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LETTERS

A Determination of the Bond Dissociation Energy (D_0(H−SH)): Threshold Ion-Pair Production Spectroscopy (TIPPS) of a Triatomic Molecule

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We present the first threshold ion-pair production spectrum of a triatomic molecule. We have recorded the ion-pair yield spectrum and TIPP spectrum for the $H_2S \rightarrow H^+ + SH^-$ ion-pair channel using single-photon excitation. From the TIPP spectrum, we have determined the H−SH bond energy (31451 ± 4 cm^{-1}) to unprecedented accuracy and demonstrated the formation of weakly bound H^+-SH^- (J') ion-pair states, with rotational excitation of the SH^- anion up to $J' = 4$. The bound nature of these states, and the assigned spectrum that results from their field dissociation suggests that this technique can be applied to many other triatomic and larger polyatomic molecules in the future, leading to energetic, spectroscopic, and dynamical information about these species.

Obtaining the bond energies of polyatomic molecules to a high degree of accuracy (to within a few wavenumbers) is of importance to both fundamental and applied areas of physical chemistry. A comparison of the experimentally determined bond energies of a species with those that are theoretically predicted provides a stringent test of the various models that are used to describe the molecular bonding, in particular the less well characterized near-dissociation region of the potential energy surface. Further, a knowledge of these bond energies to high precision can provide accurate information for modeling calculations which depend strongly upon the energetics of reactant and product channels. In contrast to diatomic molecules, where it is often possible to obtain the bond energy by extrapolation of bound-state spectroscopic data when the form of the long-range potential is known,[1] all electronic states of polyatomic molecules present a considerably more complicated potential energy surface and only a direct measurement of the bond dissociation energy will provide a reliable value.

Such direct measurements of a bond energy to wavenumber accuracy have in the past been possible for only a limited number of polyatomic molecules. In the case of NO_2, for example, the laser-induced fluorescence from the $^2B_2$ state (which is strongly coupled to the $^2A_1$ ground state) abruptly ceases when the incident photon energy corresponds to that of the bond energy, resulting in an accurately obtained D_0(O−NO) of 25128.5 ± 0.2 cm^{-1}.[2] For those molecules which dissociate into a hydrogen fragment, Doppler and time-of-flight photofragment techniques are particularly suited, although they result in an H−X bond-energy to an accuracy of typically ±20 cm^{-1}.[3]

A method has recently been developed in our laboratory to determine to unprecedented accuracy the thresholds associated with photoion-pair formation:[4] $AB(q) \rightarrow A^+(q') + B^-(q'')$, where q and q′, q″ represent the initial and final quantum states of the system. These thresholds are related by a simple energy cycle to the A−B bond energies from each quantum state q,

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the ionization potential of $A^+(q')$ and the electron affinity of $B^-(q'')$. This form of spectroscopy (dubbed threshold ion-pair production spectroscopy[4] (TIPPS)) is conceptually analogous to mass-analyzed threshold ionization[5] (MATI), and using this technique the (many) energetic thresholds corresponding to the formation of all allowed quantum states of the ion pairs from an ensemble of molecules can be determined.

In a TIPPS experiment incident, pulsed, tunable light excites the molecule, followed by the application of two sequential pulsed electric fields. If the photon energy is just below the threshold energy for a particular $AB(q) \rightarrow A^+(q') + B^-(q'')$ dissociation channel, it is possible to excite long-lived Rydberg-like vibrational levels of the A^+-B^- ion-pair state. These weakly bound "heavy Rydberg states" can be detected by field dissociation using pulsed electric fields, in the same way that weakly bound hydrogenic Rydberg states are detected in MATI spectroscopy. As in MATI, the first pulse is applied to discriminate against any nascent ions formed from above-threshold processes and the second pulse produces a peak in the spectrum exclusively from field-dissociated weakly bound ion-pair states. The spectral width of each transition from a particular ro-vibrational state is generally determined by the laser bandwidth and the magnitude of the various voltages that are applied. Typically, the high energy edge of this peak is determined by the dissociation due to the first field and any loss due to collisions of the large ($r > 2\ \mu$m) weakly bound states. Similarly, the low energy side is determined by dissociation due to the second field and any decay of the states formed in this region of the spectrum, expected to be due to lack of stabilization[6] (resulting in predissociation or autoionization) of these states.

