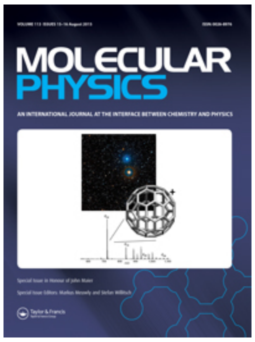

Molecular Physics

An International Journal at the Interface Between Chemistry and Physics

ISSN: 0026-8976 (Print) 1362-3028 (Online) Journal homepage: https://www.tandfonline.com/loi/tmph20

Dissociative recombination and excitation of D_5^+ by collisions with low-energy electrons

J.B.C. Pettersson, P.U. Andersson, F. Hellberg, J. Öjekull, R.D. Thomas & M. Larsson

To cite this article: J.B.C. Pettersson, P.U. Andersson, F. Hellberg, J. Öjekull, R.D. Thomas & M. Larsson (2015) Dissociative recombination and excitation of D_5^+ by collisions with low-energy electrons, Molecular Physics, 113:15-16, 2099-2104, DOI: 10.1080/00268976.2014.1003985

To link to this article: https://doi.org/10.1080/00268976.2014.1003985

Molecular Physics, 2015
Vol. 113, Nos. 15–16, 2099–2104, http://dx.doi.org/10.1080/00268976.2014.1003985

INVITED ARTICLE

Dissociative recombination and excitation of $D_5{}^+$ by collisions with low-energy electrons

J.B.C. Pettersson[a], P.U. Andersson[a], F. Hellberg[b], J. Öjekull[a], R.D. Thomas[b] and M. Larsson[b,*]

[a]*Department of Chemistry and Molecular Biology, Atmospheric Science, University of Gothenburg, Gothenburg, Sweden;* [b]*Department of Physics, AlbaNova University Center, Stockholm University, Stockholm, Sweden*

(*Received 26 November 2014; accepted 29 December 2014*)

We report results from high-resolution studies of $D_5{}^+$ cluster ion collisions with low-energy electrons performed in a heavy ion storage ring. Absolute dissociative recombination (DR) and dissociative excitation (DE) cross sections were determined for the energy range from 0.0005 to 20 eV. The DR cross sections were exceedingly large at low energies, and DR resulted in efficient internal energy redistribution and pronounced fragmentation with two main product channels: $D_2 + 3D$ (0.62 ± 0.03) and $2D_2 + D$ (0.35 ± 0.01). The DR and DE cross sections were comparable in the energy range from 0.2 to 20 eV, which suggest that the two processes follow similar dynamics and are competing outcomes of the ion–electron interaction. A simple picture of the recombination process of $D_5{}^+$ which captures the essential physics is suggested.

Keywords: dissociative recombination; dissociative excitation

1. Introduction

Hydrogen-containing ions play important roles in several types of plasmas including the interstellar medium, planetary atmospheres, man-made discharges and fusion reactors. For a low-density plasma cold enough to contain molecular components, ions are removed by dissociative recombination (DR) where a molecular ion and a free electron react to form two or more neutral fragments. In the related dissociative excitation (DE) process, the electron is not permanently transferred to the ion, it instead transfers energy to the ion, which breaks apart while the electron is re-emitted with a lower kinetic energy. The DR process may control ion and electron concentrations in the plasma and it produces radicals and highly excited molecules that may undergo subsequent reactions. The current understanding of these processes is far from complete and although DR has been treated theoretically from first principles for a handful of ions [1,2], a general theoretical framework is lacking for larger systems.

The $H_3{}^+$ ion was discovered in mass spectrometry already in 1911 [3], but its spectroscopy was not unravelled until 1980 [4], followed by the first extraterrestrial observation in the auroral regions of Jupiter in 1989 [5,6] and the first observation in the interstellar medium in 1996 [7]. The next stable ion in the H_{2n+1} family, $H_5{}^+$, was discovered by mass spectrometry in a glow discharge in 1962 [8] along with its isotopologue $D_5{}^+$, but just as for $H_3{}^+$ the spectroscopic discovery came much later [9,10], in particular the medium resolution spectroscopy of $H_5{}^+$ and $D_5{}^+$ [11,12]. The spectroscopic work and the fact that $H_5{}^+$ is the simplest molecule containing five atoms and the simplest system with two neutrals combined by a proton have stimulated much theoretical work [11–19].

Another reason for the interest in $H_5{}^+$ is the central role played by $H_3{}^+$ in interstellar chemistry [20,21], which in collision with H_2 leads to the formation of a short-lived $H_5{}^+$ complex in which proton scrambling can occur [22]. It has been estimated that interstellar $H_5{}^+$ could reach a concentration which is 40% of that of $H_3{}^+$ [23], but this estimate is grossly overestimated and flawed by the assumption that H_2 and $H_3{}^+$ are close for, unrealistically, as long as 10 ns leading to a far too high concentration. $H_5{}^+$ has never been observed in the interstellar medium.

