COMMUNICATIONS

Determination of bond dissociation energies by threshold ion-pair production spectroscopy: An improved D_0(HCl)

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A recently developed form of threshold ionization spectroscopy has been used to determine the bond energy for HCl to spectroscopic accuracy ($\pm 0.8\,\mathrm{cm}^{-1}$). This method is based on excitation to highly vibrationally excited ion-pair states using single-photon transitions from the ground state of HCl. These metastable Rydberg-like states were selectively detected using electric-field induced dissociation. By systematically varying the electric fields involved, and scanning the exciting photon energy, it was possible to determine the field-free energetic threshold for $H^{35}Cl + h\nu \rightarrow H^+ + {}^{35}Cl^-$. Using this energy, together with the known values of the ionization potential of H and electron affinity of Cl, a new estimate for the dissociation energy of HCl was obtained: $D_0(H^{35}Cl) = 35\,748.2 \pm 0.8\,\mathrm{cm}^{-1}$. © *1998 American Institute of Physics.* [S0021-9606(98)02443-X]

It is sometimes possible to determine the dissociation energies of diatomic molecules to ''spectroscopic'' accuracy ($\pm 1\,\mathrm{cm}^{-1}$). For example, the energy required to split ground state H_2 into two hydrogen atoms $D_0(H_2)$ has been experimentally determined to a precision of better than $0.1\,\mathrm{cm}^{-1}$.[1] The methods available for determining precise values of D_0 are based either on photolysis[2] or inference using bound-state spectroscopic data near the dissociation threshold.[3] However, for some molecules the best D_0 values are derived from thermochemical measurements. An example is HCl, where the oft-quoted value of D_0(HCl) in Huber and Herzberg[4] is based on a thermochemical measurement made by Rossini in 1932.[5]

In a recent paper[6] we suggested a technique for the accurate measurement of D_0 based on determination of the energetic thresholds for photoion-pair formation. This was verified in the case of O_2, since $D_0(O_2)$ is reasonably well known. The present study was undertaken with the goal of measuring a dissociation or bond energy which was less precisely known — D_0(HCl).

Measurement of the energetic threshold for splitting a diatomic molecule into ion-pairs E_{A^+,B^-} (where A and B are atoms of the molecule AB) allows one to determine D_0 if the appropriate electron affinity [$EA(B)$] and ionization potential [$IP(A)$] of the relevant fragments are known:

$$D_0(AB) = E_{A^+,B^-} - IP(A) + EA(B). \tag{1}$$

In the case of HCl, both $IP(H)$ and $EA(Cl)$ are known to better than $1\,\mathrm{cm}^{-1}$, allowing D_0(HCl) to be determined from measurement of E_{H^+,Cl^-}.

There is a specific advantage to the measurement of thresholds for ion-pair formation over neutral photolysis. For photolysis into neutrals, Wigner's threshold laws[7] dictate that the cross-section must be zero at threshold (see, for ex-

ample, Ref. 1). These laws do not necessitate that the cross-section for ion-pair formation be zero at threshold, since the two departing bodies interact with the strong Coulomb force. This situation is analogous to the relationship between photoionization and photodetachment, where photoionization cross-sections can be nonzero at threshold, whereas photodetachment cross-sections must always be zero at threshold.[8]

In 1992, Pratt *et al.*[9] demonstrated that the energetic threshold for ion-pair formation in H_2 could be accurately determined by observing the systematic lowering of the ion-pair threshold induced by application of a dc electric field to the photoexcitation region. In general, when a thermally populated sample is excited and the ion-pair yield is observed as a function of photon energy, several ion-pair thresholds will be observed, corresponding to the different amounts of initial excitation (see, for example, Fig. 6 of Ref. 10). Pratt *et al.*[9] were able to avoid this complication by using a two color multi-photon excitation through an intermediate resonance, which allowed them to ''pick'' their initial energy exclusively. With the goal of generality, a scheme has been developed for discriminating against the detection of the ion-pairs formed above the energetic threshold.[6] This allows the study of thermally populated samples with single-photon excitation, and identification of different ion-pair formation thresholds corresponding to differing amounts of rotational excitation in the sample. We have dubbed this technique: threshold ion-pair production spectroscopy (TIPPS). It relies on the selective detection of excitation into the infinite series of high-v ion-pair states approaching ion-pair asymptotes, and is conceptually analogous to the electric-field ionization of high-n Rydberg states used in both pulsed-field ionization zero-kinetic-energy (PFI-ZEKE) spectroscopy[11] and mass analyzed threshold ionization spectroscopy (MATI)[12] (see the discussion in Ref. 6).