By observing the changes in each spectrum as the magnitude of the first pulsed electric field is changed, the field-free thresholds for the ion-pair process can be determined, which can provide complete energetic information about both the initial molecule and the observed ion-pair channels. This technique has been applied to O_2,[4] HCl,[7] HF,[8] H_2, and D_2[9] to yield either bond energies or partial assignments of molecular transitions to high-lying states which couple to an ion-pair state.

The extension of the TIPPS technique from diatomics to larger molecules is of considerable interest for several reasons. As discussed above, bond energies for polyatomic molecules are generally not known to wavenumber accuracy, and the success of this experiment will motivate further studies on other polyatomics. Second, the weakly bound (and long-lived) system formed in this experiment corresponds to a proton orbiting an SH^- anion in a particular ro-vibrational state. Both the long-lived nature and field-dissociation behavior of these unusual species (that have not been previously observed) provides some additional insight into intramolecular dynamics at high internal energies. Also, since TIPPS is a spectroscopic technique, for the common cases where the ion-pair produced by pulsed field dissociation is an atomic ion plus a molecular ion, the TIPP spectrum provides detailed information about the ro-vibrational energy levels of the molecular ion.

The experimental technique was introduced in refs 4, 7, and 8 and is broadly similar to that of a MATI experiment, described in detail in refs 8−10. The tunable XUV pulsed radiation was produced through resonant four wave mixing of dye laser radiation (Lambda-Physik FL 3002 pumped by a Spectra-Physics GCR4 YAG laser) in a pulsed supersonic Kr beam, with one of the input wavelengths fixed at the 212.55 nm two-photon resonance of Kr ($4p^55p$ [1/2,0] at 94093.662 cm^{-1}).[11] The second wavelength was scanned, resulting in tunable XUV light ≈15.2 eV, with line width of ≈1 cm^{-1}. The fixed wavelength was calibrated using the two-photon Kr resonance[11] and the scanned wavelength calibrated using the known lines of a Ne:Fe hollow cathode lamp.[12] A multiphoton absorption of atomic krypton at 103314.284 cm^{-1} [11] provided added verification of the calibration. The XUV light orthogonally crossed the unskimmed, supersonic free jet of H_2S at a distance 3.5 cm downstream from the nozzle in the center of two parallel plates separated by 10 mm. H_2S of CP grade (supplied by Matheson) at a backing pressure of 2 bar was used for the expansion through the nozzle of 0.8 mm diameter. The relative populations of different $J''_{Ka,Kc}$ levels of H_2S molecules in this free jet expansion is expected to be given by that of a sample of H_2S at thermal equilibrium with rotational temperature between 100 and 200 K.

Both SH^- and H^+ ions can be formed from collisions between ions, electrons, and neutral molecules. The signal from the SH^- ions formed through such processes was observed to be considerably larger than the signal from H^+ ions, and therefore all spectra reported in this letter correspond to observing the H^+ cation. Care was taken to ensure that no contribution to the spectrum was due to the effects of collisions, which necessitated using a low density of molecules in the gas jet. During the experiments the pressure in the interaction chamber (which had a base pressure of 5×10^{-7} Torr and was pumped by a 1000 L/s Seiko Seiki turbomolecular pump) was kept relatively low, at approximately 1×10^{-6} Torr for the ion-pair yield spectra and $(2-3) \times 10^{-6}$ Torr for the TIPPS spectra. Because the cross section for the production of ion pairs from H_2S is small (with the maximum of the total ion-pair yield estimated from the experiment to be only ≈0.1% of the parent ionization signal), the average number of ion pairs produced per laser shot at the most intense TIPPS peak was ∼0.2.