DR of $H_5{}^+$ [24–27] and $D_5{}^+$ [28], i.e. $H(D)_5{}^+ + e^- \rightarrow$ neutral products, has been studied in plasma afterglow experiments. Leu *et al.* studied DR of $H_5{}^+$ [24] with a microwave afterglow apparatus combined with a mass spectrometer and determined a DR rate coefficient of $(3.6 \pm 1.0)\cdot 10^{-6}$ cm^3 s^{-1} at 205 K. MacDonald *et al.* [25] later determined the DR rate coefficient as a function of electron temperature T_e using a microwave afterglow-mass spectrometer apparatus. From ion and neutral temperatures of 128 K, the DR rate coefficient was found to be $(1.8 \pm 0.3) \times 10^{-6}\ (T_e(\mathrm{K})/300)^{-0.69}$ cm^3 s^{-1} over the range from 128 to 3000 K, with a more rapid decrease as $T_e{}^{-1}$ between 3000 and 5500 K. Pysanenko *et al.* [26] and Glosik *et al.* [27] also studied DR of $H_5{}^+$ in flowing and stationary afterglow plasmas and obtained similar values. We know of only one earlier recombination study of $D_5{}^+$ carried out by Novotny *et al.* [28].

---

[*] Corresponding author. Email: mats.larsson@fysik.su.se

None of the earlier work has addressed the recombination cross section, the product branching ratios or dissociative excitation. These are the subjects of the present paper.

2. Experiment

The experiments were performed in the heavy ion storage ring CRYRING at the Manne Siegbahn Laboratory, Stockholm University [29]. The detailed experimental procedure has been presented elsewhere [30]. $D_5{}^+$ ions were produced from pure D_2vapour in a hollow cathode ion source [31]. The ions were mass-selected by a dipole magnet and thereafter injected into the ring and accelerated to 9.28 MeV.

The ions were subsequently allowed to interact with electrons at different relative collision energies, and neutral fragments formed by DR or DE were detected by a surface barrier detector. The ions were stored in the ring for 3 s before the experiments began, which should allow for complete relaxation of vibrational excitations in the injected ions. During this time, the ion beam was merged with an electron beam over a distance of 0.85 m in the electron cooler. During this initial storage period, the electron beam was adjusted to have the same average velocity as the ion beam. The repeated passage of ions within the electron beam transferred heat from the ions to the cold electron beam, which resulted in a reduction of the translational temperature of the ions and an increase of the ion density in phase space [32].

Neutral products were generated in the electron cooler by DR of cluster ions and electrons. Neutral fragments formed by DR continued in a straight line in the forward direction, and the fragments were detected by an energy-sensitive silicon detector (SBD, diameter of active area 60 mm) mounted at a distance of 4 m from the midpoint of the electron cooler. The fragments created in a single DR event reached the detector within a short time compared with the integration time of the detector. The pulse height of the signal from the detector was proportional to the total deposited energy, and the event was recorded at the pulse height characteristic of the full beam energy. This is illustrated in Figure 1(a) where a typical energy spectrum is shown for DR of $D_5{}^+$ with 0 eV electrons. The peak observed at the total ion energy of 9.28 MeV is the DR peak and includes products of all active DR channels. A background of neutral fragments was created by collisions between ions and rest gas in the vacuum system. The background was characterised in a separate experiment with the electrons turned off and removed from the data displayed in Figure 1.

The experimental procedure and analysis used to determine absolute cross sections and to deduce thermal rate coefficients have been carefully described elsewhere [1,33]. During cross-sectional measurements after the initial cooling period, the electron energy was varied in order to determine the DR rate as a function of collision energy. The electron cooler voltage was ramped between a high and a low value crossing the cooling voltage corresponding to a centre-of-mass collision energy of 0 eV. The total ramp time was 2.0 s. A single-channel analyser amplified and monitored the signal from the SBD, followed by a multi-channel scaler giving the number of neutralisation events as a function of centre-of-mass collision energy. Simultaneously with the cross-sectional measurements, the background processes, including those due to electron capture from rest gas molecules, were monitored separately with a scintillation detector in a straight section of the ring between the accelerating system and the electron cooler. The registered count rate from this detector served as an indirect measurement of the ion beam current. The absolute beam current, which is required for a determination of the cross section, was measured by means of an ac transformer which measured the magnetic field generated by the coasting, bunched beam [34]. The DR cross section was measured from nominally 0 to 20 eV.

