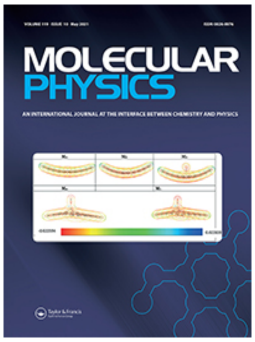

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D. Wehrli, U. Hollenstein & F. Merkt

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RESEARCH NOTE

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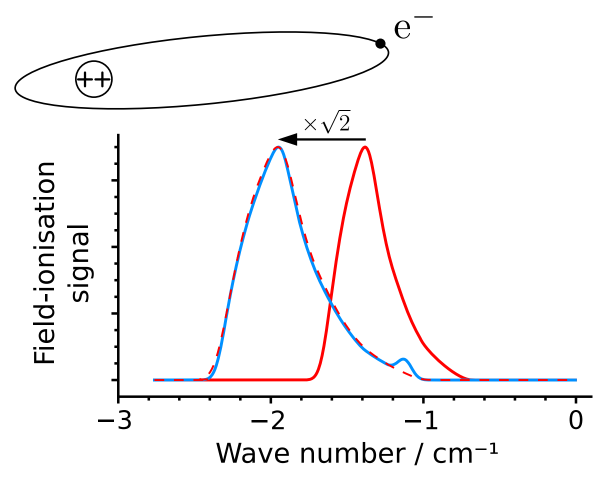
Line shapes and line positions in PFI-ZEKE photoelectron and MATI spectra of positively charged ions

D. Wehrli, U. Hollenstein and F. Merkt

Laboratory of Physical Chemistry, ETH Zurich, Zurich, Switzerland

ABSTRACT
A model developed to calculate the positions and shapes of the lines observed in pulsed-field-ionisation zero-kinetic-energy photoelectron (PFI-ZEKE-PE) and mass-analysed threshold ionisation (MATI) spectra of neutral molecules [Hollenstein et al., J. Chem. Phys. **115**, 5461 (2001)] is generalised to positively charged systems of arbitrary charge. The model assumes that the pulsed field ionisation of the high Rydberg states detected experimentally is diabatic and that their ionisation rates in the presence of electric fields can be calculated with the asymptotic expressions of Damburg and Kolosov [J. Phys. B **12**, 2637 (1979)]. We use this model to calculate the shifts of the lines with respect to the field-free ionisation thresholds and their widths and find that, to an excellent approximation, both the line shifts and line widths scale with $Z^{1/2}$. We also derive simple analytical expressions that can be used to estimate the line shifts and line widths for typical electric-field pulse sequences used in PFI-ZEKE-PE and MATI spectroscopy of positively charged cations.



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Recently, the techniques of pulsed-field-ionisation zero-kinetic-energy photoelectron (PFI-ZEKE-PE) spectroscopy [1,2] and mass-analysed threshold-ionisation (MATI) spectroscopy [3] have been used to record spectra of positively charged ions and obtain high-resolution spectroscopic information on doubly charged atomic and molecular ions [4,5]. With these methods, one monitors the pulsed electric field ionisation of Rydberg states of high principal quantum numbers ($n \gg 100$) that form pseudocontinua below the successive ionisation thresholds as a function of the frequency of the tunable radiation used for photoexcitation of the sample gas [2,6]. Single electric-field pulses or sequences of several electric-field pulses are used to select narrow energy windows of the pseudocontinua. The widths of these windows determine the spectral resolution. The shifts of the ionisation thresholds induced by the electric fields must be corrected to extract accurate field-free ionisation energies. In the case of neutral atoms and molecules (the charge of the ion core is in this case $Z = 1$), reliable procedures have been introduced to estimate the widths and field-induced shifts of the ionisation

CONTACT F. Merkt merkt@phys.chem.ethz.ch Laboratory of Physical Chemistry, ETH Zurich, Zurich CH-8093, Switzerland

thresholds and their dependence on the electric-field strengths F_i of the pulses, with index i, used in the field-ionisation sequences [7–10]. In this research note, we address questions related to the effect of the charge Z of the ion core on the line widths and threshold shifts in PFI-ZEKE and MATI spectra of systems of arbitrary positive integer Z value.

