RAPID COMMUNICATIONS

Zero-kinetic-energy electron spectroscopy of the predissociating $A\ ^2\Sigma^+$ state of HBr$^+$

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The rotationally resolved zero-kinetic-energy electron spectra for the $v^+ = 1$, 2, and 3 vibrational levels of the predissociating $A\ ^2\Sigma^+$ state of HBr$^+$ are reported. The results for the rapidly predissociating $v^+ = 2$ and 3 levels show that the high principal quantum number Rydberg states involved in the zero-kinetic-energy spectroscopy are unperturbed by ion core fragmentation. These data demonstrate the general applicability of this technique for rotationally resolved photoelectron spectroscopy.

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The method of pulsed-field ionization zero-kinetic-energy electron (PFI-ZEKE) spectroscopy allows one to measure rotationally resolved photoelectron spectra [1,2]. Although most work in PFI-ZEKE spectroscopy has used multiphoton excitation of ionization thresholds, the introduction of single-photon excitation in the vacuum ultraviolet (vuv) [3] permitted the study of systems where intermediate neutral states are either unavailable or not well enough understood, and has extended the range of thresholds accessible to higher energies. Almost all of the work to date in PFI-ZEKE spectroscopy has focused on ground electronic states of molecular ions and low vibrational levels of those states. By using very-short-wavelength coherent vuv for single-photon excitation, we have been able to apply PFI-ZEKE spectroscopy to electronically excited states of ions [4–6] and to very high vibrational levels of ions [7,8], at energies as much as 6.7 eV above the lowest ionization threshold.

These studies on excited states showed that PFI-ZEKE spectroscopy, which relies on the existence of metastable Rydberg states, could be applied to thresholds well above the lowest ionization energy. It would appear that PFI-ZEKE spectroscopy is generally applicable, and can be used to study any ionization threshold. The previous observation of the PFI-ZEKE spectrum of a fluorescing excited state [5]

showed that initially excited high principal quantum number Rydberg states, which are detected by field ionization to record the PFI-ZEKE spectrum, were not affected by fluorescence of the ion core. In this paper we wish to report observation of PFI-ZEKE spectra of predissociating excited states of a molecular ion, in which case the Rydberg electron is not affected by the dissociation of the ion core.

The current work is similar to previous studies on the photoionization of HBr [9], O$_2$ [10], and HCl [11], where superexcited states, pumped by synchrotron radiation, decayed by dissociation into excited neutral fragments, followed by autoionization of one of the neutral fragments, yielding photoelectrons with an energy independent of the excitation energy. These autoionizing atomic resonances occur at much higher excitation energies than used in this work. In the present experiments, PFI-ZEKE spectra are recorded for predissociating and nondissociating vibrational levels of the HBr$^+ A\ ^2\Sigma^+$ state. For the dissociating levels, field ionization occurs long after the ion core has fragmented, with the Rydberg electron being an unaffected spectator. Therefore, the PFI-ZEKE spectrum results from field ionization of a Br atom in a high Rydberg state, which is produced by predissociation of the initially excited HBr Rydberg state.

The electronic ground state of the HBr$^+$ ion has the configuration $(\sigma)^2(3\pi)^3$ and correlates with Br$^+(^3P)$ + H$(^2S_{1/2})$. The π hole gives rise to a strong spin-orbit interaction with a spin-orbit coupling constant of

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$A = -2651.4$ cm^{-1} [12]. The first electronically excited state $A\,^2\Sigma^+$ has the configuration $(\sigma)(3\pi)^4$, and correlates with $Br^+(^1D)+H(^2S_{1/2})$. The A-X emission spectrum of HBr$^+$ in a discharge has been studied quite thoroughly [13–15], and a set of vibrational and rotational constants for the ground state and rotational constants for the excited state have been obtained.

The onset of the predissociation occurs at $N^+=21$ and $N^+=12$ for $v^+=0$ and $v^+=1$, respectively [16], and has been attributed to the interaction with the repulsive $^4\Pi$ state, correlating with $Br^+(^3P_J)+H(^2S_{1/2})$. The energetic position of the sharp onset of the predissociation coincides closely with the lowest dissociation limit $Br^+(^3P_2)+H(^2S_{1/2})$. A recent *ab initio* calculation of the potential-energy curves of all states correlating to the first three dissociation limits explains this sharp onset of the predissociation in terms of rotationally enhanced spin-orbit interaction with the $X\,^2\Pi$ ground state [17]. The predissociation of the vibrational levels with $v^+\geq 2$ occurs through curve crossings with three different excited states, $^4\Sigma^-$, $^2\Sigma^-$, and $^4\Pi$. By calculating the lifetimes with respect to predissociation by these states separately, Banichevich, Klotz, and Peyerimhoff [17] were able to show that for lower vibrational levels, the dominating interaction is with the $^4\Sigma^-$ state, but for higher vibrational levels with the $^4\Pi$ state. The calculated lifetime for the $v^+=2$ level is 1.5×10^{-10} s, and drops by three orders of magnitude for the $v^+=3$ level and another order of magnitude for the higher vibrational levels.

