the donor state density, resulting in the exponential-increase of super-collision energy transfer efficiency. Simply, the fluorination of donors results in the exponential-increase of super-collision energy transfer efficiency.

# E. Excess excitation energy dependence of $S_1 \rightarrow S_0^*$ IC and connection with super-collision energy transfer efficiency

The plot of super-collision energy transfer efficiency shown in Figure 2-8 has a similar exponential shape to the plot of donor initial state density as the number of donor fluorine atoms seen in Figure 2-10b: namely a gradually increasing shape from MFB to Tetra-FB and a steeply increasing shape from PFB to HFB). This result may be related to the nature of electronic states for the fluorobenzenes. The study of Zgierski et al.<sup>33</sup> suggested and verified that the first electronically excited state (S<sub>1</sub>) of fluorobenzenes with 1–4 fluorine atoms has  $\pi^*$  character ( $\pi^* \leftarrow \pi$ ), while the S<sub>1</sub> state for PFB and HFB has  $\sigma^*$  character ( $\sigma^* \leftarrow \pi$ ). The different S<sub>1</sub> character originates from large electronegativity of the fluorine atoms, which causes electron density to be localized around the F atoms. In other words, during the S<sub>1</sub>  $\leftarrow$ S<sub>0</sub> transition, electrons are more likely to be promoted to the  $\sigma^*$  orbitals localized on C–F bonds in donors with more fluorine atoms, rather than to the  $\pi^*$  orbitals of the benzene ring. Their study seems to be related to super-collision energy transfer efficiency, which changes slowly for the fluorobenzenes with 1–4 fluorine atoms and change rapidly for donors with 5 or 6 fluorine atoms. If these results are

related, how are the first electronic excited states (S<sub>1</sub>) of fluorobenzenes connected to supercollision energy transfer efficiency in single collisions with CO<sub>2</sub>? From the viewpoint of collisions, it is known that CO<sub>2</sub> bath molecules collide with highly-vibrationally excited fluorobenzenes in S<sub>0</sub>\* (the vibrationally excited electronic ground state), provided by rapid internal conversion (IC) from S<sub>1</sub> to S<sub>0</sub>\*,  $\tau_{IC} = \sim 10^{-11}$  s. Meanwhile, single collisions between CO<sub>2</sub> and fluorobenzenes in S<sub>0</sub>\* have a mean gas kinetic collision time of ~4  $\mu$ s at 20 mTorr and 300 K. The short lifetime of the S<sub>1</sub> state and long the  $\mu$ s scale collision time do not seem to be connected.

To investigate the connection between  $S_1$  state of fluorobenzenes and collisions with CO<sub>2</sub>, the rate constant,  $k_{IC}$ , for internal conversion (IC) from  $S_1$  to  $S_0^*$  of aromatic molecules is obtained from Fermi's Golden Rule of time-dependent perturbation theory according to

$$k_{IC} = \frac{4\pi^2}{h} \left| V_{s_1 s_0} \right|^2 \left| \left\langle \chi_{s_1} \right| \chi_{s_0} \right\rangle \right|^2 \rho(E'),^{54}$$
(9)

where *h* is Plank's constant,  $V_{s_1s_0}$  is the electronic matrix element for IC from S<sub>1</sub> to S<sub>0</sub>\* state,  $\langle \chi_{s_1} | \chi_{s_0} \rangle$  is the vibrational overlap integral between S<sub>1</sub> and S<sub>0</sub>\* states, whose square is the Frank-Condon factor, and  $\rho(E')$  is the density of states in the S<sub>0</sub>\* state. In equation (9), the IC rate constant is directly proportional to the density of states ( $\rho(E')$ ) for aromatic molecules in S<sub>0</sub>\*, the same as the initial state of the donor in single collisions between vibrationally excited donors and CO<sub>2</sub> at 300 K. Based on the similarity of the exponential shapes of super-collision energy transfer efficiency (Figure 2-8) and the donor initial state density (Figure 2-10b), as well as the use of Fermi's Golden Rule (equation (8) and (9)) for both properties, we expect that S<sub>1</sub> $\rightarrow$ S<sub>0</sub>\* IC rates are connected to super-collision energy transfer efficiency through the donor S<sub>0</sub>\* state density.

Before investigating the connection between  $S_1 \rightarrow S_0^*$  IC and super-collision energy transfer efficiency, we must consider the possibility of collisions between  $CO_2$  and fluorobenzenes in states different from  $S_0^*$ . The donor state prior to collision with  $CO_2$  may be  $S_1$ ,  $T_1$  (the first triplet electronic excited state), or  $S_0$  (the electronic ground state after fluorescence) other than  $S_0^*$ . In considering collisions between  $CO_2$  and donors in various electronic states, keep in mind that that our measurements are performed at 1  $\mu$ s (a single collision time scale) following a UV pulse. For the  $S_1$  state, most fluorobenzenes in  $S_1$  can be ignored at 1  $\mu$ s because of rapid IC and ISC (intersystem crossing from S<sub>1</sub> to T<sub>1</sub>) that occur at ~10<sup>-11</sup> s and ~10<sup>-7</sup> s, respectively; thus, collisions between fluorobenzene in  $S_1$  and  $CO_2$  can be ignored at 1  $\mu$ s. Although collisions between CO<sub>2</sub> and fluorobenzenes in T<sub>1</sub> occur, collision energy transfer from  $T_1$  of fluorobenzenes to  $CO_2$  can be neglected due to the small  $T_1$ population. For  $S_0$  state produced by fluorescence (~10<sup>-9</sup> s lifetime), significant amounts of energy from donors to CO<sub>2</sub> cannot be transferred because the fluorescence quantum yield for the fluorobenzenes is negligible compared with the IC quantum yield from  $S_1$  to  $S_0^*$ . In addition, CO<sub>2</sub> can collide with photodissociated products following donor UV absorption. Collisions between fluorobenzene photoproducts and CO<sub>2</sub> do not affect our measurements because it is known that fluorobenzene photodissociation lifetime at 248 nm is much greater than 1  $\mu$ s and the photoproduct quantum yield is very small.<sup>55</sup> However, the sum of all possible collisions between fluorobenzenes in states other than  $S_0^*$  and  $CO_2$  can decrease super-collision energy transfer efficiency between donors and CO<sub>2</sub>. As a result, we conclude that as the  $S_1 \rightarrow S_0^*$  IC efficiency relating with the donor state density increases, the super-collision energy transfer efficiency also increases.

Based on the relationship between  $S_1 \rightarrow S_0^*$  IC rates and the donor initial state density influence of super-collision energy transfer efficiency, we suggest that the larger the  $S_1 \rightarrow S_0^*$  IC efficiency, the greater the super-collision energy transfer efficiency. According to the studies of Lim,<sup>54</sup> Hsieh et al.,<sup>56,57</sup> and Huang et al.,<sup>58</sup> IC rates exponentially or abruptly rise with increasing excess vibrational excitation energy. In studies on a number of aromatic hydrocarbons including fluorene, naphthalene, and phenanthrene, Hsieh et al.<sup>57</sup> and Huang et al.<sup>58</sup> verified that excess vibrational excitation energy dependence of IC ( $\equiv d \ln k_{IC}/dE_{vib}$ ) rate is linearly related to the  $S_1 \leftarrow S_0$  excitation energy; in these, the  $S_1 \rightarrow S_0^*$  IC rate is exponentially proportional to excess vibrational excitation energy (or excitation energy of the  $S_1 \leftarrow S_0$  transition: E'). Therefore, we propose that excess vibrational excitation energy in  $S_1$  affects  $S_1 \rightarrow S_0^*$  IC efficiency, which correlates with the density of states in  $S_0^*$  according to Fermi's Golden Rule (equation (9)).

To examine the connection between excess vibrational excitation energy  $(\Delta E_{vib})$ ,  $S_1 \rightarrow S_0^*$ IC efficiency, and super-collision energy transfer efficiency for fluorobenzene–CO<sub>2</sub> pairs, UV excitation energy of  $S_1, 0 \leftarrow S_0, 0$  transitions for various fluorobenzenes ( $\Delta E_{0.0}$ ) is listed in Table 2-5, along with oscillator strength ( $\varepsilon$ ), UV excitation energy at 248 nm (E'), and excess vibrational excitation energy at 248 nm ( $\Delta E_{vib} = E' - \Delta E_{0.0}$ ). UV excitation energies of  $S_1, 0 \leftarrow S_0, 0$  transitions for various fluorobenzenes ( $\Delta E_{0.0}$ ) were obtained from the report of Philis et al.<sup>30</sup> through UV absorption measurements. UV excitation energy at 248 nm (E') was obtained by summing thermal energy per vibrational mode ( $=\sum v_i/(\exp(v_i/kT)-1)$ ) at room temperature and 248 nm photon energy (40,323 cm<sup>-1</sup>). In this equation,  $v_i$  is the vibrational frequency for the *i*<sup>th</sup> mode. Figure 2-11 shows the plots of super-collision energy transfer efficiency and excess vibrational excitation energy as a function of the number of fluororine

Table 2-5. UV excitation energy  $(\Delta E_{0.0})^a$  from the ground vibrational level of the electronic ground state (S<sub>0</sub>,0) to the ground vibrational level of the first electronically excited state (S<sub>1</sub>,0), oscillator strengths ( $\varepsilon$ )<sup>b</sup> of the lowest singlet–singlet transitions (B<sub>2U</sub> $\leftarrow$ A<sub>1g</sub>:  $\pi^* \leftarrow \pi$ ), UV excitation energy at 248 nm (*E'*),<sup>c</sup> and excess vibrational excitation energy ( $\Delta E_{vib}$ )<sup>d</sup> for various fluorobenzenes.

Donor	$S_0, 0 \rightarrow S_1, 0$	Fransition	UV Excitation Energy	Excess Vibrational Excitation Energy				
	$\Delta E_{0-0}^{a} (\text{cm}^{-1})$	ε <sup>b</sup>	$E'^{c}$ at 248 nm (cm <sup>-1</sup> )	$\Delta E_{vib}^{\mathbf{d}}$ (cm <sup>-1</sup> )				
MFB	37,819	0.007	40,843	3,024				
12-DFB	37,827	0.008	41,025	3,198				
13-DFB	37,908	0.007	41,011	3,103				
14-DFB	36,835	0.020	41,019	4,184				
123-TFB			41,276					
124-TFB	37,126	0.018	41,200	4,074				
135-TFB	38,529	0.0017	41,192	2,664				
1234-TFB			41,274					
1235-TFB	37,965	0.0093	41,403	3,438				
1245-TFB	36,601	0.023	41,395	4,794				
PFB	36,295	0.0075	41,611	5,316				
HFB	34,521	0.0022	41,822	7,301				

Table 2-5. Continued.

a UV excitation energy of  $S_0, 0 \rightarrow S_1, 0$  transitions for various fluorobenzenes obtained from Ref. 30. Measurements for UV excitation energy of  $S_0, 0 \rightarrow S_1, 0$  transitions for various fluorobenzenes were performed using a UV absorption spectrometer with a hydrogen light source.

**b** Oscillator strength for the lowest singlet-singlet transition ( $S_1(B_{2U}) \leftarrow S_0(A_{1g})$ :  $\pi^* \leftarrow \pi$ ), obtained from

## Ref. 30.

c UV excitation energy (E') at 248 nm employed in this study, determined by adding the thermal energy

$$\left(=\sum_{i=1}^{\max} v_i / (\exp(v_i/kT) - 1))\right)$$
 at room temperature and the 248 nm photon energy (40,323 cm<sup>-1</sup>) for

various fluorobenzenes.

d Excess vibrational excitation energy obtained by subtracting UV excitation energy of the S<sub>0</sub>,0 $\rightarrow$ S<sub>1</sub>,0 transitions ( $\Delta E_{0.0}$ ) from UV excitation energy at 248 nm (*E'*) for fluorobenzene donors,  $\Delta E_{vib} = E' - \Delta E_{0.0}$ .



# of Fluorine Atoms in Fluorobenzene Donors

Figure 2-11. Relationship between super-collision energy transfer efficiency and excess vibrational excitation energy, and the number of fluorine atoms in the fluorobenzenes. Squares are excess vibrational excitation energy at 248 nm ( $\Delta E_{vib}$ ) and diamonds are super-collision energy transfer efficiency ( $\gamma x f$ ) for fluorobenzene donors in collisions with CO<sub>2</sub>. The dashed line is the fit of both squares and diamonds to an exponential function. The shape of both super-collision energy transfer efficiency and excess vibrational excitation energy versus the number of fluorine atoms in donors mirrors one another. Energy transfer collisions in the 135-TFB–CO<sub>2</sub> system have the smallest super-collision energy transfer efficiency at 248 nm ( $\Delta E_{vib}$ ).

atoms in fluorobenzene donors. Both plots in Figure 2-11 seem to have an exponentially rising shape with the increasing number of fluorine atoms. The similar results of these two plots support the correlation between super-collision energy transfer efficiency and IC rate efficiency through excess vibrational excitation energy. Therefore, excess vibrational excitation energy correlates with super- collision energy transfer efficiency measured in this work. In addition, the reason why super-collision energy transfer efficiency for 135-TFB is smallest of the fluorobenzenes as seen in Figure 2-8 can be explained by the fact that it has the smallest amount of excess vibrational excitation energy, as shown in Figure 2-11 and Table 2-5. The small excess vibrational excitation energy for 135-TFB results in the smallest IC efficiency, which is correlated to the smallest donor state density in  $S_0^*$  of the fluorobenzenes. This correlation between excess vibrational excitation energy and super-collision energy transfer efficiency allows us to conclude that excess vibrational excitation energy affects  $S_1 \rightarrow S_0^*$  IC efficiency and the donor state density, hence excess vibrational excitation energy finally influences supercollision energy transfer efficiency which is dependent on the density of states. This result suggests that the first singlet electronic excited state, S<sub>1</sub>, of fluorobenzenes is in fact connected to super-collision energy transfer events via  $S_1 \rightarrow S_0^*$  IC efficiency and the  $S_0^*$  state density. Our conclusion in this study can be used to explain the results of the study of Lendvay et al. on a  $SO_2$ -Ar collision system.<sup>52</sup> They showed that energy transfer efficiency, represented by the average energy transfer amount ( $\langle \Delta E \rangle$ ), increases linearly when the donor has low energy and quadratically when the donor possesses energy close to the dissociation threshold. In other words, as the  $\Delta E_{vib}$  increases, the  $\langle \Delta E \rangle$  increases much more than linear. Briefly, the influence of electronically excited states  $(S_1)$  on super-collision energy transfer efficiency can be explained

as follows: excess vibrational excitation energy leads to an increase of  $S_1 \rightarrow S_0^*$  IC rate that is related to the density of states, which influences super-collision energy transfer efficiency.

#### F. The effect of bending modes with low frequency on super-collision energy transfer

We have suggested that the increase in the number of fluorine atoms results in an increase of super-collision energy transfer efficiency via the density of states due to an increase in the number of low frequency modes and the IC rate. In addition, in the MFB study<sup>26</sup> we suggested that the modes with bending type character (in addition to the low frequency) play a significant role in super-collision energy transfer. In Table 2-6, all normal modes with a frequency  $< 500 \text{ cm}^{-1}$  for all the fluorobenzenes are listed using Wilson notation.<sup>59</sup> Table 2-6 also contains the total number of bending motion modes with low frequency. The total number of bending motion modes with low frequency follows the order of HFB (11) > PFB (10) >> TetraFBs (6.7) > TriFBs (6) > DFBs (5) > MFB (4). This pattern is similar to super-collision energy transfer efficiency and the excess vibrational excitation energy in Figure 2-11: a steady increasing shape for MFB-TetraFBs and a suddenly increasing shape for PFB to HFB. Based on these similarities, we suggest that low frequency, bending motion modes are strongly correlated to super-collision energy transfer. The study of Lendvay<sup>35</sup> on collision relaxation of highly vibrationally excited  $CS_2$  indicated that the bending mode of  $CS_2$  has a higher collisional energy transfer efficiency than the stretching modes. Our observation relative to the low frequency bending mode effect in this present study is in good agreement with Lendvay's study<sup>35</sup> and our previous study related to energy transfer and photochemistry of pyrazine.<sup>60</sup>

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Table 2-6. Fundamental low frequency vibrational modes with  $\nu < 500 \text{ cm}^{-1}$  along with a motion assignment for low frequency modes for various fluorobenzenes.

Mode <sup>a</sup>	The number of the fluorine-atom position in fluorobenzenes											
Widde	1 <sup>b</sup>	12 <sup>c</sup>	13°	14 <sup>c,d</sup>	123 <sup>e</sup>	124 <sup>e</sup>	135 <sup>e</sup>	1234 <sup>f</sup>	1235 <sup>f</sup>	1245 <sup>f</sup>	12345 <sup>g</sup>	123456 <sup>h</sup>
4 (οα)								169			158	249
5 ( <mark>οβ</mark> )									205			
ба ( <mark>ү</mark> )				451	480		500	459	458	485	275	264
6b (γ)							500	487		438		264
9a ( <mark>β</mark> )			330		310	358	326		310	280	470	443
9b ( <mark>β</mark> )		440		440		441	326	291	334		431	443
10a ( <mark>oβ</mark> )		275	251		210	358	250	374	258	417	391	370
10b ( <mark>oβ</mark> )		198	230	375	280	259	250	276	368	295	323	370
11 ( <mark>οβ</mark> )	249			162			206			194		215
12 ( <mark>y</mark> )								279				
15 ( <mark>β</mark> )		287	478	349	280	261			258	299	275	208
16a ( <mark>οα</mark> )	414			422							142	175
16b ( <mark>οα</mark> )	498	450	458			455				456	206	175

17a ( <mark>οβ</mark> )						156				140		
17b ( <mark>oβ</mark> )					140				139			
18a ( <mark>β</mark> )					350			325		346		
18b ( <mark>β</mark> )	400											
20a ( <mark>β</mark> )											327	315
20b (β)											304	315
Tot. bending #	4	5	5	5	6	7	5	5	7	8	10	11
Tot. #	4	5	5	6	7	7	7	8	8	10	11	13

o: out-of-plane motion

- $\alpha$  : C–C ring bending (or deformation) motion
- $\beta$  : C–F bending (or deformation) motion
- $\gamma$ : C–F stretching motion
- a : Wilson notation<sup>40</sup> expression for fundamental vibrational modes.
- b : Vibrational frequencies for MFB obtained from Refs. 61-65.
- c : Vibrational frequencies for DFB isomers obtained from Refs. 62-66.
- d : Vibrational frequencies for 14-DFB obtained from Ref. 51.
- e : Vibrational frequencies for TriFB isomers obtained from Refs. 62-65.
- f: Vibrational frequencies for TetraFB isomers obtained from Refs. 62-65, 67-70.
- g : Vibrational frequencies for PFB obtained from Refs. 62-65, 70-72.
- h : Vibrational frequencies for HFB obtained from Refs. 62-65, 73, 74.

# **IV. Conclusion**

The study of collisions between highly vibrationally excited PFB and CO<sub>2</sub> has been performed here to understand the effect of donor fluorination on collisional energy transfer. Fractional IR transient signals measured using a high-resolution ( $\Delta v = 0.0003$  cm<sup>-1</sup>) CW IRdiode laser were employed to obtain state-specific rotational populations and translational temperatures of CO<sub>2</sub> scattered into  $00^{0}$ O;J = 58–80 states by single collisions with hot PFB. The average rotational energy gain of CO<sub>2</sub>,  $\langle \Delta E_{rot} \rangle$ , was obtained from a Boltzmann distribution plotof rotational population for the scattered CO<sub>2</sub> in the J=58–80 states.  $\langle \Delta E_{rot} \rangle$  decreases with increasing the number of fluorine atoms for all fluorobenzenes. Doppler-broadened full widths at half maximum (FWHM) for each final CO<sub>2</sub> rotational state were measured to calculate translational energy gain of post-collision CO<sub>2</sub>. Large post-collision CO<sub>2</sub> translation temperatures for J = 58-80, obtained from FWHM measurements, indicate that CO<sub>2</sub> gains a large amount of translational energy in single collisions with hot PFB. The average translational energy gain of CO<sub>2</sub> ( $\langle \Delta E_{trans} \rangle$ ), obtained from state-specific translational temperatures and scattering probabilities, also has a decreasing trend with the increase in the number of the fluorine atoms. We suggest that this decreasing pattern of  $\langle \Delta E \rangle (= \langle \Delta E_{rot} \rangle + \langle \Delta E_{trans} \rangle)$  originates from the increase in the number of low frequency vibrational modes in the donors and the reduced mass of a donor-bath system. The number of low frequency vibrational modes in the donors is directly correlated with the increase of fluorine-atom number and the reduced mass may affect rotations and translations of bath molecules after collisions according to  $\Delta L = (h/2\pi)\Delta J = \mu \Delta v_{rel} \langle b_{eff} \rangle$ . In contrast, we observed that overall super-collision energy transfer efficiency increases with increasing the number of fluorine atoms. The energy transfer

probability distribution function, P(E,E'), was determined by resorting state-indexed probabilities to  $\Delta E$  dependent probabilities. P(E,E') curves were fit to a bi-exponential function to extract weak and strong collision energy transfer parameters. We found that donor state density correlates to super-collision energy transfer efficiency by using Fermi's Golden Rule related to the shape of P(E,E') and the S<sub>1</sub> $\rightarrow$ S<sub>0</sub>\* IC rate. We also observed that excess vibrational excitation energy in S<sub>1</sub> for fluorobenzenes is closely related to super-collision energy transfer efficiency by the S<sub>1</sub> $\rightarrow$ S<sub>0</sub>\* IC rate.

Therefore, we propose that the electronic excited state  $(S_1)$  for fluorobenzenes plays an important role in super-collision energy transfer via the  $S_1 \rightarrow S_0^*$  IC rate related to the density of states. Furthermore, we observed that fluorobenzene bending modes with low frequency influence super-collision energy transfer efficiency by increasing the average super-collision energy transfer amount, ( $\gamma \times f$ ). As a result, the flow diagram of the donor fluorination effect on super-collision energy transfer efficiency is suggested in Figure 2-12. Figure 2-12 shows that increasing the number of fluorine atoms in the donor increases the number of low frequency bending modes as well as the  $S_1 \rightarrow S_0^*$  IC rate, which result in increasing donor state density in  $S_0^*$  and hence, the increase in the number of fluorine atoms finally leads to an increase of supercollision energy transfer efficiency.



