

Electron photodetachment from HS⁻. The electron affinity of HS

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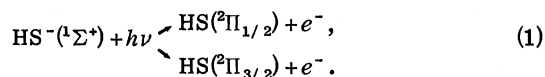
(Received 26 July 1979)

The cross section for electron photodetachment from HS⁻ has been measured using an ion cyclotron resonance (ICR) spectrometer with a tunable dye laser. A cubic spline routine is employed to remove random noise from the spectrum and allows the observation of rotational effects. The structure in the spectrum is explained in terms of a model which includes the interaction of the spin, orbital, and rotational angular momenta in HS. Comparison of the theoretically constructed photodetachment cross section predicted by this model with the experimental spectrum leads to an electron affinity for HS of 2.314 ± 0.003 eV and an estimate of the rotational temperature of the HS⁻ ions in the ICR cell.

I. INTRODUCTION

The use of a tunable dye laser as the light source in electron photodetachment spectroscopy provides a means of obtaining detailed spectroscopic information on highly reactive neutrals. Experiments of this type measure the wavelength dependence of the anion → neutral photodetachment process and can, in principle, distinguish channel openings to states in the neutral product. Recently, this technique has led^{1,2} to vibrational frequencies in CH₃S, CD₃S, and C₂H₅S in addition to the measurement of the spin-orbit splitting in CH₃S.

A previous tunable laser photodetachment experiment³ on the hydrosulfide anion (HS⁻) has produced results inconsistent with the known energy levels of the HS radical.⁴ To a first approximation, one would expect to observe two channel openings in the photodetachment spectrum corresponding to the transitions



The lowest-energy transition (to the ²Π_{3/2} state), which, by definition, is the electron affinity^{2,5} of HS, should occur at 2.31–2.32 eV. The transition to the ²Π_{1/2} state should become accessible at an energy 379.6 cm⁻¹ greater than the first transition⁴; this energy represents the spin-orbit splitting in HS. Furthermore, the spectrum should not be complicated by off-diagonal Franck-Condon transitions⁶ since R_e(HS⁻) ≈ R_e(HS). Therefore, the photodetachment spectrum might be expected to show two abrupt rises⁷ of equal intensity separated by the spin-orbit splitting as was observed for the analogous case of HSe⁻ photodetachment.⁸ The fact that this was not observed in the initial experiments on HS⁻ indicates the need for further experimental work and a more complete theoretical description of the HS⁻(¹Σ⁺) → HS(²Π_i) + e⁻ photodetachment process.

In this work we report new HS⁻ photodetachment data which, when treated with a cubic spline routine, removes random noise from the data and makes channel openings easier to observe. The experimental results can be explained by a two-step photodetachment model which includes the coupling of spin, orbital, and rotational angular momenta. This model not only correctly accounts for the experimental results but also leads to a highly accurate electron affinity (±0.003 eV) for HS and an estimate of the rotational temperature of the HS⁻ ions.

II. EXPERIMENTAL PROCEDURE

A. Instrumental

The photodetachment experiments were performed with a Varian V-5900 ion cyclotron resonance (ICR) spectrometer with a modified square-cell design.^{9,10} Satisfactory photodetachment data were obtained with the following cell conditions: Trapping potential 2.0 eV, analyzer potentials 0.0 eV, and source potentials 0.20 eV. Experiments were carried out at 4 × 10⁻⁷ torr where the trapping time was approximately 0.5 sec.

The light source employed consisted of a Coherent Radiation model 590 dye laser pumped with a Coherent Radiation model CR-12 argon ion laser. The threshold region for HS⁻ photodetachment was covered by the output of the dye coumarin 7 (Exciton). This dye lases in the region 500–560 nm with an output power of 50–100 mW when pumped with 2 W of the 476.5-nm line from the argon-ion laser. Several ml of cyclo-octatetraene were added to the dye solution to act as a triplet quencher and increase the dye laser output power. At these pump powers the dye lifetime was 3–4 hours. In order to prevent the spatial inhomogeneity of ions in the cell from producing spurious results, the laser beam was expanded to the diameter of the ICR cell (~2 cm). Approximately 4% of the beam was split into an Eppley thermopile, from which the relative

output power was recorded. After each run, the wavelength of the dye laser output was calibrated to ± 0.3 nm against a Beck wavelength reversion spectrocope.

