Recombination studies of Xe$_2^+$ following associative ionization of laser-excited Xe

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Abstract. Experiments are described where two-photon transitions in atomic xenon have been laser-excited from the $^1S_0$ ground state to Xe$^*$ np ($n=8-11$) and Xe$^*$ nf ($n=4-8$) Rydberg states in an apparatus which combines a time-of-flight mass spectrometer and a dispersive photoelectron spectrometer. Xe$^*$ atoms in nf-states, but not in np-states, undergo rapid associative ionization to form Xe$_2^+$, followed by dissociative recombination to form atoms predominantly in lower energy 6p and 5d excited states.

Orbital selectivity for associative ionization can be explained by a simple qualitative model where the Rydberg nf-electron is radially localized outside the Xe$^+$ core for long periods of time due to a larger centrifugal barrier in the effective atomic potential. This enhances the probability that excited Xe atoms in an nf state will encounter a ground state atom at those impact distances that lead to the formation of dimer ions.

1. Introduction

The scientific literature regarding gas-phase xenon (Xe) is very extensive. The electronic spectrum of atomic Xe has been well characterized for many years [1]. The atom has a large number of single and multiphoton transitions that fall in a spectral region that can be readily accessed using coherent light sources, and Xe lasing action in the infrared has been observed in low pressure discharges [2].

Significant progress has also been made towards unravelling the complex vacuum ultraviolet (VUV, wavelengths $\lambda < 200$ nm) electronic spectroscopy of Xe$_2$ using single [3] and multiphoton laser techniques [4], even at rotational resolution [5]. Xe$_2$ van der Waals molecules formed at high pressures exhibit gain in the VUV [6]. Lastly, the ground and excited states of Xe$_2^+$ have been well characterized to vibrational resolution using threshold photoelectron spectroscopy [7].

Dynamically, the dissociative recombination (DR) reaction of Xe$_2^+$:

$$\text{Xe}_2^+ + e^- \rightarrow \text{Xe}^*(n \ell) + \text{Xe}$$  \hspace{1cm} (1)

has been studied by Shiu et al [8]. Here, $n$ and $\ell$ are the principal and orbital angular momentum quantum numbers, respectively. In their experiments the formation of excited Xe$^*(6p)$ was found to dominate reaction (1), although experimentally their optical method was unable to sample channels
that led to the production of non-radiating metastable atoms, ground state atoms, or atoms in states that emitted outside the range of their wavelength detection (380 nm < λ < 890 nm). The dissociative recombination rate coefficient for Xe$_2^+$ at 300 K of $23 \times 10^{-7}$ cm$^3$s$^{-1}$ is quite large [9].

Given such a rich background one might not expect that there would be much left to learn from the xenon system. In this work however we report relatively new experimental results that show surprisingly that Xe atoms excited into Rydberg $nf$-states selectively associatively ionize to form Xe$_2^+$ ions while those excited into Xe*($np$) Rydberg states do not. A simple qualitative explanation of this phenomenon is offered.

2. Experimental arrangement

Details regarding the apparatus used in this work have been provided elsewhere [10]. Briefly, an instrument at the University of Western Ontario was used which operated either as a photoionization mass spectrometer or as a dispersive photoelectron spectrometer. In this work an ~10% Xe/He gas mixture at a backing pressure of ~0.8 MPa was introduced via a pulsed valve as a free jet into a vacuum system maintained at ~10$^{-6}$ Torr. The gas pulse duration was ~170 µs.

Tunable UV photons from a frequency-doubled Nd:YAG pumped dye laser operating at a 10 Hz repetition rate was focused with a $f = 84$ cm quartz lens into the jet ~20 mm below the nozzle pinhole to produce Xe* by resonant two-photon absorption. Depending on which Rydberg state was excited Xe* was either ionized by (2+1) resonance enhanced multiphoton ionization (REMPI) or it associatively ionized with ground state Xe to form Xe$_2^+$. In either case, the resultant ions were mass dispersed in a linear time-of-flight (TOF) mass spectrometer and detected using a microchannel plate detector.

