Ion-pair formation observed in a pulsed-field ionization photoelectron spectroscopic study of HF

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Received 24th November 1999
Published on the Web 31st March 2000

The pulsed-field ionization (PFI) photoelectron (PE) spectrum of HF has been recorded at the chemical dynamics beamline of the advanced light source over the photon energy range 15.9–16.5 eV using a time-of-flight selection scheme at a resolution of 0.6 meV. Rotationally-resolved structure in the $v^\ast=0, 1$ band systems are assigned. The spectral appearance of these systems agrees with a previous VUV laser PFI-PE study. Importantly, extensive rotationally-resolved structure between these two vibrational band systems is also observed. This is attributed to ion-pair formation via Rydberg states converging on the $v^\ast=1$ vibrational levels of the HF$^+$ ($X^2\Pi_{3/2, 1/2}$) spin–orbit states. These Rydberg states are assigned to the $^1\Sigma^+$ part of the $nd$-complexes ($\sigma$, $\pi$ and $\delta$). Ion-pair formation is observed in this study by the detection of F$^-$ ions. Some partially rotationally-resolved structure in a previously published threshold photoelectron spectrum is similarly attributed to ion-pair formation (F$^-$ detection) through a combination of the $v^\ast=17$ level of the $A^2\Sigma^+$ 3s$\sigma$ Rydberg state and the $(X^2\Pi_{3/2, 1/2}, v^\ast=1) 7d$ Rydberg states. On the basis of the present study, an accurate experimental value for the dissociation energy of the ground state of HF has been obtained, $D_0(HF) = 5.8650(5)$ eV.

I. Introduction

Pulsed-field ionization-photoelectron (PFI-PE) spectroscopy has revolutionized the field of high-resolution ionic-state spectroscopy in molecules. Historically, UV/VUV lasers dominated these studies because of their superior resolution and intensity. However, with the development of third-generation synchrotron light sources with their increased intensity and higher resolution, DOI: 10.1039/a909277c


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there is now the possibility of performing rotationally-resolved ionization studies\(^4\)–\(^11\) over much wider spectral ranges than is typical of laser based studies. Complimentary to synchrotron based PFI-PE studies is the technique of threshold photoelectron (TPE) spectroscopy\(^12\)–\(^14\) also primarily using synchrotron radiation. Recently, partially rotationally-resolved TPE spectra have been obtained in the 3 meV resolution range using the penetrating-field method of electron analysis.\(^15\)–\(^17\) In addition, conventional photoelectron spectroscopy using fixed wavelength light sources has recently been developed at Uppsala University to achieve a resolution approaching 1 meV.\(^18\)–\(^21\) The goal of all these techniques has been to understand photoionization phenomenon at the individual rotational level in molecular ion states.

The work described here consisted of a high-resolution PFI-PE study of the HF molecule in the ionization onset region encompassing the formation of the \(v^+ = 0\) and 1 vibrational band systems of the HF\(^+\)(X\(^2\)I\(^3\)i\(2\), \(1\)) spin–orbit states. In particular, this study involved the use of multibunch synchrotron radiation at the advanced light source (ALS) in conjunction with a recently developed time-of-flight detection scheme for threshold electrons.\(^22\) The spectral region covered in this study has been partially investigated in a PFI-PE study of HF using single-photon VUV laser excitation with a reported overall resolution of 1 cm\(^{-1}\).\(^23\) In addition, a TPE study of HF covering the same spectral region of this work was recently reported at a resolution of \(\sim 3\) meV.\(^17\) Both of these studies will figure prominently in the present discussion.

