Laser photodetachment determination of the electron affinities of OH, NH_2, NH, SO_2, and S_2

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Using a fixed frequency argon ion laser we have studied the energy spectra of electrons photodetached from OH^-, NH_2^-, NH^-, SO_2^-, and S_2^-. We determined the following electron affinities: $E_A(\mathrm{OH}) = 1.829^{+0.010}_{-0.014}$ eV, $E_A(\mathrm{NH_2}) = 0.779 \pm 0.037$ eV, $E_A(\mathrm{NH}) = 0.38 \pm 0.03$ eV, $E_A(\mathrm{SO_2}) = 1.097 \pm 0.036$ eV, and $E_A(\mathrm{S_2}) = 1.663 \pm 0.040$ eV. Additionally, the angular distribution anisotropy parameter β was measured for OH^- and NH_2^- at 4880 Å, as -0.993 ± 0.040, and 0.027 ± 0.012, respectively, and information about negative ion vibrational constants is presented.

I. INTRODUCTION

Experiments utilizing laser light sources have, of late, been providing new information about atomic and molecular negative ions.[1-8] These experiments fall into two categories, those using a tunable laser and observing the threshold region for photodetachment,[1,2,5,7,8] and those which utilize a fixed frequency laser and energy analyze the ejected photoelectrons.[3,4,6] This paper describes experiments which use the latter technique. Two of the ions under study, OH^- and NH_2^-, have been studied recently by the other technique[5,8] and serve as a tie point for the two measurement systems in addition to which complementary information is obtained by the two techniques.

II. APPARATUS

The apparatus used has been described extensively before.[3] Briefly, it is a crossed ion beam–laser beam apparatus as shown in Fig. 1. Negative ions are produced in a hot cathode gas discharge source, accelerated to an energy of 680 eV, focused, mass analyzed by a Wien mass filter, refocused and passed through an interaction region, and finally collected in a Faraday cup. Beam currents of the mass selected species are typically in the range of 10^{-10}–10^{-8} A.

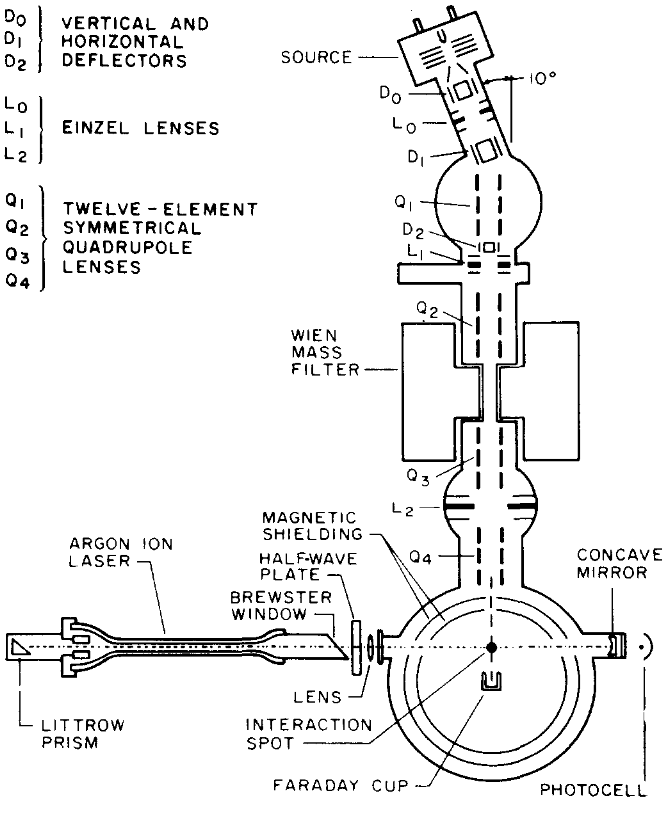

FIG. 1. An overall view of the photodetachment apparatus.

The laser is an argon ion laser which is operated at a single frequency, is linearly polarized, and contains the interaction region within its cavity. The laser mode is designed to have a waist at the interaction point, where we calculate the power density to be 300 kW/cm^2.