The electronic states of the HBr$^+$ ion have also been studied by photoelectron spectroscopy (PES) after photoionization from the ground state of the neutral molecule [18–21]. The recent study by Baltzer *et al.* [21] observed the PES after excitation with He I radiation at a resolution of 5 meV. They were able to follow the vibrational progression up to $v^+=14$, and they resolved rotational structure for high values of N^+ in $v^+=0,1,2,11,12,13$. They observe broadening of the vibrational levels consistent with a lifetime of 10^{-13} s for $v^+=3$ and 10^{-14} s for $v^+=4$.

The experimental method used has been described in detail in previous publications [4,22]. Briefly, coherent vuv radiation of the appropriate wavelength was generated by resonantly enhanced four-wave sum-frequency mixing in a pulsed jet of Kr or Xe and wavelength selected and refocused into the ionization volume by a 1-m normal incidence monochromator. The ionization volume, formed by the intersection of the vuv radiation and the collimated supersonic beam of HBr, was located between the entry grids of a double time-of-flight spectrometer. During the pulsed vuv excitation, a weak dc field (80 mV/cm) was applied between the two grids to sweep out promptly formed electrons and to field ionize very high Rydberg states just below the ionization threshold. A pulsed field of 0.8 V/cm was applied to the ionization region 1 μs after the vuv pulse, and the resulting electrons formed by field ionization were swept into the time-of-flight electron spectrometer, and detected by a channel plate multiplier. This method provided excellent discrimination against background electrons, and resulted in a threshold photoelectron energy resolution of 2 cm^{-1}. The PFI-ZEKE spectra were recorded by measuring the field ionized
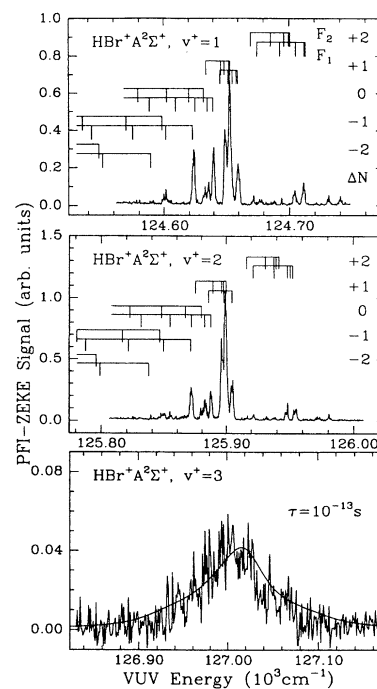

FIG. 1. PFI-ZEKE spectra of the $v^+=1,2,3$ levels of the HBr$^+$ $A\,^2\Sigma^+$ state. For $v^+=1$ and 2, the rotational transitions are grouped into branches according to the transferred angular momentum $\Delta N=N^+-N''$, with a doubling of the branches due to the spin-rotation interaction. For clarity, only $|\Delta N|\leq 2$ transitions are labeled on the figure. The solid line for $v^+=3$ is the result of a convolution of the band contour with a lifetime of 10^{-13} s.

electrons as a function of vuv photon energy, which was calibrated to an absolute energy uncertainty of less than 1 cm^{-1}.

The experimental results for HBr$^+(A\,^2\Sigma^+)$, $v^+=1,2,3$ are presented in Fig. 1. All the rotational transitions observed for the $v^+=1$ and 2 final vibrational levels are labeled and ordered into rotational branches according to the transferred angular momentum $\Delta N=N^+-N''$ [23]. The spin-rotation coupling leads to a splitting of all rotational levels, which increases linearly with the rotational quantum number. The two ensuing branches are labeled F_1 and F_2 for $J^+=N^++0.5$ and $J^+=N^+-0.5$, respectively. In both spectra, the maximum observed angular momentum transfer is $|\Delta N|\leq 3$. Line positions for rotational transitions leading to $v^+=1$ were calculated using the known constants for the HBr ground state [12] and the excited state [14]. For the transitions leading to the $v^+=2$ level, the line positions were determined, with constants calculated from the values for B_e, α_e and D_e, β_e given in Ref. [14]. Since the spin-rotation coupling constant was not known for $v^+=2$, it was linearly extrapolated from the values for $v^+=0$ and 1 [14], and set to be 1.93 cm^{-1}. With these line positions for $v^+=1$ and 2, all the observed rotational transitions could be assigned. For a qualitative understanding of the predissociation lifetime broadened $v^+=3$ level, we used our rotationally resolved results for $v^+=2$ and broadened them with a Lorentzian line

shape equivalent to a lifetime of 10^{-13} s. The result was overlaid as a full line on the experimental results for the $v^+=3$ level in Fig. 1. A detailed analysis of the spectroscopic results will be presented in a future publication [24].