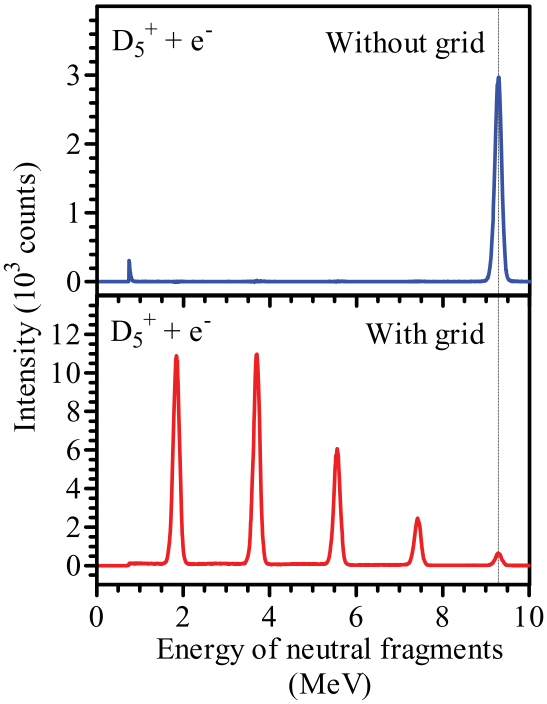

Figure 1. (a) Energy spectrum of neutral fragments produced in DR of $D_5{}^+$ measured with a surface barrier detector. (b) Same as in (a), but with a metal grid in front of the detector, which stops some of the fragments and separates the measured signal into peaks corresponding to 1–5D atoms simultaneously reaching the detector. The spectra were determined with an ion-electron centre-of-mass collision energy $E = 0$ eV. A background spectrum due to collisions with residual gas molecules has been removed from the data. The dashed line indicates the kinetic energy of $D_5{}^+$ ions in the storage ring.

The absolute cross section for DE of $D_5{}^+$ was measured for the energy range from 0.01 to 20 eV. In DE, an electron

Table 1. Energetically allowed product channels in DR and DE of $D_5{}^+$, and determined branching ratios (BRs) for DR (95% confidence interval). The energies given for DR product channels are valid when the fragments are in their rovibrational ground state.

Reaction	Product channel	BR	
Dissociative recombination			
$D_5{}^+ + e^-$ ($E = 0$ eV)	$2D_2 + D + 8.84$ eV	$0.35^{+0.01}_{-0.02}$	(*a*)
	$D_2 + 3D + 4.29$ eV	$0.62^{+0.03}_{-0.04}$	(*b*)
	$D_3\ (2p^2A_2'') + D_2 + 3.35$ eV[1]	$0.02^{+0.03}_{-0.02}$	(*c*)
	$D_4 + D + 8.79$ eV[2]	$0.01^{+0.01}_{-0.01}$	(*d*)
Dissociative excitation			
$D_5{}^+ + e^- (E \geq 0.31$ eV)	$D_3{}^+ + D_2 + e^-$	–	(*e*)
$D_5{}^+ + e^- (E \geq 4.86$ eV)	$D_3{}^+ + 2D + e^-$	–	(*f*)
$D_5{}^+ + e^- (E \geq 4.76$ eV)	$D^+ + 2D_2 + e^-$	–	(*g*)

[1] Additional short-lived D_3 states energetically allowed.
[2] Additional excited D_4 states energetically allowed.

collisionally excites the $D_5{}^+$ cluster ion to a dissociative state or to a short-lived predissociating state. We probed the formation of fragments having a mass corresponding to 2D (i.e. either formation of D_2 or 2D). Two channels resulting in the formation of either $D_3{}^+ + D_2$ or $D_3{}^+ + 2D$ were energetically allowed, see Table 1. These channels are clearly resolved from the DR channel, which occurs at 5D. A contribution to the mass 2D peak arising from collisions with residual gas molecules was subtracted in order to obtain the DE cross section. We cannot completely rule out minor contributions from additional channels listed in Table 1 in case one or several neutral fragments missed the detector due to extensive kinetic energy release.

In order to measure the branching ratios for different channels of the DR process, a metal grid with a transmission $T = 0.297 \pm 0.015$ (99% confidence interval) was inserted in front of the detector [30]. The grid technique has also been carefully described in previous work [1,30,35,36]. The grid is thick enough to stop the neutral fragments that do not pass through the holes. The probability for a neutral fragment to pass through the grid is T, and the probability for the fragment to be stopped is $(1 - T)$. Each neutral fragment carries a fraction of the total beam energy proportional to its mass. The effect of introducing the grid in front of the SBD is illustrated in Figure 1. The upper part shows the pulse-height spectrum without the grid, with a single peak at full beam energy. The lower part shows the pulse–height spectrum with the grid inserted. Particles stopped by the grid do not reach the detector and the total DR signal, therefore, splits into a series of peaks with a fraction of the full beam energy determined by mass ratios. The individual peaks in Figure 1(b) thus correspond to 1–5D atoms reaching the SBD simultaneously.