Photoelectrons generated by either ionization process could be extracted in separate experiments into a double focusing electrostatic analyzer whose entrance slit was located 180° to the flight tube of the mass spectrometer and horizontally ~5 mm from the focus of the UV laser beam in the jet. The kinetic energy full width at half maximum was experimentally determined to be ~170 mV at 5 eV pass energy.

3. Results

(2+1) REMPI excitation spectra of $^{132}$Xe between 90200 and 96800 cm$^{-1}$ is presented in figure 1. The UV laser frequency could be calibrated to a fraction of a wave number by simultaneously recording the optogalvanic spectrum of Ne in a Fe/Ne hollow cathode lamp. In this way the lines displayed were readily and unambiguously assigned using tabulated energy levels [1].

Dispersive photoelectron spectra were obtained by ionizing Xe*($n\ell$)$[1/2]_0$, $[3/2]_2$ and $[5/2]_2$ terms, $n = 8-11$, and Xe*($nf$)$[3/2]_2$ and $[5/2]_2$ terms, $n = 4-8$. The state labels for Xe follow an $n\ell[K]_J$ notation in accordance with the $(j, \ell)$ coupling scheme first proposed by Racah [11], where $K$ is the result of coupling the total angular momentum $j$ of the parent ion and the orbital angular momentum of the Rydberg electron, and $J$ is the total angular momentum formed by the vector addition of $K$ and the spin of the Rydberg electron. Typical spectra for Xe*$_{8p}[1/2]_0$ and Xe*$_{4f}[3/2]_2$ are shown in figure 2.

The two features in figure 2(a) correspond to the kinetic energy of the departing electron following (2+1) REMPI, leaving the Xe$^+$ ion-core in either its $^3P_{3/2}$ ground state (kinetic energy ~ 5.2 eV) or its higher energy $^3P_{1/2}$ spin-orbit component (kinetic energy ~ 3.7 eV). In contrast, the structure of the photoelectron spectrum shown in figure 2(b) is very different, but can be fully interpreted as kinetic energy peaks corresponding to ionization not out of Xe*$_{4f}$ but instead, primarily out of lower lying Xe*$_{5d}$ and Xe*$_{6p}$ terms. Thus, unlike the Xe*($np$) states which undergo direct ionization, Xe* in the $nf$-levels examined in this work first relax rapidly (on a time scale on the order of the pulse duration of the UV laser, ~4 ns), to the lower energy 5$d$ and 6$p$ states prior to ionization.
Figure 1. A composite of three (2+1) REMPI excitation spectra recorded for the $^{132}$Xe mass in the region between 90200 and 96800 cm$^{-1}$.

Figure 2. (a) REMPI photoelectron spectrum recorded by exciting the Xe*8p[1/2]$^0$ level; (b) REMPI photoelectron spectrum recorded by exciting the Xe*4f[3/2]$^2$ level.
4. Discussion

The rapid relaxation leading to the unusual dispersive photoelectron spectra from Xe\(^*\) \(nf\)-states is believed to proceed in two steps. The first step involves associative ionization; that is

\[
\text{Xe}^* (nf, \text{not } np) + \text{Xe} \rightarrow \text{Xe}_2^* \rightarrow \text{Xe}_2^+ + e^-
\] (2)

while the second step involves dissociative recombination of the molecular ions formed by associative ionization:

\[
\text{Xe}_2^+ + e^- \rightarrow \text{Xe}^* (5d \text{ and } 6p \text{ predominately}) + \text{Xe}
\] (3)

A complete listing of the observed kinetic energies for Xe\(^*\) \(f\)-states studied in this work is given in table II of the first paper of [10].

