

Ion-Pair Formation Observed in a Pulsed-Field Ionization Photoelectron Spectroscopic Study of HF

Andrew J. Yencha¹, M. Cristina A. Lopes², George C. King^{3,*},
Majdi Hochlaf⁴, Yang Song⁵ and Cheuk-Yiu Ng⁵

¹Department of Chemistry, State University of New York at Albany, Albany, NY 12222, USA

²Departamento de Física, ICE, Universidade Federal de Juiz de Fora, Juiz de Fora - MG, CEP 36036-330, Brazil

³Department of Physics and Astronomy, Schuster Laboratory, Manchester University, Manchester M13 9PL, UK

⁴Theoretical Chemistry Group, Université de Marne-la-Vallée, 77454 Champs-sur-Marne, France

⁵Ames Laboratory, USDOE, and Department of Chemistry, Iowa State University, Ames, Iowa 50011, USA

INTRODUCTION

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 HF⁺(X ²Π_{3/2,1/2}, v⁺=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⁺=1 vibrational levels of the HF⁺(X ²Π_{3/2,1/2}) spin-orbit states. Ion-pair formation is observed in this study by the detection of F⁻ ions. On the basis of the present study, an accurate experimental value for the dissociation energy of the ground state of HF has been obtained, D₀(HF) = 5.8650(5) eV.

RESULTS AND DISCUSSION

The full PFI-PE spectrum of HF obtained in this study utilizing the dark gap of the synchrotron period is presented in the top panel of Fig. 1. As can be seen, extensive rotationally-resolved structure is found over the entire energy region. These results are compared with the threshold photoelectron (TPE) spectrum of HF shown in the middle panel of Fig. 1 over the same photon energy range.^{1,2} It shows partially-resolved rotational structure in the v⁺=0 band system of the (X ²Π_{3/2,1/2}) states of HF⁺ that appears to be influenced by a strong resonance at about 16.06 eV, as noted earlier.¹ In the bottom panel of Fig. 1 is presented the F⁻ photoexcitation function from ion-pair formation in HF.³ 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 ¹Σ⁺ ion-pair potential based on *ab initio* calculations.³ The prominent feature at 16.062 eV has been assigned to the HF Rydberg state (A ²Σ⁺, v⁺=17) 3sσ 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 $n \geq 7$.³

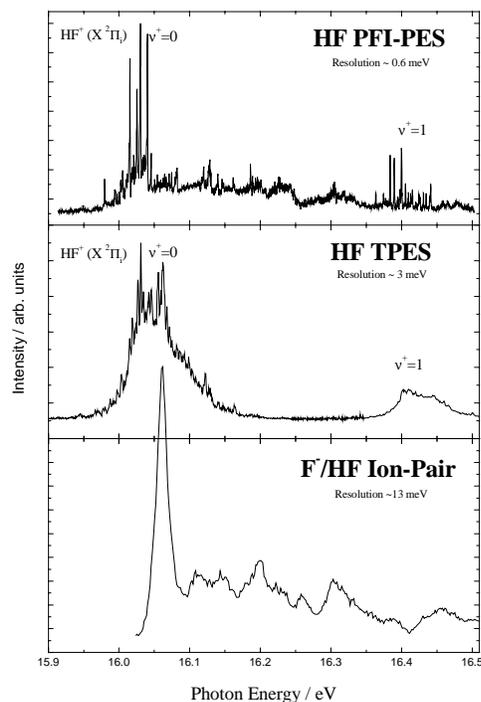


Fig. 1. Comparison of the PFI-PE spectrum of HF (top panel) with the TPE spectrum of HF (middle panel) and the F^- excitation function of HF (bottom panel) over the same photon energy region.

The two dominant series of peak structures at about 16.04 and 16.40 eV in the PFI-PE spectrum (top panel in Fig. 1) are identified with rotational structure of the $v^+=0$ and 1 bands, respectively, of $HF^+(X^2\Pi_{3/1,1/2})$. These peak structures are assigned to resolved rotational lines of the two spin-orbit components F_1 and F_2 based on previously published assignments.^{4,5} The relative intensities of the rotational profiles in these two vibrational bands are essentially identical to those observed in the VUV laser PFI-PE spectrum of Mank et al.⁴ except for small variations due to different resolutions and temperature conditions in the two experiments. Based on our analysis of these systems, we find the $R_1(0)$ 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 et al.⁴

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 (compare the top and bottom panels in Fig. 1). 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 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. The slow moving F^- ions are then swept from the interaction region towards the TOF detection system by the dc pushing potential used in the experimental

procedure. 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. 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).

We now consider 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 study¹ 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 $(A^2\Sigma^+, v^+=17)$ $3s\sigma$ Rydberg state. It is unlikely that such a prominent feature is due to threshold electrons because the magnitude of the coupling of the $3s\sigma$ Rydberg state to the ionization continuum is expected to be very low.³ 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 top panel in Fig. 1), it is interpreted as being due primarily to the detection of F^- ions.

REFERENCES

1. A.J. Yencha, A.J. Cormack, R.J. Donovan, A. Hopkirk and G.C. King, *J. Phys. B*, **32** (1999) 2539.
2. A.J. Cormack, Ph.D. Thesis, Department of Chemistry, The University of Edinburgh, 1998.
3. A.J. Yencha, A. Hopkirk, J.R. Grover, B-M. Cheng, H. Lefebvre-Brion and F. Keller, *J. Chem. Phys.*, **103** (1995) 2882.
4. A. Mank, D. Rodgers and J.W. Hepburn, *Chem. Phys. Lett.*, **219** (1994) 169.
5. K. Wang, V. McKoy, M.-W. Ruf, A.J. Yencha and H. Hotop, *J. Electron Spectrosc. Relat. Phenom.*, **63** (1993) 11.

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Contact person: Andrew J. Yencha, Department of Chemistry, State University of New York at Albany.
Email: AJY26@cnsvox.albany.edu. Telephone: (518) 442-4416.