The number of counts in each of the five sharp peaks observed in the energy spectrum was used to determine the branching ratios. A set of linear equations connecting the number of dissociations into the different channels N_a, N_b, N_c and N_d (see Table 1) to the measured numbers of events in the five peaks was set up. The measured numbers of events in the different peaks were represented by N(D), N(2D), N(3D), N(4D) and N(5D). The following set of equations relates the number of events in each peak to the number of dissociations into the different channels:

$$\begin{pmatrix} N(5D) \\ N(4D) \\ N(3D) \\ N(2D) \\ N(1D) \end{pmatrix} = \begin{pmatrix} T^3 & T^4 & T^2 & T^2 \\ T^2(1-T) & 3T^3(1-T) & 0 & T(1-T) \\ 2T^2(1-T) & 3T^2(1-T)^2 + T^3(1-T) & T(1-T) & 0 \\ 2T(1-T)^2 & 3T^2(1-T)^2 + T(1-T)^3 & T(1-T) & 0 \\ T(1-T)^2 & 3T(1-T)^3 & 0 & T(1-T) \end{pmatrix} \times \begin{pmatrix} N_a \\ N_b \\ N_c \\ N_d \end{pmatrix}. \quad (1)$$

By solving this set of equations, the branching ratios were obtained after normalisation to the total number of dissociations

$$n_i = \frac{N_i}{N_a + N_b + N_c + N_d} \quad \text{with} \quad i = a, b, c, d \quad (2)$$

3. Results and discussion

The absolute DR cross section for $D_5{}^+$ as a function of centre-of-mass collision energy is shown in Figure 2. The cross section decreases monotonically over the energy range up to 1 eV, with an increasing slope above approximately 0.02 eV and again further increasing above approximately 0.2 eV. A broad distribution that peaks around 8 eV is observed at higher energies. Fits to selected energy ranges

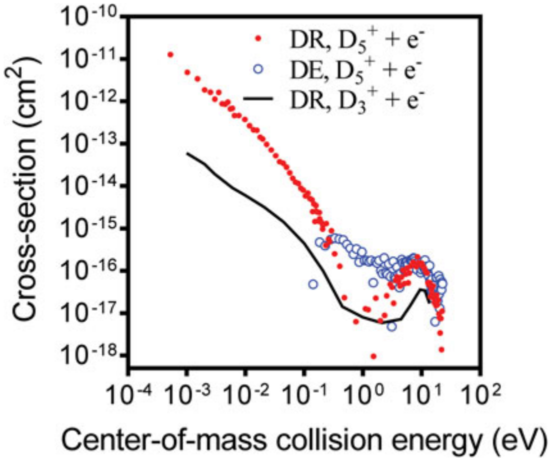

Figure 2. Absolute cross sections for DR and DE of $D_5{}^+$ as a function of centre-of-mass energy. Literature data for $D_3{}^+$ [38].

give (with E used numerically in the expressions for the cross section):

$$\sigma(E) = 10^{-14.87\pm0.20} \times E^{-1.20\pm0.08}\,\text{cm}^2,\quad 0.0005 \le E < 0.017\,\text{eV} \tag{3}$$

$$\sigma(E) = 10^{-15.93\pm0.12} \times E^{-1.78\pm0.10}\text{cm}^2,\quad 0.017 \le E < 0.159\,\text{eV} \tag{4}$$

$$\sigma(E) = 10^{-17.50\pm0.35} \times E^{-3.75\pm0.54}\text{cm}^2,\quad 0.159 \le E \le 1.0\,\text{eV}, \tag{5}$$

where error limits are given as 95% confidence intervals for fits to the experimental data. The data in the low-energy range show an $E^{-1.2}$ dependence which is not too far from the E^{-1} dependence predicted by the Wigner threshold law [37]. Figure 2 also display DR cross-sectional data for D_3]. At energies below 0.01 eV, the cross section for D [38]. At energies below 0.01 eV, the cross section for $D_5{}^+$ is more than 100 times larger than for $D_3{}^+$. The DR cross section for $D_5{}^+$ is similar to the cross sections observed for the cluster ions $D^+(D_2O)_2$ [39] and $D^+(ND_3)_{2,3}$ [40], but the effect of adding a D_2 unit to $D_3{}^+$ is considerably larger than to add D_2O or ND_3 to the other cluster ions.