II. Experimental

The procedure for obtaining the PFI-PE spectrum presented here has been described in detail recently,\(^22\) so only a brief account will be given. Synchrotron radiation emanating from the advanced light source (ALS) storage ring entered the chemical dynamics beamline consisting of a 10 cm period undulator, a gas harmonic filter, a 6.65 m off-plane Eagle mounted monochromator and a photoelectron–photoion spectrometer. PFI-PE spectra of HF were taken in small energy regions \((\sim 0.04\) eV\) in 0.2 meV steps covering the total energy range studied (15.9–16.5 eV). These were joined, with overlapping portions, to produce a single PFI-PE spectrum. The conditions for recording the spectrum were as follows. An ambient temperature, effusive gas jet of HF interacted with the focused monochromatic photon beam (spot size 0.2 \(\times\) 0.3 mm\(^2\)) at the center of the ionization region of the apparatus. Threshold electrons were detected during the 112 ns dark gap of the synchrotron period in the following manner: After an elapsed time of \(\sim 20\) ns from the start of the dark gap an electric field pulse of 1.5 V cm\(^{-1}\) was applied across the interaction region for a duration of 40 ns. This applied field resulted in field ionization of any long-lived Rydberg states of HF created during the light-on portion of the synchrotron period and acted to accelerate the threshold electrons produced into the time-of-flight (TOF) electron spectrometer. Prior to the pulsed electric field a small dc field \((0.04–0.2\) V cm\(^{-1}\)) was applied across the interaction region to push any hot electrons that might have been present due to autoionization or direct ionization towards the electron detector as soon as they were formed. Near the end of the pulsed-field period a gate was opened in the output of the electron detector for 10 ns and electrons collected in this period were accumulated. The triggering of the gate was accomplished by a bunch-marking pulse provided by the ALS, whose position in time was arbitrary. The opening of the electron collection gate was set to coincide with the flight time of electrons initially created in the synchrotron dark gap with zero kinetic energy to arrive at the electron detector. The repetition rate for the above procedure was set to correspond to the operating frequency of the ALS, namely 1.52 MHz.

The photon energy scale of the PFI-PE spectrum in HF was calibrated by measuring threshold electrons produced from PFI of argon and neon under identical conditions as for the HF experiment. A resolution of 0.5 meV was determined from the full width at half maximum (FWHM) of the \(\text{Ar}^+\) (\(^3\)P\(^{1}\)) peak and 0.6 meV (FWHM) from one of the sharpest features in the HF spectrum using slit settings on the monochromator of 10 \(\mu\)m and a 2400 lines mm\(^{-1}\) grating. The HF gas pressure in the apparatus was \(2 \times 10^{-6}\) mbar. The HF gas used in this experiment was purchased from Matheson Tri-Gas, Inc. (Cucamonga, CA) with a stated purity of 99.0%. No further purification of the gas was performed except to remove the hydrogen gas that accumulated due to decomposition of HF on the walls of the cylinder. This was accomplished by pumping on the liquid-nitrogen cooled cylinder just prior to use.

III. Results and discussion

The full PFI-PE spectrum of HF obtained in this study is presented in the top panel of Fig. 1 over the photon energy range 15.9–16.5 eV at an overall resolution of ~0.6 meV. As can be seen, extensive rotationally-resolved structure is found over the entire energy region. Before an analysis of these features can be made it is necessary to introduce additional spectral results. In the middle panel of Fig. 1 is the TPE spectrum of HF over the same photon energy range at a resolution of ~3 meV.\textsuperscript{17,24} It shows partially-resolved rotational structure in the \( v^+ = 0 \) band system of the \((X^2\Pi_{3/2, 1/2})\) states of HF\(^+\) that appears to be influenced by a strong resonance at about 16.06 eV, as noted earlier.\textsuperscript{17} In the bottom panel of Fig. 1 is presented the F\(^-\) photoexcitation function from ion-pair formation in HF at a resolution of ~13 meV.\textsuperscript{25} This spectrum has been shifted from the originally published spectrum by 8.5 meV to lower energy for the present comparison. This was done so that the prominent onset feature in the F\(^-\) excitation function coincides in energy with the intense resonance feature in the HF TPE spectrum at 16.062 eV, which we believe to have a common origin. All of the structure observed in the F\(^-\) excitation function has been attributed to ion-pair formation via photoexcited Rydberg states that are predissociated by the \( V^1\Sigma^+ \) ion-pair potential based on \textit{ab initio} calculations.\textsuperscript{25} The prominent feature at 16.062 eV has been assigned to the HF Rydberg state \((A^3\Sigma^+, v^+ = 17)\) while essentially all other features in the F\(^-\) excitation function were assigned to overlapping HF Rydberg states \((X^2\Pi_{3/2, 1/2}, v^+ = 1)\) nd for \( n \geq 7.\textsuperscript{25}\)