To discriminate against ion-pairs formed above threshold, the molecules are excited with a pulsed light source. Shortly following photoexcitation (300 ns), an electric field is applied to the excitation volume which removes free ion-pairs from the region if they have been formed. This takes a certain amount of time, after which a larger electric field of opposite polarity to the first is applied. This field dissociates a range of high-v ion-pair states, and draws the resulting fragments into a time-of-flight spectrometer, where they are detected (see Fig. 1 in Ref. 6). This signal is recorded as a function of excitation energy to produce TIPPS spectra. The discrimination field also depletes a range of high-v states below threshold. Later, it will be shown how this may be exploited to determine the field-free ion-pair dissociation threshold of HCl.

The first observation of photoion-pair formation in HCl was made by Yencha et al.[13] using synchrotron radiation. They characterized this process by collecting total Cl$^-$ ions as a function of photon energy, from the energetic threshold at 14.4 eV to 16.3 eV. The structure in this spectrum was then modeled theoretically as an indirect process: Rydberg states are excited, which then predissociate into ion-pairs.

In the present work, the approximately 14.4 eV photons used to study the threshold region were generated by four-wave sum-frequency mixing in xenon,[14,15] in a modified version of an apparatus described previously.[16] Frequency doubled light from one dye laser (ν_1) was tuned to approximately match a two-photon resonance in Xe [$2\nu_1 = 80\,119.5\,\text{cm}^{-1}$[17]]. Frequency doubled light from a second dye laser (ν_2) was overlapped with the ν_1 beam, and focused into a free jet of Xe. The desired harmonic: $2\nu_1 + \nu_2$, was separated from the fundamentals and unwanted harmonics using a monochromator, then refocused into the main experimental chamber. The final photon energy was varied by scanning ν_2. The VUV beam crossed a pure HCl beam at right angles. The HCl beam was expanded from a 1 mm diameter pulsed valve, with a backing pressure of 20 psi, and travelled 5.2 cm before intersection with the VUV beam.

The VUV energy was calibrated using the relationship $\nu_{\text{VUV}} = 2\nu_1 + \nu_2$. The values of ν_1 and ν_2 were determined by calibrating the fundamentals of the two dye lasers using known optogalvanic transitions in uranium, observed using the optogalvanic effect in a hollow cathode discharge lamp.[18] The grating drive mechanism in the dye lasers exhibited a small periodic nonlinearity which was corrected for by collecting etalon fringes together with the optogalvanic spectra. The estimated accuracy of the calibration of the final VUV energy is $0.2\,\text{cm}^{-1}$. To check the VUV energy calibration, the position of an autoionizing resonance in Kr was measured near the HCl ion-pair formation threshold. The observed energy location agreed with the literature value ($116\,528.8 \pm 0.2\,\text{cm}^{-1}$)[19] to within the combined uncertainties of the determination ($0.2\,\text{cm}^{-1}$) and tabulated value.

Figure 1 shows a TIPPS spectrum covering the energetic thresholds for $\text{HCl}(X\,^1\Sigma, v = 0, J) + h\nu \rightarrow \text{H}^+ + \text{Cl}^-(^1S)$. Each peak corresponds to the signal due to the electric field induced dissociation of a range of unresolved highly vibrationally excited ion-pair states excited from a unique initial J level of HCl. Since the energetic ion-pair threshold is inde-
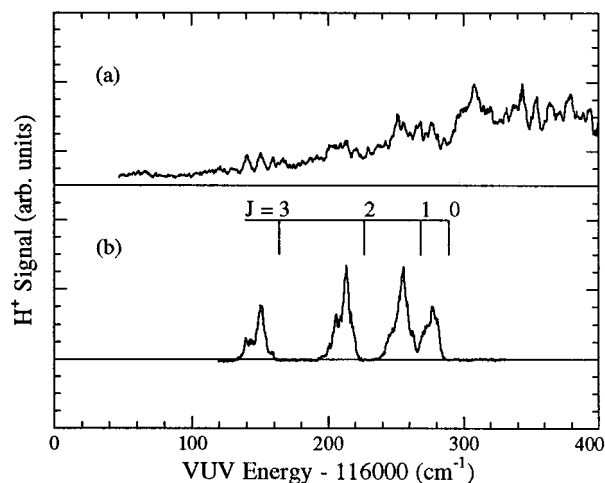