Thermal DR rate coefficients were calculated from the absolute cross-sectional data by folding the cross section with an isotropic Maxwellian electron-velocity distribution [1]. The calculated rate coefficient in the temperature range from 10 to 1000 K is well described by (with T_e used numerically)

$$\alpha(T_e) = (6.96 \pm 0.02) \times 10^{-5} T_e^{-(0.672\pm0.001)} - (3.45 \pm 0.03) \cdot 10^{-7}\text{cm}^3\text{s}^{-1}. \tag{6}$$

Table 2 contains results from earlier determinations of the DR rate coefficients for $D_5{}^+$ and $H_5{}^+$ at a few different temperatures and the result from the present work at 300 K. The afterglow results are consistently higher than the merged-beam result from CRYRING. A possible explanation for this is that it was recently discovered that the H_2-assisted ternary recombination rate coefficient is very large and that this could have had the effect of ternary recombination domination over binary recombination, resulting in an apparent too large binary recombination rate coefficient [41].

The DE cross-sectional data in Figure 2 show two broad peaks that may be associated with the energetic thresholds of 0.31 and 4.86 for the $D_3{}^+ + D_2$ and $D_3{}^+ + 2D$ channels, respectively. Finite cross sections at energies below 0.31 eV may be due to the thermal excitation (at 300 K) of $D_5{}^+$ ions in the storage ring. The onset of DE around 0.3 eV coincides with a rapid decrease in DR cross section in the same energy range. A comparison between the absolute DR and DE cross sections in the energy range below 3 eV suggests that electron capture process follows the same overall behaviour in this range and that DR and DE are competing outcomes of the ion–electron interaction. As the DE channel becomes energetically accessible around 0.3 eV, autoionisation is strongly favoured over DR. The DR cross sections for $D_5{}^+$ and $D_3{}^+$ are comparable around 1 eV, and the DR and DE data at higher energies both show a broad distribution that peaks around 8 eV. This is due to a resonant process where autoionisation and DR are competing outcomes that have comparable cross sections. The resonant state into which the electron is captured is the same for both processes, but whereas DR leads to dissociation, DE leads to autoionisation. Similar resonant peaks have been observed in DR and DE of $D_3{}^+$ [38]. What is striking with the data in Figure 2 is that this is the first time, to the best of our knowledge, a DE cross section has been measured for a cluster ion ($D_5{}^+$) and made a comparison with the smaller $D_3{}^+$ possible.

The measured product branching ratios are given in Table 1. The dominant channels are $2D_2 + D$ (0.35) and $D_2 + 3D$ (0.62), whereas all other channels are essentially

Table 2. Experimental rate coefficients for $H_5{}^+$ and $D_5{}^+$.

α [10^{-6} cm^3 s^{-1}]	Ion	T_e (K)	Technique	Reference
3.6 ± 1	$H_5{}^+$	205	Afterglow	[24]
1.8 ± 0.3	$H_5{}^+$	300	Afterglow	[25]
3.5 ± 0.4	$H_5{}^+$	195	Afterglow	[26]
$(2 - 3.5)$	$H_5{}^+$	$195 - 220$	Afterglow	[27]
3 ± 1	$D_5{}^+$	190	Afterglow	[28]
1.16 ± 0.02	$D_5{}^+$	300	Storage ring	This work

zero. As pointed out by one of the referees, only the $N = K = 0$ rotational level of the $2p^2 A_2''$ in D_3 has a sufficiently long lifetime to survive to the detector, which must be a very small fraction of all states in D_3. The D_4 channel must also be negligible since only dispersion forces are acting in D_4. The dominance of the three-body break-up has been noted for many molecular ions [1,35,42]; however, in this particular case, a comparison with other cluster ions is more relevant but results for comparison are more limited. Cluster ions have typical bond energies in the range 0.2 –1 eV, with the binding energy of 0.37 eV between $H_3{}^+$ and H_2 falling in this range [43]. The product branching ratio for the water channel $2D_2O + D$ for DR of the cluster ion $D_5O_2{}^+$ was measured in CRYRING to be 0.94 ± 0.04 [39], which is substantially larger than the 0.35 measured for $D_5{}^+$. It is also known from imaging experiments in CRYRING that $D_5O_2{}^+ + e^- \rightarrow 2D_2O + D$ leads to substantial heating of the water molecules [44]; out of the maximum kinetic energy release, as much as 4 eV goes into vibrational energy of the water molecules. It was concluded for $D_5O_2{}^+$ that the single-electron transition model proposed by Bates [45] and termed super-dissociative recombination was less likely to be operative for $D_5O_2{}^+$ [44] since only an indirect recombination process could create the conditions needed for the deuteron to vibrationally heat up D_2O.