B. Anion generation

A clean, direct source of hydrosulfide anions in the gas phase is low-energy dissociative electron attachment to H_2S . The lowest resonance capture maximum for this process is at¹¹ 2.2 eV and electron energies of 2.2–2.9 eV produced strong HS^- signals.

C. Data analysis

Techniques for data acquisition and analysis have been previously described.¹ To keep any long-term changes in the ion trapping conditions from changing the ion-photon overlap and producing artifacts, small sections (six points) of the photodetachment cross section were measured and then pieced together by overlapping points to produce the complete spectrum.

III. RESULTS

The relative photodetachment cross section for HS^- is shown in Fig. 1. These data represent the average of three runs; the size of the data points reflects the uncertainty in the cross section. Any abrupt changes in slope in Fig. 1 can be associated with channel openings to excited states of HS . To make any changes in slope more obvious, the cross section was fit to a cubic spline which was chosen such that random noise was eliminated from the data¹²; the spline was then differentiated with the result shown in Fig. 2. This experimental curve is the result of fitting a cubic spline function to the photodetachment data at wavelengths shorter than 535 nm and a second spline to the data at

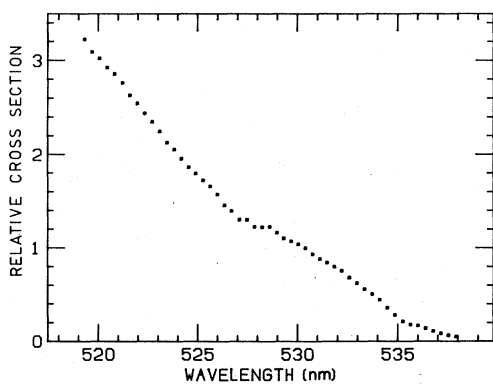


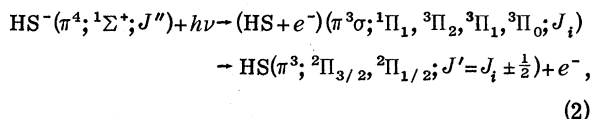
FIG. 1. Relative photodetachment cross section of HS^- .

wavelengths greater than 535 nm. The derivative of these two splines is then normalized at 535 nm. The wavelengths at which the experimental maxima in Fig. 2 appear are 522.8 ± 0.5 , 525.5 ± 0.5 , 530.8 ± 0.5 , 534.4 ± 0.2 , and 536.6 ± 0.2 nm.

IV. DISCUSSION

A. Photodetachment model

Previous negative-ion photodetachment experiments which have involved channel openings to fine-structure states of the neutral^{1,13-16} have indicated the need for a two-step photodetachment model. This geometrical model^{17,18} considers the bound-continuum photodetachment process to proceed through an electron-neutral complex which then separates to a free electron and the appropriate final state of the neutral. For HS^- photodetachment, this model can be described schematically as



where J'' is the angular momentum of the negative ion and J' is the angular momentum of the final-state neutral. The quantum number J_i represents the total angular momentum of the neutral-electron complex. It should be noted that J_i also describes the total angular momentum of ion+photon and radical product+free electron and, therefore, does not change throughout the photodetachment process. The electron configuration of the intermediate neutral-electron complex is $\pi^3\sigma$ since the departing electron is best described as an s