For the ion-pair yield spectrum, an electric field extraction pulse of 30 V/cm was applied to the interaction region 200 ns after the light pulse and the H^+ ions recorded using boxcar detection in ion-counting mode (described in detail in ref 9). To obtain a high-resolution TIPP spectrum over the same range, the excitation took place under an ambient stray (≈0.1 V/cm) electric field, and 200 ns after the light pulse an electric field discrimination pulse of duration 1 μs and magnitude 4 V/cm was applied. This forced the H^+ ions formed from above threshold processes and those (if any) formed from field dissociation toward the detector to arrive at a particular time. At a time of 1.5 μs after the application of this pulse, an electric field pulse of greater magnitude (7 V/cm) was applied to the interaction region. At those photon energies just below each field-free ion-pair threshold, where long-lived weakly bound ion-pair states were created, this second pulse then field-dissociated these species, and the nascent cations were accelerated along the time-of-flight tube, and onto the front surface of an MCP detector, to arrive at a time ≈1 μs after the "prompt" ions.

The H^+ yield spectrum recorded over the range from 122100 to 122650 cm^{-1}, which to our knowledge has not been observed before, is shown in Figure 1a. Within this energy range are the thresholds corresponding to excitation to the (several) ion-pair limits ($H^+ + SH^-(X^1\Sigma^+, v' = 0, J')$) from the (many) initially populated rotational levels of H_2S (($\tilde{X}^1A_1, J''_{Ka,Kc}$). It is not clear from the spectrum where these thresholds lie, although the spectrum appears reasonably free from sharp resonant enhancement, implying that the cross section at threshold for each transition is not strongly dependent upon the particular quantum states of either the H_2S molecule or the SH^- ion produced.[9]

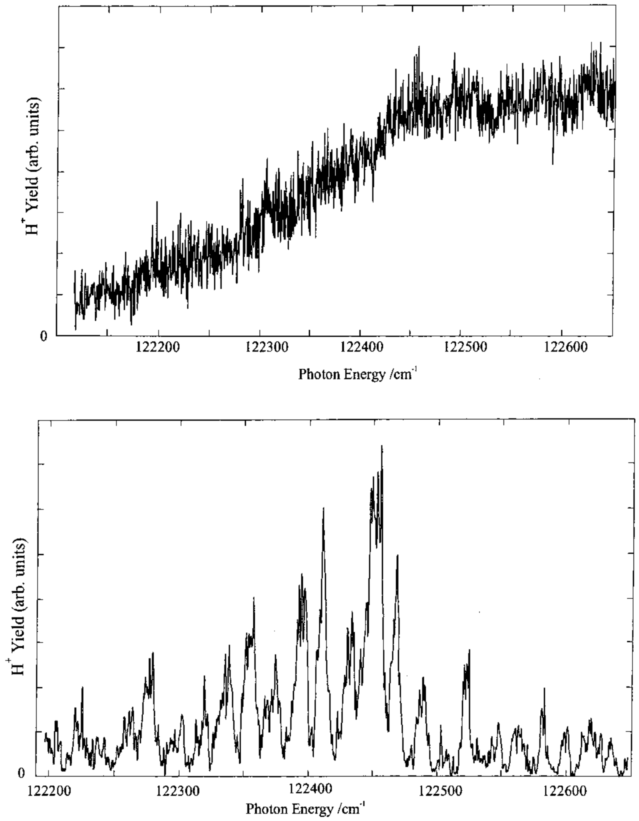

Figure 1. (a) The H$^+$ ion-pair yield spectrum from H_2S recorded with single-photon excitation from 122100 to 122650 cm^{-1}, employing an extraction field of 30 V/cm at a time 200 ns after the light pulse. (b) The TIPP spectrum for H_2S taken with a discrimination field of 4 V/cm and extraction field of 7 V/cm over a similar energy region. The highly structured spectrum reflects the formation and field-dissociation of weakly bound ion-pair states just below each field-free threshold.

The TIPP spectrum (normalized by light flux) is shown in Figure 1b and takes the form that is expected, with peaks increasing in intensity as the photon energy is increased toward ≈122400 cm^{-1} and more peaks with steadily decreasing intensity toward higher energy. As this spectrum is the summation of data collected over several days the relative intensities of individual peaks are probably reproducible to within a factor of 2. Each peak (which may be composed of several unresolved peaks) results from field dissociation of weakly bound H$^+$–SH$^-$ ($v' = 0$, J') ion-pair states formed through photon absorption by a particular $J''_{Ka,Kc}$ level of H_2S. The high-energy edge of each peak should be increasingly eroded away as the magnitude of the discrimination field is increased, due to the field dissociation of increasingly more strongly bound ion-pair states. Indeed, spectra of isolated peaks taken at different values of discrimination field, which display differences only at their high energy edges, are evidence of the observation of these weakly bound states. A detailed study of the field dissociation behavior is quite complex, but the ion-pair threshold in a field is, by analogy with field ionization behavior, predicted to be reduced by a value proportional to the square root of applied field,[13] and this has been observed previously for thresholds that are known to be well-separated.[7,9]