Electrons photodetached into a small solid angle, 0.00628 sr, enter a hemispherical energy analyzer, and those electrons with energies within the passband of the analyzer (0.03 eV full width at half maximum) are transmitted and registered by a counting chain consisting of an electron multiplier, an amplifier, a discriminator, and a multichannel analyzer. (See Fig. 2.) Digital circuitry allows us to vary the acceptance energy, and the mass of the ion being transmitted by the Wien filter can also be selected automatically, allowing energy spectra of electrons photodetached from different ions to be accumulated rapidly. Rotation of the plane of polarization of the photon beam permits measurements of the angular distribution of the photodetached electrons.

The zero for the energy scale is set by observing photodetachment from a negative ion of known electron photodetachment energy. For all of our experiments we have used O^- and we take the electron affinity as $1.462^{+0.003}_{-0.007}$ eV.[6] The energy scale calibration requires the determination of an "effective electron affinity" which corresponds to the center of the observed photodetachment peak. We calculate this "effective electron affinity" to be $1.465^{+0.004}_{-0.008}$ eV by weighting and summing the fine structure contributions to the $O^- \rightarrow O$ transition.[3,9]

III. OH^-

The spectrum of photodetached electrons ejected from an OH^- beam is shown in Fig. 3. The energy scale has been determined with the use of O^- photodetachment data obtained alternately with the OH^- data, and also shown in Fig. 3. The negative ions were obtained from a discharge in NH_3 at approximately 50 μm pressure with some residual air present. The ion beam was sorted

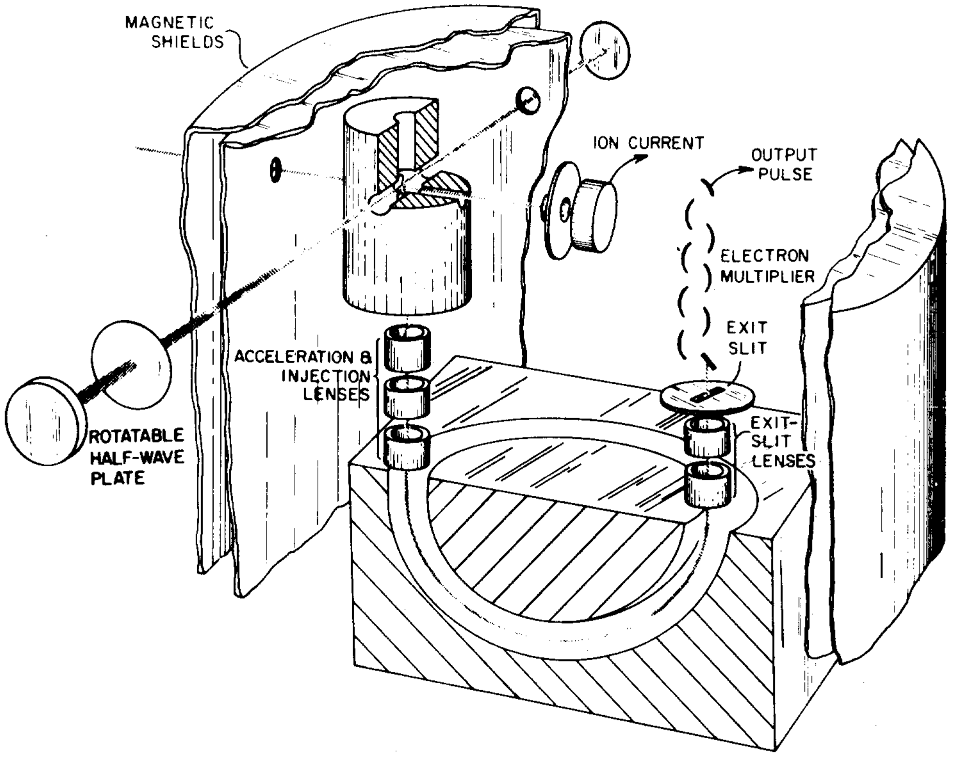

FIG. 2. A view of the interaction region including the electron energy analyzer.

into two components, of mass 16 and mass 17, and data were accumulated separately, over the two energy ranges, with the masses being switched every 8 msec to eliminate errors due to slow drifts in surface potentials in the electron energy analyzer.