The experimental evidence for reaction (2) is shown in figures 3(a-c). In figures 3(a) and (b) features can be seen near \(m/z = 130\) amu which correspond to the formation of Xe\(^*\) by (2+1) REMPI. However, the diffuse feature near \(m/z = 270\) amu which is present only in figure 3(a), is attributed to the formation of Xe\(_2^+\) by associative ionization. Dimer ion formation from excitation of Xe\(^*\) \(np\)-states could be observed but only when the backing pressure of the jet was high enough for three-body association reactions to occur within the expansion (figure 3(c)):

\[
\text{Xe}^* + \text{Xe} + \text{Xe} \rightarrow \text{Xe}_2^* + \text{Xe}
\] (4)
Figure 4. Photoelectron signals obtained by gating the electron spectrometer detection for (a) the fast electrons produced by (2+1) REMPI and (b) the slow electrons produced by Xe$_2^*$ autoionization.

Additional evidence for associative ionization is shown in figure 4. In figure 4(a) the electron spectrometer was gated to detect the fast electrons (1.5 – 4 eV) produced by (2+1) REMPI, while in figure 4(b) the spectrometer was gated to detect slow electrons near zero kinetic energy formed by Xe$_2^*$ autoionization following associative ionization.

While we cannot present direct evidence for the dissociative recombination reaction of Xe$_2^*$ that produces predominately Xe$^*$($5d$ and $6p$), reaction (3), the spectroscopy of Xe$_2^*$($5d$) strongly supports this mechanism. The simplest picture of a molecular Rydberg state is that of a molecular ion-core and a non-bonding, non-interacting Rydberg electron. Symmetry dictates that the gerade $5d$ states of Xe$_2$ are built upon either the $\text{B}^2\Pi_{3/2g}$ or $\text{B}^2\Pi_{1/2g}$ ion-cores [4]. The latter ion-core is almost entirely repulsive [12] and therefore any molecular states built upon it could easily cross the Xe$_2^*$ potential curve providing the necessary conditions for facile dissociative recombination. Simple modeling of the heteronuclear rare gas potential curves has shown that $5d$-$6p$ mixing in rare gas dimers is prevalent [13]. This may be one mechanism leading to the formation of Xe$^*$($6p$) by reaction (3) in the homonuclear systems.

What is surprising is the orbital selectively associated with the associative ionization process in step 1. Janev and Mihajlov [14] and others [15] have modeled collisions leading to associative ionization. In those models the probability of associative ionization becomes large when the atoms approach within distances that are smaller than the mean orbital radius of the Rydberg electron, provided the relative velocity of the colliding pair is smaller than the orbital velocity of the Rydberg electron (a condition readily achieved in supersonic expansions). Since the mean radii of Rydberg states scale as $n^2$ [16] while the Rydberg electron velocities scale as $n^{-1}$, the associative ionization rates as a function of $n$ are expected and have been observed [17] to maximize at some intermediate value of $n$ and then decrease monotonically.

The mean radii for Xe$^*$($n, \ell$) orbitals with $4 \leq n \leq 11$ and $\ell = 1$ and 3, calculated by Hartree-Fock methods in this work are in excellent agreement with estimates obtained from the well known hydrogenic formula:

$$\langle r_{n,\ell} \rangle = \frac{n^2}{z} \left[ 1 + \frac{1}{2} \left( 1 - \frac{\ell(\ell + 1)}{n^2} \right) \right] a_o$$

(5)
where \( n^* = n - \delta \) with \( \delta \) being the quantum defect and \( z \) the effective nuclear charge (assumed for the calculations to be equal to unity). The orbital radii vary from \( \sim 8.7 \) atomic Bohr units (a.u.) for \( \text{Xe}^*(6p) \) to \( \sim 84.8 \) a.u. for \( \text{Xe}^*(11p) \), and increase from 17.5 a.u. for \( \text{Xe}^*(4f) \) to 115.1 a.u. for \( \text{Xe}^*(9f) \). The excellent agreement between the two methods of calculation has been noted previously [18], and indicates that the inner electrons of the \( \text{Xe}^+ \) core effectively shield the Rydberg electron from the nuclear charge. The orbital radii for the \( f^- \) and \( p^- \)-series are comparable although for states of similar energy the \( f^- \)-states are larger (figure 5).