The results of varying the magnitude of the first pulse for the (most intense) sharp peak at 122411 cm^{-1} is shown in Figure 2. For purely practical reasons the polarity of the pulses for these spectra were arranged so that the first pulse forced H$^+$ ions away from the detector and the second pulse accelerated any H$^+$ ions formed due to field dissociation toward the detector. The three (unscaled) spectra were taken with the first pulse at 3, 5, and 7 V/cm and the second pulse set for all spectra to 10 V/cm. In all cases the low energy side of the peak does not change appreciably, providing conclusive evidence that the signals originate from field-dissociated ion-pair states. The high-energy side of the peak is eroded away, as expected from the paragraph above. The change in intensity in the middle of the peak implies that this peak is composed of several unresolved peaks corresponding to several thresholds, each of which have their high energy edges modified by the change in F1. This is confirmed by the assignment presented below.

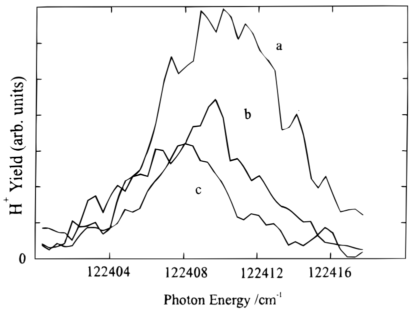

Figure 2. The TIPP spectrum of H_2S in the region of the peak at 122411 cm^{-1}, taken with applied discrimination fields of (a) 3.0, (b) 5.0, and (c) 7.0 V/cm. The high-energy side of all (unresolved) transitions within this peak are gradually eroded away with increasing discrimination field.

Since the rotational constants of the ground vibronic states of both H_2S ($\tilde{X}^1A_1$) and SH$^-$($X^1\Sigma^+$) are known, it is possible to fit this spectrum by assuming a line shape function at each energetic threshold, including the effects of rotational degeneracy and nuclear statistics and weighting for each J' channel. Such a fit should determine to high accuracy the field-free thermodynamic ion-pair production threshold (the minimum energy required to excite H_2S from the ground state ($\tilde{X}^1A_1$, $J''_{Ka,Kc} = 0_{00}$) to a separated proton and SH$^-$ anion in its ground state ($X^1\Sigma^+$, $J' = 0$)), and also provide qualitative insight into the possibilities of forming various rotationally excited states of the SH$^-$(J') anion within the weakly bound molecule.

In its ground vibronic state, H_2S has a H–S bond length of 1.34 Å, and H–S–H angle of 92° and rotational constants of $A = 10.359$ cm^{-1}, $B = 9.015$ cm^{-1}, and $C = 4.731$ cm^{-1}.[14] The lower levels of all transitions therefore have energies determined by those of an asymmetric rotor, and are labeled $J_{Ka,Kc}$, where J is the total angular momentum and Ka and Kc are the projection of J on the a and c axes, respectively. The B constant of the SH$^-$ anion is known from velocity modulation spectroscopy[15] to be 9.5627 cm^{-1} and for our simulation the SH$^-$ rotational energies are given by the usual $BJ'(J'+1)$ formula.

Using an initial value of the field free ion-pair production threshold v_{IPP}, a simulation spectrum was synthesized containing peaks at each calculated transition energy with line shapes corresponding to those expected[9] for 4 and 7 V/cm for the two pulses. The intensities of all transitions to a particular SH$^-$ J' level were assumed to be determined solely by the initial rotational population of each $J''_{Ka,Kc}$ level. The temperature, v_{IPP}, and the relative strengths of the transitions to different J' levels were fit to the experimental spectrum. The first value was determined predominately by the low energy edge of the spectrum, the second by the position of all peaks in the spectrum, and the last value by the high-energy tail of the spectrum.