The laser was operated at 4880 Å (2.54 eV) and was linearly polarized with the plane of polarization perpendicular to the direction of the electron acceptance aperture.

The vertical detachment energy can be calculated by using the expression,[3]

$$E_{VD}(OH) = E_A'(O) + [\Omega(O) - \Omega(OH)] + mW(1/M_O - 1/M_{OH}).$$

Here $E_{VD}(OH)$ is the vertical detachment energy corresponding to the center of the OH^- peak, and $E_A'(O)$ is the "effective electron affinity" of O. $\Omega(O)$ and $\Omega(OH)$ are the measured kinetic energies of the O^- and OH^- detached electrons, respectively. The last term is a kinetic correction. Here M_O and M_{OH} are the respective ion masses, m is the electron mass, and W is the ion beam energy.

The energy difference $\Omega(O) - \Omega(OH)$ is obtained by nonlinear least squares fitting[3] a slightly asymmetric gaussian line shape to each photodetachment peak and calculating the energy difference. A small correction, approximately 2%, is applied to this energy difference to compensate for minor electron-optical effects.[3] This correction procedure has been thoroughly tested with the use of known neutral molecule energy levels.[4]

Using an effective electron affinity of O = 1.465 eV, a beam energy of 680 eV and a measured energy difference $\Omega(O) - \Omega(OH)$ of 0.367 eV, we obtain a vertical detachment energy of 1.833 eV.

The errors in this value are principally systematic. The only statistical errors present come from the precision with which the fitting procedure can locate the peak centers and therefore determine the energy difference $\Omega(O) - \Omega(OH)$. We estimate that each peak center is determined to a precision of ±0.5 meV. A worst case estimate of the error in the 2% correction factor applied to our energy difference would be ±0.5%. This contributes an error of ±0.002 eV to the vertical detachment energy. An error can be introduced if the geometry of the photodetachment region is slightly skewed. This error has been tested[3] and should be limited to less than ±0.001 eV. We add an uncertainty of $^{+0.003}_{-0.007}$ eV, which is the error estimate given by Hotop, Bennett, and Lineberger[6] in the O affinity determination. It is also possible that due to variations in source temperatures or lack of knowledge about relative intensities of different fine structure, the adjustment which we apply to obtain the effective electron affinity of O, 1.465 eV, is not correct. We estimate an error of ±0.001 eV in our calculation of the effective electron affinity. We therefore arrive at

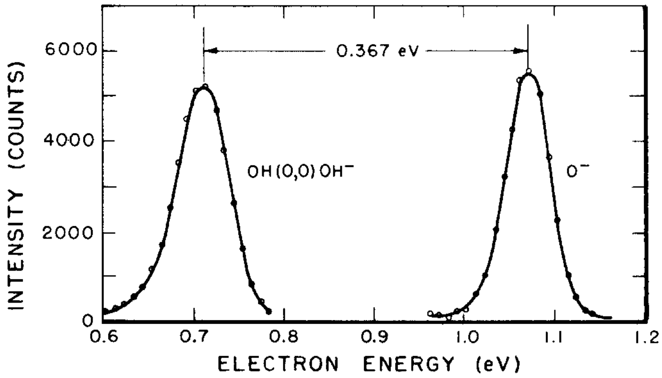

FIG. 3. Photodetachment data for both O^- and OH^- and fits to the data.

an overall error estimate of $^{+0.008}_{-0.012}$ eV.

In order to obtain a value for the electron affinity of OH based solely on our own measurement of the vertical detachment energy corresponding to the center of our OH peak, the intensities of the various rotational transitions and their positions within the spectrum would have to be calculated. However, a recent photodetachment study of OH$^-$ has been performed by Hotop, Patterson, and Lineberger,[5] where the tunable laser procedure was used. From their measurements they are able to calculate the energy difference between the electron affinity and the value of the vertical detachment energy that corresponds to the center of the photodetachment peak as it appears in our work. This difference is 0.004 ± 0.002 eV. Hence, our experiment produces the values $1.829^{+0.010}_{-0.014}$ eV for the electron affinity of OH. A value of 1.8255 ± 0.002 eV was obtained directly by Hotop, Patterson, and Lineberger.[5,6]