Figure 2-12. Flow Diagram of donor fluorination effect on super-collision energy transfer efficiency. This diagram shows that donor fluorination influences super-collision energy transfer efficiency by increasing excess vibrational excitation energy and decreasing local vibrational frequency, resulting in the increase of donor state density ( $\rho(E')$ ) at S<sub>0</sub>\* state.

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Chapter 3

Vibrational Relaxation Dynamics of Highly Vibrationally Exited Pyrazine in Single Collisions with N<sub>2</sub>O: I. Rotational and Translational Energy

Gain of N<sub>2</sub>O in the High J Tail (J=59–75)

# **I. Introduction**

Highly activated molecules undergoing chemical reactions have long been a focus in combustion, environmental, surface, and biological chemistry due to their impact on reaction mechanisms and product yield efficiency. Activated molecules have also been of interest in the study of collisional energy transfer processes since the 1920's when Lindemann and Hinschelwood recognized that collisional processes could account for activation and deactivation of species undergoing unimolecular chemical reactions.<sup>1,2</sup> Experiments designed to measure energy loss of activated molecules in collisions with bath molecules have been performed using a variety of spectroscopic methods including time-resolved IR fluorescence (IRF),<sup>3,4</sup> UV absorption (UVA),<sup>5</sup> and kinetically controlled selective ionization (KCSI).<sup>6,8</sup> While these studies provide the average amount of energy transfer and the energy transfer probability distribution function, P(E,E'), using KCSI, state-specific vibrational, rotational, and translational energy transfer information is required to understand the collisional energy transfer mechanism.

Recently, our group<sup>9-15</sup> and the Mullin group<sup>16-21</sup> have studied collisional energy transfer between a variety of highly vibrationally excited donors and room temperature CO<sub>2</sub> bath molecules by measuring bath energy gain using the transient high-resolution IR probing technique developed by Flynn and coworkers.<sup>22-26</sup> In these bath energy gain studies we have found that physical properties of donor molecules, such as mass, permanent dipole moment, state density, the number of low frequency vibrational modes, and excess excitation energy in an electronically excited state, strongly influence bath energy gain efficiency in collisional energy transfer.

In addition, there has been interest in understanding how the properties of bath molecules in collisions with hot donors influence the kinetics and dynamics of energy transfer. A number

of theoretical and experimental studies have been performed and compared to investigate the effect of bath physical properties on collisional energy transfer. For example, Li et al.<sup>27</sup> have studied collisional relaxation of highly vibrationally excited pyrazine by CO<sub>2</sub> using classical trajectory calculations (CTC). They observed that moment of inertia of the bath molecule strongly governs energy partitioning into bath rotations and translations. Through simulation for collisions of pseudo-linear H<sub>2</sub>O, -linear HOO, and  $CO_2$  with pyrazine, they proposed that translational energy gain of bath increases with the increase of moment of inertia for bath. Zalesskaya and coworkers<sup>28</sup> have experimentally studied the effect of the reduced mass of a collision complex on collisional energy transfer using a time-resolved IRF method. They reported that increasing the reduced mass of the collision complex decreases collision energy transfer probability. They also noticed that the complexity and mass of bath molecules have negative effect on V $\rightarrow$ T energy transfer by comparing results of collision systems composed of various donors (acetophenone, benzophenone, and anthraquinone) and bath molecules (Ar, C<sub>2</sub>H<sub>4</sub>,  $SF_6$ ,  $CCl_4$ , and  $C_5H_{12}$ ). Miller and Barker<sup>3</sup> have experimentally studied collisional deactivation of excited pyrazine in collisions with various bath molecules (19 bath gases) by measuring energy loss of pyrazine. In contrast to Zalesskaya's work, they observed that increasing bath mass increases the average energy transfer amount,  $\left< \Delta E \right>_d$ , in agreement with the calculations of Li et al.<sup>27</sup> As noted previously, donor loss studies do not provide detailed information about the dynamics of energy transfer and may not provide the detailed information necessary to sufficiently correlate bath molecule properties with energy transfer efficiency.

Mullin and coworkers, measuring state-specific bath energy gain, have reported experimental results on vibrational relaxation of pyrazine ( $E' = 38,900 \text{ cm}^{-1}$ ) in collisions with  $H_2O^{29}$  and DCl,<sup>30</sup> and have compared these results with the results obtained from the study of

 $CO_2$  energy gain in collisions with pyrazine.<sup>16</sup> In the H<sub>2</sub>O–pyrazine study, Fraelich et al.<sup>29</sup> discussed the attractive interaction between the electron-rich- $\pi$ -cloud of pyrazine and the large permanent dipole moment of water and how the rotation frequency per collision affects  $V \rightarrow T$ energy transfer amount. They suggested that the increase of attractive interaction between donor and bath decreases the V $\rightarrow$ T energy transfer amount resulting in the overall decrease of overall V→RT energy transfer, while the increase of rotation frequency due to bath moment of inertia results in more contact of hydrogen atoms with pyrazine and leading to probable rotational energy gain of H<sub>2</sub>O. In the DCl-pyrazine study, Li et al.<sup>30</sup> explored the effect of angular momentum and electrostatic attraction between donor and bath on collision energy transfer. Using the results of CO<sub>2</sub>-, H<sub>2</sub>O-, and DCl-pyrazine systems, they concluded that two factors are most responsible for collision energy transfer efficiency. First, they found that bath moment of inertia relating to mass affects bath angular momentum change ( $\Delta J_{\text{bath}}$ ) and ends up with governing relative velocity change ( $\Delta v_{rel}$ ). Second, they suggested that collisional dynamics, including relative rotational motion, long-range attractive interaction, and availability of reaction pathways, strongly correlates with energy partitioning into bath molecules.

In this study, we explore a variety of bath physical properties that potentially influence translational and rotational energy gain of N<sub>2</sub>O in vibrational relaxation of hot pyrazine and elucidate the effect of bath physical properties on energy transfer in particular P(E,E) by comparison with bath energy gain results of previous  $CO_2-$ ,<sup>24</sup> H<sub>2</sub>O-,<sup>29</sup> and DCl-pyrazine<sup>30</sup> studies. While Li et al.<sup>30</sup> have compared the energy gain results of CO<sub>2</sub>, DCl, and H<sub>2</sub>O with a pyrazine donor, those three bath molecules have very different physical properties, including mass, structure, moment of inertia, the number of vibrational modes, and so on, which make it difficult to interpret which property is more responsible for influencing collision energy transfer

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both in terms of amount and probability. The choice of  $N_2O$  in this work gives us a good standard to discuss the dominant bath physical factors that govern collision energy transfer efficiency because  $N_2O$  and  $CO_2$  have many similar properties (isoelectronic configuration, same mass, same structure, same number of vibrational modes) with slight differences (different permanent dipole moment:  $N_2O = 0.166$  D while  $CO_2 = 0$  D). This study is mainly aimed to investigate the effect of each bath physical property on rotational and translational energy gain results of bath molecules and determine which physical property is more significant in supercollision energy transfer efficiency.

#### **II. Experimental**

The experiments presented here to study the vibrational relaxation of highly vibrationally excited pyrazine in single collisions with N<sub>2</sub>O in the vibtationally ground state have been described in detail elsewhere;<sup>9</sup> therefore, only a brief description is presented here. A 1:1 mixture of gas phase pyrazine and N<sub>2</sub>O with a total pressure of 20.0 mTorr flows through a 300 cm collision cell at 300 K. 248 nm UV light (1 Hz pulse) generated from a KrF excimer laser (Lamda Physik Complex 201) is propagated collinearly with a IR probe beam into the collision cell to excite pyrazine molecules via the S<sub>2</sub> $\leftarrow$ S<sub>0</sub> electronic transition followed by rapid radiationless internal conversion into vibrationally excited states of the electronic ground level, S<sub>0</sub>\* $\leftarrow$ S<sub>2</sub>. UV power density to excite pyrazine was maintained at 4~6 mJ/cm<sup>2</sup> to ensure single photon absorption.<sup>31</sup> A tunable CW IR diode laser (Laser Components) with 0.0003 cm<sup>-1</sup> resolution, which generates photons at  $\lambda = ~4.6 \ \mu m$ , was used to probe the anti-symmetric stretching ro-vibrational transition (00<sup>0</sup>1;J±1  $\leftarrow 00^{0}0$ ;J = 59–75) of N<sub>2</sub>O scattered by collisions with hot pyrazine (E' = ~41,000 cm<sup>-1</sup>). After passing through the collision cell the IR beam is

focused into a single grating monochromator (Acton Research Corporation, SpectraPro 500i) to select a single laser mode and onto a liquid-nitrogen-cooled (77 K) InSb diode detector (Judson Technologies). The combined rise time of the detector and pre-amplifier (Perry Amplifer, 100 ns rise time) is ~400 ns, shorter than mean gas collision time, 4  $\mu$ s. The IR signal is amplified and recorded by a digital oscilloscope (LeCroy LT364, 500 MHz) using a dual channel technique.<sup>24</sup> The IR transient absorption signal, collected at 1  $\mu$ s (1/4 the mean gas kinetic collision time) after every UV pulse, is obtained from a ratio of AC ( $\Delta I$ ) to DC ( $I_0$ - $\Delta I$ ) signals,  $\Delta I/(I_0$ - $\Delta I$ ); the fractional IR transient absorption signal for calculating the scattered N<sub>2</sub>O number density corresponds to  $\Delta I/I_0$  (=1-exp( $-\alpha \rho I$ )), where  $\alpha$  is the absorption coefficient,  $\rho$  is the density of the probed molecule, and l is the collision cell length. This dual-channel method is also useful to stabilize short-term drifts in IR light intensity ( $I_0$ ).<sup>32, 33</sup> Transient absorption signals are averaged over ~100 UV pulses by the oscilloscope and then transferred to a computer for further analysis.

About 4 % of the IR diode laser light is split off and directed to a 100 cm long reference cell. This reference beam passes through a second monochromator and is focused onto a second liquid-nitrogen-cooled (77 K) InSb detector and pre-amplifier. The reference signal from the second detector is sent to a lock-in amplifier (Standard Research Systems) to correct for longterm drifts of the IR diode laser frequency by locking the laser frequency to the rovibrational transition center peak of the scattered  $N_2O$ , while the transient absorption signal is measured.

The population of  $N_2O$  scattered by single collisions with hot pyrazine was determined using the transient absorption signal and a Doppler-broadened linewidth at each final rotational state of the scattered  $N_2O$ . The Doppler-broadened full width at half maximum (FWHM) was obtained by locking the IR diode laser frequency to a fringe of a scanning Fabry-Perot etalon (Laser Components, free spectral range=289 MHz) in place of the reference cell and measuring

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transient absorption signals at 40 frequencies evenly distributed over the rovibrational transition peaks of the scattered  $N_2O$ , averaged over 100 UV shots at each frequency.

The divergence of the UV laser over the 300 cm collision cell produces errors in calculating the collision rate constants; therefore, a calibration method to correct the UV divergence was used.<sup>9</sup> The pyrazine– $N_2O$  scattering results obtained using a 20 cm cell under the same condition as employed with the 300 cm cell was used to obtain a scaling factor applied to determine an absolute energy transfer rate constant.

Pyrazine (Aldrich, 99+ % purity) was purified using 3 freeze-pump-thaw cycles prior to use. N<sub>2</sub>O gas (Intermountain Airgas Inc., 99.9999+ % purity) was used without any purification.

# **III. Results**

#### A. Detection of N<sub>2</sub>O excited by single collisions with vibrationally hot pyrazine

N<sub>2</sub>O molecules excited into the high J states of the ground level (00<sup>0</sup>0) by single collisions with highly vibrationally hot pyrazine (E' = ~41,000 cm<sup>-1</sup>) were detected as a function of time ( $\mu$ s scale) by probing the anti-symmetric stretch transition of N<sub>2</sub>O (00<sup>0</sup>1;J±1  $\leftarrow$  00<sup>0</sup>0;J = 59–75). The transient IR absorption signal for the N<sub>2</sub>O transition (00<sup>0</sup>1;J=63  $\leftarrow$  00<sup>0</sup>0;J=64) at  $\nu_0$ = 2156.4020 cm<sup>-1</sup>, averaged over 100 shots during the detection, is shown in Figure 3-1. The state-specific transient IR absorption signal following UV pulse in Figure 3-1 was obtained using a high-resolution ( $\Delta \nu = 0.0003$  cm<sup>-1</sup>) solid state IR diode laser. N<sub>2</sub>O molecules that are scattered into the excited rotational state of 00<sup>0</sup>0 by single collisions with vibrationally hot pyrazine can be represented by the growth of transient absorption signals at early times. That is, the linear growth of the transient absorption signal up to ~4  $\mu$ s characterizes the increase of N<sub>2</sub>O molecules



Figure 3-1. Transient IR absorption signal of N<sub>2</sub>O scattered into the J = 64 state of the vibrational ground state (00<sup>0</sup>0) by single collisions with highly vibrationally excited pyrazine (E' = ~41,000 cm<sup>-1</sup>) on the  $\mu$ s scale. The signals were measured by probing the N<sub>2</sub>O transition (00<sup>0</sup>1;J=63  $\leftarrow$  00<sup>0</sup>0;J=64). The signals obtained at 1  $\mu$ s following UV pulse were used to calculate the number density of the scattered N<sub>2</sub>O into the 00<sup>0</sup>0;J=64 state in order to count only the population change by a single collision with hot pyrazine. 1  $\mu$ s is 1/4 the mean gas kinetic collision time of ~4  $\mu$ s at 20 mTorr and 300 K.

scattered into a specific J state by single collisions with hot donors at 20 mTorr and 300 K.<sup>34</sup> The absorption cross section obtained from the HITRAN database<sup>35</sup> for N<sub>2</sub>O anti-symmetric stretch transition was also employed with the transient signal at the transition center and Doppler broadened full width at half maximum ( $\Delta v_{obs}$ ) to determine the state-specific post-collision N<sub>2</sub>O population.

#### B. Rotational energy gain of N<sub>2</sub>O from single collisions with hot pyrazine

State-specific population for N<sub>2</sub>O scattered by single collisions with vibrationally hot pyrazine were measured for J=59–75 of the vibrational ground state (00<sup>0</sup>0). IR absorption signals at 1  $\mu$ s after UV excitation of pyrazine at 248 nm were directly converted to the number density of scattered N<sub>2</sub>O. The obtained state-specific populations were used to obtain a Boltzmann distribution of post-collision N<sub>2</sub>O scattered by collisions with hot pyrazine. Figure 3-2 displays a plot of ln( $N_J/(2J+1)$ ) vs.  $E_{rot}$ , where  $N_J$  is the number density of post-collision N<sub>2</sub>O molecules in the J state and  $E_{rot}$  is the final N<sub>2</sub>O rotational energy. The slope obtained from the plot shown in Figure 3-2 was used to determine a single rotational temperature;  $T_{rot} = 930 \pm 50$ K. As seen in previous diode probe energy transfer studies, a single rotational temperature describes the rotational energy distribution of post-collision N<sub>2</sub>O molecules in the J=59–75 range. This large post-collision rotational temperature indicates that N<sub>2</sub>O gains a large amount of rotational energy in single collisions with vibrationally hot pyrazine, compared to the initial temperature of pre-collision N<sub>2</sub>O distribution (300 K).



Rotational Energy for Scattered NO,  $E_{rot}=BJ(J+1)$  (cm<sup>-1</sup>)

Figure 3-2. Boltzmann plot for the state-specific rotational population distribution of N<sub>2</sub>O scattered into the J = 59–75 of the ground vibrational level (00<sup>0</sup>0) in single collisions with hot pyrazine. The line is the best linear least squares fit of the data. The slope corresponds to  $T_{rot} = 930 \pm 50$  K, which is related to the average final rotational energy ( $\langle E_{rot} \rangle_f$ ) of N<sub>2</sub>O in the range of 00<sup>0</sup>0;J=59–75.

#### C. Translational energy gain of N<sub>2</sub>O from single collisions with hot pyrazine

Doppler broadened line profiles of the transient IR absorption signals at 1  $\mu$ s following a 248 nm UV pulse were measured for J=59–75 states to determine the translational energy gain of N<sub>2</sub>O scattered by single collisions with vibrationally hot pyrazine. Figure 3-3 shows a Doppler broadened line profiles for the N<sub>2</sub>O transition (00<sup>0</sup>1;J=72  $\leftarrow$  00<sup>0</sup>0;J=73). The solid dots in Figure 3-3 represent the fractional IR absorption, averaged over 100 shots at near frequencies from the line center. The solid line was obtained by fitting the measured transient absorption signals to a Gaussian function. The full width at half maximum (FWHM) for the N<sub>2</sub>O transition determined from the Gaussian fit is  $\Delta v_{obs} = 0.0104 \pm 0.0010 \text{ cm}^{-1}$ , which corresponds to a lab-frame translational temperature of  $T_{trans} = 2020 \pm 160 \text{ K}$ . The linewidths (FWHM) for the rovibrational transitions of N<sub>2</sub>O scattered into 00<sup>0</sup>0,J=59–75 are listed in Table 3-1, along with N<sub>2</sub>O rotational energy, lab-frame translational temperature ( $T_{trans}$ ), and center-of-mass translational temperature ( $T_{COM}$ ) calculated according to

$$T_{COM} = T_{trans} + \left(T_{trans} - T_{cell}\right) \left(\frac{m_{N_2O}}{m_{pyrazine}}\right),\tag{1}$$

where  $T_{cell}$  is the cell temperature (300 K) and  $m_{N_2O}/m_{pyrazine}$  is the ratio of N<sub>2</sub>O-pyrazine mass. Figure 3-4 displays translational temperature for each measured state in both lab-frame and center-of-mass frame as a function of the final N<sub>2</sub>O rotational state. In Figure 3-4, translational temperature increases linearly with the final N<sub>2</sub>O rotational state. This relationship between the translational temperature and bath rotational state agrees with the classical collision viewpoint that the angular momentum change correlates with the change in relative recoil velocity,  $(h/2\pi)\Delta J = \mu\Delta v_{rel}b$ , and indicates that the impact parameter (*b*) of the collisions is small and constant in the J = 59–75 range.


Relative Frequency to the Center of the Peak $\lambda v$  (cm<sup>-1</sup>)

Figure 3-3. State-specific Doppler broadened line profiles for the transient absorption signals of the N<sub>2</sub>O transition (00<sup>0</sup>1;J=72  $\leftarrow$  00<sup>0</sup>0;J=73) measured at 1  $\mu$ s after UV excitation of pyrazine. Solid dots are the absorption signals collected and averaged over 100 shots at 40 positions evenly distributed near the center frequency of the 00<sup>0</sup>1;J=72  $\leftarrow$  00<sup>0</sup>0;J=73 transition ( $v_0$  = 2144.7320 cm<sup>-1</sup>). The solid line is the best non-linear least squares fit of the absorption signals to a Gaussian function and the dashed line is the Gaussian fit for Doppler broadening at 300 K. The solid line fit results in  $\Delta v_{obs}$  = 0.0104 ± 0.0010 cm<sup>-1</sup>, corresponding to  $T_{trans}$  = 2040 ± 160 K and  $T_{COM}$  = 2990 ± 240 K. For comparison,  $\Delta v_{obs}$  at 300 K is 0.0040 cm<sup>-1</sup>.

$N_2O(00^00)$	$Pyrazine^{E'} + N_2O (00^00) \rightarrow Pyrazine^{E' \Delta E} + N_2O (00^00;J)$			
J state	$E_{rot} \left( \mathrm{cm}^{-1} \right)^{d}$	$\Delta v_{obs} (\mathrm{cm}^{-1})^{\mathrm{a}}$	$T_{trans}(\mathbf{K})^{\mathbf{b}}$	$T_{COM}$ (K) <sup>c</sup>
59	1483.260	$0.0086 \pm 0.0006$	$1360 \pm 120$	$1940 \pm 160$
61	1584.658	$0.0096 \pm 0.0008$	$1710\pm150$	$2490\pm190$
62	1636.614	$0.0099 \pm 0.0006$	$1820\pm120$	$2650\pm170$
64	1743.040	$0.0102 \pm 0.0007$	$1910\pm130$	$2800\pm190$
66	1852.818	$0.0098 \pm 0.0005$	$1780\pm100$	$2600\pm150$
68	1965.948	$0.0104 \pm 0.0008$	$2000\pm160$	$2940 \pm 240$
69	2023.770	$0.0106 \pm 0.0008$	$2090 \pm 160$	$3070 \pm 240$
73	2263.438	$0.0104 \pm 0.0008$	$2040\pm160$	$2990 \pm 240$
74	2325.450	$0.0108 \pm 0.0008$	$2160\pm170$	$3180\pm260$
75	2388.300	$0.0118 \pm 0.0008$	$2610\pm210$	$3880\pm310$

Table 3-1. State-specific full width at half maximum (FWHM) for Doppler-broadened line shapes,<sup>a</sup> labframe translational temperatures<sup>b</sup> and center-of-mass translational temperatures<sup>c</sup> for N<sub>2</sub>O scattered into J = 59-75 at  $00^{0}0$  by single collisions with highly vibrationally excited pyrazine (E' = ~41,000 cm<sup>-1</sup>).

a Full width at half maximum (FWHM) for Doppler-broadened line shapes, which were measured by fitting transient IR absorption signals for the N<sub>2</sub>O ( $00^01$ ;J-1  $\leftarrow 00^00$ ;J) transition to a Gaussian function. Transient IR absorption signals at 1  $\mu$ s following UV excitation of pyrazine at 248 nm, distributed evenly around the center of the absorption line, were collected and averaged over 100 shots.

b Lab-frame translational temperature determined from  $T_{trans} = (m_{N_2O}c^2/8k_B \ln 2)(\Delta v_{obs}/v_0)^2$ , where  $m_{N_2O}$  is the mass of N<sub>2</sub>O, *c* is the speed of light,  $k_B$  is the Boltzmann constant,  $v_0$  is the frequency at the center of the absorption line, and  $\Delta v_{obs}$  is the experimentally measured Doppler-broadened full width at half maximum (FWHM).

c Center-of-mass (COM) translational temperature determined using Equation (1).

d Rotational energy of N<sub>2</sub>O scattered into J=59–75 at the vibraionally ground state by single collisions with hot pyrazine.  $E_{rot}$  is obtained from  $E_{rot} = BJ(J+1)$ , where *B* is the rotational constant for N<sub>2</sub>O in this study; B = 0.419 cm<sup>-1</sup>.



