Dynamics and energetics of photoion-pair formation in HF/DF

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Abstract. Preliminary results of a high resolution coherent vacuum ultraviolet study of photoion-pair formation in HF/DF are reported. These results include threshold ion-pair production (TIPPS) and total photoion-pair yield spectra, which show sharp resonances due to predissociating Rydberg states. Detailed analysis of the spectra provides precise energies for the ion-pair thresholds, and insight into the mechanism for ion-pair formation.

1. Introduction
Photoion-pair formation is common in small molecules where it is possible to dissociate into stable ionic fragments [1], and the mechanism for this process can be either direct or indirect:

\[ AB + h\nu \rightarrow A^+ + B^- \quad \text{(direct)} \]
\[ AB^{**} \rightarrow A^+ + B^- \quad \text{(indirect)} \]

In the indirect mechanism, \( AB^{**} \) is a highly excited Rydberg state, which predissociates into the ion-pair continuum, while in the direct mechanism the continuum is excited. The indirect mechanism typically dominates, as most Franck-Condon accessible excited states have very little ionic character at \( R \approx R_e \). The process of predissociation into ion-pairs is not well understood theoretically, even for simple systems.

By using high resolution single photon excitation from a coherent vacuum ultraviolet light source, the current study reveals detailed information about the dynamics of photoion-pair formation in HF/DF that have previously been unavailable. Further, by combining this high resolution spectroscopy with our recently developed technique of threshold ion-pair production spectroscopy, precise information was obtained on the energetics and dynamics of photoion-pair formation in this prototypical system.

Threshold Ion-Pair Production Spectroscopy (TIPPS) is a high resolution threshold photoionization technique developed in our laboratory [2] which can determine to unprecedented accuracy the energetic thresholds associated with the process: \( AB(\alpha) \rightarrow A^+(\beta^+) + B^-(\beta^-) \), where \( \alpha \) and \( \beta^+, \beta^- \) represent the initial and final quantum states of the system [3]. It involves the excitation of neutral molecules to highly vibrationally excited levels just below the \( A^+(\beta^+) + B^-(\beta^-) \) dissociation threshold. These states behave like the high-\( n \) Rydberg states used for zero kinetic energy photoelectron (ZEKE) or mass analyzed threshold ionization (MATI) spectroscopy [4,5], and can be detected by pulsed field dissociation. Ion-pair dissociation thresholds can be determined to an accuracy better than 0.1 meV by TIPPS, determining the neutral bond dissociation energy \( D_0 \) to similar accuracy [6,7]. Here, the bond energies of HF and DF were determined, as in our previous work on HCl/DCl [8]. Such results allow for the probing of Born-Oppenheimer breakdown effects in these systems [9].
The photoion-pair yield spectra for HF and DF were first measured by Berkowitz et al. [10] and then by Yencha et al. [11]. Both experiments were carried out at significantly lower resolution than this work, and over a broader range of photon energies. These lower resolution studies showed that for both HF and DF, the photoion-pair yield spectra are dominated by a sharp resonance just above the ion-pair threshold, followed by a series of weaker resonances at higher energies. Berkowitz et al. proposed an indirect mechanism, with ion-pairs formed through predissociation of Rydberg states converging to low vibrational levels of the HF$^+\text{X}^2\Pi$ state, a conclusion supported by later work on the autoionizing resonances in the spectra of HF and DF [12]. Yencha et al. proposed a different mechanism based on MQDT calculations, with most important resonances assigned to the Rydberg states with highly vibrationally excited A$^2\Sigma^+$ ion cores [11]. In recent work carried out at CRYRING [13], a high resolution study on resonant ion-pair formation in HF (e$^-+$HF $\rightarrow$ H$^+$+F$^-$) found the same resonance structure as was observed in the earlier photoionization experiments, and so no refinement of the assignments or mechanism was proposed. The present results provide new assignments for the Rydberg states involved in the formation of photoion-pairs, and clarify the mechanism for this process in HF/DF.