In OH$^-$ we see only one transition although we have carefully scanned the area in which the OH(1, 0)OH$^-$ transition would appear. These two regions are shown in Fig. 4. The noise in the OH(1, 0)OH$^-$ region is of order ± 40 counts and we take this as an upper limit on the OH(1, 0)OH$^-$ intensity. The relative intensity of the OH(0, 0)OH$^-$ transition is approximately 64,000 counts when corrected for a 4 : 1 integration time factor, which gives a maximum intensity ratio, $I(1,0)/I(0,0) < 0.0006$. It is unlikely that the angular distribution for the (1, 0) transition is significantly different than that for the (0, 0) transition. Using an expression due to Branscomb,[10] this implies a difference between the internuclear distance of the neutral and the negative ion of less than 3×10^{-4} Å, although the theoretical assumptions lose their validity long before this limit.

The angular distribution of photodetached electrons was measured using 4880 Å light and is displayed in Fig. 5. Two complete cycles are shown because the polarization of the laser light goes through two rotations as our half-wave plate polarizer rotates through one. The points are the data corrected for variations in laser intensity as a function of angle and ion beam noise. The smooth curve is the best least squares fit to the function,

$$I(\theta)=A[1+B\sin(\theta/2+\alpha)]$$
$$\times\{[1+\beta P_2\,(\cos\theta)]+D[1+\beta P_2\,(\cos(\theta+\pi/2))]\}$$

Here θ is the polarization angle, $I(\theta)$ is the intensity of emitted photoelectrons, β is the anisotropy parameter, P_2 is a Legendre polynomial. The multiplicative correction term accounts for mechanical problems in the half-wave plate motion. The term with $D(\simeq 0.01)$ accounts for the slightly imperfect linear polarization. From this fit we obtain a value for β of -0.933 ± 0.040.

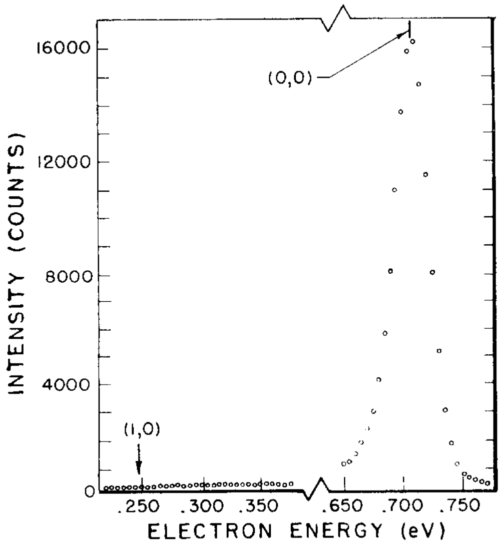

FIG. 4. Photodetachment data for the OH(0, 0)OH$^-$ and the OH(1, 0)OH$^-$ transitions.

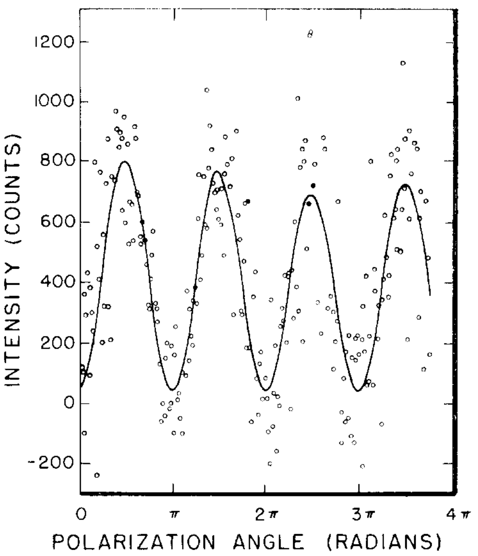

FIG. 5. Data and fit for angular distribution of ejected electrons for the OH(0, 0)OH$^-$ transition. Data were corrected for background counts.