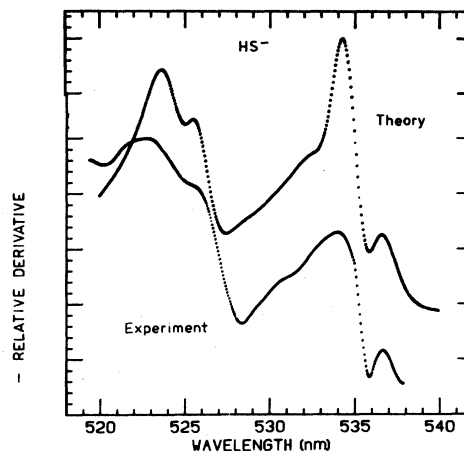


FIG. 2. Experimental (bottom) and theoretically constructed (top) photodetachment cross sections of HS^- . The theoretical spectrum was constructed for a rotational temperature of 300 K.

wave.^{2,7} The two-step designation for photodetachment has been employed in the calculation of the relative transition intensities to multiplet states in atomic photodetachment.¹⁸

In order to use this model to determine the relative transition intensities to the possible final states of HS, one must first find the relative intensities for the transitions to the various states of the electron-neutral complex, and then determine how the complex projects onto the allowed final states. For the sake of computational simplicity, it is assumed that the intermediate state is pure ¹Π which decomposes to the allowed final states, according to some Clebsch-Gordan coefficients. The matrix elements for such an angular momentum transformation have been determined

previously.¹⁹ The simplifying assumption that the electron-neutral complex may be labeled as pure ¹Π allows us to neglect any interference effects in the calculation and is made with the intention of determining accurate transition energies for the various photodetachment processes without necessarily having an exact knowledge of the transition intensities. Such an analysis is the most tractable method for determining the electron affinity of HS through the comparison of theory and experiment.

The HS⁻ photodetachment spectrum can be constructed, therefore, by determining the relative energies and intensities of the transitions from a particular *J''* in HS⁻ to all the allowed final states and summing over *J''*. There are 12 possible transitions from a given *J''* in HS⁻. They are

R branch:

$$J'' - J_i = J'' + 1 \begin{cases} {}^2\Pi_{3/2} J' = J'' + \frac{3}{2} (R_3^*), & J' = J'' + \frac{1}{2} (R_3^-) \\ {}^2\Pi_{1/2} J' = J'' + \frac{3}{2} (R_1^*), & J' = J'' + \frac{1}{2} (R_1^-) \end{cases} \quad (3)$$

Q branch:

$$J'' - J_i = J'' \begin{cases} {}^2\Pi_{3/2} J' = J'' + \frac{1}{2} (Q_3^*), & J' = J'' - \frac{1}{2} (Q_3^-) \\ {}^2\Pi_{1/2} J' = J'' + \frac{1}{2} (Q_1^*), & J' = J'' - \frac{1}{2} (Q_1^-) \end{cases} \quad (4)$$

P branch:

$$J'' - J_i = J'' - 1 \begin{cases} {}^2\Pi_{3/2} J' = J'' - \frac{1}{2} (P_3^*), & J' = J'' - \frac{3}{2} (P_3^-) \\ {}^2\Pi_{1/2} J' = J'' - \frac{1}{2} (P_1^*), & J' = J'' - \frac{3}{2} (P_1^-) \end{cases} \quad (5)$$

The labeling of these transitions is consistent with that used for HO⁻ photodetachment.¹⁵ The subscript indicates whether the final state is $\Omega' = \frac{3}{2}$ or $\frac{1}{2}$ while the superscript labels whether the photoelectron has departed with spin up or down. By this scheme, there are several transitions which are indistinguishable in terms of energy: $P_3^+ = Q_3^-$, $Q_3^+ = R_3^-$, $P_1^+ = Q_1^-$, and $Q_1^+ = R_1^-$.