A difference between $D_5{}^+$ and $D_5O_2{}^+$ is that the channel giving rise to excited $D_3{}^*$ and D_2 in DR of $D_5{}^+$ is open, whereas the corresponding channel $D_2O + D_3O^*$ is not. Emission from transitions between $H_3{}^*$ Rydberg states has been observed with the characteristic Doppler-like broadening arising from DR of $H_5{}^+$ [46], an effect observed for the first time in afterglow studies of recombining $Ne_2{}^+$ forming energetic Ne atoms as a result of DR of $Ne_2{}^+$ [47]. The lower $n = 2$ Rydberg state in these $H_3{}^*$ transition couples to the repulsive ground state of H_3, which dissociates into three H atoms [48]. This would account for the $D_2 + 3D$ channel, which is the dominant channel for $D_5{}^+$.

The picture emerging for DR of $D_5{}^+$ is thus the single-electron super-dissociative recombination process suggested by Bates [45], where the electron recombines with the $D_3{}^+$ ion in the slightly asymmetric $D_5{}^+$ ion [43], and the single-electron capture is possible because of the vicinity of a D_2 molecule, which can absorb the kinetic energy of the free electron and make the capture possible. The neutral products in the recombination of $D_3{}^+$ with electrons have never been measured; however, there are data for the other three isotopologues and they all ($H_3{}^+$ [49,50]; H_2D^+ [51]; D_2H^+ [52]) show a clear inclination for the three-body break-up, with branching ratios similar that for the $D_2 + 3D$ channel. This suggests that the D_2 molecule in this case has a quite passive role, mainly acting as a third body that enhances the recombination process. If the electron capture occurs when D^+ is about midway between the two D_2 molecules, the break-up occurs into $2D_2 + D$. This is of course a simplified and qualitative picture, but is supported by the experimental results and captures the essential physics. It should be a challenge to the theoretical community to address the recombination process of $D_5{}^+$ with the sophisticated theoretical methods that are available.

4. Conclusions

This paper presents the first experiment in which the absolute cross section and the product branching ratios in dissociative recombination of $D_5{}^+$ with electrons have been measured. The cross section is between one and two orders or magnitude larger than the one for $D_3{}^+$, which suggests that the vicinity of a D_2 molecule to $D_3{}^+$ in the $D_5{}^+$ cluster ion enhances the recombination process by supplying a third body that can absorb the kinetic energy of the electron and hence stabilise the capture. In electron recombination of $D_3{}^+$, the ion must itself stabilise the capture, something which is much less effective. The single-electron super-dissociative recombination model proposed by Bates [45] seems to capture the essential physics.

The neutral products in DR of $D_5{}^+$ are dominated by the $D_2 + 3D$ channel, as predicted by Bates' model [45]. The $2D_2 + D$ channel is also quite large, with a branching ratio of 0.35. The $D_5{}^+$ cluster ion can be described as a slightly asymmetric $D_2 \cdot D^+ \cdot D_2$ complex [43], where the D^+ ion vibrates between the two D_2 molecules. If the electron is captured when the D^+ is about midway between the molecules, recombination would result in the $2D_2 + D$ decay channel. When metastable $D_5{}^{+*}$ is formed, it decays to $D_3{}^+$ and D_2 [53], whereas the $2D_2 + D^+$ channel is absent.

In denser hydrogen plasmas, such as the atmospheres of the gaseous planets Jupiter, Saturn, Uranus and Neptune, $H_5{}^+$ should exist because of the presence of a third body that could stabilise the short-lived $H_5{}^+$ complex formed in $H_2 + H_3{}^+$ collisions. It seems very unlikely that $H_5{}^+$ is present in the interstellar medium.

Acknowledgements

The authors would like to thank the staff of the Manne Siegbahn Laboratory operating the CRYRING facility for technical assistance, B.J. McCall and T. Oka for valuable discussions, and an anonymous referee for valuable comments.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This work was supported by the Swedish Research Council under contract C0250701.

References

[1] M. Larsson and A.E. Orel, *Dissociative Recombination of Molecular Ions* (Cambridge University Press, Cambridge, 2008).

[2] R. Johnsen and S.L. Guberman, Adv. At. Mol. Opt. Phys. **59**, 75 (2010).