Our value for E_A(OH), $1.829^{+0.010}_{-0.014}$ eV, can be compared to the value obtained by Branscomb,[10] 1.83 ± 0.04 eV, or the more recent results of Hotop, Patterson, and Lineberger,[5,6] 1.8255 ± 0.002 eV. In both cases the agreement is excellent. Of our error estimate, $^{+0.003}_{-0.007}$ eV are due to the error bars put on the O electron affinity.[6] Hence, we measure the electron affinity of OH relative to the value for E_A(O) with a precision of ± 0.007 eV. If we choose to make use of the recent results of Hotop, Patterson, and Lineberger[5,6] and use their absolute determination of E_A(OH) as our standard, we could say that the $E_A(\text{O}) = 1.4585\pm0.007$ eV relative to E_A(OH) = 1.8255 eV, or on an absolute basis, including the errors bars on E_A(OH), we get $E_A(\text{O}) = 1.4585\pm0.009$ eV.

The value of the upper limit for Δr_e between OH and OH$^-$ is 3×10^{-4} Å as compared to 2×10^{-3} Å as obtained by Branscomb. Of course, $\omega_e x_e$ might be different for the two molecules and the simple harmonic oscillator approximation would not be valid.

No previous measurements have been reported of the angular distribution. The value of almost − 1 for the anisotropy parameter indicates a strong p-like character for the bound electron to be promoted, which then comes out as s and d waves, which interfere to produce an almost pure $\sin^2\theta$ distribution, θ being the angle be-

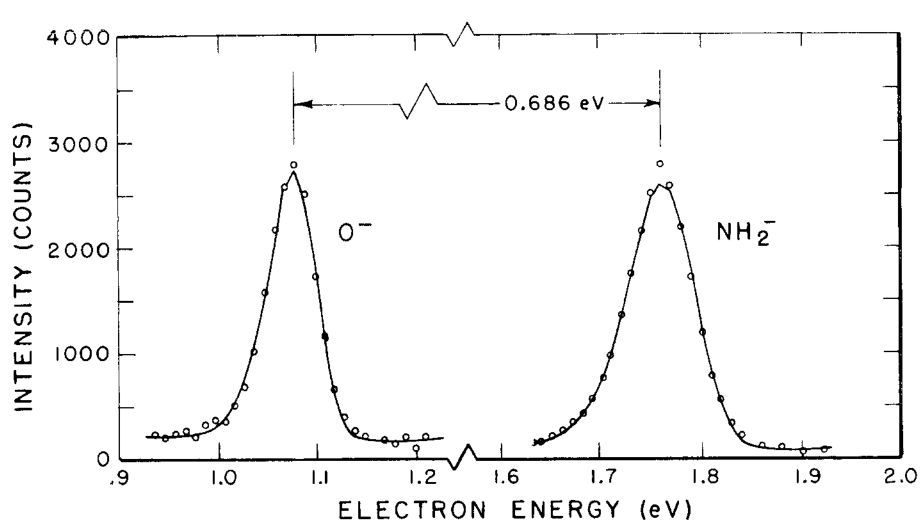

FIG. 6. Photodetachment data and fits to the data for NH_2^- and O^-.

tween the E vector of the light and the electron collection direction in the plane containing the ion beam.

IV. NH_2^- AND NH^-

In the photodetachment spectrum of NH_2^-, as with OH^-, only one peak was observed. This peak is shown in Fig. 6 as is the corresponding O^- calibration peak. The source gas used was again NH_3. The energy scale was calibrated as in Sec. III and a value for the electron affinity of NH_2 of 0.779 eV was obtained. The error estimate consists of statistical errors of ±0.002 eV, energy scale errors of ±0.005 eV, and an angular error of possibly ±0.002 eV. Additionally, an error of $^{+0.004}_{-0.008}$ eV comes from the O^- calibration procedure. This gives a total error in the determination of $^{+0.013}_{-0.017}$ eV.

There is another type of error which is more difficult to evaluate. What we measure is really the vertical detachment energy between the negative ion and the neutral, summed over a distribution of initial rotational and vibrational populations and various rotational transitions. Only in the limit of identical spectroscopic parameters for the neutral and its negative ion can we use this vertical detachment energy for the electron affinity. We see only one peak in the photodetachment spectrum indicating that the two systems have quite similar structure, but this is not sufficient to establish the electron affinity. We estimate that in this case it is highly unlikely that the electron affinity differs from the vertical detachment energy by more than ±0.020 eV. Hence our total error estimate is ±0.037 eV.