The procedures used for the case $Z = 1$ are based on detailed characterisation of the ionisation of Rydberg states of alkali-metal atoms by pulsed electric fields [11, 12], and in particular on the insight that the states of high principal quantum numbers detected in PFI-ZEKE-PE and MATI spectroscopic experiments follow a diabatic (also called hydrogenic) field-ionisation mechanism [7]. For instance, Chupka [7] has shown that the low-wave-number onset $\tilde{\nu}_{\mathrm{LWO}}$ (with respect to the field-free ionisation threshold) of a line in a PFI-ZEKE photoelectron spectrum recorded by collecting the signal generated by a pulse of strength F is given in good approximation by

$$\tilde{\nu}_{\mathrm{LWO}}/\mathrm{cm}^{-1} = -4\sqrt{F/(\mathrm{V/cm})}, \tag{1}$$

from which one may infer that the spectral width $\tilde{\Gamma}_i$ of the lines in a spectrum recorded using pulse F_i of a sequence of pulses of the same polarity should be (see also Refs. [6–8,13])

$$\tilde{\Gamma}_i/\mathrm{cm}^{-1} = 4\left(\sqrt{F_i/(\mathrm{V/cm})} - \sqrt{F_{i-1}/(\mathrm{V/cm})}\right), \tag{2}$$

and that the shifts of the line centres with respect to the field-free ionisation thresholds are approximately given by

$$\Delta\tilde{\nu}/\mathrm{cm}^{-1} = -2\left(\sqrt{F_i/(\mathrm{V/cm})} + \sqrt{F_{i-1}/(\mathrm{V/cm})}\right). \tag{3}$$

These expressions have been verified [10] in numerical simulations of line shapes that take into account the ionisation rates Γ of Rydberg states in dependence of the electric field strength based on asymptotic expressions derived for the hydrogen atom ($Z = 1$) by Damburg and Kolosov [14,15] and which we have generalised to arbitrary Z value in the present work as (in atomic units)

$$\Gamma = \frac{Z^2(4R)^{(2n_2+m+1)}}{n^3 n_2!(n_2+m)!}\exp\left(-\frac{2R}{3} - \frac{n^3}{4Z^3}\left(34n_2^2 + 34n_2 m + 46n_2 + 7m^2 + 23m + \frac{53}{3}\right)F + O(F^2)\right), \tag{4}$$

with

$$R = (-2E_0)^{3/2}/F, \tag{5}$$

and

$$\begin{aligned} E_0 = {} & -\frac{Z^2}{2n^2} + \frac{3}{2}\frac{n}{Z}(n_1 - n_2)F \\ & - \frac{1}{16}\frac{n^4}{Z^4}\left[17n^2 - 3(n_1 - n_2)^2 - 9m^2 + 19\right]F^2 \\ & + \frac{3}{32}\frac{n^7}{Z^7}(n_1 - n_2)[23n^2 - (n_1 - n_2)^2 \\ & + 11m^2 + 39]F^3 - \frac{1}{1024}\frac{n^{10}}{Z^{10}}\left[5487n^4 + 35182n^2\right. \\ & - 1134m^2(n_1 - n_2)^2 + 1806n^2(n_1 - n_2)^2 \\ & - 3402n^2m^2 + 147(n_1 - n_2)^4 - 549m^4 \\ & \left. + 5754(n_1 - n_2)^2 - 8622m^2 + 16211\right]F^4 + O(F^5). \end{aligned} \tag{6}$$

In these equations, E_0 is the energy of the Rydberg states with respect to the ionisation threshold up to fourth order in the field (see, e.g. Ref. [16]) and n, n_1, n_2 and m are the quantum numbers used in the solution of the Schrödinger equation of the hydrogen atom in parabolic coordinates [17].