We now turn to an analysis of the PFI-PE spectrum shown in the top panel of Fig. 1. The two dominant series of peak structures at about 16.04 and 16.40 eV are identified with rotational

\textbf{Fig. 1} Comparison of (a) the PFI-PE spectrum of HF (top panel) over the photon energy region encompassing the \( v^+ = 0 \) and 1 vibrational bands of HF\(^+(X^2\Pi_{3/2, 1/2})\) with (b) the TPE spectrum of HF (middle panel) (refs. 17 and 24) and (c) the F\(^-\) excitation function of HF (bottom panel) (ref. 25) over the same photon energy region.
structure of the $v^+ = 0$ and 1 bands, respectively, of $\text{HF}^+ (X^2\Pi_{3/2, 1/2})$. These two band systems are displayed in Figs. 2 and 3, respectively, in expanded form. The peak structures in these figures are assigned to resolved rotational lines of the two spin–orbit components $F_1$ and $F_2$ based on previously published assignments.\textsuperscript{23,26} It should be noted that the relative intensities of the rotational profiles in these two figures are essentially identical to those observed in the VUV laser PFI-PE spectrum of Mank \textit{et al.}\textsuperscript{23} except for small variations due to different resolutions and temperature conditions in the two experiments. Based on the spectral results of Figs. 2 and 3 we find the $R_{2}(0)$ transition energies in the $v^+ = 0$ and 1 bands to be at 16.0456(4) and 16.4056(4) eV, respectively, in good agreement with the results of Mank \textit{et al.}\textsuperscript{23} Thus, we confidently conclude that our synchrotron based PFI-PE method is equivalent to the VUV laser based method.

Fig. 2 Rotational assignment of the $v^+ = 0$ vibrational band of the spin–orbit $F_1$ and $F_2$ components of $\text{HF}^+ (X^2\Pi_{3/2, 1/2})$ obtained by the PFI-PE method employed in this study.

Fig. 3 Rotational assignment of the $v^+ = 1$ vibrational band of the spin–orbit $F_1$ and $F_2$ components of $\text{HF}^+ (X^2\Pi_{3/2, 1/2})$ obtained by the PFI-PE method employed in this study.

The remaining part of this paper will focus on the highly structured region between the $v^+ = 0$ and 1 vibrational bands in the PFI-PE spectrum of HF given in the top panel of Fig. 1 and the TPE and ion-pair results presented in the middle and bottom panels of Fig. 1, respectively. We attribute all of the structure in the PFI-PE spectrum between the $v^+ = 0$ and 1 bands to ion-pair formation with the detection of F$^-$ ions by our TOF spectrometer. To support our view we present in Fig. 4 an overlay of the F$^-$ excitation function onto the PFI-PE spectrum. Although the match in band features is not perfect, there is a high correspondence between the two spectra except for the prominent F$^-$ peak at 16.062 eV. We point out that a perfect match would not really be expected since the means of carrying out the two experiments are quite different (e.g., differences may be expected in the collection efficiencies and the gas temperature was different in the two experiments). We rationalize the F$^-$ signal in the PFI-PE spectrum as being due to a dc F$^-$ signal produced during the entire light-on portion of the synchrotron period under field-free conditions. The non-appearance in the PFI-PE spectrum of the prominent (16.062 eV) F$^-$ peak in the excitation function is thought to be due to the fact that the F$^-$ ions associated with this peak are created with essentially zero kinetic energy, since they are formed at the threshold for ion-pair formation. There is, therefore, a high probability that they will recombine with the threshold H$^+$ ions that are also formed in the interaction region. On the other hand, at photon energies above the threshold for ion-pair formation the ion pairs are formed with varying amounts of finite relative kinetic energy and can separate from each other. Because of the mass difference between the H and F atoms, ~95% of the excess internal energy will be carried away as kinetic energy of the H$^+$ ion. The slow moving F$^-$ ions are then swept from the interaction region towards the TOF detection system by the dc pushing potential described in the experimental section. This results in a nearly constant stream of F$^-$ ions through the TOF spectrometer where they are detected whenever the threshold electron detection gate is opened.