This indicates that orbital size alone cannot account for the selectivity associated with the associative ionization process. Here, it is also important to consider the multielectron potential in which the Rydberg electron moves:

\[
V(r) = V_{\text{Coulomb}}(Z, r) + \frac{\ell(\ell + 1)\hbar^2}{2m_e r^2}
\]

where \( Z \) is the atomic number of the element, and \( m_e \) is the electron mass. \( V_{\text{Coulomb}}(Z, r) \) is not a simple Coulomb function as is the case for hydrogen because multielectron systems contain an electronic core. Goeppert Mayer [19] was the first to show that the many-electron potential for \( \ell = 3 \) Rydberg states (each \( n \)) has a double well structure (shown qualitatively in figure 6). The physical origin of the double well can be easily understood. The potential for the Rydberg electron at large \( r \) (region 1 in figure 6) is dominated by the first, attractive Coulombic term in (6) that incorporates screening by the \( (Z-1) \) electrons in the core. As \( r \) decreases the second, repulsive centrifugal barrier term in (6) becomes important and forms the outer well (region 2 in figure 6). At even shorter \( r \), the Rydberg electron will penetrate the electronic core, and experience a stronger non-Coulombic attraction due to a rapidly decreasing \( r \)-dependent screening. This causes \( V(r) \) to drop dramatically within the core (region 3 in figure 6). This will be offset as \( r \) decreases even further because the centrifugal barrier term \( (r^2) \) again dominates (region 4 in figure 6). \( V(r) \) will then rise steeply to produce the inner well.

The influence of this potential form for \( f^- \)-states is so profound that Connerade has labeled these terms “non-Rydberg-like” [20]. The wave function density for every \( \text{Xe}^* nf \)-state \( (Z = 54) \) is localized in the outer well of its potential. The transition in the periodic table where the \( nf \)-state wave function density is found entirely in the inner well, or orbital collapse, occurs a \( Z = 57 \) for lanthanum, and reestablishes the Aufbau ordering of multielectron atomic orbitals [21].
Thus for Xe\(^*\) \(nf\)-states the centrifugal barrier prevents the Rydberg electron from entering the core. The centrifugal barrier is much less important for \(np\)-states, allowing the Rydberg \(p\)-electron to penetrate the core closer to the nucleus. Not surprisingly, this has an effect on the average Rydberg electron velocities as a function of \(n\) and \(\ell\). They range from 0.25 \(v_0\) for Xe\(^*\)(4\(f\)) to 0.11 \(v_0\) for Xe\(^*\)(9\(f\)) where \(v_0\) is the electron velocity in the first Bohr orbit = 2.18765 \(\times 10^6\) ms\(^{-1}\). The velocities are notably larger for the \(np\)-states but drop from 0.53 \(v_0\) to 0.24 \(v_0\) going from Xe\(^*\)(6\(p\)) to Xe\(^*\)(11\(p\)). Therefore, the origin of the orbital selectivity observed in associative ionization can be attributed to a combination of centrifugal barrier and dynamical effects. Associative ionization will only occur if the Rydberg electron “samples” the critical internuclear separation long enough. Compared to electrons in Rydberg \(np\) states, electrons in \(nf\) states are slower and more “radially” localized outside the core (see figure 5). Thus the probability of finding Xe\(^*\)(nf) at the optimum distance is higher than for Xe\(^*\)(np) states where the Rydberg electron moves faster and spends a larger proportion of its time near the core.

5. Conclusions

Under appropriate experimental conditions, the explanation proposed in this work for the orbital selectivity in associative ionization is expected to be general for every neutral element with \(Z < 57\). Furthermore, compared with conventional optical methods which are limited to measuring dissociative recombination reactions on the \(\mu\)sec time scale or longer, photoelectron spectroscopy provides a new means of detecting dissociative recombination on the nsec time scale.

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