To determine the relative intensities of the transitions listed above, $I(J'', J_i, J', \Omega')$, we have solved the following equation:

$$I(J'', J_i, J', \Omega') = \text{Boltz}(J'') \times \text{H-L}(J'', J_i) \times \text{Proj.}(J_i, J', \Omega'). \quad (6)$$

Boltz (*J''*) describes the relative Boltzmann population of the rotational states of the anion at a chosen rotational temperature. As a first approximation, the temperature was taken²¹ to be 300 K. The H-L(*J''*, *J_i*) are the Hönl-London factors for a ¹Π - ¹Σ transition²² which include the (2*J''* + 1) degeneracy of the *J''*th state:

$$R \text{ branch: } \text{H-L}(J'', J'' + 1) \propto (J'' + 2), \quad (7)$$

$$Q \text{ branch: } \text{H-L}(J'', J'') \propto (2J'' + 1), \quad (8)$$

$$P \text{ branch: } \text{H-L}(J'', J'' - 1) \propto (J'' - 1). \quad (9)$$

These Hönl-London formulas are valid only when the interaction of rotation and electronic motion is negligible [Hund's case (a)]. This would appear to be the case in HS (at 300 K), where the frequency of precession of the spin angular momentum about the internuclear axis is approximately ten times the frequency of rotation of the internuclear axis.^{1,20} Proj. (*J_i*, *J'*, Ω') is simply the angular momentum transformation which describes the decomposition of the intermediate ¹Π state to the appropriate ²Π_{3/2} or ²Π_{1/2} state.¹⁹ The values of Proj. (*J_i*, *J'*, Ω') for the four possible transitions from a given *J_i* are listed in Table I. For a Q branch the final states would be labeled (from left to right), Q_3^+ , Q_1^+ , Q_3^- , and Q_1^- .

In Fig. 3, we present the relative position and intensity of the 12 rotational branches calculated according to Eq. (6). Also shown is the superposition of all the rotational branches. Each of these branches is made up of individual lines, but we present the results in this manner for the sake of

TABLE I. Relative intensities to final-state HS.

| J_i | $J' = J_i + \frac{1}{2}$ $\Omega' = \frac{3}{2}$ | $J' = J_i + \frac{1}{2}$ $\Omega' = \frac{1}{2}$ | $J' = J_i - \frac{1}{2}$ $\Omega' = \frac{3}{2}$ | $J' = J_i - \frac{1}{2}$ $\Omega' = \frac{1}{2}$ |
|-------|---|---|---|---|
| 0 | 0.000 | 1.000 | 0.000 | 0.000 |
| 1 | 0.523 | 0.144 | 0.000 | 0.333 |
| 2 | 0.437 | 0.163 | 0.086 | 0.314 |
| 3 | 0.407 | 0.166 | 0.116 | 0.311 |
| 4 | 0.393 | 0.162 | 0.128 | 0.317 |
| 5 | 0.389 | 0.157 | 0.132 | 0.322 |
| 6 | 0.389 | 0.149 | 0.132 | 0.330 |
| 7 | 0.392 | 0.142 | 0.130 | 0.336 |
| 8 | 0.394 | 0.135 | 0.126 | 0.345 |
| 9 | 0.399 | 0.127 | 0.121 | 0.353 |
| 10 | 0.403 | 0.120 | 0.116 | 0.361 |
| 11 | 0.408 | 0.114 | 0.110 | 0.368 |

clarity. The separation of the strongest lines in each branch is Q_3^+ , 7.8 cm^{-1} ; Q_3^- , 11.1; Q_1^+ , 11.6; Q_1^- , 8.3; R_3^+ , 26.7; R_3^- , 7.8; R_1^+ , 30.5; R_1^- , 10.6; P_3^+ , 11.1; P_3^- , 30.0; P_1^+ , 7.8; P_1^- , 27.2 cm^{-1} .

It is instructive to analyze the results of this calculation. As expected from the Hönl-London factors [Eqs. (7)–(9)], the Q branches dominate. Furthermore, the intensity of each Q branch is augmented by the degeneracies listed earlier ($P_3^+ = Q_3^-$, $R_3^- = Q_3^+$, $P_1^+ = Q_1^-$, and $R_1^- = Q_1^+$). These effects give rise to four of the five peaks when the rotational branches are superimposed, the fifth peak being due to the strong R_3^+ branch. Owing to the definition of the electron affinity (EA) of HS,

$$\text{HS}^{-}(^1\Sigma^+, J''=0) \rightarrow \text{HS}(^2\Pi_{3/2}, J'= \frac{3}{2}) + e^-, \quad \text{EA} = \Delta E^\circ \quad (10)$$