To further support our contention that the highly structured features between the $v^+ = 0$ and 1 bands in the top panel of Fig. 1 are due to ion-pair formation, we present in Fig. 5 the calculated energy positions of the $nd\pi$ Rydberg series converging on the two spin–orbit components of the $v^+ = 1$ band system. It is the 'Σ' part of the $nd\pi$ Rydberg states that couples to the 'Σ' ion-pair state. For these calculations we used the accurate ionization value of 132 333.3 cm$^{-1}$ for the R$_j(0)$ rotational line in the $v^+ = 1$ band given by Mank et al. and the measured fine-structure splitting of 36 meV in the $v^+ = 1$ band given by Wang et al. In addition, we used a quantum defect for the $d\pi$ Rydberg states of $-0.01$. Although these Rydberg resonances are expected to

![Fig. 4](image_url)
Fig. 5  Calculated positions of the ndt Rydberg members in the series converging on the $v^+ = 1$ vibrational levels of the HF$^+$($X^2\Pi_{3/2, 1/2}$) spin-orbit states.

be rather narrow (about 5 cm$^{-1}$ for 7d$^p$),$^{25}$ they are likely broadened by interaction with the dissociative ion-pair continuum and the inclusion of the mixing with other members of the d-complex (σ and δ) Rydberg states may be sufficiently wide in energy to account for the results shown in Fig. 5. The σ and δ members do not have $1\Sigma^+$ symmetry but can be mixed with the π member by rotational interaction.$^{27}$ Clearly, the energy positions of the two Rydberg series shown in Fig. 5 could well account for the $F^-$ structure observed in the PFI-PE spectrum.

The rotational structure in the band-like features observed in the region between the $v^+ = 0$ and 1 bands of the HF$^+$($X^2\Pi_{3/2, 1/2}$) system in the PFI-PE spectrum must be due to the intermediate nd-complex Rydberg states as the $1\Sigma^+$ part of these states is coupled to the dissociative continuum of the ion-pair state (see above). Analysis of these Rydberg rotational lines will be given in a future publication.

We now return to considering the TPE spectrum shown in the middle panel of Fig. 1. Here we try to explain the appearance of the pronounced resonance (anomalous high intensity) feature at 16.062 eV in the spectrum and the rather unusual high-energy tails on both the $v^+ = 0$ and 1 vibrational bands. There are two possible explanations for these features. They can be either due to threshold electrons or due to threshold F$^-$ ions, since the penetrating-field method employed in this study$^{17}$ detects both of these species equally well, i.e., there is no mass discrimination in the analyzer system. Considering first the resonance at 16.062 eV, as discussed above, we believe that this feature is due to the presence of the ($\Lambda ^2\Sigma^+, v^+ = 17$) 3σ Rydberg state. It is unlikely that such a prominent feature is due to threshold electrons because the magnitude of the coupling of the 3σ Rydberg state to the ionization continuum is expected to be very low.$^{25}$ We, therefore, conclude that this feature is due to the production of threshold F$^-$ ions. Next we consider the structured high-energy tail of the $v^+ = 0$ band in the TPE spectrum. It is likely that this region of the TPE spectrum contains some contributions from both electrons and F$^-$ ions. However, because most of this tail extends well beyond the contour of the $v^+ = 0$ vibrational band (see the top panel in Fig. 1), it is interpreted as being due primarily to the detection of F$^-$ ions.