In the classical treatment of the ionisation in a potential consisting of a Coulomb ($-Z/r$) and an electric-field (eFz) potential term, the field-induced shift of the ionisation energy can be obtained from the position of the saddle point in the potential as [4,12]

$$\tilde{\nu}_{\mathrm{LWO}}/\mathrm{cm}^{-1} = -6.12\sqrt{ZF/(\mathrm{V/cm})}. \tag{7}$$

This equation suggests a $Z^{1/2}$ scaling of the widths and field-induced shifts of the lines in PFI-ZEKE-PE and MATI spectra of positively charged ions. However, it is not obvious that the Z dependence of the ionisation rates in Equation (4) should result in such a scaling. We have therefore performed numerical simulations of line shapes for different Z values and for typical electric-field pulse sequences used in high-resolution PFI-ZEKE-PE and MATI spectroscopy following the procedure described in Ref. [10].

Representative results are depicted in Figure 1, which shows the line shapes calculated for sequences of two pulses of the same (panels (a) and (c)) and opposite (panels (b) and (d)) polarity for values of Z up to 3. In panels (c) and (d), the lines calculated for $Z = 1$, corresponding to the ionisation of a neutral atom or molecule, are depicted as full red lines. The origin of the wave-number scale is set at the field-free ionisation energy. The dashed red lines represent the same line profiles, but multiplied by $\sqrt{2}$ and $\sqrt{3}$ along the wave-number axis. These scaled line profiles correspond almost exactly to the line profiles calculated for $Z = 2$ (blue line) and 3 (green line). The only significant difference concerns