[3] J.J. Thomson, Phil. Mag. **21**, 225 (1911).
[4] T. Oka, Phys. Rev. Lett. **45**, 531 (1980).
[5] L. Trafton, D.F. Lester, and K.L. Thompson, Astrophys. J. **343**, L73 (1989).
[6] P. Drossart, J.-P. Maillard, J. Caldwell, S.J. Kim, J.K.H. Watson, W.A.S. Majewski, J. Tennyson, S. Miller, S.K. Atreya, J.T. Clarke, J.H. Waite, Jr., and R. Wagener, Nature **340**, 539 (1989).
[7] T.R. Geballe and T. Oka, Nature **384**, 334 (1996).
[8] P.H. Dawson and A.W. Tickner, J. Chem. Phys. **37**, 672 (1962).
[9] M. Okumura, L.I. Yeh, and Y.T. Lee, J. Chem. Phys. **88**, 79 (1988).
[10] Y.K. Bae, Chem. Phys. Lett. **180**, 179 (1991).
[11] T.C. Cheng, B. Bandyopadyay, Y. Wang, S. Carter, B.J. Braams, J.M. Bowman, and M.A. Duncan, J. Phys. Chem. Lett. **1**, 758 (2010).
[12] T.C. Cheng, L. Jiang, K.R. Asmis, Y. Wang, J.M. Bowman, A.M. Ricks, and M.A. Duncan, J. Phys. Chem. Lett. **3**, 3160 (2012).
[13] Z. Xie, B.J. Braams, and J.M. Bowman, J. Chem. Phys. **122**, 224307 (2005).
[14] A. Aguado, P. Barragán, R. Prosmiti, G. Delgado-Barrio, P. Villareal, and O. Roncero, J. Chem. Phys. **133**, 024306 (2010).
[15] S. Gomez-Carrasco, L. Gonzalez-Sanchez, A. Aguado, C. Sanz-Sanz, A. Zanchet, and O. Roncero, J. Chem. Phys. **137**, 094303 (2012).
[16] A. Aguado, C. Sanz-Sanz, P. Villarreal, and O. Roncero, Phys. Rev. A **85**, 032514 (2012).
[17] H. Song, S.-Y. Lee, M. Yang, and Y. Lu, J. Chem. Phys. **138**, 124309 (2013).
[18] Z. Lin and A.B. McCoy, J. Chem. Phys. **140**, 114305 (2014).
[19] A. Valdés and R. Prosmiti, Phys. Chem. Chem. Phys. **16**, 6217 (2014).
[20] T. Oka, Phil. Trans. R. Soc. A **370**, 4991 (2012).
[21] B.J. McCall, K.H. Hinkle, T.R. Geballe, G.H. Moriarty-Schieven, N.J. Evans II, K. Kawaguchi, S. Takano, V.V. Smith, and T. Oka, Astrophys. J. **567**, 391 (2002).
[22] T. Oka and E. Epp, Astrophys. J. **613**, 349 (2004).
[23] M. Barbatti and M.A.C. Nascimento, Int. J. Quant. Chem. **112**, 3169 (2012).
[24] M.T. Leu, M.A. Biondi, and R. Johnsen, Phys. Rev. A **8**, 413 (1973).
[25] J. Macdonald, M.A. Biondi, and R. Johnsen, Planet. Space Sci. **32**, 651 (1984).
[26] A. Pysanenko, O. Novotny, P. Zakouril, R. Plasil, V. Poterya, and J. Glosik, Czech. J. Phys. **52**, D681 (2002).
[27] J. Glosik, O. Novotny, A. Pysanenko, P. Zakouril, R. Plasil, P Kudrna, and V. Poterya, Plasma Sources Sci. Technol. **12**, S117 (2003).
[28] O. Novotny, J. Glosik, A. Pysanenko, P. Zaukoril, R. Plasil, and M. Tichy, 12th International Congress on Plasma Physics – ICPP, Nice, 2004.
[29] K. Abramsson, G. Andler, L. Bagge, E. Beebe, P. Carlé, H. Danared, S. Egnell, K. Ehrnstén, M. Engström, C.J. Herrlander, J. Hilke, J. Jeansson, A. Källberg, S. Leontein, L. Liljeby, A. Nilsson, A. Paal, K.-G. Rensfelt, U. Rosengård, A. Simonsson, A. Soltan, J. Starker, M. af Ugglas, and A. Filevich, Nucl. Instr. Methods Phys. Res. B **79**, 269 (1993).
[30] A. Neau, A. Al Khalili, S. Rosén, A. Le Padellec, A.M. Derkatch, W. Shi, L. Vikor, M. Larsson, J. Semaniak, R. Thomas, M.B. Någård, K. Andersson, H. Danared, and M. af Ugglas, J. Chem. Phys. **113**, 1762 (2000).
[31] J.R. Peterson, A. Le Padellec, H. Danared, G.H. Dunn, M. Larsson, Å. Larson, R. Peverall, C. Strömholm, S. Rosén, M. af Ugglas, and W.J. van der Zande, J. Chem. Phys. **108**, 1978 (1998).