Rotational Quantum Number of Scattered NO, J

Figure 3-4. State-specific lab-frame and center-of-mass translational temperatures as a function of the final rotational state of scattered N<sub>2</sub>O (00<sup>0</sup>0) in the J = 59–75 range. Lab-frame translational temperatures,  $T_{trans}$ , (left Y axis) were directly obtained from  $\Delta v_{obs}$  and center-of-mass translational temperatures,  $T_{COM}$ , (light Y axis) were calculated according to Equation (1). The approximately linear increase of translational temperature with final J state (J=59–75) for the scattered N<sub>2</sub>O indicates that N<sub>2</sub>O–pyrazine collisions in this study have a constant impact parameter.

# D. State-specific V $\rightarrow$ RT energy transfer rate constants of collisions between hot pyrazine and N<sub>2</sub>O

Rotational state-specific V $\rightarrow$ RT energy transfer rate constants were measured using the rotational and translational energy gain information of scattered N<sub>2</sub>O for the V $\rightarrow$ RT energy transfer process

$$Pyrazine^{E} + N_2 O(00^0 0) \xrightarrow{k_2^J} Pyrazine^{E^-\Delta E} + N_2 O(00^0 0; J, V),$$
(2)

where E' (= ~41,000 cm<sup>-1</sup>) is the initial pyrazine energy,  $\Delta E$  is the energy transferred in a single collision,  $N_2O(00^00; J, V)$  represents N<sub>2</sub>O molecules that gain energy  $\Delta E$  and are scattered into the rotational state (*J*) with recoil velocity *V*, and  $k_2^J$  is the state-specific energy transfer rate constant. At early times (1  $\mu$ s) compared to the mean gas kinetic collision time (~4  $\mu$ s), the rate constant described by equation (2) can be calculated according to

$$k_{2}^{J} = \frac{[N_{2}O(00^{0}0; J, V)]_{t}}{[N_{2}O]_{0}[pyrazine^{E}]_{0}t},$$
(3)

where  $[N_2O]_0$  and  $[pyrazine^{E'}]_0$  are the initial number density of N<sub>2</sub>O (00<sup>0</sup>0) and pyrazine (E' = ~41,000 cm<sup>-1</sup>) prior to collisions, respectively, *t* is 1  $\mu$ s, and  $[N_2O(00^00;J,V)]_t$  is the post-collision number density of N<sub>2</sub>O scattered into 00<sup>0</sup>0;J with velocity *V* determined from the IR absorption signals at 1  $\mu$ s.  $[N_2O]_0$  is obtained from the initial pressure in the collision cell and  $[pyrazine^{E'}]_0$  is obtained from the number of UV photons absorbed by pyrazine at t = 0. The state-specific energy transfer rate constants,  $k_2^J$ , for scattering into a range of final rotational states, J=59–75, are listed in Table 3-2, along with the scattering probabilities that are obtained by dividing  $k_2^J$  by the Lennard-Jones collision rate constant,  $P_J = k_2^J/k_{LJ}$ . The Lennard-Jones collision rate

N <sub>2</sub> O (00 <sup>0</sup> 0)	pyrazine <sup>E'</sup> + N <sub>2</sub> O(00 <sup>0</sup> 0) $\rightarrow$ pyrazine <sup>E' \Delta E</sup> + N <sub>2</sub> O(00 <sup>0</sup> 0; J, V)		
J state	$k_2^{Ja}$ (10 <sup>-12</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$P_J^{b}(10^{-3})$	
59	$2.6 \pm 0.3$	$5.0 \pm 0.6$	
61	$1.9\pm0.2$	$3.7\pm0.4$	
62	$1.8\pm0.2$	$3.4\pm0.3$	
64	$1.7\pm0.2$	$3.3 \pm 0.3$	
66	$1.7\pm0.2$	$3.2\pm0.3$	
68	$1.4 \pm 0.3$	$2.8\pm0.5$	
69	$1.4 \pm 0.2$	$2.6 \pm 0.3$	
73	$1.3 \pm 0.3$	$2.4 \pm 0.5$	
74	$1.1 \pm 0.2$	$2.1 \pm 0.4$	
75	$0.9 \pm 0.2$	$1.7 \pm 0.4$	

Table 3-2. State-specific energy transfer rate constants  $(k_2^J)^a$  and scattering probabilities  $(P_J)^b$  for the processes of pyrazine<sup>E'</sup> + N<sub>2</sub>O(00<sup>0</sup>0)  $\rightarrow$  pyrazine<sup>E'-\Delta E</sup> + N<sub>2</sub>O(00<sup>0</sup>0;J,V).

a State-specific energy transfer rate constant,  $k_2^J$ , for the process of pyrazine<sup>E</sup> + N<sub>2</sub>O(00<sup>0</sup>0)  $\rightarrow$  pyrazine<sup>E-\DeltaE</sup> + N<sub>2</sub>O(00<sup>0</sup>0;J,V) determined using Equation (3).

b The scattering probability obtained from  $P_J = k_2^J/k_{LJ}$ .  $k_{LJ}$  is the Lennard-Jones gas kinetic collision rate constant defined as  $k_{LJ} = \pi [(d_{N_2O} + d_{pyrazine})/2]^2 \sqrt{(8k_BT/(\pi\mu)}\Omega_{12})$ , where  $d_{N_2O} = 4.2$  Å,<sup>36</sup>  $d_{pyrazine} = 5.27$  Å,  $k_B$  is the Boltzmann constant, and  $\mu$  is the reduced mass of N<sub>2</sub>O and pyrazine.  $\Omega_{12}$  is the Lennard-Jones well depth collisional integral determined from  $\Omega_{12} = [0.636 + 0.567\log(k_BT/\epsilon_{12})]^{-1}$ ,<sup>37</sup> where the well depth potential,  $\varepsilon_{12}$ , is  $\varepsilon_{12} = \sqrt{\varepsilon_{pyrazine}}\varepsilon_{N_2O}$ .  $\varepsilon_{pyrazine}/k_B = 412$  K and  $\varepsilon_{N_2O}/k_B = 210$  K is obtained from Refs. 38 and 39. The Lennard-Jones well depth collision rate constant,  $k_{LJ}$ , at 300 K is  $5.19 \times 10^{-10}$  cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup> for the pyrazine and N<sub>2</sub>O pair. constant,  $k_{LJ}$ , for collisions between pyrazine (E' = ~41,000 cm<sup>-1</sup>) and N<sub>2</sub>O at 300 K is  $5.19 \times 10^{-10}$  cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup>.

## **IV. Discussion**

The use of N<sub>2</sub>O gas as a bath for collisions with pyrazine at 248 nm in the present work is aimed at understanding the effect of bath physical properties on V $\rightarrow$ RT energy transfer by comparing previous studies of pyrazine– $CO_2$ ,<sup>24</sup>–DCl,<sup>30</sup> and – $H_2O^{29}$  collision systems and the current pyrazine–N<sub>2</sub>O results. In these previous studies, Mullin and coworkers suggested that some bath physical properties (i.e. mass, moment of inertia, and angular momentum) are correlated to  $V \rightarrow RT$  energy transfer efficiency through the direct comparison of the results. However, the physical properties of CO<sub>2</sub>, DCl, and H<sub>2</sub>O are very different and may make it difficult to find simple correlations between  $V \rightarrow RT$  energy transfer efficiency and bath physical properties. In this study, we chose N<sub>2</sub>O as a bath molecule to investigate bath physical properties and V $\rightarrow$ RT energy transfer results because N<sub>2</sub>O and CO<sub>2</sub> are isoelectronic and have the same mass, structure, and number of vibrational modes, but different dipole moments (N<sub>2</sub>O has 0.166 D dipole moment and  $CO_2$  has no dipole moment). In this investigation of the effect of bath physical properties on V $\rightarrow$ RT energy transfer we compare the rotational and translational energy gain and V $\rightarrow$ RT energy transfer probability distribution function (P(E,E')) for N<sub>2</sub>O and CO<sub>2</sub>, as well as DCl and H<sub>2</sub>O.

It should be noted that this study on the pyrazine $-N_2O$  collision pair was performed at 248 nm excited as was the pyrazine $-CO_2$  study of Flynn and coworkers,<sup>24</sup> while the  $H_2O^{29}$  and  $DCl^{30}$  studies were performed at 266 nm. We also noticed that energy transfer is not dependent

on the change of donor internal energy in the range of E' =  $36,000-41,000 \text{ cm}^{-1}$ : 271-248 nm. Wall et al.<sup>40</sup> reported the UV energy dependent study for collisions between vibrationally excited pyrazine and CO<sub>2</sub> and observed that rotational and translational energy gain amounts for CO<sub>2</sub> scattered into the high J states of the ground vibrational level ( $00^{0}0$ ) have no UV energy dependence as UV excitation energy is altered from ~36,000 to ~ $41,000 \text{ cm}^{-1}$ . However, they have shown that the energy transfer rate constant applied to calculate energy transfer probability distribution, P(E,E'), changes with donor internal energy; thus, P(E,E') will separately be discussed from the energy gain amounts. From their results, we could assume that rotational and translational energy gain amounts of H<sub>2</sub>O and DCl by collisions with pyrazine have no UV energy dependence in the UV energy range. Based on this assumption, we can directly compare V $\rightarrow$ RT energy gain information of DCl<sup>30</sup> and H<sub>2</sub>O<sup>29</sup> at 266 nm with the energy gain results from this present N<sub>2</sub>O study and previous CO<sub>2</sub><sup>24</sup> study at 248 nm to investigate the effect of bath physical properties on collision energy transfer.

#### A. Comparison of translational energy gain for bath molecules by collisions with pyrazine

State-specific translational energy gain of N<sub>2</sub>O scattered into J=59–75 of the ground vibrational state by collisions with vibrationally hot pyrazine is compared with the results of pyrazine– $CO_2$ ,<sup>24</sup> –H<sub>2</sub>O,<sup>29</sup> and –DCl<sup>30</sup> by plotting the center-of-mass translational temperature ( $T_{COM}$ ) in Figure 3-5, as a function of the final rotational energy of the bath molecules. Final rotational energy was used instead of the final J state so that the translational energy gain of bath molecules can be directly compared. Figure 3-5 shows that CO<sub>2</sub> gains the largest and H<sub>2</sub>O gains the smallest amount of translational energy per single collision with hot pyrazine, with N<sub>2</sub>O slightly smaller than CO<sub>2</sub> and HCl slightly greater than H<sub>2</sub>O in the  $E_{rot} = 1,000-3,000$  cm<sup>-1</sup> range.



Rotational Energy for Scattered Bath,  $E_{rot}$  (cm<sup>-1</sup>)

Figure 3-5. Comparison of center-of-mass translational temperatures for  $N_2O$ ,  $CO_2$ , DCl, and  $H_2O$  in collisions with hot pyrazine vs. the final rotational energy for bath molecules. Triangles represents  $N_2O$  data measured in this study, while diamonds, circles, and squares represent data for  $CO_2$  (Ref. 24), DCl (Ref. 30) and  $H_2O$  (Ref. 29), respectively. The dotted line is a best linear least squares fit of  $N_2O$  data.

It is interesting to note that the translational energies for CO<sub>2</sub> and N<sub>2</sub>O increase steeply with the increase of  $E_{rot}$ , while those of DCl and H<sub>2</sub>O have a little or no  $E_{rot}$  dependence (i.e. no J dependence). This feature indicates that the translation energy gain of CO<sub>2</sub> and N<sub>2</sub>O is strongly related to  $E_{rot}$ , while those of DCl and H<sub>2</sub>O have a little or no relation to  $E_{rot}$ . The correlation (or lack thereof) between translational energy gain and rotational excitation must be related to physical properties of bath molecules. Some of the bath physical properties potentially responsible for this behavior are listed in Table 3-3 and discussed in the following sections. Table 3-3 also includes other parameters of the collision results between pyrazine and bath molecules, such as the rotational temperature ( $T_{rot}$ ), average change of rotational states ( $<\Delta J >$ ), average translational energy gain ( $<\Delta E_{trans}>$ ), and average total energy gain ( $<\Delta E_{total}>$ ) in the high J tail measured for V—RT pathway.

### 1. Mass/size effect on $V \rightarrow T$ energy transfer

The mass/size of bath molecules is one of the most important physical property factors influencing velocity of a particle after collisions. In general, a heavier/bigger molecule moves slower than a lighter/smaller one at the same energy. To make both heavier and lighter molecules move at the same speed following a collision, it is necessary to give more energy to the heavier/bigger molecule than to the lighter/smaller molecule. As classically considered in terms of mass/size for bath molecules, if the mass/size is large, bath molecules move slowly and the collision duration time increases. Zalesskaya and coworkers<sup>28</sup> studied the efficiency of vibrational energy transfer in collisions through time-resolved delayed fluorescence experiments for various collision systems. They reported that the vibrational energy transfer duration time increases with the mass of bath molecules. An other study performed by Miller and Barker<sup>3</sup> on

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Table 3-3. Comparison of physical properties (mass, rotational constant,<sup>a</sup> dipole moment, and structure), rotational temperatures,<sup>b</sup> average change of rotational angular momentum ( $<\Delta J>$ ),<sup>c</sup> average amount of translational energy gain ( $<\Delta E_{trans}>$ ),<sup>d</sup> and average amount of total energy gain ( $<\Delta E_{total}>^{e}$ ) for bath molecules in the *pyrazine*<sup>E'</sup> + *Bath*  $\xrightarrow{k_2^{-i}}$  *pyrazine*<sup>E'-\Delta E</sup> + *Bath*  $\stackrel{\Delta E}{\rightarrow}$  process.

$pyrazine^{E'} + Bath \xrightarrow{k_2^J} pyrazine^{E' - \Delta E} + Bath^{\Delta E}$				
	$H_2O^f$	DCl <sup>g</sup>	N <sub>2</sub> O	$\text{CO}_2^{\text{h}}$
Mass (g/mol)	18.0	37.5	44.0	44.0
$B^{\mathrm{a}}(\mathrm{cm}^{-1})$	27, 14, 9	5.39	0.419	0.394
Dipole moment (D)	1.85	1.05	0.166	0
Structure	Bent tri-atomic	Linear di-atomic	Linear tri-atomic	Linear tri-atomic
$T_{rot}^{b}(\mathbf{K})$	$920\pm100$	$755 \pm 90$	$930 \pm 40$	$1300\pm100$
$<\Delta J>^{c}$	~5	~7	~32	~37
$<\Delta E_{trans}>^{d}$	340	490	2410	2890
$<\Delta E_{total}>^{\rm e}$	990	810	2850	3590

a Rotational constant, B.

b Rotational temperature obtained from the slope of the plot of  $\ln(N_J/(2J+1))$  vs.  $E_{rot}$ , where  $N_J$  is the number density of bath molecules scattered into the J state at the vibrationless level,  $E_{rot}$  is the final rotational energy of the scattered bath molecules, and (2J+1) is the rotational degeneracy for linear bath molecules in this study; for H<sub>2</sub>O (bent tri-atomic), the rotational degeneracy is (2J+1)<sup>2</sup>.

c The average rotational quantum number change obtained from  $\langle \Delta J \rangle \approx \sqrt{\langle J_f \rangle^2 - \langle J_i \rangle^2}$  (Ref. 30), where  $\langle J_i \rangle$  and  $\langle J_f \rangle$  are the average initial and final rotational state, respectively, obtained using rotational and cell temperatures of the collision complex for simple comparison.  $\langle J_i \rangle$  for N<sub>2</sub>O, DCl, and H<sub>2</sub>O were determined from  $\langle J_i \rangle \approx \sqrt{(N/2 \times kT_{cell})/B}$  when  $\langle E_{rot} \rangle_i = N/2 \times kT_{cell} =$  $B \langle J_i \rangle (\langle J_i \rangle + 1) \approx B \langle J_i \rangle^2$ , while  $\langle J_i \rangle$  for CO<sub>2</sub> is  $\sim 28$ .<sup>24</sup>  $\langle J_f \rangle$  was determined from

$$\langle J_f \rangle \approx \sqrt{(N/2 \times kT_{rot})/B}$$
 when  $\langle E_{rot} \rangle_f = N/2 \times kT_{rot} = B \langle J_f \rangle (\langle J_f \rangle + 1) \approx B \langle J_f \rangle^2$ . In these equations, *k* is the Boltzmann constant, *B* is the rotational constant, *T<sub>cell</sub>* is the collision cell temperature (= 300 K), and *N* is the degrees of rotational freedom for bath molecules.  $N = 3$  for H<sub>2</sub>O and  $N = 2$  for DCl, N<sub>2</sub>O, and CO<sub>2</sub>. For H<sub>2</sub>O, the average rotational constant obtained from  $B_{ave} = (ABC)^{1/3} = \sim 15$  cm<sup>-1</sup> (Ref. 41) was used to calculate the average initial rotational state,  $\langle J_i \rangle$ .

d The average translational energy gain obtained from  $\langle \Delta E_{trans} \rangle = \sum \left( \langle \Delta E_{trans}^J \rangle \times k_2^J / k_{LJ} \right) / \sum k_2^J / k_{LJ}$ when  $\langle \Delta E_{trans}^J \rangle \cong E_{trans}^J - \langle E_{trans} \rangle_i$  (Ref. 30), where  $\langle E_{trans} \rangle_i = 3/2 \times kT_{cell}$  and  $E_{trans}^J = 3/2 \times kT_{COM}$ . For  $\langle \Delta E_{trans} \rangle$ , J = 59–75 for N<sub>2</sub>O, J = 58–82 for CO<sub>2</sub>, J = 15–21 for DCl, and J = 7–10 for H<sub>2</sub>O.

e The average total energy gain of bath molecules, scattered in the high J states of the ground vibrational state (00<sup>0</sup>0) by single collisions with hot pyrazine (E' = ~41,000 cm<sup>-1</sup>), obtained from  $<\Delta E_{total}>$  =

$$<\Delta E_{trans}> + <\Delta E_{rot}>$$
 when  $<\Delta E_{rot}> = N/2 \times k (T_{rot} - T_{cell}).$ 

f Experimental values for  $H_2O$  are obtained from Ref. 29.

g Experimental values for DCl are obtained from Ref. 30.

h Experimental values for  $CO_2$  are obtained from Ref. 24.

pyrazine and various bath molecules displayed that average energy loss of donors,  $\langle\langle\Delta E\rangle\rangle$ , increases when the size and mass of bath molecules increase. In a pyrazine–CO<sub>2</sub> classical trajectory calculation (CTC) study, Li and coworkers<sup>27</sup> also showed that chattering collision time increases with the mass of bath molecules. They concluded that multiple chattering collisions, defined as the multiple contacts between vibrationally hot donor and bath molecules resulting from flick motions, are responsible for ~50 % of V $\rightarrow$ RT supercollision energy transfer while short-range repulsive collisions are responsible for the rest. They suggested that the increase of multiple chattering collisions increases the efficiency of V $\rightarrow$ RT supercollision energy transfer.

It is well known that V $\rightarrow$ T energy transfer is dominant in a V $\rightarrow$ RT energy transfer process;<sup>24, 32, 33</sup> thus, the increase of chattering collisions must be correlated with the V $\rightarrow$ T energy transfer efficiency. In a benzene–Ar collision CTC study, Clary et al.<sup>42</sup> reported that supercollision energy transfer in donor vibrational relaxation occurs through a "flick" motion (a 40~60 fs period) within the collision duration (a few ps). In an azulene–Xe collision study, Clarke et al.<sup>43</sup> suggested that the large  $\Delta E$  collision energy transfer events occur through multiple chattering collisions composed of a number of flick motions. These previous studies are in good agreement with the results of this study given that the chattering collisions increases with the mass/size of bath molecules, resulting in an increase of V $\rightarrow$ T energy transfer amounts. Figure 3-5 shows that the heavier/bigger bath molecules gain more translational energy in collisions with hot pyrazine; the average translational energy gain,  $\langle \Delta E_{trans} \rangle$ , decreases with an order of CO<sub>2</sub> > N<sub>2</sub>O > DCl > H<sub>2</sub>O as listed in Table 3-3. Even though the masses of CO<sub>2</sub> and N<sub>2</sub>O are the same, the reason that  $\langle \Delta E_{trans} \rangle$  is bigger for CO<sub>2</sub> than for N<sub>2</sub>O may be a result of the size given that the hard sphere diameter of CO<sub>2</sub> (= 0.45 nm) is bigger than that of N<sub>2</sub>O (= 0.42 nm). Therefore, we conclude that the mass/size factor of bath molecules positively affects the amount of  $V \rightarrow T$  energy transfer.