FIG. 1. (a) Prompt ion-pair yield from HCl. An extraction field of 60 V/cm was pulsed on 0.2 μs following photoexcitation. No discrimination field was used. No attempt was made to ensure 100% collection efficiency for fast H$^+$. (b) TIPPS spectrum of HCl. The discrimination field was 2 V/cm, pulsed on 0.3 μs following photoexcitation. The extraction field was 60 V/cm, pulsed on 4.1 μs after the discrimination field. The field-free ion-pair formation thresholds for each initial J level have been superimposed (see Fig. 3 and text).

pendent of J, the relative spacing of these peaks is given by the well known rotational constants of ground state HCl. This spacing has been superimposed on the figure. Also shown over the same energy range is the prompt H$^+$ ion yield recorded by pulsing on an extraction field 0.2 μs following photoexcitation and not using a discrimination field. This spectrum illustrates the difficulty in identifying the thresholds for photoion-pair formation unless some form of discrimination is used.

The spectrum in Fig. 1 corresponds to one scan with a fixed discrimination field of 2 V/cm. Figure 2 illustrates the effect of varying this field from 10.2 V/cm to 25 V/cm. As expected, increasing the discrimination field pushes the blue edge down in energy, since larger discrimination fields deplete more of the high-v ion-pair states. In analogy with the behavior observed with Rydberg states in ZEKE/MATI
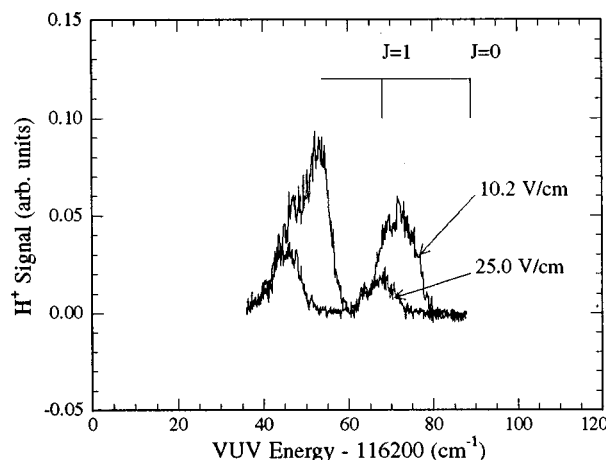

FIG. 2. TIPPS Spectra of HCl for two different discrimination fields. Conditions are identical to Fig. 1, except for the magnitude of the discrimination field.
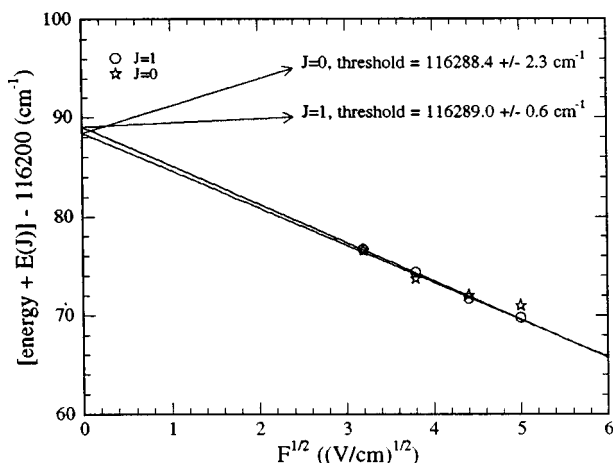
FIG. 3. Extrapolation to determine the field-free ion-pair formation threshold. The positions of the blue edges of a series of spectra taken at different discrimination fields are plotted as a function of the square root of the discrimination field. The $J=1$ data has been shifted up in energy by the $J=0$, $J=1$ energy level difference in the HCl ground vibronic state. The extrapolated zero-field thresholds for the two J levels are labeled.

spectroscopy,[20] one would expect the leading blue edge of the peaks in the TIPPS spectrum to be shifted down from the field-free dissociation threshold in proportion to the square root of the discrimination field. In Fig. 3, the position of the blue edge of several TIPPS spectra have been plotted as a function of the square root of the discrimination field F. The data from the $J=1$ line have been shifted up in energy by the $J=0$, $J=1$ splitting using the previously known spectroscopic constants.[4] The data points fit reasonably well to a straight line, allowing extrapolation to zero-field strength.

This procedure for extrapolation has been tested by collecting MATI spectra of Argon at the $^2P_{1/2}$ ionization threshold with different discrimination fields using the same spectrometer.[21] The extrapolated field-free ionization threshold agrees with the literature value to within the combined uncertainties.