2. Experimental

The methods used for recording TIPP spectra and total ion-pair yield spectra have been described in recent papers [2,3,6], so only a brief description is given here. The molecules were excited by a pulsed coherent VUV light source in the photon energy range corresponding to the threshold for forming ion-pairs (15.95 eV to 16.15 eV). The coherent VUV radiation was generated through resonant four-wave mixing $\nu = 2\nu_1 + \nu_2$ in a pulsed supersonic Kr beam [14]. The VUV photon energy resolution was about 0.1 meV, and the photon energy was calibrated to an absolute accuracy of $\pm0.04$ meV.

The VUV light was separated from the fundamental by a one meter focal length normal incidence monochromator, which also focused the VUV into an uncollimated pulsed jet of HF or DF (from a General Valve Series 9 pulsed source) about 5 cm downstream from the nozzle. Both HF (U.H.P. grade, Matheson) and DF (99%, Cambridge Isotope Laboratories, Inc.) gases were used directly without further purification, and the stagnation pressure in the source was about 1 bar.

For the total ion-pair yield spectrum, an extraction field pulse of 35 V/cm was applied to the interaction region 2 $\mu$s after the laser pulse and the positive ions were detected in a time of flight mass spectrometer. For the TIPP spectrum, a discrimination field pulse of a few V/cm and 1 $\mu$s duration was applied 300 ns after the laser to repel any ions formed from above threshold processes. At a delay time of 2 $\mu$s after the laser, an extraction field pulse of larger magnitude was applied to field dissociate long-lived Rydberg-like ion-pair states and extract the resulting H$^+$ or D$^+$ ions into the mass spectrometer.

3. Results and discussion

The total ion-pair yield and TIPP spectra of DF are shown in figure 1. The spectrum covers the excitation range of DF($^1\Sigma, \nu' = 0, J'' \leq 6$) + h$\nu \rightarrow$ D$^+ (^1S_0) + F^- (^1S_0)$. Similar spectra were recorded for HF, but are not shown here (they will be given in a later publication on this work). For both HF and DF, the total yield spectra show very sharp resonances, with the cross section peaked very sharply at the ion-pair threshold. At threshold, the yield of H$^+$/D$^+$ is comparable with that of parent ion HF$^+$/DF$^+$. This contrasts with the normal case, where ion-pair yield is orders of magnitude smaller than the parent ion yield, and is due to the very close ion-pair and molecular ionization threshold energies (for HF, the ion-pair threshold is 16.06 eV [15] and the ionization energy is 16.04 eV [16]).

3.1. Assignment of resonances in the total ion-pair yield spectra

While the overall structure of the present ion-pair yield spectra agrees with previous work, in that the cross section for ion-pair formation peaks sharply at the threshold, there was no indication of anything but a single resonance at threshold in any of the previous work. As a result, all previous analyses were based on a single Rydberg resonance dominating the ion-pair yield spectrum. Since the present results show
many sharp resonances in the threshold region, one can hope to provide a more definitive assignment for the Rydberg states involved in photoion-pair formation through an analysis of the observed rotational structure.

Definitive assignments for $J''$ can be made for any resonances that are observed in the TIPP spectra, based on the fact that the observation of TIPPS signal places the upper resonant state within the field dissociation range just below the ion-pair threshold. Starting from this, combination differences can be used to identify and assign other resonances. Once this is done, excited state energy levels can be assigned core rotation quantum numbers, based on an $^2\Pi$ rotational structure. While this is not an exact model for the rotational structure of the Rydberg states, we can expect it to be approximately true. Preliminary analysis of the spectra found three Rydberg states, and effective rotational constants for these Rydberg states. The assignment of one of these bands is shown in figure 1, and the results of the fit are given in table 1.