#### 2. Angular momentum change effect on $V \rightarrow T$ energy transfer

The angular momentum change,  $\Delta J$ , for a collision complex may also be an important factor related to V $\rightarrow$ T energy transfer because  $\Delta J$  is directly related to the relative velocity change  $(\Delta v_{rel})$  according to classical collision theory,  $(h/2\pi)\Delta J = \mu b \Delta v_{rel}$ , where h is Plank's constant,  $\mu$  is the reduced mass of the collision complex, and b is the impact parameter. Prior to discussing the correlation between  $\Delta J$  and  $\langle \Delta E_{trans} \rangle$ , we consider the moment of inertia which is directly related to the bath mass and size. As the moment of inertia increases, B decreases. The decrease of B indicates that if the same amount of energy is transferred in a collision, the bath must be excited to higher rotational state. Thus, because the energy gap between rotational states  $(\Delta J_{J \to J \pm 1} \approx 2B)$  of a bath with a larger moment of inertia decreases,  $\Delta J$  gets larger for a constant energy change. Larger  $\Delta J$  also increases  $\Delta v_{rel}$ , resulting in an increase of  $\langle \Delta E_{trans} \rangle$ , since  $\langle \Delta E_{trans} \rangle$  is related to  $1/2 \mu (\Delta v_{rel})^2$ . The results of  $\langle \Delta E_{trans} \rangle$  in this study verify that the angular momentum change ( $\Delta J$ ) is affected by the moment of inertia. As seen in Table 3-3,  $<\Delta E_{trans}>$  is ordered as CO<sub>2</sub> > N<sub>2</sub>O >> DCl > H<sub>2</sub>O, the same as the moment of inertia, which is inversely proportional to the rotational constant, B. In this study, for simple comparison of bath molecules we use the average angular momentum change,  $\langle \Delta J \rangle \approx \sqrt{\langle J_f \rangle^2 - \langle J_i \rangle^2}$ ,<sup>30</sup> instead of  $\Delta J$ , where  $\langle J_i \rangle$  and  $\langle J_f \rangle$  are the average initial and final rotational states, respectively, obtained using rotational and cell temperatures of the collision complex; for CO<sub>2</sub>,  $\langle J_i \rangle = -28$ 

was employed according to the study of Mullin et al.<sup>24</sup>  $< \Delta J >$  for the different bath molecules are also listed in Table 3-3. The increasing pattern of  $< \Delta J >$  exactly matches that of  $< \Delta E_{trans} >$ :  $CO_2 > N_2O >> DCl > H_2O$ . From these same patterns, we could conclude that  $< \Delta J >$  is one of important physical parameters influencing V $\rightarrow$ T energy transfer.

However, it is interesting that although the mass/size and the moment of inertia factors of N<sub>2</sub>O and CO<sub>2</sub> are very similar, CO<sub>2</sub> has somewhat larger  $<\Delta E_{trans}>$  than does N<sub>2</sub>O (by about 500 cm<sup>-1</sup>). This indicates that other physical properties may have a greater effect on V $\rightarrow$ T energy transfer than do the mass/size and the moment of inertia. Li et al.<sup>27</sup> suggested that the moment of inertia may have a larger effect on the energy partitioning in a V $\rightarrow$ RT energy transfer process than the mass alone based on a comparison of H<sub>2</sub>O, DCl, and CO<sub>2</sub> results. In this work, we also found that the moment of inertia cannot be the dominant property for the V $\rightarrow$ T energy transfer because the amount of translational energy gain for CO<sub>2</sub> is quite a bit larger even though the moment of inertia of N<sub>2</sub>O and CO<sub>2</sub> is similar. This suggests that the angular momentum change ( $<\Delta J >$ ) may have a larger effect on V $\rightarrow$ T energy transfer than do the mass/size and the moment of inertia because the  $<\Delta E_{trans}>$  difference between CO<sub>2</sub> and N<sub>2</sub>O (~500 cm<sup>-1</sup>) can be explained by the  $<\Delta J >$  difference; N<sub>2</sub>O has  $<\Delta J > = ~32$  while CO<sub>2</sub> has  $<\Delta J > = ~37$ .

#### 3. Dipole moment effect on $V \rightarrow T$ energy transfer

This present work was performed by measuring V $\rightarrow$ RT energy transfer from vibrationally hot pyrazine to vibrational ground state N<sub>2</sub>O molecules. It is well known that V $\rightarrow$ RT energy transfer originates from short-range impulsive collisions, while V $\rightarrow$ V energy transfer is due to long-range attractive collisions.<sup>25</sup> However, we must consider the efficiency of

 $V \rightarrow V$  relaxation since an increased  $V \rightarrow V$  efficiency leads to a reduction in  $V \rightarrow RT$  collision energy transfer events. Wall and coworkers<sup>16</sup> investigated the influence of a donor permanent dipole moment on vibrational relaxation through pyridine–CO<sub>2</sub> collision experiments. They observed that  $V \rightarrow V$  energy transfer probability is considerably enhanced for pyridine, which has a large dipole moment (2.2 D) when compared to pyrazine with no dipole moment, in collisions with CO<sub>2</sub>. They suggested that the V $\rightarrow$ V energy transfer enhancement in pyridine–CO<sub>2</sub> collisions results from the dipole coupling between the donor permanent dipole moment and a large change of dipole in the anti-symmetric stretching vibrational motion of  $CO_2$  (00<sup>0</sup>1). They also showed that the population of scattered  $CO_2$  in the high J states of  $00^01$  is almost negligible; therefore, vibrationally excited  $(00^{0}1)$  CO<sub>2</sub> molecules in collisions with hot pyridine have almost no translational and rotational energy gain. They concluded that a large donor dipole moment increases the relative efficiency of long-range  $V \rightarrow V$  collisions thereby reducing the relative efficiency of short-range impulsive collisions and decreasing the  $V \rightarrow RT$  energy transfer efficiency, which is related to  $V \rightarrow T$  energy transfer efficiency. Because it is known that vibrational motion can change the dipole moment of non-polar molecules and non-polar molecules can be dipole-coupled with polar molecules, we wonder how the permanent dipole moment of bath molecules affects  $V \rightarrow V$  and in turn  $V \rightarrow T$  energy transfer.

Table 3-3 lists the permanent dipole moment of each bath molecule studied; the bath dipole moment is ordered as H<sub>2</sub>O (1.85 D) > DCl (1.05 D) > N<sub>2</sub>O (0.166 D) > CO<sub>2</sub> (0 D), which is opposite to translational energy gain amount of those bath molecules. Based on these results, it appears that a bath permanent dipole moment has a negative effect on the V $\rightarrow$ RT energy transfer by enhancing coupling between the donor vibrational motions (or the  $\pi$  electron cloud on the donor) and the permanent dipole moment of bath molecules. The large difference of the

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permanent dipole moment between DCl (or H<sub>2</sub>O) and N<sub>2</sub>O matches the large difference in V $\rightarrow$ T energy transfer amount. The difference in  $\langle \Delta E_{trans} \rangle$  between N<sub>2</sub>O and CO<sub>2</sub> may also result from coupling between pyrazine's vibrational motions (or  $\pi$  electron cloud) and the bath permanent dipole moment. We assume that it is easier for CO<sub>2</sub> to move away after collisions than N<sub>2</sub>O due to the lack of dipole coupling between CO<sub>2</sub> and pyrazine even though the mass/size and moment of inertia factors are similar for N<sub>2</sub>O and CO<sub>2</sub>. For H<sub>2</sub>O, the two hydrogen bondings (positive charge on hydrogens) increase the coupling with pyrazine  $\pi$  electron cloud (negative charge). Larger coupling between H<sub>2</sub>O and pyrazine may result in a larger decease of translational energy gain;  $\langle \Delta E_{trans} \rangle$  of H<sub>2</sub>O is the smallest among bath molecules, as can be interpreted using this technique.

#### B. Comparison of rotational energy gain for bath molecules by collisions with pyrazine

In addition to a comparison of translational energy gain, a comparison of the degree of rotational excitation may also provide insight into the bath properties associated with energy transfer. A rotational temperature, representing the average rotational energy of bath molecules scattered into the high J states of vibrationally ground level, is listed in Table 3-3 and may be used to compare rotational energy gain and explore the effect of bath physical properties. The rotational temperatures for CO<sub>2</sub>, N<sub>2</sub>O, H<sub>2</sub>O, and DCl are 1300 K, 930 K, 920 K, and 755 K, respectively. When considering with the effect of mass/size, moment of inertia, and dipole moment on rotational energy gain of bath molecules investigated in this work, we expect similar pattern to that observed for translational energy gain. This is because both V $\rightarrow$ T and V $\rightarrow$ R energy transfer result from short-range impulsive interactions. However, for H<sub>2</sub>O and DCl, the pattern is not followed. The average rotational energy gain ( $<\Delta E_{rot} >$ ) for H<sub>2</sub>O is larger than

that for DCl.  $\langle \Delta E_{rot} \rangle$  for H<sub>2</sub>O obtained from  $3/2 \times k(T_{rot} - T_{cell})$  is 650 cm<sup>-1</sup> while  $\langle \Delta E_{rot} \rangle$  for DCl obtained from  $k(T_{rot} - T_{cell})$  is 320 cm<sup>-1</sup>;  $T_{cell}$  is 300 K and k is the Boltzmann constant. The large amount of  $\langle \Delta E_{rot} \rangle$  for H<sub>2</sub>O further results in a larger total V $\rightarrow$ RT energy gain  $(\langle \Delta E_{total} \rangle)$  for H<sub>2</sub>O (990 cm<sup>-1</sup>) compared to  $\langle \Delta E_{total} \rangle$  for DCl (810 cm<sup>-1</sup>).

Why is  $\langle \Delta E_{rot} \rangle_{\text{H2O}}$  bigger than  $\langle \Delta E_{rot} \rangle_{\text{DCI}}$  even though the mass/size, the moment of inertia, and angular momentum change are larger for DCl than H<sub>2</sub>O and the permanent dipole moment is larger for H<sub>2</sub>O than DCl? Let's briefly consider factors that influence translational and rotational energy gain before we answer this question. First of all, the mass/size factor positively affects the amount of V $\rightarrow$ R energy transfer and V $\rightarrow$ T energy transfer, by increasing collision duration time and chattering collisions. In addition, the increase of moment of inertia decreases energy gap between rotational states, resulting in a large  $\langle \Delta J \rangle$ . A large  $\langle \Delta J \rangle$  leads to a large translational energy gain because  $\Delta J$  is proportional to  $\Delta v_{rel}$ . Finally, the bath permanent dipole moment reduces V $\rightarrow$ RT energy transfer due to coupling between pyrazine  $\pi$ electron cloud and bath dipole moment. These factors (mass/size, moment of inertia, angular momentum change, and permanent dipole moment) provide some insight into how bath physical parameters affect V $\rightarrow$ R energy transfer as well as V $\rightarrow$ T energy transfer. However, we could not explain the reason why  $\langle \Delta E_{rot} \rangle_{H2O}$  is larger than  $\langle \Delta E_{rot} \rangle_{DCI}$  using those bath physical parameters. Here we consider some bath physical parameters and the influence on V $\rightarrow$ R energy transfer in order to unveil the reason why  $\langle \Delta E_{rot} \rangle_{H2O}$  is greater than  $\langle \Delta E_{rot} \rangle_{DCI}$ .

#### 1. Moment of inertia effect on $V \rightarrow R$ energy transfer

First of all, the reason that  $\langle \Delta E_{rot} \rangle_{\text{H2O}}$  is larger than  $\langle \Delta E_{rot} \rangle_{\text{DCI}}$  can be investigated with a detailed consideration of the moment of inertia. A larger moment of inertia decreases the energy gap between rotational states and it ends up with larger  $\langle \Delta J \rangle$ . A large  $\langle \Delta J \rangle$  correlates to a large rotational energy gain because  $\langle \Delta E_{rot} \rangle$  is proportional to  $B(\langle J_f \rangle^2 - \langle J_i \rangle^2)$ ; see Table 3-3. However, one must be cautious since  $\langle \Delta J \rangle$  and *B* are both required to determine  $\langle \Delta E_{rot} \rangle$ .  $\langle \Delta J \rangle$  for H<sub>2</sub>O and DCl are ~5 and ~7, respectively, while the rotational constant (*B*) for H<sub>2</sub>O and DCl is ~15<sup>41</sup> and 5.39 cm<sup>-1</sup>, respectively. *B* is much larger for H<sub>2</sub>O than for DCl so that the larger *B* for H<sub>2</sub>O may overwhelm the difference of  $\langle \Delta J \rangle$  between H<sub>2</sub>O and DCl. Therefore, the reason that  $\langle \Delta E_{rot} \rangle_{\text{H2O}}$  is larger than  $\langle \Delta E_{rot} \rangle_{\text{DC1}}$  may result from  $B_{\text{H2O}} \rangle B_{\text{DC1}}$ rather than  $\langle \Delta J \rangle_{\text{H2O}} \rangle \langle \Delta J \rangle_{\text{DC1}}$ . As a result, we suggest that the moment of inertia may be the reason that  $\langle \Delta E_{rot} \rangle_{\text{H2O}}$  is larger than  $\langle \Delta E_{rot} \rangle_{\text{DC1}}$  and is one of bath physical factors that affects  $V \rightarrow R$  energy transfer.

#### 2. Structure effect on $V \rightarrow R$ energy transfer

In addition to the moment of inertia effect, the structure of bath molecules can also be an important factor for rotational energy gain in collisions with hot donors. H<sub>2</sub>O has two light H atoms on either end of the molecule (oxygen is almost at the center-of-mass) while DCl has only one light D atom at the edge (Cl is almost at the center-of-mass). When hot pyrazine collides with either bath molecule, it is twice as likely to contact the H atoms on H<sub>2</sub>O than the D atom on DCl, if H<sub>2</sub>O and DCl rotate with same speed. However, according to the studies of Fraelich et al.<sup>29</sup> and Li et al.,<sup>30</sup> H<sub>2</sub>O rotates ~2 times, while DCl rotates ~1 time in ~1 ps collision duration.

Thus, H atoms on H<sub>2</sub>O interact more frequently (about 4 times more often) with pyrazine than D atom of DCl. This results in more V $\rightarrow$ R energy transfer to H<sub>2</sub>O than to DCl.

# C. The effect of the number of bath vibrational modes on $V \rightarrow RT$ supercollision energy transfer

The number of vibrational modes of bath molecules may be another physical property that influences collisional energy transfer. If the bath molecule has many vibrational modes, the possibility that vibrational energy in the donor is transferred to the vibrational modes of the bath will increase. If we assume that the Lennard-Jones collision rate constant  $(k_{LJ})$  is approximately same as the total collisional energy transfer rate constant  $(k_{total} = k_{V \to RT} + k_{V \to V})$ ,<sup>20</sup> the integrated scattering probability,  $k_2^{int}/k_{LJ}$ , in the high J tail measured in this work can be a measure of V $\rightarrow$ RT supercollision energy transfer efficiency.

Before examining  $k_2^{\text{int}}/k_{LJ}$  for the V $\rightarrow$ RT supercollision energy transfer efficiency, we need to note that the measurements of V $\rightarrow$ RT energy transfer for the pyrazine–N<sub>2</sub>O and –CO<sub>2</sub> were performed at 248 nm, while the measurements of the pyrazine–H<sub>2</sub>O and –DCl were carried out at 266 nm. The study of Wall et al.<sup>40</sup> reported that the energy transfer rate constants of the pyrazine–CO<sub>2</sub> collisions measured at 266 nm are about one half of the rate constants obtained at 248 nm; this measurement is only limited for the high J tail (J = 56–76). If we employ their results to provide a more accurate comparison to the work performed at 248 nm, the energy transfer rate constants for the pyrazine–H<sub>2</sub>O<sup>29</sup> and –DCl<sup>30</sup> measured at 266 nm should be doubled ( $k_{2248nm}^{J} \approx 2 \times k_{2266nm}^{J}$  for the pyrazine–H<sub>2</sub>O and –DCl collisions in the high J tail only). This approach is also in good agreement with the study of Park et al.<sup>44</sup> on energy-dependent relaxation of the pyridine–CO<sub>2</sub> collisions at 273–251 nm and our previous study<sup>10</sup> on the pyridine–CO<sub>2</sub> at 248 nm in that  $k_2^J$  for the high J tail of CO<sub>2</sub> at 248 nm is about twice magnitudes of  $k_2^J$  at 266 nm for pyridine–CO<sub>2</sub> collisions. Figure 3-6 shows the comparison of scattering probabilities,  $k_2^J/k_{LJ}$ , for the pyrazine–CO<sub>2</sub>, –N<sub>2</sub>O, –DCl, and –H<sub>2</sub>O collisions as a function of state-specific total energy gain ( $\Delta E_{total}^J = <\Delta E_{trans}^J > + <\Delta E_{rol}^J >$ ) after the above application ( $k_{2\,248nm}^J \approx 2 \times k_{2\,266nm}^J$ ) was employed for DCl and H<sub>2</sub>O. In Figure 3-6,  $k_2^J/k_{LJ}$  values for CO<sub>2</sub> and N<sub>2</sub>O for  $\Delta E_{total}^J > ~5,000$  cm<sup>-1</sup> is larger than  $k_2^J/k_{LJ}$  for DCl, while  $k_2^J/k_{LJ}$  for CO<sub>2</sub> and N<sub>2</sub>O for  $\Delta E_{total}^J < ~3,000$  cm<sup>-1</sup> is smaller than  $k_2^J/k_{LJ}$  for DCl.  $k_2^J/k_{LJ}$  for H<sub>2</sub>O is the lowest in the entire  $\Delta E_{total}^J$  range.

To accurately compare the efficiency of V $\rightarrow$ RT supercollision energy transfer for those collision pairs according to the number of vibrational modes for bath molecules, the integrated energy transfer rate constant ( $k_2^{\text{int}}$ ) and the integrated scattering probability ( $k_2^{\text{int}}/k_{LJ}$ ) are listed in Table 3-4, along with fundamental vibrational frequencies of bath molecules. Note that  $k_2^{\text{int}}$  was obtained for only the high J states to compare V $\rightarrow$ RT supercollision energy transfer (above  $\Delta E_{total}^J = \sim 1,000 \text{ cm}^{-1}$ ). DCl has the largest scattering probability ( $k_2^{\text{int}}/k_{LJ}=0.258$ ) for V $\rightarrow$ RT supercollision energy transfer in comparison with CO<sub>2</sub> (0.095), N<sub>2</sub>O (0.054), and H<sub>2</sub>O (0.044). The reason for the largest  $k_2^{\text{int}}/k_{LJ}$  for DCl could be found in that the existence of only one vibrational mode decreases the possibility of V $\rightarrow$ V energy transfer, while CO<sub>2</sub> and N<sub>2</sub>O have four vibrational modes and H<sub>2</sub>O has three vibrational modes. Thus, we suggest that as the number of bath vibrational modes increases, V $\rightarrow$ RT energy transfer probability decreases and V $\rightarrow$ V energy transfer probability increases.



Figure 3-6. The comparison of scattering probabilities for the process of  $Pyrazine^{E'}$  + Bath(00<sup>0</sup>0)  $\rightarrow$  $Pyrazine^{E' \Delta E}$  + Bath(00<sup>0</sup>0;J), where Bath is N<sub>2</sub>O, CO<sub>2</sub> (Ref. 24), DCl (Ref. 30), or H<sub>2</sub>O (Ref. 29). For DCl and H<sub>2</sub>O, the energy transfer rate constants for the high J tail at 248 nm were estimated as  $2 \times k_{2266nm}^{J}$  as described in the text.

Table 3-4. The integrated energy transfer rate constants  $(k_2^{\text{int}})^a$  and the integrated scattering probabilities  $(k_2^{\text{int}}/k_{LJ})^b$  for single collision energy transfer from hot pyrazine to various bath molecules, along with fundamental vibrational frequencies for each bath molecule.

$pyrazine^{E'} + Bath \xrightarrow{k_2^J} pyrazine^{E' - \Delta E} + Bath^{\Delta E}$ at 248 nm				
Bath molecule	$k_2^{\text{inta}}$ (×10 <sup>-12</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$k_2^{\rm int}/k_{LJ}^{\rm b}$	Vibrational frequency (cm <sup>-1</sup> )	
$H_2O^{c}$	36	0.044	3657, 1595, 3756	
DCl <sup>d</sup>	141	0.258	2090	
$N_2O$	28	0.054	1285, 589 <sup>f</sup> , 2224	
$\text{CO}_2^{\text{e}}$	58	0.095	1388, 667 <sup>f</sup> , 2349	

a The integrated energy transfer rate constant obtained from  $\sum k_2^J$ , where J=59–75 for N<sub>2</sub>O, J=58–82 for

CO<sub>2</sub>, J=15–21 for DCl, and J=7–10 for  $H_2O$ .

**b** The integrated scattering probability obtained from  $k_2^{\text{int}}/k_{LJ}$ .

c Values obtained from Ref. 29. Note for comparison to N<sub>2</sub>O and CO<sub>2</sub> collected at 248 nm,  $k_2^{\text{int}}$  and

 $k_2^{\text{int}}/k_{LJ}$  are assumed to be twice the literature values obtained at 266 nm; see the text for full description.

d Values obtained from Ref. 30. Note for comparison to N<sub>2</sub>O and CO<sub>2</sub> collected at 248 nm,  $k_2^{\text{int}}$  and

 $k_2^{\text{int}}/k_{LJ}$  are assumed to be twice the literature values obtained at 266 nm; see the text for full description.

e Values obtained from Ref. 24.

f The fundamental vibrational bending modes for N<sub>2</sub>O and CO<sub>2</sub> are doubly degenerated.

Based on the effect of the bath vibrational mode number, H<sub>2</sub>O would have the second largest  $k_2^{\text{int}}/k_{LJ}$  for V→RT energy transfer because H<sub>2</sub>O has 3 vibrational modes while CO<sub>2</sub> and N<sub>2</sub>O have 4 vibrational modes. However, as seen in Table 3-4, H<sub>2</sub>O has the smallest  $k_2^{\text{int}}/k_{LJ}$ among those bath molecules. If we consider this together with the permanent dipole moment that decreases V→RT energy transfer efficiency by dipole coupling between donors and baths, the smallest  $k_2^{\text{int}}/k_{LJ}$  for the pyrazine–H<sub>2</sub>O collision energy transfer may be clarified. The reason that  $k_2^{\text{int}}/k_{LJ}$  for CO<sub>2</sub> is larger than that for N<sub>2</sub>O could also be explained by the N<sub>2</sub>O dipole moment that decreases the V→RT energy transfer efficiency. The another reason that  $k_2^{\text{int}}/k_{LJ}$  for CO<sub>2</sub> is greater than that for N<sub>2</sub>O may result from the fact that the vibrational frequencies of N<sub>2</sub>O are smaller than those of CO<sub>2</sub>, if lower vibrational frequencies of N<sub>2</sub>O result in more probable V→V energy transfer. As a result, we suggest that the number of fundamental vibrational modes in bath molecules and these frequencies may play a role in the efficiency of V→RT supercollision energy transfer.