[32] H. Danared, Phys. Scripta **T59**, 121 (1995).
[33] A. Al-Khalili, S. Rosén, H. Danared, A.M. Derkatch, A. Källberg, M. Larsson, A. Le Padellec, A. Neau, J. Semaniak, R. Thomas, M. af Ugglas, L. Vikor, W. Zong, W.J. van der Zande, X. Urbain, M.J. Jensen, R.C. Bilodeau, O. Heber, H.B. Pedersen, C.P. Safvan, L.H. Andersen, M. Lange, J. Levin, G. Gwinner, L. Knoll, M. Scheffel, D. Schwalm, R. Wester, D. Zajfman, and A. Wolf, Phys. Rev. A **68**, 042702 (2003).
[34] A. Paal, A. Simonsson, A. Källberg, J Dietrich, and I. Mohos, Proceedings of 6th European Workshop on Beam Diagnostics and Instrumentation for Particle Accelerators (DIPAC 2003), Mainz, 2003, p. 240.
[35] R.D. Thomas, Mass Spectrom. Rev. **27**, 485 (2008).
[36] W.D. Geppert and M. Larsson, Chem. Rev. **113**, 8872 (2013).
[37] E.P. Wigner, Phys. Rev. **73**, 1002 (1948).
[38] A. Le Padellec, M. Larsson, H. Danared, Å. Larson, J.R. Peterson, S. Rosén, J. Semaniak, and C. Strömholm, Phys. Scripta **57**, 215 (1998).
[39] M.B. Någård, J.B.C. Pettersson, A.M. Derkatch, A. Al Khalili, A. Neau, S. Rosén, M. Larsson, J. Semaniak, H. Danared, A. Källberg, M. af Ugglas, and F. Österdahl, J. Chem. Phys. **117**, 5264 (2002).
[40] J. Öjekull, P.U. Andersson, M.B. Någård, J.B.C. Pettersson, A. Neau, S. Rosén, R.D. Thomas, M. Larsson, J. Semaniak, H. Danared, A. Källberg, F. Österdahl, and M. af Ugglas, J. Chem. Phys. **125**, 194306 (2006).
[41] P. Dohnal, P. Rubovic, A. Kalosi, M. Hejduk, R. Plasil, R. Johnsen, and J. Glosik, Phys. Rev. A 90, 042708 (2014).
[42] M. Larsson and R. Thomas, Phys. Chem. Chem. Phys. **3**, 4471 (2001).
[43] H. Müller and W. Kutzelnigg, Phys. Chem. Chem. Phys. **2**, 2061 (2000).
[44] R.D. Thomas, V. Zhaunerchyk, A. Ehlerding, W.D. Geppert, F. Hellberg, E. Bahati, M.E. Bannister, M.R. Fogle, C.R. Vane, P.U. Andersson, J. Öjekull, J.B.C. Pettersson, A. Petrignani, W.J. van der Zande, and M. Larsson, J. Phys. Chem. A **114**, 4843 (2010).
[45] D.R. Bates, J. Phys. B **25**, 3067 (1992).
[46] C.A. Miderski and G.I. Gellene, J. Chem. Phys. **88**, 5331 (1988).
[47] T.R. Connor and M.A. Biondi, Phys. Rev. **140**, A778 (1965).
[48] H. Helm, in *Dissociative Recombination: Theory, Experiment and Applications*, edited by B.R. Rowe, J.B.A. Mitchell, and A. Canosa (NATO ASI Series B: Physics Vol. 313, New York, Plenum Press, 1993), p. 145.
[49] S. Datz, G. Sundström, Ch. Biedermann, L. Broström, H. Danared, S. Mannervik, J.R. Mowat, and M. Larsson, Phys. Rev. Lett. **74**, 896 (1995).
[50] B.J. McCall, A.J. Huneycutt, R.J. Saykally, N. Djuric, G.H. Dunn, J. Semaniak, O. Novotny, A. Al-Khalili, A. Ehlerding, F. Hellberg, S. Kalhori, A. Neau, R. Thomas, A. Paal, F. Österdahl, and M. Larsson, Phys. Rev. A **70**, 052716 (2004).
[51] M. Larsson, S. Lepp, A. Dalgarno, C. Strömholm, G. Sundström, V. Zengin, H. Danared, A. Källberg, M. af Ugglas, and S. Datz, Astron. Astrophys. **309**, L1 (1996).
[52] V. Zhaunerchyk, R.D. Thomas, W.D. Geppert, M. Hamberg, M. Kaminska, E. Vigren, and M. Larsson, Phys. Rev. A **77**, 034701 (2008).
[53] N.J. Kirchner and M.T. Bowers, J. Phys. Chem. **91**, 2573 (1987).