Table 1. Assignment of three Rydberg states in HF/DF ion-pair yield spectra. Energies are in cm$^{-1}$.

| molecule | $B'_{\text{eff}}$ | assigned ion core | $B_{\text{eff}}$ | $n^*$ |
|----------|------------------|-------------------|-----------------|------|
| DF       | 6.75             | $X^2\Pi_1/2$, $v^+ = 7$ | 7.07 | 2.91 |
| HF       | 14.67            | $X^2\Pi_1/2$, $v^+ = 3$ | 15.37 | 3.60 |
| HF       | 13.00            | $X^2\Pi_1/2$, $v^+ = 5$ | 13.68 | 2.92 |
As can be seen in figure 1, the assignment of the few resonances in the TIPP spectrum is critical to the credibility of our assignment, and is enough to provide a preliminary value for the effective rotational constant of the Rydberg state $B'_{\text{eff}}$. While our simple model for the rotational structure of the Rydberg resonances makes a detailed interpretation of $B'_{\text{eff}}$ uncertain, one would expect the fitted value to be close to the $B_{\text{eff}}$ of the ion core for the Rydberg state. Thus, in table 1 values for the probable ion core states are also given. For HF$^+$, literature values were used [17], while for DF$^+$, $B_{\text{eff}}$ was calculated from the HF$^+$ values [18].

3.2. Dynamics of ion-pair production

In contrast with all previous work, we have assigned the principal resonances in the HF and DF spectra to low-$n$ Rydberg states with a vibrationally excited HF$^+$/DF$^+$ $X^2\Pi_{1/2}$ core. (Corresponding Rydberg states with an $X^2\Pi_{3/2}$ core are below threshold for producing ion-pairs.) The high resolution HF$^+$ photoion yield spectrum over the same energy range near the ion-pair (and ionization) threshold has many more and different resonances, which correspond to higher-$n$ Rydberg states with low vibrational level ion cores. Thus, low-$n$ Rydberg states with a vibrationally excited HF$^+$/DF$^+$ $X^2\Pi_{1/2}$ core preferentially predissociate into ion-pairs, while the higher-$n$ Rydberg states with low vibrational level cores preferentially autoionize to HF$^+$/DF$^+$. The reason for this is clear if the potential curves shown in figure 2 are examined. A range of possible Rydberg states can be excited in the Franck-Condon region, and the potential for an $n = 3$ state shown could be coupled strongly to the B state, while the equivalent energy low $v$ high-$n$ state will not be strongly coupled, but will couple to the ionization continuum.

3.3. Bond dissociation energies of HF/DF

As shown in figure 1, there are some intense resonance peaks present in the TIPP spectra of both HF and DF. The energetic levels of the resonance states are within tens of wavenumbers to the ion-pair limit but do not give the exact value for the threshold. Although not obvious in figure 1, there is a contribution to the TIPPS signal from direct excitation of the ion-pair quasi-continuum, and the blue edges of TIPPS peaks coming from this direct excitation shift according to expected Stark ionization behavior [21], while the positions of resonance peaks do not shift. By recording TIPPS spectra at several
Table 2. Results from HF/DF TIPP spectra. Energies are in cm$^{-1}$. There are two major uncertainties for the IPD values: ±0.3 cm$^{-1}$ for wavelength calibration and ±0.8 cm$^{-1}$ for extrapolation to zero electric field. $D_0$ is the bond dissociation energy from $v = 0$, and $D_e$ is the classical BDE.

|       | HF          | DF          |
|-------|-------------|-------------|
| IPD   | 129557.1 ± 0.9 | 130135.0 ± 0.9 |
| $D_0$ | 47310.8 ± 0.9  | 47858.8 ± 0.9  |
| $D_e$ | 49361.6 ± 0.9  | 49349.2 ± 0.9  |

different magnitudes of the pulsed field, one can extrapolate the blue edge of the TIPPS peaks to obtain the zero-field dissociation threshold. These results are given in table 2. The HF ion-pair threshold agrees with our previous measurement [15], while the DF value is reported for the first time. Combined with the ionization energy of H(D) [22] and electron affinity of F [23], the bond dissociation energies of HF/DF could be determined.

To provide a more accurate measurement of Born-Oppenheimer breakdown effects, a comparison of HF and DF TIPPS recorded under identical conditions using a mixed beam of HF and DF gave the difference in classical bond dissociation energy of $D_e$(HF)$-D_e$(DF) = 12.4 ± 0.5 cm$^{-1}$, which provides a benchmark for studying these effects in this simple system.

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