To improve the precision of the extrapolation it would be desirable to extend the points in Fig. 3 to lower discrimination fields. Unfortunately it was found that the lower discrimination field TIPPS spectra had blue edges which were shifted by ion-density (due to $HCl + h\nu \rightarrow HCl^+ + e^-$). This could be eliminated by lowering the VUV power (going to lower ion-densities) at the expense of worsened signal to noise. Given the practical constraints of time, $F = 10.2$ V/cm was the lowest discrimination field possible for extrapolation. The points in Fig. 3 were tested to make sure they did not shift as ion-density was reduced.

HCl has two abundant natural isotopomers: $H^{35}Cl$ (75%) and $H^{37}Cl$ (25%). Since H^+ was collected instead of Cl^- it was not possible to distinguish the TIPPS spectra originating from the two isotopomers. Assuming the simple harmonic oscillator model for the ground state potential, the zero point vibrational energy of $H^{37}Cl$ is 1.1 cm^{-1} less than that of $H^{35}Cl$. Thus it is expected that the TIPPS spectra for $H^{37}Cl$ will be shifted 1.1 cm^{-1} to higher energy with respect to $H^{35}Cl$. A simple model for the blue edge line shapes predicts that the field-free threshold obtained using the composite spectra ($H^{35}Cl$ and $H^{37}Cl$) is shifted 0.28 cm^{-1} higher in

energy than that for pure $H^{35}Cl$.[21] Thus, the extrapolated threshold is corrected by this amount, to give an isotopomer specific threshold. The error in this correction is unlikely to be greater than 0.1 cm^{-1}. Combining the uncertainties in the extrapolation, photon energy calibration and isotopomer correction, the uncertainty in the field-free ion-pair formation threshold is estimated to be 0.6 cm^{-1}. Thus we have determined the minimum energy required to split $H^{35}Cl$ from its ground electronic state, $J=0$, $v=0$ into the ion-pairs H^+ and $^{35}Cl^-$ to be $116\,288.7 \pm 0.6$ cm^{-1}.

The ionization potential of H is accurately known,[22] and the electron affinity of Cl has been measured by Trainham et al.[23] to be $29\,138.3 \pm 0.5$ cm^{-1}. When $IP(H) = 109\,678.8$ cm^{-1}, $EA(Cl) = 29\,138.3 \pm 0.5$ cm^{-1}, and $E_{H^+,^{35}Cl^-} = 116\,288.7 \pm 0.6$ cm^{-1} are substituted into Eq. (1), $D_0(H^{35}Cl) = 35\,748.2 \pm 0.8$ cm^{-1} is obtained.

As mentioned, previous estimates of $D_0(HCl)$ are thermochemical in origin. Knowledge of the heat of formation of HCl from H_2 and Cl_2 together with $D_0(H_2)$ and $D_0(Cl_2)$ allows the determination of $D_0(HCl)$. Rossini[5] measured the heat of formation of HCl at room temperature using flame calorimetry. This can be corrected to give the hypothetical heat of formation at 0 K (from the elements in their standard states). The JANAF tables[24] quote $\Delta H_{f0}^{\ominus}(HCl) = -92.128 \pm 0.21$ kJ mol^{-1} $(-7701 \pm 18$ cm$^{-1})$. Substituting the JANAF[24] recommended values: $D_0(H_2) = 36\,118.3$ cm^{-1} and $D_0(Cl_2) = 19\,999.1$ cm^{-1} into:

$$D_0(HCl) = \tfrac{1}{2}D_0(H_2) + \tfrac{1}{2}D_0(Cl_2) - \Delta H_{f0}^{\ominus}(HCl) \qquad (2)$$

gives $D_0(HCl) = 35\,760 \pm 18$ cm^{-1}. The value of $D_0(HCl)$ in Huber and Herzberg is $35\,759$ cm^{-1} and said to be derived "from $D_0(H_2)$, $D_0(Cl_2)$, and $\Delta H_{f0}^{\ominus}(HCl)$." Therefore it is most likely that this is based on Rossini's heat of formation and thus has a comparable error (± 18 cm^{-1}). The present determination of $D_0(H^{35}Cl) = 35\,748.2 \pm 0.8$ cm^{-1} is within these error bars.

We have also applied this technique to the measurement of $D_0(HF)$,[21,25] and hope to investigate bond energies of polyatomics in the future.

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