The angular distribution of the outgoing photodetached electron was measured and a value for β of 0.027±0.012 was obtained. This corresponds to an almost perfectly isotropic angular distribution.

The value of 0.779±0.037 eV obtained for the electron affinity can be compared to the recent measurements of Smyth and Brauman,[8] 0.744±0.022 eV, and of Feldman,[11] 0.76±0.04 eV. Both of these measurements were made by the threshold technique using filtered conventional light sources. Their error estimates refer to experimental problems and do not include the possibility that the observed vertical detachment threshold does not correspond to the electron affinity.

Older determinations include 1.20±0.09 eV by Page,[12] ≤0.6 eV by Dorman,[13] 1.20 eV by Ritchie and Wheeler,[14] 1.05±0.1 eV by Fischer and Henderson,[15] 1.12±0.1 eV by Bayley,[16] and 1.12 eV by Page and Goode.[17] We have no explanation for the apparent clustering of results about two values.

During the course of the NH_2^- measurements we observed photodetachment from a small quantity of mass fifteen ion. We are fairly confident that this ion is NH^- being produced in our NH_3 discharge. Only one photodetachment peak was observed, although the low beam intensity would have prevented the observation of any additional peaks with intensity a factor of ten smaller. On the basis of this peak location we calculate $E_A(\mathrm{NH}) = 0.38 \pm 0.03$ eV. It should be made clear that isotope substitution was not used to confirm the identity of this ion as it was in the other cases due to the low intensity of the beam. We offer only plausibility arguments that the mass fifteen negative ion formed in an NH_3 discharge is NH^-.

The only value we find for $E_A(\mathrm{NH})$ is due to a calculation of Cade,[18] who obtains 0.22±0.20 eV, in agreement with this determination.

V. SO_2^-

Using SO_2 as the source gas, the photodetachment spectrum of the mass 64 negative ion was measured and is presented in Fig. 7. Five prominent peaks are seen with a smaller peak at approximately 1.57 eV. Each of the five major peaks is seen to have a subsidiary peak on its low energy side. The energy differences between the main peaks correlate well with the symmetric stretch frequency of the neutral SO_2 molecule.[19] The energy difference between the subsidiary peaks on the low energy side of the main peaks and the main peaks themselves is just the bending mode frequency of the neutral SO_2 molecule.[19] Since we know that the SO_2^- molecule has a similar geometry to that of SO_2,[20] we shall assume that we are observing a progression in final states starting with the transition $SO_2(0,0,0;0,0,0)SO_2^-$. We are using the notation $(\nu_1', \nu_2', \nu_3'; \nu_1'', \nu_2'', \nu_3'')$. The transitions are la-