#### **D.** V $\rightarrow$ RT Energy Transfer Probability Distribution Function, P(E,E')

Energy Transfer Probability Distribution Function, P(E,E'), calculated from stateresolved energy transfer data,<sup>26</sup> has been used in our group<sup>9-15</sup> to compare the overall V $\rightarrow$ RT energy transfer efficiency. To calculate P(E,E') from J-specific energy gain information, the initial rotational state and velocity are required to obtain the total energy transfer amount,  $\Delta E$ . As discussed elsewhere,<sup>9</sup> in the absence of an exact initial state, the average initial state may be used with only a small error. The average initial rotational state,  $\langle J_i \rangle$ , for N<sub>2</sub>O, H<sub>2</sub>O, and DCl was obtained from  $\langle E_{rot} \rangle_i = N/2 \times kT_{cell} = B \langle J_i \rangle (\langle J_i \rangle + 1)$ , where N is the number of rotational

degrees of freedom, k is the Boltzmann constant,  $T_{cell}$  is the initial cell temperature (= 300 K), and B is the rotational constant. The average initial rotational states at 300 K were determined as  $\langle J_i \rangle_{\text{N2O}} = \sim 21, \ \langle J_i \rangle_{\text{DC1}} = \sim 5, \text{ and } \langle J_i \rangle_{\text{H2O}} = \sim 4 \text{ when } B_{\text{ave,H2O}} = (27 \times 14 \times 9)^{1/3} = \sim 15.0.^{41} \text{ For}$ CO<sub>2</sub>, the average initial state,  $\langle J_i \rangle_{CO2} = \sim 28$ , was obtained using a gap law model applied to temperature dependent data.<sup>24</sup> The average initial velocity,  $\langle v_i \rangle$ , was obtained from a translational gap law model. The total energy transfer amount,  $\Delta E$ , was then determined using the average initial information and the state-specific final energy gain information. The energy transfer probability distribution functions for the pyrazine $-N_2O_2$ ,  $-CO_2$ , <sup>24</sup> and  $-DCl^{30}$  are compared for  $\Delta E = 2,000-7,000 \text{ cm}^{-1}$  in Figure 3-7. Figure 3-7 shows that energy transfer probability for collisions with pyrazine is greatest for CO<sub>2</sub> followed by N<sub>2</sub>O and then DCl for  $\Delta E$ >4,500 cm<sup>-1</sup>, while for energy transfer amount < 3,000 cm<sup>-1</sup> the order of the probability is reversed. Thus, CO<sub>2</sub> has the greatest probability of large  $\Delta E$  supercollision events. Although the probability for H<sub>2</sub>O is not compared in Figure 3-7, H<sub>2</sub>O has the smallest probability for those supercollision events according to the study of Li et al.<sup>30</sup> showing that H<sub>2</sub>O has the smallest probability on V $\rightarrow$ RT supercollision energy transfer in the entire  $\Delta E$  range studied when compared to CO<sub>2</sub>, N<sub>2</sub>O, and DCl.

To more specifically compare V $\rightarrow$ RT supercollision energy transfer efficiency in this study, P(E,E') was fit to a normalized bi-exponential function suggested by Troe<sup>45</sup> to separate strong and weak collisions,

$$P(E,E') = \frac{(1-f)\exp\{-(E'-E)/\alpha\} + f\exp\{-(E'-E)/\gamma\}}{(1-f)(\alpha+\beta) + f(\gamma+\delta)} \text{ for } E' > E.$$
(4)

Here  $\alpha$  and  $\gamma$  are the average "weak" and "strong (super)" energy transfer magnitude for downward collisions, respectively, while  $\beta$  and  $\delta$  is the average "weak" and "strong" energy



Total Energy Transfer Amount,  $\Delta E$  (cm<sup>-1</sup>)

Figure 3-7. Comparison of energy transfer probability distribution functions, P(E,E'), for CO<sub>2</sub>, N<sub>2</sub>O, and DCl in single collisions with hot pyraizine. Data used to calculate P(E,E') for CO<sub>2</sub> and DCl were obtained from Ref. 24 and 30, respectively.

transfer magnitudes for upward collisions, respectively, and *f* is defined as the strong collision "fraction."  $\alpha$  and  $\beta$ , as well as  $\gamma$  and  $\delta$ , are related each other and can be described by the detailed balance.<sup>37, 45, 46</sup> In this study,  $\beta$  and  $\delta$  are obtained by fitting the data to equation (4) and extrapolating the fit which requires that the fraction be normalized and detail balance is satisfied. The bi-exponential fit of P(E,E') is shown in Figure 3-8, along with the experimentally obtained P(E,E'). As can be seen in Figure 3-8, the experimental P(E,E') for the pyrazine–N<sub>2</sub>O collisions is in good agreement with the bi-exponential fit for  $\Delta E > \sim 2,000$  cm<sup>-1</sup>. This implies that the strong collision magnitude ( $\gamma$ ) and fraction (*f*) obtained from fitting P(E,E') to the bi-exponential function are reliable; however, the weak collision parameters are only an estimate. Using the parameters from the bi-exponential fit, we can obtain the average amount of downward energy transfer,  $\langle \Delta E \rangle_{\alpha}$ , according to

$$\left\langle \Delta E \right\rangle_d \approx \frac{(1-f) \cdot \alpha^2 + f \cdot \gamma^2}{(1-f) \cdot \alpha + f \cdot \gamma}.$$
<sup>46</sup> (5)

The bi-exponential parameters ( $\gamma$ ,  $\alpha$ , and f) and  $\langle \Delta E \rangle_d$  for the pyrazine–N<sub>2</sub>O, –CO<sub>2</sub>, and –DCl are listed in Table 3-5.  $\langle \Delta E \rangle_d$  is largest for collisions with DCl and smallest for collisions with N<sub>2</sub>O. This ordering is similar to the effect of the number of bath vibrational modes on V $\rightarrow$ RT energy transfer: DCl > CO<sub>2</sub> > N<sub>2</sub>O. Therefore, we suggest that  $\langle \Delta E \rangle_d$  may represent the V $\rightarrow$ RT energy transfer efficiency for the whole downward  $\Delta E$  range.

On the other hand, our previous study<sup>15</sup> on the fluorobenzene–CO<sub>2</sub> systems suggested that the product of  $\gamma$  and f,  $\langle \Delta E \rangle_s$ , can be defined as a V—RT supercollision energy transfer efficiency, similar to  $\langle \Delta E \rangle_d$ . Using the bi-exponential parameters, we obtained  $\langle \Delta E \rangle_s = 211$ 



Total Energy Transfer Amount,  $\Delta E$  (cm<sup>-1</sup>)

Figure 3-8. The bi-exponential fit (solid line) of the experimentally obtained P(E,E') data (dots) for the pyrazine<sup>E'</sup> + N<sub>2</sub>O(00<sup>0</sup>0)  $\rightarrow$  pyrazine<sup>E'-\Delta E</sup> + N<sub>2</sub>O(00<sup>0</sup>0;J) process when E' = ~41,000 cm<sup>-1</sup>. The bi-experimental fit parameters shown in the box were obtained using equation (4). The integration of bi-exponential fit is normalized to 1.

Table 3-5. Parameters obtained from the bi-exponential fit of experimentally obtained P(E,E'): the characteristic magnitude of strong  $(\gamma)^{a}$  and weak collisions  $(\alpha)^{b}$  the strong collision "fraction"  $(f)^{c}$  and the average energy transferred in downward collisions  $(\langle \Delta E \rangle_{d})^{d}$ .

Bath	$\gamma^{a}$ (cm <sup>-1</sup> )	$\alpha^{b}$ (cm <sup>-1</sup> )	$f^{c}$	$\left<\Delta E\right>_d^{\mathbf{d}} (\mathrm{cm}^{-1})$
CO <sub>2</sub> <sup>e</sup>	2340	531	0.09	849
$N_2O$	2625	797	0.04	829
DCl <sup>f</sup>	4867	1025	0.01	898

a The characteristic strong collision magnitude obtained by fitting experimental P(E,E') data to a biexponential function; see equation (4).

b The characteristic weak collision magnitude obtained by fitting experimental P(E,E') data to a biexponential function; see equation (4).

c The strong collision fraction obtained by fitting experimental P(E,E') data to a bi-exponential function; see equation (4). The weak collision fraction is defined as (1-*f*) because the energy transfer probability distribution function, P(E,E'), is normalized.

d The average amount of total energy transfer for downward energy transfer collisions from hot donor to bath molecules.  $\langle \Delta E \rangle_d$  was obtained from equation (5) (Ref. 46).

e Bi-exponential fit parameters of P(E,E') data for the pyrazine–CO<sub>2</sub> system obtained from Ref. 24.

f Bi-exponential fit parameters of P(E,E') data for the pyrazine–DCl obtained from Ref. 30.

cm<sup>-1</sup> for CO<sub>2</sub>, 105 cm<sup>-1</sup> for N<sub>2</sub>O, and 49 cm<sup>-1</sup> for DCI. Although we have not calculated P(E,E') for H<sub>2</sub>O given the small  $P_J$  magnitudes in this  $\Delta E$  range,  $\langle \Delta E \rangle_s$  for H<sub>2</sub>O will be even smaller than that for DCI. This order is in excellent agreement with our interpretation of the mass/size, moment of inertia, and dipole moment effect for the various bath molecules discussed here on V $\rightarrow$ RT supercollision energy transfer. In other words, P(E,E) results are consistent with the trends in bath molecule properties as discussed above. One note of caution must be considered as noted previously that we have scaled the collision rate constants and probability (and therefore P(E,E')) for the pyrazine–H<sub>2</sub>O and –DCl systems to make the results of these various studies more comparable. This scaling may result in errors in obtaining  $\langle \Delta E \rangle_s$  as well as bi-exponential fit parameters for the pyrazine–H<sub>2</sub>O and –DCl systems. In addition, all of these probabilities are determined using a Lennard-Jones potential. Given the errors in their intermolecular potential,<sup>20</sup> these may be additional errors in the rate constants. A more accurate comparison can be made by repeating these studies at a 266 nm excitation. Those results could be directly compared for all four bath molecules, using previously obtained pyrazine–CO<sub>2</sub> results at 266 nm.<sup>40</sup>

### V. Conclusion

The vibrational relaxation of highly vibrationally excited pyrazine ( $E' = ~41,000 \text{ cm}^{-1}$ ) in single collisions with N<sub>2</sub>O of the ground vibrational level ( $00^{0}0$ ) was studied using a transient absorption probe technique. The state-specific rotational and translational energy distribution for N<sub>2</sub>O scattered into  $00^{0}0$ , J = 59–75 by single collisions with hot pyrazine was measured by probing N<sub>2</sub>O transitions ( $00^{0}1$ ;J±1  $\leftarrow 00^{0}0$ ;J=59–75). The measured state-specific energy distribution information for N<sub>2</sub>O was then compared with the previous studies (pyrazine–CO<sub>2</sub>,<sup>24</sup>  $-DCl_{,30}^{,30}$  and  $-H_2O^{29}$ ) to explore the influence of bath molecule physical properties on V $\rightarrow$ RT supercollision energy transfer. Several physical properties of the bath molecules seem to play a role in governing the magnitude and probability of large  $V \rightarrow RT$  energy transfer events. These include the mass/size (or moment of inertia), angular momentum change, dipole moment, and the number and frequency of vibrational modes. We observed that the mass/size (or moment of inertia) and angular momentum change of bath molecules increases the amount of  $V \rightarrow RT$ energy transfer, while the dipole moment and the number of vibrational modes decrease the overall  $V \rightarrow RT$  energy transfer efficiency. The correlation between the mass/size (or moment of inertia) and the amount of  $V \rightarrow RT$  energy transfer originates from chattering collisions and the increasing time of the collision event. The angular momentum change,  $\Delta J$ , also positively affects V  $\rightarrow$  RT energy transfer amount; i.e.  $\Delta J \propto \Delta v_{rel}$  and  $\langle \Delta E_{rot} \rangle$ . On the other hand, the dipole moment decreases the V $\rightarrow$ RT energy transfer efficiency by increasing the dipole coupling between donor's  $\pi$  electron cloud and bath polarity; as the dipole coupling increases, V  $\rightarrow$  V energy transfer increases due to the increase of long-range attractive collisions, while  $V \rightarrow RT$ energy transfer decreases. In addition, more vibrational modes increase  $V \rightarrow V$  energy transfer probability, so that  $V \rightarrow RT$  energy transfer probability decreases in collisions between hot pyrazine and bath molecules with more vibrational modes. The energy transfer probability distribution function, P(E,E'), was obtained from the state-specific energy gain information and compared with the previous studies to further investigate the effect of bath physical properties on V $\rightarrow$ RT supercollision energy transfer. The P(E,E') for different bath molecules are also consistent with the correlation of bath molecule physical properties.

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Chapter 4

Vibrational Relaxation Dynamics of Highly Vibrationally Exited Pyrazine in Single

Collisions with  $N_2 O\colon II.$  Rotational and Translational Energy

Gain of N<sub>2</sub>O in the Mid J Tail (J=37–57)

# I. Introduction

Collisional energy transfer processes between highly vibrationally excited donors and small room temperature bath molecules have been investigated using a variety of spectroscopic approaches, such as UV absorption (UVA),<sup>1,2</sup> IR fluorescence (IRF),<sup>3-5</sup> kinetically controlled selective ionization (KCSI),<sup>6-8</sup> and high-resolution transient IR absorption.<sup>9-24</sup> Transient absorption measures energy gain of bath molecules by probing state-specific transient IR absorption, while UVA, IRF, and KCSI measure energy loss of donor molecules after collisions. Flynn,<sup>9-11</sup> Mullin,<sup>12-16</sup> and our group<sup>17-24</sup> have used transient absorption spectroscopy to obtain energy the transfer probability distribution function, P(E,E'), from the state-specific energy gain information of bath molecules. However, until recently the obtained energy transfer probability distribution only part of the energy gain data (only in the high J tail) to the entire range of  $\Delta E$ . This was due to experimental limitations including saturation of absorption signals and the difficulty of distinguishing the molecules scattered into a state from the ambient background signals in the low J states; both of these make it difficult to measure the energy gain of bath molecules in low J states.

Recently, Havey et al.<sup>25</sup> have proposed a new approach to measure the population change of post-collision bath molecules in low J states by probing overtone or combination bands with small absorption coefficients. Probing transitions with small absorption coefficients could avoid the limitation of absorption signal saturation. Another limitation, background population, can be avoided by distinguishing between appearance and depletion population of bath molecules. This is done by fitting the experimental line shape profiles to a double parametric Gaussian function, which distinguishes between molecules that scatter into a rotational state and those that scatter out. Finally, the energy transfer probability distribution with partial extrapolation in the low  $\Delta E$ 

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region has been improved by measuring the energy gain of bath molecules for the whole J range in the Mullin group.<sup>26-28</sup> They reported fully measured energy transfer probability distribution without any extrapolation of energy gain data.

Since the time that Hinschelwood<sup>29</sup> recognized "strong" collision energy transfer as a competing process with chemical reactions, many researchers have anticipated being able to separately observe weak and strong collision energy transfer processes. For example, Troe<sup>30-32</sup> formulated strong and weak collision energy transfer models for the energy transfer probability distribution function and applied these models to master equation modeling in order to obtain accurate unimolecular reaction rates. The theoretical studies of Bernshtein and Oref<sup>33, 34</sup> have reported supercollision efficiency on unimolecular reactions and separated strong and weak collision efficiency using a modified bi-exponential energy transfer probability formula. Other theoretical studies performed by Lendvay et al.,<sup>35</sup> Clary et al.,<sup>36</sup> and Li et al.<sup>37</sup> using classical trajectory calculations (CTC) have shown the importance of supercollisions in chemical reactions by comparing strong collisions with weak collisions, which are described as large and small energy transfer amounts, respectively. Their work has further reported on the effect of donor molecular physical properties on collision energy transfer. In contrast to these theoretical studies, until recently experimental studies have only been capable of measuring large energy transfer or average energy transfer.

Recently the Mullin group have performed studies on pyrazine–HOD,<sup>26</sup> –CO<sub>2</sub>,<sup>28</sup> and –DCl<sup>27</sup> collisions to measure energy transfer into the whole J range of bath molecules. They observed weak collisions for HOD (J < 10), DCl (J < 15), and CO<sub>2</sub> (J < 50) in comparison with strong collisions by observing different rotational and translational temperature distributions in different final bath state ranges.

In this work, we also observed a turning point between weak to strong collisions, which is shown in the rotational and translational energy distributions. This turning point (J = 55) corresponds to the end point of the range that the scattered-out N<sub>2</sub>O population appears from thermally populated N<sub>2</sub>O prior to collisions with hot pyrazine. As a result of this correspondence, we discuss the correlation between weak collisions and scattered-out N<sub>2</sub>O population. The assumption that the scattered-out population must be equal to the scattered-in population according to conservation of matter enabled us to compare the scattered-in Boltzmann probability with scattered-out Boltzmann probability for post-collision N<sub>2</sub>O and obtain the Jdependence of N<sub>2</sub>O energy gain. Using this, we can determine the average initial J value of N<sub>2</sub>O,  $< J_{ini} >$ .

The goal of this study is to extend the N<sub>2</sub>O energy gain measurements to the mid J states (J = 37-57) and to analyze the data obtained from the mid J range measurements along with data obtained from our previous study<sup>23</sup> of the high J tail (J = 59–75). Doppler broadened absorption line profiles with Gaussian dips shown in the J = 37–54 region were fit to a double parametric Gaussian function so that the scattered-out N<sub>2</sub>O population could be distinguished from the scattered-in N<sub>2</sub>O population. Boltzmann probabilities for scattered-in and scattered-out N<sub>2</sub>O in single collisions with hot pyrazine were compared and a new approach to obtain the average initial N<sub>2</sub>O rotational state is presented. Rotational and translational energy distributions for the scattered-in N<sub>2</sub>O were characterized with weak and strong collisions from J = 55 turning point. The weak collision distribution was then determined  $T_{rot_mid} = 500$  K and  $T_{trans_mid} = 600-1,000$  K for J = 37–54, while the strong collision distribution was determined as  $T_{rot_high} = 940$  K and  $T_{trans_high} = 1,000-2,600$  K for J = 55–75 of scattered-in N<sub>2</sub>O molecules. Comparison of the integrated scattering probability with the normalized Boltzmann probability for the measured

scattered-in N<sub>2</sub>O gives evidence that the Lennard-Jones collision rate constant  $(k_{LJ})$  used in this study is an underestimation of the true collision rate constant by a factor of two. Another evidence of this underestimation is obtained from the average rate constant,  $\langle k_{out}^J \rangle$ , for scatteredout N<sub>2</sub>O. The correct  $k_{col}$  estimated from the evidence is in good agreement with results of a previous study on energy loss measurements and the agreement is shown through comparison of the downward average energy transfer,  $\langle \Delta E \rangle_d$ .

### **II. Experimental**

Vibrational relaxation of highly vibrationally excited pyrazine due to single collisions with room temperature N<sub>2</sub>O molecules has been observed by measuring the energy gain of N<sub>2</sub>O in the J = 37–57 range using a high-resolution transient IR absorption spectroscopic method. The detailed description of this experiment has been given previously;<sup>17</sup> only the brief description is presented here. A 1:1 20.0 mTorr mixture of pyrazine and N<sub>2</sub>O flows through a 200 or 100 cm long collision cell. Highly vibrationally excited pyrazine was prepared through a rapid radiationless internal conversion from S<sub>2</sub> to S<sub>0</sub>\* following 248 nm UV absorption of pyrazine by a KrF excimer laser (Lamda Physik Complex 201). UV light was propagated through the collision cell collinearly with  $\lambda = ~4.6 \ \mu m$  light generated from a narrow ( $\Delta \nu =$ 0.0003 cm<sup>-1</sup>) IR probe laser (Laser Components). The UV light intensity was maintained at 4 – 6 mJ/cm<sup>2</sup> to minimize multiphoton absorption;<sup>38</sup> multiphoton absorption was not detected in that intensity range. IR light was used to probe anti-symmetric stretching ro-vibrational transitions (00<sup>0</sup>1;J±1(-00<sup>0</sup>0;J=37-57) for N<sub>2</sub>O populated in single collisions with hot pyrazine. State-specific Doppler broadened line profiles were obtained by scanning the IR laser over the range of  $\Delta v = \pm 0.01$  cm<sup>-1</sup> near the center frequency of the probe transitions and measuring the transient absorption signal 1  $\mu$ s after the UV pulse. Doppler broadened line shape profiles for J = 37–54 were used not only to calculate the number density of post-collision N<sub>2</sub>O molecules, but also to obtain full widths at half maximum (FWHM), while the line profiles measured for J = 55–57 were only used to obtain full widths at half maximum. The IR absorption signals were averaged over ~100 shots for each position. The number density of scattered-in N<sub>2</sub>O at J = 55–57 was determined by measuring and calibrating IR absorption signals at the center frequency of the transitions.

Pyrazine (Aldrich, 99+ % purity) was degassed using three freeze-pump-thaw cycles prior to use, while  $N_2O$  gas (Intermountain Airgas Inc., 99.9999+ % purity) was used without any purification.

# **III. Results**

### A. Transient IR Absorption Signals for Post-collision N<sub>2</sub>O in Collisions with Pyrazine

N<sub>2</sub>O transient IR absorption signals at 1  $\mu$ s following the UV pulse were measured for J = 37–57 of vibrational ground state (00<sup>0</sup>0) using a high-resolution solid state IR diode laser. The transient absorption signals were obtained by probing the anti-symmetric stretching ro-vibrational transition of N<sub>2</sub>O (00<sup>0</sup>1;J-1  $\leftarrow$  00<sup>0</sup>0;J) scattered into and out of J states in single collisions with vibrationally hot pyrazine. We expected an increase in the transient IR absorption signals at early times (< 4  $\mu$ s) with a decrease in J state. However, the IR absorption signals measured at center frequency of the probe transitions for J = 37–54 decrease as J

decreases, while the IR absorption signals for  $J \ge 55$  increase with the decrease of J state. Figure 4-1 shows the transient IR absorption signals measured for J = 53, 55, and 57 of N<sub>2</sub>O. The unexpected decrease of the IR signal for J = 53 at early times, in comparison with the IR signal for J = 55, is clearly shown.