The simulation, together with combs displaying each family of peaks with common J' rotational quantum number of the SH$^-$ ion that is produced, can be seen in Figure 3. The rotational

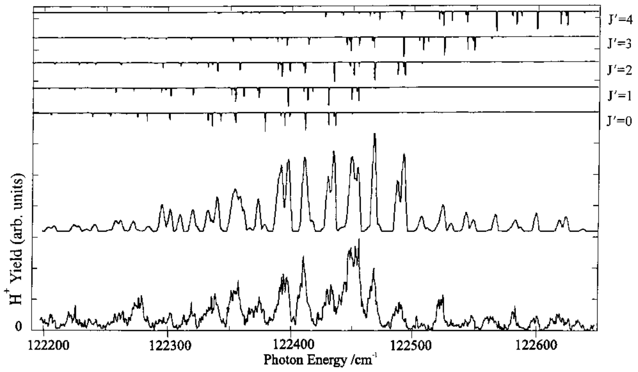

Figure 3. The simulation (above) composed of peaks near each threshold with line shapes and intensity as described in the text. The experimental TIPP spectrum is shown below.

temperature obtained was 105 K, which is a reasonable value for the beam conditions used. The value obtained for υ_{IPP} was 122458 ± 3 cm^{-1} and the ratio of the peak heights of the transitions from a particular $J''_{Ka,Kc}$ to each $M_{J'}$ sublevel of $J' = 0, 1, 2, 3, 4, 5$ was 1:2.5:2.5:0.3:0.3:0.0. The error quoted for υ_{IPP} is largely due to fitting the simulated spectrum to an experimental one composed of many blended lines. The assumptions which were used will be discussed in more detail below but within the errors of the experiment, the simulation is an excellent fit and it is highly unlikely that the results would be appreciably changed should a more complicated model be assumed.

The bond dissociation energy (D_0(H−SH)) can be deduced from this value for υ_{IPP} by subtracting the ionization potential[16] for the hydrogen atom (109678.772 cm^{-1}) and adding the electron affinity of the SH radical. This latter value can be accurately determined from photodetachment spectroscopy, and a spectrum from such an experiment has been published.[17] Although no numerical value from the data was given in this paper, the value 18672 ± 2 cm^{-1} can be read from the spectrum. We have deduced the value for the bond energy to be 31451 ± 4 cm^{-1}, which can be compared with that obtained from photofragment measurements[18] (31440 ± 20 cm^{-1}). Our result is in agreement with previous measurements, but has a precision which is greater by a factor of 5.

The ratio of peak heights corresponding to the formation of SH^- in different rotational levels provides some information about the coupling from H_2S ($\tilde{X}^1A_1$, $J''_{Ka,Kc}$) to each $H^+ + SH^-(J')$ ion-pair curve. The distribution is seen to be peaked at $J' \sim 1-2$, and falls off with increasing J' above this. A similar degree of rotational excitation is observed in the ultraviolet fragmentation channel into the neutral products (H + SH)[18] and reflects a direct dissociation from a bent parent molecule. Indeed, a simple, classical calculation of the angular momentum imparted to the SH^- anion by releasing a kinetic energy corresponding to the bond energy results in the SH^- anion being produced in J' between 1 and 2.

As stated above, there are some assumptions within the model that are only approximate, and should this model be compared with the spectrum in a more quantitative manner, a breakdown of these assumptions might be observed. One of the more interesting assumptions is that which supposes all transitions from $J''_{Ka,Kc}$ to a particular J' level are independent of $J''_{Ka,Kc}$, and the degree to which this is true and the propensity for forming ion-pair states with $J' > 2$ are of considerable interest. We hope to pursue such studies soon.

In conclusion, we present the first threshold ion-pair production spectrum of a triatomic molecule. We have investigated the $H_2S \rightarrow H^+ + SH^-$ ion pair channel using single photon excitation by recording both the ion-pair yield spectrum and TIPPS spectrum and subsequently D_0(H−SH) to unprecedented accuracy. The TIPP spectrum demonstrates the formation of weakly bound H^+-SH^- ion-pair states, some of which contain a rotationally excited SH^- anion. This form of spectroscopy has considerable potential to obtain energetic, structural and dynamical information about both neutral and ionic polyatomic molecules which are of fundamental importance to chemistry.

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