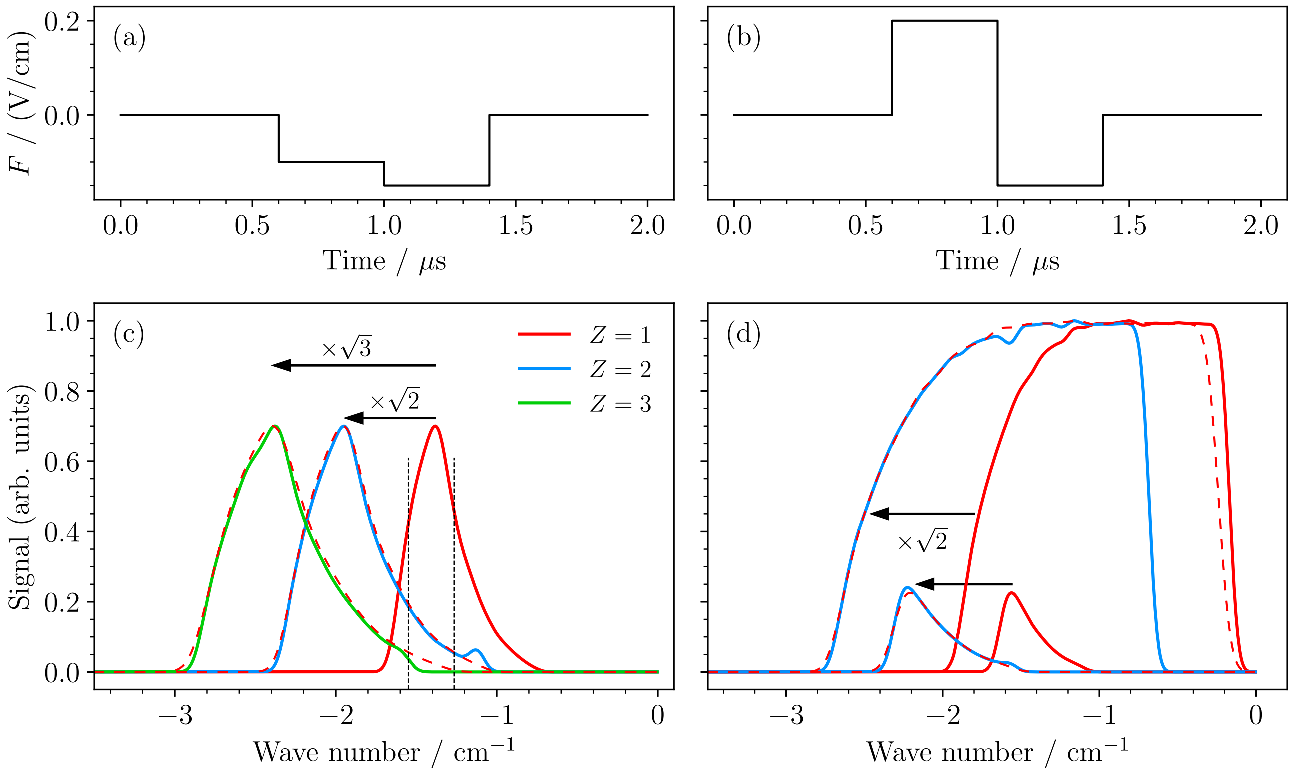

Figure 1. (a) and (b) Typical electric-field pulse sequences used in high-resolution PFI-ZEKE photoelectron spectroscopy involving two subsequent pulses of (a) the same polarity ($F_1 = -0.1$ V/cm; $F_2 = -0.15$ V/cm), and (b) opposite polarity ($F_1 = +0.2$ V/cm; $F_2 = -0.15$ V/cm), which lead to the calculated line shapes depicted in panels (c) and (d), respectively. (c) Line shapes calculated for the second pulse (F_2) of the sequence depicted in panel (a) for $Z = 1$ (full red line), 2 (blue) and 3 (green). The dashed red lines were obtained by multiplying the wave numbers used for the $Z = 1$ case by $\sqrt{2}$ and $\sqrt{3}$. (d) Line shapes calculated for the two pulses of the sequence depicted in panel (b) for $Z = 1$ (full red lines) and 2 (blue). The dashed red lines were obtained by multiplying the wave numbers used for the $Z = 1$ case by $\sqrt{2}$. The vertical dashed black lines in panel (c) correspond to the shifts calculated with Equation (1) for F_1 and F_2. The origin of the wave-number scale is set at the field-free ionisation energy (see text for details).

the high-wave-number edge of the blue line in panel (d), which is significantly displaced compared to the high-wave-number edge of the dashed red line. This difference is an artefact of the calculations, which we have restricted to principal quantum numbers n below 800. The binding energy of Rydberg states scales as Z^2/n^2 and the difference in the high-frequency edges merely reflects the highest n values considered in the calculations.

These results, as well as similar results (not shown) obtained for a much broader range of pulse sequences demonstrate that the widths and field-induced shifts of the lines observed in PFI-ZEKE-PE and MATI spectra of neutral and charged gas-phase species scale as $Z^{1/2}$. The dashed vertical black lines in panel (c) further illustrate the use of Equation (2) to estimate the widths of the lines, which for systems with $Z > 1$ must be replaced by

$$\tilde{\Gamma}_i/\mathrm{cm}^{-1} = 4\sqrt{Z}\left(\sqrt{F_i/(\mathrm{V/cm})} - \sqrt{F_{i-1}/(\mathrm{V/cm})}\right). \tag{8}$$

The pulse sequences involving a reversal of the sign of the electric field lead to different shifts and shapes because, upon rapid reversal of the field polarity, Rydberg states with positive (negative) Stark shifts are converted into Rydberg states with negative (positive) Stark shifts, which ionise at different rates [12]. This property has been exploited to improve the resolution of PFI-ZEKE-PE spectroscopy, as has been explained in detail in Refs. [6,8,10]. The data presented in Figure 1 show that the $Z^{1/2}$ scaling of line shapes and widths also apply in this case.

With the development of powerful narrow-band free-electron lasers, we expect that it will soon be possible to record high-resolution PFI-ZEKE-PE and MATI spectra of a broad range of singly, doubly and even multiply charged cations. We expect that the simple $Z^{1/2}$ scaling of the widths and field-induced shifts of the lines in such spectra demonstrated here will be useful in the planning and analysis of the measurements.

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Disclosure statement

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

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