The decrease of IR signals is due to molecules that are scattered out of rotational states J < 55 and scattered into other states, as seen in the Gaussian dip in Figure 4-2. The IR absorption line profiles in Figure 4-2 were measured at 50–60 different frequencies near the center frequency of the probed transition  $(00^{0}1;J=53 \leftarrow 00^{0}0;J=54, \nu_0=2168.7416 \text{ cm}^{-1})$ . The dip at the center of a Doppler broadened line shape in Figure 4-2 is a result of N<sub>2</sub>O molecules scattered out of J = 54, while the broadened rising signals represent N<sub>2</sub>O molecules scattered into J = 54 by single collisions with hot pyrazine.

#### B. Double Gaussian Fit for Doppler-broadened Line Shapes of N<sub>2</sub>O Absorption Signals

The Gaussian dip at the center frequency was observed in the Doppler broadened line shape measurements for J = 37-54 of N<sub>2</sub>O, while the line shapes for  $J \ge 55$  of N<sub>2</sub>O, including the measurements for J = 59-75 in our previous study,<sup>23</sup> have no dip at the center. This indicates that Doppler broadened line shapes measured for J < 55 must be fit to a double Gaussian function to account for N<sub>2</sub>O population scattered out of the J state, shown as a negative Gaussian dip, and N<sub>2</sub>O population scattered into the J state, shown as a positive Gaussian. The best nonlinear least squares fit of the absorption line profiles to double Gaussian functions is shown in Figure 4-3, which displays Doppler broadened line profiles for J = 54 and J = 46. Double Gaussian fit in Figure 4-3 was obtained using



Time (s)

Figure 4-1. Transient IR absorption signals of post-collision N<sub>2</sub>O scattered by single collisions with highly vibrationally excited pyrazine ( $E' = \sim 41,000 \text{ cm}^{-1}$ ) on the  $\mu$ s time scale, measured for J = 53 (dotted line), 55 (short-dashed line), and 57 (dashed line). The signals were measured by probing the anti-symmetric stretching ro-vibrational transition ( $00^{0}1;J-1 \leftarrow 00^{0}0;J$ ) for post-collision N<sub>2</sub>O. The magnitude of signals obtained at 1  $\mu$ s following UV pulse is ordered as J = 55 > 53 > 57.



Relative Frequency to the Center of the Peak  $\nu$  (cm<sup>-1</sup>)

Figure 4-2. The early (1  $\mu$ s) transient absorption line profile for post-collision N<sub>2</sub>O molecules of J = 54. Squares represent the transient absorption signals at 1  $\mu$ s after UV pulse and dash line is the best nonlinear least squares fit to a double Gaussian function. The Gaussian dip at the center frequency of the transition peak results from N<sub>2</sub>O molecules scattered out of J = 54 by single collisions with hot pyrazine, while the rising signals on either side of the dip originate from the increase of N<sub>2</sub>O molecules scattered into J = 54.



Relative Frequency to the Center of the Peak  $\nu$  (cm<sup>-1</sup>)



Relative Frequency to the Center of the Peak $\lambda v$  (cm<sup>-1</sup>)

Figure 4-3. Double Gaussian fit of the transient absorption line profiles for post-collision N<sub>2</sub>O in (a) J = 54 and (b) J = 46. Squares represent the transient absorption signals at 1  $\mu$ s after a UV pulse. The solid line is the best non-linear least squares fit of the absorption line profile to a double Gaussian function. Dashed and dotted lines are the best non-linear least squares fits to a single Gaussian function of scattered-in and scattered-out N<sub>2</sub>O absorption line profiles, respectively. For (a) J = 54, the measured full widths at half maximum (FWHM) for scattered-in and scattered-out N<sub>2</sub>O are  $\Delta v_{in} = 0.0068 \pm 0.0005$  cm<sup>-1</sup>

and  $\Delta v_{out} = 0.0024 \pm 0.0003 \text{ cm}^{-1}$ , respectively, which correspond to  $T_{trans,in} = 880 \pm 50 \text{ K}$  and  $T_{trans,out} = 100 \pm 30 \text{ K}$ , respectively. For (b) J = 46 the measured FWHM for scattered-in and scattered-out N<sub>2</sub>O are  $\Delta v_{in} = 0.0069 \pm 0.0004 \text{ cm}^{-1}$  and  $\Delta v_{out} = 0.0035 \pm 0.0005 \text{ cm}^{-1}$ , respectively, which correspond to  $T_{trans,in} = 870 \pm 90 \text{ K}$  and  $T_{trans,out} = 230 \pm 60 \text{ K}$ , respectively.  $\Delta I_{in}$  and  $\Delta I_{out}$  obtained from this double Gaussian fit are used to calculate the number density of scattered-in and scattered-out N<sub>2</sub>O molecules, respectively.

$$\Delta I_{tot} = \Delta I_{in} \exp\left[-4\ln 2\left(\frac{v-v_0}{\Delta v_{in}}\right)^2\right] - \Delta I_{out} \exp\left[-4\ln 2\left(\frac{v-v_0}{\Delta v_{out}}\right)^2\right] + m(v-v_0) + \Delta I_{int}, \quad (1)$$

where  $\Delta I_{tot}$  and  $\Delta I_{int}$  are the total absorption intensity and the baseline intensity at the center frequency of the probe transition ( $v_0$ ), respectively.  $\Delta I_{in}$  and  $\Delta I_{out}$  are the absorption intensities at  $v_0$  for scattered-in and scattered-out N<sub>2</sub>O, respectively, while  $\Delta v_{in}$  and  $\Delta v_{out}$  are the observed full widths at half maximum (FWHM) for scattered-in and scattered-out N<sub>2</sub>O, respectively. ( $v - v_0$ ) represents the relative frequency ( $\Delta v$ ) to  $v_0$  and m is the slope of the baseline for the double Gaussian fit. Obtaining  $\Delta I_{in}$  and  $\Delta I_{out}$  from a double Gaussian fit allows us to correct for the decrease of the transient absorption signal at line center observed in J < 55. As seen in Figure 4-3, FWHM for scattered-in and scattered-out N<sub>2</sub>O for J = 54 are  $\Delta v_{in} = 0.0068 \pm 0.0005$ cm<sup>-1</sup> and  $\Delta v_{out} = 0.0024 \pm 0.0003$  cm<sup>-1</sup>, respectively, while the FWHM for scattered-in and scattered-out N<sub>2</sub>O for J = 46 are  $\Delta v_{in} = 0.0069 \pm 0.0004$  cm<sup>-1</sup> and  $\Delta v_{out} = 0.0035 \pm 0.0005$  cm<sup>-1</sup>, respectively.

These FWHM can be directly converted to a lab-frame translational temperature,  $T_{trans}$ , according to

$$T_{trans} = \frac{m_{N_2O}c^2}{8R\ln 2} \left(\frac{\Delta v_{obs}}{v_0}\right)^2,\tag{2}$$

where  $m_{N_2O}$  is the mass of N<sub>2</sub>O, *R* is the gas constant, and  $\Delta v_{obs}$  is the observed FWHM determined by fitting Doppler broadened line profiles to a Gaussian function. Hereafter  $\Delta v_{obs}$  is designated by  $\Delta v_{in}$  for scattered-in N<sub>2</sub>O and  $\Delta v_{out}$  for scattered-out N<sub>2</sub>O for the specific J state. In Figure 4-3,  $\Delta v_{in}$  for (a) J = 54 and (b) J = 46 corresponds to  $T_{trans,in} = 880 \pm 50$  K and  $870 \pm 90$ K, respectively, while  $\Delta v_{out}$  for (a) J = 54 and (b) J = 46 results in  $T_{trans,out} = 100 \pm 30$  K and 230  $\pm$  60 K, respectively. For comparison,  $\Delta v_{obs}$  at 300 K is ~0.0040 cm<sup>-1</sup>. Lab-frame translational temperatures for scattered-in ( $T_{trans,in}$ ) and scattered-out N<sub>2</sub>O molecules ( $T_{trans,out}$ ) are listed in Table 4-1 and Table 4-2, respectively, along with full widths at half maximum obtained from single or double Gaussian fitting ( $\Delta v_{in}$  and  $\Delta v_{out}$ ), depending on the J state.

# C. Boltzmann Distribution for Post-collision N<sub>2</sub>O in Collisions with Hot Pyrazine

 $\Delta I_{in}$  and  $\Delta I_{out}$  obtained from double Gaussian fits of Doppler broadened line shapes for J < 55 were used to calculate the population of N<sub>2</sub>O scattered-in and scattered-out of various J states in single collisions with hot pyrazine. Note that Doppler broadened line shapes for J = 55–57 in this work and J = 59–75 in our previous study<sup>23</sup> exhibit only a single Gaussian shape, which indicates that N<sub>2</sub>O population scattered out of the J state by single collisions with hot pyrazine is negligible in comparison with the absorption intensity for N<sub>2</sub>O molecules scattered into the state. Combining  $\Delta I_{in}$  for J = 37–54 obtained by double Gaussian fits and the linecenter measurements for J = 55–75, we obtained two different Boltzmann distributions for scattered-in N<sub>2</sub>O: one for J = 37–55 and another for J = 55–75. Figure 4-4 displays these two different Boltzmann plots. The Boltzmann plot for scattered-in N<sub>2</sub>O for J = 37–55 corresponds to  $T_{rot,mid}$  = 500 ± 180 K and the plot of J = 55–75 results in  $T_{rot,high}$  = 940 ± 50 K. The logarithm of population for scattered-out N<sub>2</sub>O from J = 37 to 54 (ln(N<sub>1</sub>/(2J+1))), using  $\Delta I_{out}$  obtained from the double Gaussian fits, is also plotted in Figure 4-4 as a function of N<sub>2</sub>O rotational energy to determine a rotational temperature,  $T_{rot,out}$  = 245 ± 90 K.

From these two different rotational temperatures for scattered-in N<sub>2</sub>O, we define pyrazine–N<sub>2</sub>O collisions resulting in J < 55 of N<sub>2</sub>O rotational states to be weak collisions, while

$N_2O(00^00)$	$Pyr^{E'} + N_2O(00^{0}0;J_i) \xrightarrow{k_m^J} Pyr^{E'-\Delta E} + N_2O(00^{0}0;J)$				
J state	$E_{rot} \left( \mathrm{cm}^{-1} \right)^{d}$	$\Delta v_{in} (\mathrm{cm}^{-1})^{\mathrm{a}}$	$T_{transin}$ (K) <sup>b</sup>	$T_{COM}$ (K) <sup>c</sup>	
37	589.11	$0.0060 \pm 0.0009$	660 ± 190	860 ± 300	
41	721.52	$0.0059 \pm 0.0006$	$610\pm130$	$780 \pm 200$	
45	867.33	$0.0071 \pm 0.0005$	$910\pm130$	$1240\pm200$	
46	905.88	$0.0069 \pm 0.0004$	$870\pm90$	$1190 \pm 140$	
47	945.26	$0.0065 \pm 0.0008$	$780\pm200$	$1050\pm300$	
48	985.49	$0.0074 \pm 0.0002$	$990 \pm 40$	$1380 \pm 60$	
49	1026.55	$0.0075 \pm 0.0005$	$1020\pm140$	$1420\pm210$	
50	1068.45	$0.0073 \pm 0.0006$	$980 \pm 160$	$1350\pm250$	
54	1244.43	$0.0068 \pm 0.0005$	$880\pm50$	$1200 \pm 80$	
55	1290.52	$0.0075 \pm 0.0002$	$1020 \pm 40$	$1420 \pm 60$	
56	1337.45	$0.0075 \pm 0.0004$	$1020 \pm 50$	$1420\pm80$	
57	1385.21	$0.0075 \pm 0.0004$	$1040 \pm 50$	$1450\pm80$	

Table 4-1. State-specific full width at half maximum (FWHM)<sup>a</sup> for Doppler-broadened line shapes, labframe<sup>b</sup> and center-of-mass translational temperatures<sup>c</sup> for N<sub>2</sub>O scattered into J = 37–57 of 00<sup>0</sup>0 by single collisions with highly vibrationally excited pyrazine ( $E' = \sim 41,000 \text{ cm}^{-1}$ ).

a Full width at half maximum (FWHM) for Doppler-broadened line shapes, which were measured by fitting transient IR absorption profiles for anti-symmetric stretching ro-vibrational transitions of N<sub>2</sub>O(00<sup>0</sup>1;J-1) ← N<sub>2</sub>O(00<sup>0</sup>0;J) to a double or single Gaussian function. Transient IR absorption signals at 1 μs following UV excitation of pyrazine at 248 nm, distributed evenly near center frequency of the transition, were collected and averaged over 100 shots. FWHM for J = 37–54 were obtained from a double Gaussian fit (equation (5)), while FWHM for J = 55–57 were obtained from a single Gaussian fit. b Lab-frame translational temperature determined from using Equation (2). c Center-of-mass (COM) translational temperatures determined using Equation (3).

d Rotational energy of N<sub>2</sub>O scattered into J = 37–57 of  $00^{0}0$  level by single collisions with hot pyrazine.  $E_{rot}$  is obtained from  $E_{rot} = BJ(J+1)$ , where *B* is the rotational constant for the bath molecule (N<sub>2</sub>O in this study).

N <sub>2</sub> O (00 <sup>0</sup> 0)	$Pyr^{E'} + N_2 O(00^0 0; J) \xrightarrow{k_{out}^{J}} Pyr^{E''} + N_2 O(00^0 0; J')$			
J state	$E_{rot} (\mathrm{cm}^{-1}) \qquad \Delta v_{out} (\mathrm{cm}^{-1})^{\mathrm{a}}$		T <sub>transout</sub> (K) <sup>b</sup>	
37	589.11	$0.0039 \pm 0.0011$	$290 \pm 160$	
41	721.52	$0.0032 \pm 0.0007$	$180 \pm 70$	
45	867.33	$0.0040 \pm 0.0005$	$290\pm70$	
46	905.88	$0.0035 \pm 0.0005$	$230\pm60$	
47	945.26	$0.0036 \pm 0.0007$	$240\pm90$	
48	985.49	$0.0038 \pm 0.0005$	$260 \pm 60$	
49	1026.55	$0.0034 \pm 0.0006$	$220\pm70$	
50	1068.45	$0.0039 \pm 0.0009$	$280 \pm 110$	
54	1244.43	$0.0024 \pm 0.0003$	$100 \pm 30$	

Table 4-2. State-specific full width at half maximum (FWHM) for Doppler-broadened line shapes,<sup>a</sup> lab-

frame translational temperatures<sup>b</sup> for N<sub>2</sub>O scattered out of J=59–54 of  $00^{0}0$  by single collisions with

highly vibrationally excited pyrazine ( $E' = \sim 41,000 \text{ cm}^{-1}$ ).

a Full width at half maximum (FWHM) for Gaussian dip portion, which were measured by fitting transient IR absorption profiles for anti-symmetric stretching ro-vibrational transitions of N<sub>2</sub>O(00<sup>0</sup>1;J-1)  $\leftarrow$  N<sub>2</sub>O(00<sup>0</sup>0;J) to a double Gaussian function.

b Lab-frame translational temperature determined using Equation (2).



Rotational Energy for Post-collision NO,  $E_{rot}$  (cm<sup>-1</sup>)

Figure 4-4. Boltzmann distributions for N<sub>2</sub>O scattered into J = 37–75 and N<sub>2</sub>O scattered out of J = 37–54 in single collisions with vibrationally hot pyrazine. Boltzmann distributions for J = 37–54 of scattered-in (squares) and scattered-out N<sub>2</sub>O (circles) were obtained from  $\Delta I_{in}$  and  $\Delta I_{out}$ , respectively, using a Double Gaussian fit, while Boltzmann distribution for J = 55–75 (diamonds) were obtained from linecenter measurements. Boltmann plots for J = 37–55 and J = 55–75 of scattered-in N<sub>2</sub>O correspond to  $T_{rot_{mid}}$  = 500 ± 180 K and  $T_{rot_{high}}$  = 940 ± 50 K. A Boltzmann plot for J = 37–54 of scattered-out N<sub>2</sub>O corresponds to  $T_{rot_{out}}$  = 245 ± 90 K. The turning point between weak and strong collision was determined to be J = 55.

A rotational temperature obtained from a Boltzmann plot represents the average rotational energy for molecules characterized by the Boltzmann distribution.

collisions resulting in J  $\ge$  55 of N<sub>2</sub>O are defined to be strong collisions. Rotational temperature,  $T_{rot}$ , obtained by Boltzmann plots is related to the average rotational energy for post-collision N<sub>2</sub>O in single collisions with hot pyrazine. Using the equipartition theorem, the average rotational energy for scattered-in N<sub>2</sub>O in the J = 37–55 range is determined  $\langle E_{rot} \rangle_{mid} = kT_{rot_mid} \approx$ 348 cm<sup>-1</sup>, while the average rotational energy for scattered-in N<sub>2</sub>O for J = 55–75 is  $\langle E_{rot} \rangle_{high} =$   $kT_{rot_high} \approx 653$  cm<sup>-1</sup>, where k is the Boltzmann constant. Defining weak and strong collision energy transfer using the average rotational energy for post-collision N<sub>2</sub>O, the turning point from weak to strong collision energy transfer is determined to be J = 55 ( $E_{rot} = 1290.52$  cm<sup>-1</sup>).

### **IV. Discussion**

### A. Translational Energies for Post-collision N<sub>2</sub>O

State-specific post-collision translational energies for N<sub>2</sub>O scattered by collisions with hot pyrazine were measured by fitting Doppler broadened line profiles of J = 37-57 to a double or single Gaussian function. The Double Gaussian line shapes for IR absorption signals were observed for J = 37-54, while N<sub>2</sub>O scattered into J = 55-57 were fit to a single Gaussian line shape; note that our previous pyrazine–N<sub>2</sub>O study<sup>23</sup> for the high J tail (J = 59-75) indicated that only single Gaussian shapes were observed in that range. Lab-frame translational temperatures ( $T_{trans,out}$ ) for scattered-out N<sub>2</sub>O in the J = 37-54 range are displayed in Figure 4-5, along with lab-frame translational temperatures ( $T_{trans,in}$ ) for scattered-in N<sub>2</sub>O in the J = 37-75 range. The  $T_{trans,in}$  are accurately fit to a single exponential function while  $T_{trans,out}$  are almost invariant except for J = 41 and 54. We assume that smaller  $T_{trans,out}$  for J = 41 and 54, compared to  $T_{trans,out}$ for other J states, are due to experimental errors; see  $T_{trans,in}$  for J = 41 and 54 that are smaller



Rotational State for Post-collision  $NO, J_f$ 

Figure 4-5. State-specific lab-frame translational temperatures for scattered-in N<sub>2</sub>O in the J = 37–75 and scattered-out N<sub>2</sub>O for J = 37–54. Squares are the lab-frame translational temperatures for scattered-in N<sub>2</sub>O of J = 37–57, while circles are the lab-frame translational temperatures for scattered-out N<sub>2</sub>O of J = 37–54. Diamonds are the lab-frame translational temperatures for scattered-in N<sub>2</sub>O of J = 59–75 obtained in our previous study (Ref. 23).  $T_{trans,out}$  for J < ~54 show almost constant values (~250 K), while  $T_{trans,in}$  for J < 55 show gradual decreasing values, 600–1,000 K (as an average value of ~850 K).

than the exponential fit line (Figure 4-5) by similar amount. Translational temperatures for scattered-in and scattered-out N<sub>2</sub>O molecules in J = 37-54 change very little or not at all with approximate temperatures of  $T_{trans,in} = -850$  K and  $T_{trans,out} = -250$  K. This result is in good agreement with previous studies on pyrazine–CO<sub>2</sub>,<sup>28</sup>–HOD,<sup>26</sup> and –DCl<sup>27</sup> in that translational temperatures of low J states are nearly constant. For example, the studies on pyrazine– $CO_2$ ,<sup>28</sup> -HOD,<sup>26</sup> and -DCl<sup>27</sup> show that lab-frame translational temperatures for appearance  $(T_{trans,in})$  are nearly constant at ~740 K for J  $\leq$  52 for scattered-in CO<sub>2</sub>, ~580 K for J  $\leq$  7 for scattered-in HOD, and ~680 K for J  $\leq$  12 for scattered-in DCl. In addition,  $T_{trans,out}$  for scattered-out CO<sub>2</sub>, HOD, and DCl are invariant at ~350 K for  $J \le 38$ , ~330 K for  $J \le 7$ , and ~170 K for  $J \le 7$ , respectively. According to these studies,  $^{26-28}$  the depletion Doppler line widths ( $\Delta v_{out}$ ) represent the velocity distribution of bath molecules prior to collisions. This indicates that N<sub>2</sub>O molecules, as has been seen with CO<sub>2</sub>, HOD, and DCl scattered into low J states during single collisions with hot pyrazine, gain only a small amount of translational energy in the range of J < 55. That is, the small variance in low translational temperatures ( $T_{trans,in} = 600-1,000$  K) for J = 37–54 suggests that collisions that scatter  $N_2O$  into J = 37-54 are weak collisions, while the linear increase of high lab-frame translational temperatures ( $T_{trans.in} = 1,020-2,610$  K) for J = 55-75 are collisions where  $N_2O$  gains a large amount of translational energy from hot pyrazine, defined as strong collisions.