The detection of F$^-$ ions over such a wide photon energy range can be explained by the fact that the penetrating-field analyzer used in this study$^{17}$ has an acceptance energy window from zero to about 3 meV with a finite high-energy tail extending out to about 20 meV. For illustrative purposes, if the detected F$^-$ ions have kinetic energies up to 3 meV, when this energy range is converted into an excess internal energy associated with the excitation process for the production of F$^-$ ions, this would amount to an energy range above the dissociation limit of from zero to
about 60 meV. Since this photon energy range would cover most of the high-energy tail in the TPE spectrum starting at the prominent resonance structure at 16.062 eV, we conclude that these features in the TPE spectrum are due to threshold to slightly above threshold (0–3 meV) F~ ions.

We further conclude that the rotational structure observed in this tail is due to the 7d Rydberg states discussed above. Why all of the highly structured region between the € = 0 and 1 bands in the PFI-PE spectrum does not appear in the TPE spectrum is explained by the fact that the F~ ions created beyond a photon energy of about 16.122 eV (16.062 ± 0.060) possess kinetic energies in excess of 3 meV, and therefore would not be detected using the penetrating-field analysis method.

Finally, we take the information we have gained in this study to derive a value for the dissociation energy of the HF(X 1Σ+) state. If we assume that the prominent peak at 16.0622(5) eV in the TPE spectrum is an accurate reflection of the threshold energy for the production of F~ + H+ [E(H+ + F~)], we can derive the dissociation energy, D(0)(HF), as follows:

\[ E(H^+ + F^-) = D(0)(HF) + IE(H) - EA(F) \]

where \( E(H^+ + F^-) = 16.0622 \text{ eV} \), \( IE(H) = 109.678.7 \text{ cm}^{-1} \) or 13.598 43 eV \( ^{28} \) is the ionization energy for H, and \( EA(F) (= 3.401 \text{ 190 eV})^{29} \) is the electron affinity for F. This yields a value of \( D(0)(HF) = 5.8650(5) \text{ eV}, \) in excellent agreement with the calculated value \( ^{30} \) of 5.8658(6) eV.

IV. Conclusions

A rotationally-resolved PFI-PE spectrum of HF has been obtained at the chemical dynamics beamline of the advanced light source using the time-of-flight method for threshold electron detection during the dark gap in the synchrotron period. It yielded results that were very similar to a VUV laser based PFI-PE spectrum over the € = 0 and 1 vibrational bands of HF~(X 2Π\(_{3/2, 1/2}\)). More importantly, the PFI-PE spectrum displayed extensive rotationally-resolved structure between the € = 0 and 1 band systems. This is attributed to ion-pair formation via Rydberg states converging on the € = 1 vibrational levels of the spin–orbit split (X 2Π) state of HF~ that are produced during the light-on portion of the synchrotron period. The Rydberg series assigned for the production of this structure are nd-complexes (σ, π and δ) for n = 7–14. The appearance of a signal due to negative ions in the PFI-PE method used here must be kept in mind in future studies. However, it also offers a novel way to perform high-resolution ion-pair formation studies. Similarly, it has been found that TPE studies using the penetrating-field method are also susceptible to ion-pair formation processes, and these must be taken into account in the analysis of TPE spectra, a fact that was already recognized in the analysis of the TPE spectrum of HI. \(^{31}\) This report demonstrates the utility and importance of doing complimentary studies to gain a fuller understanding of photoexcitation and photoionization phenomena in molecules.

Acknowledgements

This work was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Science Division of the U.S. Department of Energy under contract no. W-7405-ENG-82 for the Ames Laboratory and contract no. DE-AC03-76SF00098 for the Lawrence Berkeley Laboratory and in part by the EPSRC. AJY thanks Dr. Helene Lefebvre-Brion for many helpful discussions.

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