(which is defined as zero energy in Fig. 3), the Q_3^+ branch lies very close to EA(HS) with the Q_3^-

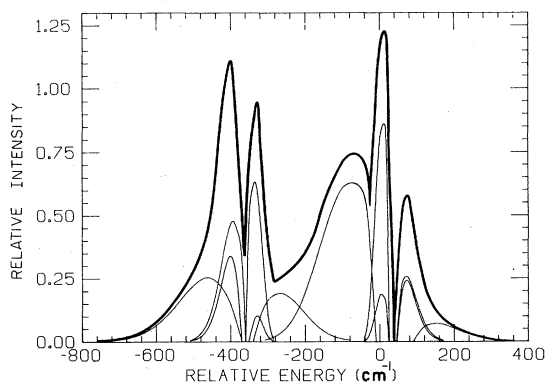


FIG. 3. Relative position and intensity of rotational branches in HS^- photodetachment. The branches, from left to right, are R_1^+ , Q_1^+ , R_1^- , Q_1^- , P_1^+ , P_1^- , R_3^+ , Q_3^+ , R_3^- , Q_3^- , P_3^+ , and P_3^- . The heavy line represents the superposition of these branches.

branch at lower energy. The Q_1^+ and Q_1^- branches are centered about the $^2\Pi_{1/2} \rightarrow ^1\Sigma^+$ transition at $\sim -380 \text{ cm}^{-1}$ in Fig. 3.

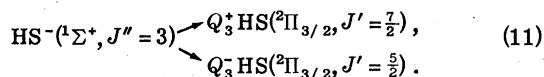
To compare the results of this model with our experimental results, we need to convolve each of the rotational lines calculated above with a theoretical description of HS^- photodetachment in the absence of rotational effects. In previous work, we have utilized a simple one-electron photodetachment model to account for the cross section behavior of negative ions.^{1, 2, 12, 23} Applying this theory to HS^- we calculate the *electronic* photodetachment cross section to follow an $E_k^{1/2}$ behavior where E_k is the energy above threshold.²⁴ To combine the theoretical electronic cross section with the rotational lines, we have convolved the $E_k^{1/2}$ threshold behavior with each of the $I(J'', J_i, J', \Omega')$ for $J''=0$ to $J''=11$. The calculated cross section, being an integral spectrum like the experimental data in Fig. 1, is then differentiated so that we can compare it directly with the differentiated experimental data in Fig. 2. The differentiated theoretically constructed spectrum is presented with the experimental results in Fig. 2. The best agreement with the experimental data is achieved when the wavelength scale is anchored such that the electron affinity of HS is at 2.314 eV. The agreement between the calculated cross section and our experimental results is excellent—each cross section shows four strong features which appear at approximately the same wavelength. The shoulder in the experimental data at $\sim 531 \text{ nm}$ is probably real in the light of the strong R_3^+ branch which is expected in that region of the spectrum (cf. Fig. 3). The magnitude of the vertical scale in Fig. 2 is not relevant since the size of the derivative for the experimental data in Fig. 2 depends upon the amount of smoothing. However, the relative heights of the peaks in a particular curve are related to the relative intensities of the rotational branches giving rise to the fine structure.¹² The relative peak heights of the experimental and theoretical curves in Fig. 2 are in qualitative agreement indicating that the HS^- photodetachment model described in Eq. (2) provides a satisfactory means of estimating the rotational line intensities. Thus, the fine structure observed in the photodetachment spectrum is not due to individual rotational lines or rotational branches, but is due to the superposition of the 12 possible rotational branches. These results are consistent with those recently obtained²⁵ using high-resolution photoelectron spectroscopy.²⁶ This technique^{25, 26} offers the possibility of obtaining accurate branching ratios and angular distributions of ejected electrons which will provide a further test of photodetachment models.