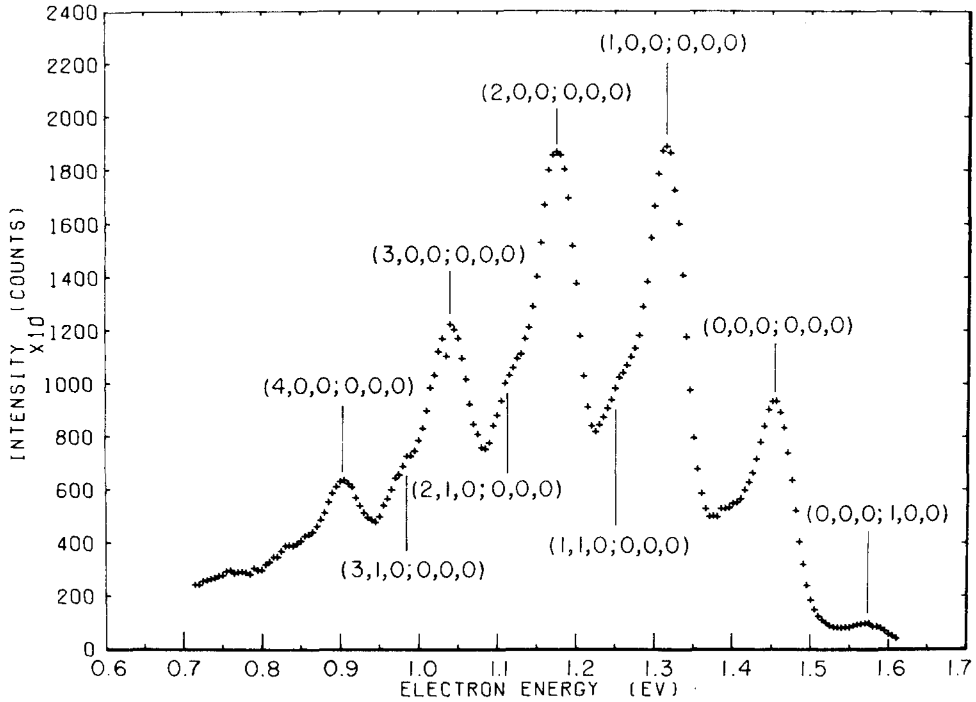

FIG. 7. Photodetachment spectrum of SO_2^- with vibrational transitions labeled.

beled in Fig. 7. The main features are then seen to be transitions from the ground vibrational state of $SO_2^-(0,0,0)$ to the progression of symmetric stretch states of the neutral, $\nu_1' = 0,1,2,3,4$, with bending modes $\nu_2' = 0,1$.

This structure all rests on a nonzero background which is due to hot bands as evidenced by the peak to the right of the figure. This peak is due to negative ions originating in the state $SO_2^-(1,0,0)$ and therefore it should be shifted from the next peak to the left by just the value of ν_1'' for SO_2^-. The energy interval we measure is 122.5 meV as compared to 122 meV determined from rare gas matrix spectroscopy.[20] The progression of transitions beginning on this state but ending on vibrationally excited states of the neutral contributes to the background intensity under the main progression.

Assuming we have correctly identified the peak shown in Fig. 7 at approximately 1.45 eV as corresponding to the $SO_2(0,0,0;0,0,0)SO_2^-$ transition, we can calculate a nominal value for the electron affinity of SO_2. Again using the O electron affinity standard, we obtain 1.097 eV for the electron affinity. The errors in this determination are estimated to be ±0.002 eV from statistics, ±0.003 eV from the energy scale calibration, ±0.003 eV from a possible angular misalignment, and $^{+0.004}_{-0.008}$ eV from the O^- calibration procedure, for a total of $^{+0.012}_{-0.016}$ eV.

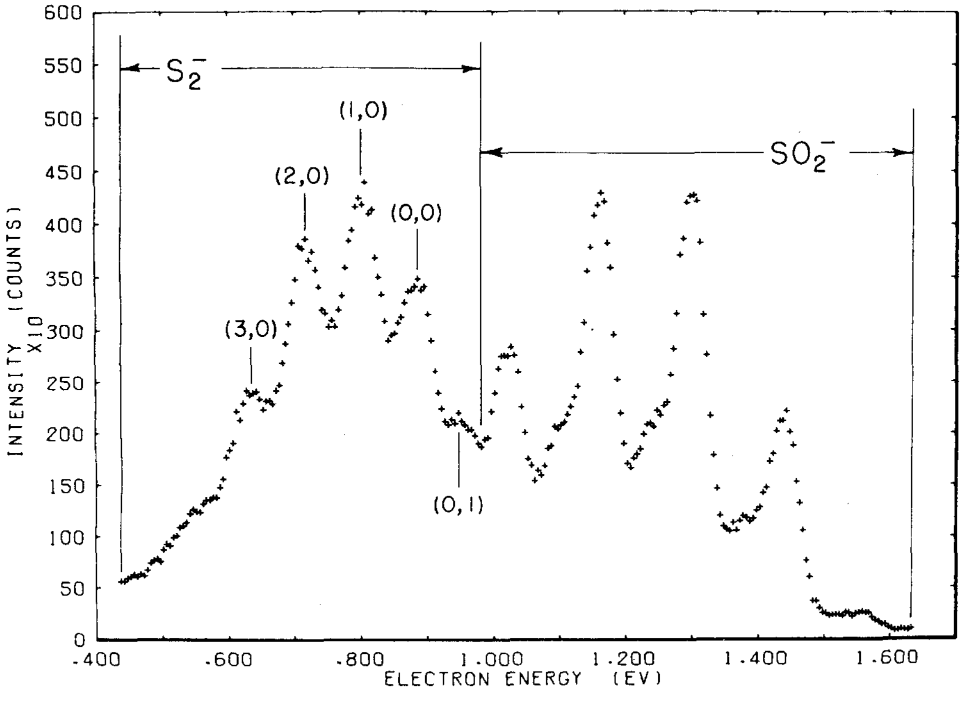

FIG. 8. Photodetachment spectra of S_2^- and SO_2^- with S_2^- transitions labeled.