The center-of-mass translational temperature ( $T_{COM}$ ) can be obtained from the lab-frame translational temperature ( $T_{trans}$ ) in order to determine the state-specific translational energy gain of post-collision N<sub>2</sub>O in single collisions with hot pyrazine ( $E' = \sim 41,000 \text{ cm}^{-1}$ ). The following equation is used to convert  $T_{trans}$  to  $T_{COM}$ .

$$T_{COM} = T_{trans} + \left(\frac{m_{N_2O}}{m_{pyr}}\right) (T_{trans} - T_{cell}),$$
(3)

where  $m_{N_2O}$  and  $m_{pyr}$  are masses of N<sub>2</sub>O and pyrazine, respectively, and  $T_{cell}$  is the cell temperature, 300 K.  $T_{COM}$  for each J state has been used elsewhere to determine the statespecific translational energy gain for scattered-in bath molecules in single collisions with hot donors according to  $\langle \Delta E_{trans}^J \rangle_{in} = 3/2 \cdot k (T_{COM} - T_{cell})$ ,<sup>26, 39</sup> where *k* is the Boltzmann constant. However, we must consider the effect of scattered-out bath molecules to determine the actual translational energy gain of post-collision bath molecules. Until now, no research groups have accounted for the effect of scattered-out bath molecules to calculate the actual translational energy gain. For example, the studies of pyrazine–CO<sub>2</sub>,<sup>28</sup>–HOD,<sup>26</sup> and –DCl<sup>27</sup> have displayed translational energy gain ( $\langle \Delta E_{rel} \rangle$ ) only from state-specific energy gain information for scatteredin bath molecules without any consideration of scattered-out bath molecules.

Here we determine the actual translational energy gain using both scattered-in and scattered-out N<sub>2</sub>O translational temperatures. Generally, the initial translational energy distribution prior to collisions is thermally equilibrated at 300 K. Based on this, we assume that collisional energy transfer from pyrazine to N<sub>2</sub>O occurs in collisions with somewhat slower N<sub>2</sub>O molecules because the translational temperatures of scattered-out N<sub>2</sub>O are below room temperature, ~250 K. As a result, we suggest that the translational energy of scattered-out N<sub>2</sub>O molecules must be included for the actual translational energy gain as in the following equation

$$\left\langle \Delta E_{trans}^{J} \right\rangle_{gain} = \left\langle \Delta E_{trans}^{J} \right\rangle_{in} + \left\langle \Delta E_{trans}^{J} \right\rangle_{out} \tag{4}$$

where  $\langle \Delta E_{trans}^J \rangle_{in}$  and  $\langle \Delta E_{trans}^J \rangle_{out}$  are the average state-specific translational energy changes for scattered-in and scattered-out N<sub>2</sub>O, respectively, and  $\langle \Delta E_{trans}^J \rangle_{gain}$  is the actual translational

energy gain for post-collision N<sub>2</sub>O in single collisions with hot pyrazine.  $\langle \Delta E_{trans}^J \rangle_{gain}$  is listed in Table 4-3 along with  $\left< \Delta E_{trans}^J \right>_{in}$  and  $\left< \Delta E_{trans}^J \right>_{out}$ . The obtained  $\left< \Delta E_{trans}^J \right>_{eain}$  is plotted against the post-collision N<sub>2</sub>O rotational state in Figure 4-6. Figure 4-6 shows that the  $\left<\Delta E_{trans}^{J}\right>_{eain}$  plot is accurately fit to an exponential function and that there are two different patterns: a steady increase in translational excitation for J < 60 and a steep increase in translational excitation for J > 60. These patterns seem to be related to rotational angular momentum change ( $\langle \Delta J \rangle$ ) and relative velocity change ( $<\Delta v_{rel}>$ ), according to  $(h/2\pi)<\Delta J>=\mu b_{eff}<\Delta v_{rel}>$ , where h is the Plank's constant,  $\mu$  is the reduced mass of pyrazine and N<sub>2</sub>O, and  $b_{e\!f\!f}$  is the average effective impact parameter. In other words, for the large  $\langle \Delta J \rangle$  (J > 60) the effective impact parameter is almost constant while for the low  $\langle \Delta J \rangle$  (J  $\langle 60 \rangle$ )  $b_{eff}$  varies according to rotational state. This indicates that collision energy transfer between N<sub>2</sub>O and hot pyrazine for J > 60 occurs due to short-range impulsive collisions ( $b_{eff}$  is small and constant in J > 60 due to steep linearity between  $<\Delta J >$  and  $<\Delta v_{rel} >$ ), while collisions for J < 60 occurs due to long-range (large  $b_{eff}$ ), but still generally impulsive collisions.

# B. Rotational Energy Distribution for Post-collision N<sub>2</sub>O

As seen in Figure 4-4, the rotational Boltzmann distribution for scattered-in N<sub>2</sub>O molecules in single collisions with hot pyrazine has a distinct shape with two different rotational temperatures,  $T_{rot_{mid}} = 500 \pm 180$  K for J = 37–55 and  $T_{rot_{high}} = 940 \pm 50$  K for J = 55–75.

$N_2O(00^00)$	Average energy change of $N_2O$ in single collisions with Pyrazine <sup>E'</sup>			
J state	$\left\langle \Delta E_{trans}^{J} \right\rangle_{in}^{a} (\text{cm}^{-1})$	$\left<\Delta E_{trans}^{J}\right>_{out}^{\mathbf{b}}$ (cm <sup>-1</sup> )	$\left<\Delta E_{trans}^{J}\right>_{gain}^{c}$ (cm <sup>-1</sup> )	
37	580	10	590	
41	500	130	630	
45	980	10	990	
46	930	80	1010	
47	780	60	840	
48	1120	40	1160	
49	1160	90	1250	
50	1100	20	1120	
54	940	210	1150	
55	1170		1170	
56	1170		1170	
57	1200		1200	

Table 4-3. State-specific translational energy changes for scattered-in<sup>a</sup> and scattered-out<sup>b</sup>  $N_2O$ , and actual translational energy gain<sup>c</sup> for post-collision  $N_2O$ .

a Relative state-specific translational energy change for scattered-in N<sub>2</sub>O molecules obtained from

$$\left\langle \Delta E_{trans}^{J} \right\rangle_{in} = 3/2 \cdot k (T_{COM} - T_{cell}).$$

b Relative state-specific translational energy change for scattered-out N<sub>2</sub>O molecules obtained from

$$\left\langle \Delta E_{trans}^{J} \right\rangle_{out} = 3/2 \cdot k \left| T_{cell} - T_{transout} \right|.$$

c Actual state-specific translational energy gain for post-collision N<sub>2</sub>O molecules obtained from

$$\left\langle \Delta E_{trans}^{J} \right\rangle_{gain} = \left\langle \Delta E_{trans}^{J} \right\rangle_{in} + \left\langle \Delta E_{trans}^{J} \right\rangle_{out}.$$



Rotational State for post-collision NO,  $J_f$ 

Figure 4-6. Actual average translational energy gain of post-collision  $N_2O$  as a function of post-collision  $N_2O$  rotational state. Squares are the actual average translational energy gain amounts of  $N_2O$  obtained from Equation (4) and shown with experimental errors. Thick line is the best non-linear squares fit line to an exponential function.

Alternatively, the rotational Boltzmann distribution for  $N_2O$  scattered into J = 37-75 can be obtained by fitting the population of the entire J range to a two-component exponential function,

$$\frac{N_J}{(2J+1)} = \left[ A \cdot \exp\left(\frac{-E_{rot}}{kT_{mid}}\right) + B \cdot \exp\left(\frac{-E_{rot}}{kT_{high}}\right) \right] / Q_{rot}$$
(5)

where  $N_J$  is the scattered-in N<sub>2</sub>O population for each J state, (2J+1) is the rotational degeneracy,  $Q_{rot}$  is the rotational partition function,  $E_{rot}$  is the rotational energy for post-collision N<sub>2</sub>O in each J state, k is the Boltzmann constant, A and B are the parameters related to the total scattered-in N<sub>2</sub>O population,  $N_0$ , and  $T_{mid}$  and  $T_{high}$  are rotational temperatures obtained from fitting to this equation. Figure 4-7 shows the nascent experimental Boltzmann distribution for scattered-in N<sub>2</sub>O for the J = 37–75 range fit to equation (5), along with  $T_{mid}$  and  $T_{high}$ .  $T_{mid}$  = 450 K for  $E_{rot}$  = 500–1,300 cm<sup>-1</sup> and  $T_{high}$  = 930 K for  $E_{rot} \ge 1,300$  cm<sup>-1</sup> obtained from the fit are in good agreement within experimental error with  $T_{rot_mid}$  = 500 ± 180 K and  $T_{rot_high}$  = 940 ± 50 K, obtained from two single Boltzmann plots in Figure 4-4.

This distinct distribution is further evidence of both weak and strong collisions in pyrazine–N<sub>2</sub>O collisions because the average rotational energies ( $\langle E_{rot} \rangle = kT_{rot}$ ) determined from rotational temperatures are considerably different for the J = 37–55 and the J = 55–75 ranges;  $\langle E_{rot} \rangle_{\text{weak}} = kT_{mid} \approx 313 \text{ cm}^{-1}$  and  $\langle E_{rot} \rangle_{\text{strong}} = kT_{high} \approx 646 \text{ cm}^{-1}$ . For comparison, the average rotational energy of the initial N<sub>2</sub>O at 300 K prior to collisions with hot pyrazine is  $\langle E_{rot} \rangle_{\text{ini}} = kT_{cell} = 208.5 \text{ cm}^{-1}$ . This Boltzmann distribution with weak and strong collision character also seems to the correlate with the translational energy distribution, as seen in Figure 4-6. Figure 4-6 shows that the translational temperature slowly decreases from J = 59 to lower J states, while the translational temperature for J > 59 rapidly increases. For scattered-in N<sub>2</sub>O with J < 55, it is



Final Rotational Energy for Scattered NO,  $E_{rot}$  (cm<sup>-1</sup>)

Figure 4-7. Fit of experimental rotational Boltzmann distribution (squares) for J = 37-75 of scattered-in N<sub>2</sub>O in single collisions with vibrationally hot pyrazine to a two-component double exponential function; see Equation (5). Rotational temperatures obtained from the two-component double exponential fit are  $T_{mid} = 450$  K for  $E_{rot} = 500-1,300$  cm<sup>-1</sup>, and  $T_{high} = 930$  K for  $E_{rot} \ge 1,300$  cm<sup>-1</sup>.

interesting to note that this range corresponds to both low rotational temperature and slowly decreasing translational temperatures (600–1,000 K). That is, weak and strong collisions for the pyrazine–N<sub>2</sub>O pair can be distinguished at approximately J = 55.

The feature that post-collision N<sub>2</sub>O has two different rotational temperatures (for weak and strong collisions) has also been seen in the study of pyrazine–CO<sub>2</sub> collisions,<sup>28</sup> where  $T_{rot} =$ ~440 K for J < 50 and ~1150 K for J > 50. However, studies of pyrazine–HOD<sup>26</sup> and –DCl<sup>27</sup> are described by a single rotational temperature for the entire J range,  $T_{rot} = ~430$  K and ~880 K, respectively. Thus, in terms of the energy partitioning into bath molecules, N<sub>2</sub>O with weak and strong collisions observed in this study has similar collision energy transfer dynamics to CO<sub>2</sub>, while HOD and DCl have different collision energy transfer dynamics in collisions with pyrazine.

One way to see whether weak or strong collisions contribute more to energy transfer between pyrazine and N<sub>2</sub>O is to plot the weak and strong collision parameters obtained from the two-component double Boltzmann exponential fit independently. Figure 4-8 is a plot of the fractional N<sub>2</sub>O population following collisions with pyrazine that result from weak and strong collisions as well as overall post-collision Boltzmann distribution. Weak collisions are about three times more prevalent than strong collisions in V $\rightarrow$ RT collision energy transfer; weak and strong collision fractions are 76 % and 24 %, respectively. On the other hand, the initial bulk N<sub>2</sub>O density is [N<sub>2</sub>O]<sub>0</sub> = 3.22×10<sup>14</sup> molecule/cm<sup>3</sup> determined using the ideal gas law at P = 10 mTorr and T = 300 K, while the overall scattered-in N<sub>2</sub>O density at *t* = 1  $\mu$ s calculated using N<sub>0</sub>, obtained from the fit to equation (5), is  $\Sigma[N_2O]_t^T = 4.17\times10^{12}$  molecule/cm<sup>3</sup> when J = 0–100. It is interesting that the overall scattered-in N<sub>2</sub>O population change corresponds to only about 1.3

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# Boltzmann Distribution of Scattered-in N<sub>2</sub>O

Final Rotational State for Scattered NO,  $J_f$ 

Figure 4-8. Plot of Boltzmann probability using parameters of the two-component double exponential fit for the whole range of post-collision N<sub>2</sub>O rotational states. Open square boxes are experimental Boltzmann probabilities for scattered-in N<sub>2</sub>O obtained from Boltzmann distribution,  $N_J/N_0$ , where  $N_J$  is the J-specific population and  $N_0$  is the total population for scattered-in N<sub>2</sub>O molecules. The solid line is the best fit to the data using the double exponential function (Equation (5)). The dashed and dotted lines are obtained from the experimental Boltzmann plots using the weak and strong collision parameters, respectively, from the double exponential fit. The Strong collision fraction is 24 %, while the weak collision fraction is 76 % of all V→RT collision energy transfer events.

% of the initial bulk N<sub>2</sub>O population. This indicates that most of N<sub>2</sub>O molecules have not been involved in a collision with pyrazine at 1  $\mu$ s and is in agreement with previous studies using CO<sub>2</sub>.<sup>9-11</sup>

Knowledge of the average initial rotational state,  $< J_{ini} >$ , is necessary to determine the amount of rotational energy gain. In previous studies,  $< J_{ini} >$  has been obtained from temperature-dependent experiments performed by Flynn and coworkers.<sup>9-11</sup> For example, the studies of Mullin et al.,<sup>9</sup> Michaels et al.,<sup>10</sup> and Sevy et al.<sup>11</sup> employed the average initial CO<sub>2</sub> rotational state obtained from temperature-dependent experiments:  $< J_{ini} > \approx 29$  on pyrazine–CO<sub>2</sub>,  $< J_{ini} > \approx 31$  on perfluorobenzene–CO<sub>2</sub>, and  $< J_{ini} > \approx 26$  on methylpyrazine–CO<sub>2</sub> collisions. Previous studies performed in our lab<sup>17-22, 24</sup> have omitted temperature-dependent experiments because small changes in  $< J_{ini} > \approx 26$ , obtained from the average of three values of  $< J_{ini} >$  obtained in the temperature-dependent experiments,<sup>9-11</sup> was used to obtain state-specific energy gain amounts. Studies using bath molecules other than CO<sub>2</sub> have found  $< J_{ini} >$  from the thermal population distribution at 300 K prior to collisions; e.g.  $kT_{cell} = B < J_{ini} > (< J_{ini} > +1)$ , where *B* is the bath molecule rotational constant.<sup>23, 27, 28, 39-42</sup>

In this study, we have used a different approach to obtain the average initial state. In Figure 4-4, we plotted the experimentally measured scattered-out N<sub>2</sub>O population as well as scattered-in N<sub>2</sub>O population. Comparing these Boltzmann probability profiles for scattered-in and scattered-out N<sub>2</sub>O molecules may provide the J-dependence of energy transfer. Figure 4-9 shows Boltzmann probability plots for scattered-in and scattered-out N<sub>2</sub>O as a function of postcollision N<sub>2</sub>O J state ( $J_f$ ), along with the J-dependence of energy gain for N<sub>2</sub>O scattered by single collisions with hot pyrazine. The J-dependence of N<sub>2</sub>O energy gain in Figure 4-9 was determined by subtracting the scattered-out N<sub>2</sub>O Boltzmann probability from the scattered-in



J-Dependence of N<sub>2</sub>O Energy Gain

Final Rotational State of Scattered NO,  $J_f$ 

Figure 4-9. J-dependence of N<sub>2</sub>O energy gain in single collisions with vibrationally hot pyrazine. Filled and open squares are experimental Boltzmann probabilities for scattered-in and scattered-out N<sub>2</sub>O molecules, respectively. Solid and dotted lines are the Boltzmann plots obtained by fitting experimental scattered-in and scattered-out N<sub>2</sub>O probabilities over the entire N<sub>2</sub>O J range, respectively. The solid line was obtained using a two-component double exponential Boltzmann fit to the data, while the dotted line was obtained using a single exponential Boltzmann function. The dashed line was obtained by subtracting the scattered-out Boltzmann probability from the scattered-in Boltzmann probability for each

J state, which is defined as J-dependence of N<sub>2</sub>O energy gain. The inversion point of the J-dependence of N<sub>2</sub>O energy gain is between J = 24 and 25. This point represents the point that  $\langle \Delta J \rangle$  become positive; see in the text. Therefore, J = 24 can be used as the average initial rotational state,  $\langle J_{ini} \rangle$ , for N<sub>2</sub>O in single collisions with hot pyrazine.

N<sub>2</sub>O Boltzmann probability. In Figure 4-9, the J-dependence for N<sub>2</sub>O energy gain becomes positive at J = 25. This indicates that scattered-in N<sub>2</sub>O starts dominating over scattered-out N<sub>2</sub>O at J = 25. It is known that the average rotational state change is defined as  $\langle \Delta J \rangle = J_f - \langle J_{ini} \rangle$ .<sup>11</sup> We also recognize that positive  $\langle \Delta J \rangle$  result in positive energy gain of a bath molecule according to  $(h/2\pi) \langle \Delta J \rangle = \mu b_{eff} \langle \Delta v_{rel} \rangle$ . Based on this, we suggest that the average initial N<sub>2</sub>O rotational state is  $\langle J_{ini} \rangle = 24$  in this study.

### C. Energy Transfer Rate Constants and Scattering Probabilities

The collision energy transfer process for N<sub>2</sub>O scattered into J = 37-75 of the ground vibrational level, (00<sup>0</sup>0), in single collisions with hot pyrazine (*Pyr*<sup>*E*'</sup>) can be described as

$$Pyr^{E'} + N_2 O \xrightarrow{k_m^J} Pyr^{E' - \Delta E} + N_2 O (00^0 0; J),$$
(6)

where  $Pyr^{E'-\Delta E}$  is the pyrazine molecules that end up with  $E'-\Delta E$  after single collisions with  $N_2O$ at 300 K,  $N_2O$  (00<sup>0</sup>0;*J*) is the post-collision N<sub>2</sub>O molecule scattered into 00<sup>0</sup>0;J states, and  $k_{in}^J$  is the energy transfer rate constant for N<sub>2</sub>O scattered into the J state.  $k_{in}^J$  is obtained using

$$k_{in}^{J} = \frac{[N_2 O(00^0 0; J)]_{in}}{[Pyr^{E'}]_0 [N_2 O]_0 t}.$$
(7)

In equation (7),  $[N_2O(00^00;J)]_{in}$  is the number density of N<sub>2</sub>O molecules scattered into the J state at 1  $\mu$ s (*t*) following 248 nm UV absorption of pyrazine, and  $[Pyr^{E'}]_0$  and  $[N_2O]_0$  are the number densities of pyrazine and N<sub>2</sub>O molecules prior to collisions, respectively.  $[Pyr^{E'}]_0$  and  $[N_2O]_0$ were here applied to calculate  $k_{in}^J$  because  $[Pyr^{E'}]_0$  and  $[N_2O]_0$  can be treated as constants given that  $Pyr^{E'}$  and  $N_2O$  are nearly the same before and after single collisions ( $[Pyr^{E'}]_0 \approx [Pyr^{E'}]_t$  and  $[N_2O]_0 \approx [N_2O]_t$ ). The collision energy transfer process for N<sub>2</sub>O scattered out of  $00^{0}0$ ; J = 37–54 in single collisions with hot pyrazine can be described as

$$Pyr^{E'} + N_2 O\left(J\right) \xrightarrow{k_{out}^J} Pyr^{E''} + N_2 O\left(J'\right),\tag{8}$$

where  $Pyr^{E''}$  are pyrazine molecules that end up with E'' following collision energy transfer to  $N_2O(J)$  at 300 K, J and J' are the probed N<sub>2</sub>O rotational state and any state other than J, respectively, and  $k_{out}^J$  is the energy transfer rate constant for N<sub>2</sub>O scattered out of the J state by single collisions with  $Pyr^{E'}$ .  $k_{out}^J$  is obtained using

$$k_{out}^{J} = \ln \left( \frac{[N_2 O(J)]_0}{[N_2 O(J)]_t} \right) / [Pyr^{E'}]_0 t.$$
(9)

In equation (9),  $[N_2O(J)]_0$  and  $[N_2O(J)]_t$  are the number densities of N<sub>2</sub>O molecules in the J state prior to collisions and after collisions, respectively.  $[N_2O(J)]_t$  is the N2O density at time *t* that is obtained by subtracting the scattered-out N<sub>2</sub>O density from  $[N_2O(J)]_0$ ; i.e.  $[N_2O(J)]_t = [N_2O(J)]_0$  $- [N_2O(00^00;J)]_{out}$ , where  $[N_2O(00^00;J)]_{out}$  is the number density of scattered-out N<sub>2</sub>O at 1  $\mu$ s after a UV pulse obtained from the area of the Gaussian dip. Alternatively, equation (9) can be rewritten as

$$k_{out}^{J} = \ln \left( \frac{[N_2 O(J)]_0}{[N_2 O(J)]_0 - [N_2 O(00^0 0; J)]_{out}} \right) / [Pyr^{E'}]_0 t$$

$$= \ln \left( \frac{1}{1 - [N_2 O(00^0 0; J)]_{out} / [N_2 O(J)]_0} \right) / [Pyr^{E'}]_0 t \approx \frac{[N_2 O(00^0 0; J)]_{out}}{[Pyr^{E'}]_0 [N_2 O(J)]_0 t}$$
(10)

In equation (10), the logarithmic term can be simplified to  $[N_2O(00^00;J)]_{out}/[N_2O(J)]_0$  since  $[N_2O(J)]_0$  is much larger than  $[N_2O(00^00;J)]_{out}$ ;  $[N_2O(00^00;J)]_{out}/[N_2O(J)]_0 << 1$ .  $k_{in}^J$  for J = 37–57 and  $k_{out}^J$  for J = 37–54 are listed in Table 4-4, along with scattering probabilities obtained using  $k_{in}^J/k_{LJ}$ , where  $k_{LJ}$  is the Lennard-Jones gas kinetic collision rate constant.