The PFI-ZEKE spectra shown in Fig. 1 are for a nondissociating level of the $A\ ^2\Sigma^+$ state ($v^+=1$) and two predissociating levels ($v^+=2$ and 3). For the $v^+=2$ level, the $\sim 10^{-10}$ s lifetime will not lead to any observable line broadening at the resolution of the present spectra, and thus it is interesting to compare the PFI-ZEKE spectra for the $v^+=1$ and $v^+=2$ bands. The bands shown in Fig. 1 are the same, except for the expected differences in spectroscopic constants for the two vibrational levels, and the overall intensities. Spectra simulations using the model developed by Buckingham, Orr, and Sichel [25] show that the rotational line strengths are essentially the same for the two bands [24], and the relative intensities of the two bands are in reasonable agreement with the Franck-Condon factors to the HBr $X\ ^1\Sigma^+$ ($v=0$) level [17].

The similarity between the PFI-ZEKE spectra of the two levels stands in contrast to the known differences between the two levels. All of the rotational levels of $v^+=1$ observed in the spectrum are below the dissociation limit, and will thus only decay by fluorescence, with a lifetime of 4.0 ± 0.4 μs [26], while all rotational levels of $v^+=2$ predissociate, with a calculated lifetime of 1.5×10^{-10} s. Although there is no experimental value for this predissociation lifetime, the complete extinction of fluorescence for all levels above the dissociation limit shows that the lifetime must be close to the calculated value. Thus it would appear that the dissociation of the ion core seems to have no effect on the subsequent field ionization detection of the metastable Rydberg states. This is demonstrated again by the spectrum of $v^+=3$ shown in Fig. 1. Although the signal-to-noise ratio is not as good because the spectrum is spread over a larger energy range, it is certain that the lifetime broadened $v^+=3$ level is being observed, with the spectral broadening in good agreement with the calculated lifetime for this level. Furthermore, the integrated band intensity for the $v^+=3$ band is in reasonable accord with the Franck-Condon factors, when compared with the $v^+=0$, 1, and 2 PFI-ZEKE bands.

It should be stressed that the spectra shown in Fig. 1 are purely the results of weak-field ionization of high principal quantum number Rydberg states, which are initially excited by the vuv pulse. Any electrons formed at the time of laser excitation would be removed by the weak dc field present, and the expected dependence of the line shapes for individual rotational lines on the strength of the pulsed field [22] was observed for both the nondissociating $v^+=1$ and the dissociating $v^+=2$ levels (the broadening of $v^+=3$ made the measurement impossible for this level). From these results, we are led to the following mechanism for the PFI-ZEKE spectra of the predissociating levels. The initial step is single-photon excitation of the Rydberg states just below the

threshold to form a predissociating state. Since the ion core is promoted into the predissociating level, it dissociates immediately after excitation to give $H(^2S_{1/2})+Br^+(^3P_2)$. The recoil velocity of the Br^+ ion in the $v^+=2$ vibrational state is ≈0.38 Å/ps, which has to be compared to the orbital velocity of ≈ 100 Å/ps for a Rydberg electron with $n\approx200$. The Rydberg electron follows the recoiling Br^+, with little or no change in principal quantum number, and the subsequent field ionization produces an electron and a Br^+ ion.

The fact that the initially excited Rydberg electron is essentially undisturbed by the dissociation of the HBr^+ core is shown by the strength of the PFI-ZEKE signal for $v^+=2$ and 3, and by the similarity between the field dependence of the $v^+=1$ and 2 line shapes. Since the PFI-ZEKE signal results from metastable Rydberg states, which can be Stark ionized at fields between the applied dc field and the pulsed field, anything that increases or decreases the principal quantum number of the Rydberg state, such that it is removed from this range between vuv excitation and field ionization, will lead to a loss in PFI-ZEKE signal. The similarity of the Stark field shift of the ionization thresholds for dissociating and nondissociating levels implies that the "survival" of Rydberg states does not depend significantly on principal quantum number, at least for $n>150$.

This observation of adiabatic decay of high Rydberg states,

$$HBr^*(n\sim200)\rightarrow H+Br^*(n\sim200),$$
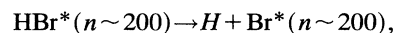
where HBr^* is a Rydberg state converging to a predissociating level of HBr^+ and Br^* is a Rydberg state with a $Br^+(^3P_2)$ core, is similar to what has been observed in PFI-ZEKE of van der Waals complexes [27]. In the case of the van der Waals complex, the predissociation can be viewed in terms of a vibrational relaxation of the ion core leading to the departure of a rare-gas atom, instead of the dissociation of the chemical bond in the ion core, followed by ejection of an H atom.

In this Rapid Communication, we are reporting results of PFI-ZEKE spectroscopy for the $A\ ^2\Sigma^+$, $v^+=1$, 2, and 3 vibrational levels of the HBr^+ ion. Our results were obtained at a resolution of 2 cm^{-1} (0.25 meV), thus enabling the resolution not only of the rotational structure of the $v^+=1$ and 2 levels, but also the spin-rotation splitting even for low N^+. No difference in the intensity has been observed between the nondissociating $v^+=1$ level and the predissociating $v^+=2$ level. The $v^+=3$ level is observed to be considerably broadened, consistent with a lifetime of 10^{-13} s.

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