B. Electron affinity

Since there is excellent agreement between the calculated and experimental cross sections when the electron affinity of HS is chosen to be 2.314 eV, we conclude that $EA(HS) = 2.314 \pm 0.003$ eV where the uncertainty reflects the reproducibility of the observed peaks in the differentiated experimental cross section and the sensitivity of the calculated cross section to the choice of electron affinity. This result is in good accord with previous low-resolution determinations,^{2,5} but does not agree with the value reported by Eyler and Atkinson³ (2.301 ± 0.001 eV). However, these workers assigned the first rise in the cross section to the adiabatic electron affinity while our analysis shows the electron affinity to be at a greater energy than this. Furthermore, most of the periodic features observed by Eyler and Atkinson do not correspond to any structure one should expect to observe.

C. Rotational temperature

The structure we have predicted and observed in HS⁻ photodetachment offers the interesting possibility of assigning a rotational temperature to the HS⁻ ions formed and trapped in our ICR cell. At 300 K, $I(J'', J_i, J', \Omega')$ for Q branches reaches a maximum for $J'' = 3$. To a first approximation, we consider the two maxima at longest wavelengths to be due to the transitions



These two transitions should be separated by approximately 60 cm⁻¹. If the ion rotational temperature is raised to 400 K, $I(J'', J_i, J', \Omega')$ is at a maximum for $J'' = 4$ and the tops of the Q_3^+ and Q_3^- peaks would be separated by 76 cm⁻¹; i.e., the separation of the maxima in the Q_3^+ and Q_3^- branches is temperature dependent (this is also true for the Q_1^+ and Q_1^- branches). We have explored this phenomenon by calculating the spectra expected at different temperatures. These spectra were obtained in the same manner as the theoretical spectrum in Fig. 2; i.e., the intensity and position of all the rotational transitions are convolved with an $E_k^{1/2}$ function which is then differentiated. The calculated separations of the pairs of peaks at longest wavelength (Q_3^+/Q_3^-) and shortest wavelength (Q_1^+/Q_1^-) are presented in Table II. As expected, the separation increases with temperature, but is slightly larger than predicted by the simple model

TABLE II. Calculated separation of peaks in theoretical spectra.

| Temperature (K) | Q_1^+/Q_1^- separation (cm ⁻¹) | Q_3^+/Q_3^- separation (cm ⁻¹) |
|-----------------|--|--|
| 200 | 51 | 70 |
| 300 | 67 | 78 |
| 400 | 82 | 85 |
| 500 | 89 | 92 |
| 600 | 97 | 96 |

above due to the presence of other branches.

To obtain a rotational temperature, we simply measure the separation between peaks at longest wavelength in the experimental data and compare it with the values in the right-hand column of Table II. The peaks at longest wavelengths are chosen since they have the smallest uncertainty associated with them. The experimental spacing is 77 ± 7 cm⁻¹ which indicates an ion rotational temperature of $\sim 300 \pm 100$ K. This result is in accord with the notion that the HS⁻ ion will efficiently lose any excess rotational energy *via* collision²¹ with H₂S.

V. SUMMARY

We have observed rotational structure in the photodetachment spectrum of HS⁻. A model which includes the mixing of spin, orbital, and rotational angular momenta is used to assign the observed structure. The electron affinity of HS is determined to be 2.314 ± 0.003 eV. The spacing of the structure in the HS⁻ spectrum allows an estimate of the rotational temperature of the HS⁻ ions: 300 ± 100 K.

ACKNOWLEDGMENTS

We are grateful to the National Science Foundation for support of this research and fellowship support (to B.K.J.). J.I.B. is pleased to acknowledge fellowship support from the J. S. Guggenheim Foundation. We are grateful to Professor Hans C. Andersen and Professor Richard N. Zare (Stanford University), Professor Graham Richards (Oxford University), and Professor Robert W. Field (M.I.T.) for helpful discussions, to Professor Paul C. Engelking (University of Oregon) for his many useful comments, and to Professor H. Hotop (Universität Kiel) for sending us unpublished data from the thesis of Dr. F. Breyer.

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