Table 4-4. State-specific energy transfer rate constants  $(k_{in}^J)^a$  and scattering probabilities  $(k_{in}^J/k_{LJ})^b$  for the process of  $Pyr^{E'} + N_2O \xrightarrow{k_{in}^J} Pyr^{E'-\Delta E} + N_2O(00^00;J)$  and state-specific energy transfer rate constants  $(k_{out}^J)^c$  for the  $Pyr^{E'} + N_2O(J) \xrightarrow{k_{out}^J} Pyr^{E''} + N_2O(J')$  process.

Post-collision	Collisions between $Pyr^{E'}$ and N <sub>2</sub> O (00 <sup>0</sup> 0)				
N <sub>2</sub> O J state	$k_{in}^{J a}$ (10 <sup>-12</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	$k_{in}^{J}/k_{LJ}^{b}$ (10 <sup>-3</sup> )	$k_{out}^{J \ c} (10^{-10} \ cm^3 molecule^{-1} s^{-1})$		
37	$14.6\pm6.0$	$28.1 \pm 11.8$	$12.7 \pm 4.5$		
41	$11.5 \pm 1.3$	$22.2\pm2.5$	$11.1 \pm 4.3$		
45	$7.4 \pm 1.9$	$14.3\pm3.8$	$15.0\pm6.5$		
46	$7.0 \pm 1.2$	$13.5\pm2.4$	$11.6 \pm 2.3$		
47	$7.0 \pm 2.4$	$13.4\pm4.6$	$13.6\pm5.5$		
48	$8.3 \pm 0.4$	$15.9\pm0.8$	$15.1\pm1.6$		
49	$7.9 \pm 3.6$	$15.3\pm6.9$	$16.6\pm11.0$		
50	$4.4\pm1.7$	8.4 ± 3.2	$14.4\pm7.1$		
54	$4.1 \pm 0.5$	$7.9 \pm 1.0$	$6.1 \pm 3.3$		
55	$3.8\pm0.9$	$7.4 \pm 1.7$			
56	$4.0 \pm 1.1$	$8.0 \pm 2.2$			
57	$3.2 \pm 0.3$	$6.1\pm0.6$			
$\left\langle k_{out}^{J} ight angle ^{d}$			$12.9 \pm 5.1$		

a State-specific energy transfer rate constant,  $k_{in}^J$ , for the process of  $Pyr^{E'} + N_2O \xrightarrow{k_{in}^J} Pyr^{E'-\Delta E} +$ 

 $N_2 O(00^0 0; J)$  determined by Equation (7).

b State-specific scattering probability obtained from  $k_{in}^J/k_{LJ}$ .  $k_{LJ}$  is the Lennard-Jones gas kinetic collision rate constant defined as  $k_{LJ} = \pi [(d_{N_2O} + d_{pyrazine})/2]^2 \sqrt{(8k_BT/(\pi\mu)\Omega_{12})}$ , where  $d_{N_2O} = 4.2$  Å,<sup>43</sup>
$d_{pyrazine} = 5.27$  Å,  $k_B$  is the Boltzmann constant, and  $\mu$  is the reduced mass of N<sub>2</sub>O and pyrazine.  $\Omega_{12}$  is the Lennard-Jones well depth collisional integral,  $\Omega_{12} = [0.636 + 0.567 \log(k_B T/\epsilon_{12})]^{-1}$ ,<sup>30</sup> where the well depth potential,  $\epsilon_{12}$ , is  $\epsilon_{12} = \sqrt{\epsilon_{pyrazine}} \epsilon_{N_2O}$ .  $\epsilon_{pyrazine}/k_B = 412$  K and  $\epsilon_{N_2O}/k_B = 210$  K are obtained from Ref. <sup>44</sup> and <sup>45</sup>, respectively. The Lennard-Jones well depth collision rate constants,  $k_{LJ}$ , at 300 K is  $5.19 \times 10^{-10}$  cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup> for the pyrazine and N<sub>2</sub>O pair.

c State-specific energy transfer rate constant,  $k_{out}^J$ , for the process of  $Pyr^{E'} + N_2O(J) \xrightarrow{k_{out}^J} Pyr^{E''} + N_2O(J')$  determined using Equation (10).

d Average energy transfer rate constant for J = 37-54 of scattered-out N<sub>2</sub>O molecules in single collisions with vibrationally hot pyrazine.

It is interesting that  $\langle k_{out}^{J} \rangle = (12.9 \pm 5.1) \times 10^{-10} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$  for J = 37–54 is about two times larger than  $k_{LJ} = 5.19 \times 10^{-10} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ . The studies of Du et al.<sup>27</sup> and Havey et al.<sup>28</sup> showed that the average energy transfer rate constant for scattered-out bath molecules,  $\langle k_{dep} \rangle$ , corresponds to  $k_{LJ}$  for collisions with pyrazine. Although in this study energy transfer measurements for scattered-out N<sub>2</sub>O in single collisions with vibrationally hot pyrazine were performed for only J = 37–54 (Du et al.<sup>27</sup> and Havey et al.<sup>28</sup> measured for the entire DCl or CO<sub>2</sub> J range), the two times larger value of  $\langle k_{out}^{J} \rangle$ , in comparison with  $k_{LJ}$ , suggests that there may be a problem with eiter the Lennard-Jones rate constant for pyrazine–N<sub>2</sub>O collisions or the absolute rate constants reported in this study. Thus, this disagreement of  $\langle k_{out}^{J} \rangle$  with  $k_{LJ}$  requires further study.

The measured scattering probability,  $k_{in}^{J}/k_{LJ}$ , describing the fraction of N<sub>2</sub>O that gains a certain amount of energy ( $\Delta E$ ) from hot pyrazine and is scattered into the J state, is plotted as a function of post-collision N<sub>2</sub>O J state in Figure 4-10, along with the normalized Boltzmann probability fit obtained using the measured scattered-in N<sub>2</sub>O population. The measured probability,  $k_{in}^{J}/k_{LJ}$ , is also fit to a two-component double exponential function using two different rotational temperatures ( $T_{rot_mid} = 450$  K and  $T_{rot_high} = 930$  K) obtained in this study. As shown in Figure 4-10, the integrated  $k_{in}^{J}/k_{LJ}$  is much larger (= 1.68) than the normalized Boltzmann probability (= 1). This indicates that  $k_{LJ}$  for the pyrazine–N<sub>2</sub>O system is smaller than the collision rate constant should be because the sum of the energy transfer rate constants for the entire J range should be closer to the true collision rate constant. If the total energy transfer rate constants



Rotational State of Post-collision NO,  $J_f$ 

Figure 4-10. Scattering probability plot for scattered-in N<sub>2</sub>O as a function of post-collision N<sub>2</sub>O rotational state. The solid line is the two-component ( $T_{rot} = 930$  and 450 K) double exponential fit to the experimentally obtained scattering probability data (squares:  $k_{in}^J/k_{LJ}$ ) over the entire N<sub>2</sub>O rotational states, while the dashed line is the plot of normalized Boltzmann probability for the measured scattered-in N<sub>2</sub>O molecules. The sum of the normalized Boltzmann probabilities for each J state is 1, while the sum of scattering probabilities for each J state is 1.68. This suggests that  $k_{LJ}$  for the pyrazine–N<sub>2</sub>O system is smaller than the collision rate constant should be.

 $(k_{tot} = \Sigma k_{V \to RT} + \Sigma k_{V \to V})$ , the addition of  $\Sigma k_{V \to V}$  means that  $k_{LJ}$  is even smaller than it should be. According to this analysis,  $k_{LJ}$  for the pyrazine–N<sub>2</sub>O system should be roughly twice as big as the calculated value. The corrected value of  $k_{LJ}$  estimated from this analysis (~10 × 10<sup>-10</sup> cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup>) is in good agreement with the average energy transfer rate constant for J = 37–54 of scattered-out N<sub>2</sub>O molecules ( $\langle k_{out}^J \rangle = (12.9 \pm 5.1) \times 10^{-10}$  cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup>), as noted above. One potential reason for apparent underestimation of  $k_{LJ}$  may be due to the extrapolation of  $k_{in}^J/k_{LJ}$  for low J states (J < 37).  $k_{in}^J/k_{LJ}$  for low J states may not follow the trend of Boltzmann distribution shape and hence decrease or increase the integrated  $k_{in}^J/k_{LJ}$ . The measurement of the pyrazine–N<sub>2</sub>O energy transfer in the low J states (J < 37) must be performed to determine an accurate value of  $k_{coll}$  and thereby a correction of  $k_{LJ}$ . We plan to perform

## **D.** Energy Transfer Probability Distribution, P(E,E')

The energy transfer probability distribution, P(E,E'), for pyrazine–N<sub>2</sub>O collisions was obtained using the energy gain information from this study (J = 37–57), and data from our previous report on the pyrazine–N<sub>2</sub>O collisions for the high J tail (J = 59–75).<sup>23</sup> The experimental P(E,E') curve obtained from the energy transfer data for J = 37–75 is plotted as a function of the amount of energy transferred ( $\Delta E$ ) in Figure 4-11, along with the P(E,E') curve obtained in our previous study.<sup>23</sup> The sum of P(E,E') in the  $\Delta E = 1,000-7,000$  cm<sup>-1</sup> range obtained from the extrapolation of J = 37–75 data,  $\Sigma P(E,E')$ , is 0.0293/cm<sup>-1</sup>, while the sum of P(E,E') obtained from the extrapolation of J = 59–75 data<sup>23</sup> is 0.0272/cm<sup>-1</sup>. This points out that P(E,E') directly determined from the experimental data of the mid J range, along with the high J



Figure 4-11. Comparison of the energy transfer probability distribution for  $\Delta E = 1,000-7,000 \text{ cm}^{-1}$ obtained from J = 37–75 data with P(E,E') obtained from the extrapolation of J = 59–75 data for postcollision N<sub>2</sub>O. The negative  $\Delta E$  values describe downward collisional energy transfer from vibrationally hot pyrazine to N<sub>2</sub>O. The sum of P(E,E'),  $\Sigma P(E,E')$ , in  $\Delta E = 1,000-7,000 \text{ cm}^{-1}$  obtained from J = 37–75 data is 0.0293/cm<sup>-1</sup>, while the sum of P(E,E') obtained from J = 59–75 data is 0.0272/cm<sup>-1</sup>.

range, corrects P(E,E') values obtained from an extrapolation of only the high J range and increases a small amount of energy transfer probability in the  $\Delta E = 1,000-3,000 \text{ cm}^{-1}$  range. The increase of energy transfer probability based on direct measurements in the mid J range is  $\sim 0.002/\text{cm}^{-1}$ .

For specific comparison in terms of weak and strong collisions, the experimental P(E,E') curve measured in this work was fit to a bi-exponential function according to

$$P(E,E') = \frac{(1-f)\exp\{-(E'-E)/\alpha\} + f\exp\{-(E'-E)/\gamma\}}{(1-f)(\alpha+\beta) + f(\gamma+\delta)} \text{ for } E' > E^{30-32},$$
(11)

where  $\alpha$  and  $\gamma$  are the average "weak" and "strong (super)" energy transfer magnitudes for downward collisions, respectively, and *f* is defined as the strong collision fraction.  $\beta$  and  $\delta$  are the average "weak" and "strong" energy transfer magnitudes for upward collisions, respectively.  $\alpha$  and  $\beta$  as well as  $\gamma$  and  $\delta$  are related to each other and can be described by detailed balance.<sup>32,46</sup> Bi-exponential parameters ( $\alpha$ ,  $\gamma$ , and *f*) for the experimentally obtained P(E,E') in this work are listed in Table 4-5, along with the bi-exponential parameters obtained from our previous study using only the high J tail data (J = 59–75). Comparison of measured P(E,E') between this study and the previous study<sup>23</sup> can be made using the super-collision energy transfer efficiency ( $\langle \Delta E \rangle_s$ ), obtained by multiplying  $\gamma$  with *f*;  $\langle \Delta E \rangle_s$  was described in detail in our previous studies.<sup>19, 22, 23</sup>  $\langle \Delta E \rangle_s$  values obtained from measurements of J = 37–75 and J = 59–75 ranges are 146.5 and 105.0 cm<sup>-1</sup>, respectively. If super-collision energy transfer is considered to be collisions where  $\Delta E > \sim 1,000$  cm<sup>-1</sup>, it is then not surprising that the super-collision energy transfer efficiency obtained using the J = 37–75 data has a larger efficiency than that obtained from the J = 59–75 data because P(E,E') from J = 59–75 used extrapolated data under the

Table 4-5. Bi-exponential fit parameters obtained from the fit of P(E,E') to a bi-exponential function: the characteristic strong  $(\gamma)^{a}$  and weak collision magnitudes  $(\alpha)^{b}$ , the strong collision fraction  $(f)^{c}$ , and the average amount of total energy transfer for downward collisions  $(\langle \Delta E \rangle_{d})^{d}$ .

Experimentally measured N <sub>2</sub> O range	$\gamma^{a}$ (cm <sup>-1</sup> )	$\alpha^{b}$ (cm <sup>-1</sup> )	$f^{c}$	$\left<\Delta E\right>_d^{\mathbf{d}}$ (cm <sup>-1</sup> )
$J = 59 - 75^{\circ}$	2625	797	0.04	829
J = 37 - 75	2093	729	0.07	780

a The characteristic strong collision magnitude obtained by fitting experimental P(E,E') data to a biexponential function; see equation (11).

b The characteristic weak collision magnitude obtained by fitting experimental P(E,E') data to a bi-

exponential function; see equation (11).

c The strong collision fraction obtained by fitting experimental P(E,E') data to a bi-exponential function; see equation (11).

d The average amount of total energy transfer for downward collisions from hot donor to bath molecules.

 $\langle \Delta E \rangle_d$  was obtained from equation (12).

e Bi-exponential fit parameters obtained from Ref. 23.

assumption that the translational temperature for the mid J range decreases linearly with same trend as the translational temperatures for J = 59-75. However, as seen in Figure 4-5  $T_{trans}$  does not decrease linearly and measured values in this mid J range are larger than ones predicted by the linear assumption. The increase of super-collision energy transfer efficiency for the corrected P(E,E') obtained from the J = 59-75 data (Figure 4-11) originates in part because translational temperatures for J < 55 decrease less than ones predicted by a linear extrapolation of the J = 55-75 data as used previously.<sup>23</sup>

In Table 4-5, the average downward collision energy transfer amount,  $\langle \Delta E \rangle_d$ , was determined using  $\alpha$ ,  $\gamma$ , and f as given by<sup>32, 46</sup>

$$\left\langle \Delta E \right\rangle_d \approx \frac{(1-f) \cdot \alpha^2 + f \cdot \gamma^2}{(1-f) \cdot \alpha + f \cdot \gamma}.$$
 (12)

 $\langle \Delta E \rangle_d$  for P(E,E') from the extrapolation of the J = 37–75 data (780 cm<sup>-1</sup>) is smaller than obtained from the J = 59–75 data (829 cm<sup>-1</sup>). This is due to the greater probability of energy transfer in the  $\Delta E$  = 1,000–3,000 cm<sup>-1</sup> range; this increase results in decreased values of  $\gamma$  and  $\alpha$ (see Table 4-5). As a result of the decrease of both  $\gamma$  and  $\alpha$ ,  $\langle \Delta E \rangle_d$  decreases according to equation (12). However, neither of these studies include experimentally obtained energy gain information for J < 37; this study still uses extrapolated energy transfer parameters for the low J states (J < 37) to calculate P(E,E'). Even though energy transfer measurements for J < 37 are required to obtain a complete P(E,E'), it is noteworthy that the use of P(E,E') data obtained in this study can be compared with other studies of energy loss, since P(E,E') obtained here is within 10 % of that obtained with a greater degree of extrapolation, as seen in Figure 4-11.

 $\langle \Delta E \rangle_d$  obtained from this study can be compared with the study of Miller and Barker<sup>4</sup> on collisional deactivation of highly vibrationally excited pyrazine by various bath molecules. They

used a time-resolved IR fluorescence technique to measure the energy loss from hot pyrazine to 19 bath molecules and reported an average total energy transfer,  $\langle \Delta E \rangle$ , for pyrazine–CO<sub>2</sub> collisions of  $-275 \pm 30 \text{ cm}^{-1}$  with an average downward energy transfer,  $\langle \Delta E \rangle_d$ , of  $\sim 380 \pm 60$  $cm^{-1}$  when E' is ~40,640 cm<sup>-1</sup>. As discussed before, we observed that collisions for the pyrazine–N<sub>2</sub>O and –CO<sub>2</sub> systems are governed by similar energy transfer dynamics. We also know that the average energy transfer amounts for N2O and CO2 obtained from our previous study<sup>23</sup> are nearly the same. Based on these, we assume that  $\langle \Delta E \rangle_d$  for the pyrazine–CO<sub>2</sub> system from the energy loss study of Miller and Barker<sup>4</sup> may also be similar to  $\langle \Delta E \rangle_d$  for the pyrazine–N<sub>2</sub>O collisions (~400 cm<sup>-1</sup>). However, this value is nearly a half of  $\langle \Delta E \rangle_d = 780 \text{ cm}^{-1}$ measured in this study. The study of Hippler et al.<sup>47</sup> showed that the average energy loss is inversely related to the Lennard-Jones collision rate constant,  $\langle \Delta E \rangle \cong d \langle E(t) \rangle / Z_{LJ}[M] dt$ , where  $\langle E(t) \rangle$  is the average energy of donor at t,  $Z_{LJ}$  is the Lennard-Jones collision frequency, and [M] is the number density of bath molecules. That is, according to the study of Hippler et al.  $\langle \Delta E \rangle_d$ is inversely proportional to  $k_{LJ}$ . As discussed above, it is possible that  $k_{LJ}$  used in this study is an underestimate of the true pyrazine–N<sub>2</sub>O collision rate by about a factor of 2. Thus, if  $k_{LJ}$  were doubled to correct for this underestimation,  $\langle \Delta E \rangle_d = 780 \text{ cm}^{-1}$  measured in this study would become ~390 cm<sup>-1</sup>, since  $\langle \Delta E \rangle \propto 1/Z_{LJ}$ .<sup>47</sup> This value ( $\langle \Delta E \rangle_d = ~390$  cm<sup>-1</sup>) is in good agreement with  $\langle \Delta E \rangle_d = \sim 400 \text{ cm}^{-1}$  obtained from the study of Miller and Barker.<sup>4</sup> Therefore, if the corrected  $k_{LJ}$  is used, the results from this study are consistent with previous studies obtained from energy loss measurements. However, the measurements for low J states (J < 37) of postcollision  $N_2O$  must be performed to obtain overall P(E,E') without extrapolation and determine an accurate collision rate constant.

## V. Conclusion

Vibrational relaxation of highly vibrationally excited pyrazine ( $E' = \sim 41,000 \text{ cm}^{-1}$ ) in collisions with  $N_2O$  molecules was investigated by measuring rotational and translational energy gain of post-collision  $N_2O$  for J = 37-57 range. The measurements were analyzed by including the results of a previous study measured in the J = 59-75 range of post-collision N<sub>2</sub>O in single collisions with hot pyrazine. A Gaussian dip at the center frequency of Doppler broadened absorption line profiles was observed in J = 37-54, while no Gaussian dip was observed in J =55–75. Transient IR absorption signals at 1  $\mu$ s after a UV pulse measured from Gaussian dips were used to calculate the number density of N<sub>2</sub>O scattered out of the J state, while normal Gaussian transient IR signals were used to determine the number density of N<sub>2</sub>O scattered into the J state by single collisions with hot pyrazine. Strong and weak collision dynamics were observed in both rotational ( $T_{rot mid} = 500$  K and  $T_{rot high} = 940$  K) and translational temperature distributions ( $T_{trans \text{ mid}} = 600-1,000 \text{ K}$  and  $T_{trans \text{ high}} = 1,000-2,600 \text{ K}$ ) measured for N<sub>2</sub>O molecules scattered into J = 37-75. The turning point from weak to strong collisions (J = 55) is in good agreement with the range of states with measured out-scattering (J = 37-54). The fraction of strong collisions obtained by fitting scattered-in N<sub>2</sub>O Boltzmann distribution to a twocomponent double exponential function is  $\sim 24$  % of overall V $\rightarrow$ RT pathway, while the fraction of weak collisions is ~76 %. A new approach to determine the average initial rotational state,  $\langle J_{ini} \rangle$ , for N<sub>2</sub>O molecules was proposed and  $\langle J_{ini} \rangle = 24$  was determined using J-dependence of N<sub>2</sub>O energy gain obtained from Boltzmann probability fits of scattered-in and scattered-out N<sub>2</sub>O molecules.

Energy transfer rate constants and scattering probabilities,  $k_{in}^J/k_{LJ}$ , for rotational and translational energy gain of post-collision N<sub>2</sub>O were obtained in the J = 37–75 range and

extrapolated to J = 0. The integrated scattering probability for the entire J range,  $\sum k_{in}^J/k_{LJ}$ , is 1.68 times larger than the normalized Boltzmann probability for measured post-collision N<sub>2</sub>O, while the average energy transfer rate constant for scattered-out N<sub>2</sub>O,  $\langle k_{out}^J \rangle$ , is about twice as large as  $k_{LJ}$ . The results of  $\sum k_{in}^J/k_{LJ}$  and  $\langle k_{out}^J \rangle$  suggest that the Lennard-Jones collision rate constant is smaller than the actual collision rate constant by roughly a factor of two. The comparison of  $\langle \Delta E \rangle_d = 780$  cm<sup>-1</sup> obtained from P(E,E') in this study and  $\langle \Delta E \rangle_d = \sim 400$  cm<sup>-1</sup> from the energy loss study of Miller and Barker<sup>4</sup> on pyrazine–CO<sub>2</sub> collisions and our previous study<sup>23</sup> further suggest that the Lennard-Jones collision rate constant,  $k_{LJ}$ , for pyrazine–N<sub>2</sub>O collisions is to small. This suggestion is in agreement with the study of Hippler et al.<sup>47</sup> Energy gain measurements for low J states (J < 37) for N<sub>2</sub>O following collisions with pyrazine must be performed to obtain accurate collision rate constants as well as complete P(E,E') free from any extrapolation.

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