There has been no attempt made to correct the electron affinity obtained for differences in the rotational energy of the negative ion and neutral or to include the effect of rotational selection rules on the observed line shape. The possible errors caused by these effects are difficult to calculate, although an estimate of ±0.020 eV should be more than adequate. We obtain therefore a total error estimate of ±0.036 eV.

Our value for the electron affinity 1.097±0.036 eV can be compared with the value 1.0±0.05 eV obtained by Feldmann[21] for the minimal detachment energy. Since the minimal detachment energy will be affected by the transition we observe originating in the vibrationally excited SO_2^- ion, it is expected that Feldmann's value will be somewhat below the electron affinity.

VI. S_2^-

A photodetachment spectrum of mass 64 ion is shown in Fig. 8. The source gas in this case was 23 μm of SO_2 and traces of COS and CS_2. The structure to the right is easily identified as being due to SO_2^- photodetachment (see Fig. 7), while the left-hand portion of the spectrum can be attributed to S_2^- photodetachment. Source discharges run in pure COS produced the S_2 spectrum without the SO_2 structure, but the number of hot bands present made identification of vibrational structure impossible.

The four main peaks are separated by the vibrational interval for neutral S_2 and have a Franck–Condon intensity envelope reminiscent of our previous measurements on NO and O_2^-.[3,4] We shall assume that the highest energy peak observable, with the correct ground state neutral vibrational energy difference, corresponds to the $S_2(v'=0, v''=0)S_2^-$ transition. The transitions are labeled in Fig. 8 and constitute a vibrational progression in the neutral ground state. The small peak to the right of the $S_2(0,0)S_2^-$ transition is the analogue to that present in the O_2^- spectrum.[4] It originates in the $v''=1$ state of S_2^- and is the first member of the progression to vibrationally excited S_2 final states. Hence, it is the lowest energy member of a progression shifted by the first vibrational interval of the ground state of S_2^-. We measure the interval, $\Delta G''_{1/2}$, to be 0.065±0.015 eV. It is, as expected, smaller than the neutral frequency because of the antibonding character of the additional electron in the negative ion.

Interpreting the S_2^- spectrum in analogy with the O_2^- spectrum we find a value for the electron affinity $E_A(S_2) = 1.663 \pm 0.040$ eV. Of the ±0.040 eV error estimate, ±0.015 eV is due to scale calibration factors and statistical errors, and the ±0.025 eV is due to our not making any adjustments for rotational or fine structure effects.

The only value for $E_A(S_2)$ is that due to Jäger and Henglein[22] as measured by electron attachment. They obtained a value of $\gtrsim 2.0$ eV.

VII. SUMMARY

By means of fixed frequency laser photodetachment spectroscopy we have measured the following electron affinities: $E_A(\mathrm{OH}) = 1.829^{+0.010}_{-0.014}$ eV, $E_A(NH_2) = 0.779 \pm 0.037$ eV, $E_A(SO_2) = 1.097 \pm 0.036$ eV, $E_A(S_2) = 1.663 \pm 0.040$ eV, and $E_A(\mathrm{NH}) = 0.38 \pm 0.03$ eV.

The angular distribution anisotropy parameter β has been measured for OH^- and NH_2^- at 4880 Å as -0.933 ± 0.040 and 0.027 ± 0.012, respectively.

The OH result serves as a tie point with the tunable-laser, threshold type experiments, and the agreement is excellent. Used in conjunction with recent absolute results for $E_A(\mathrm{OH})$, these data can be used as a check on the electron affinity of atomic oxygen.

The SO_2^- photodetachment spectrum is particularly encouraging because it was relatively simple to understand and points the way to further photodetachment study of triatomics.

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