

Photodetachment Cross Section, Electron Affinity, and Structure of the Negative Hydroxyl Ion*

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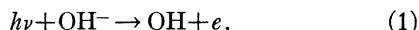
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Experimental data on the cross section for photodetachment of OH^- and OD^- ions are given and used to argue that the equilibrium internuclear distance $r_e(\text{OH}^-) = r_e(\text{OH}) \pm 0.002 \text{ \AA}$, that the vibrational frequency $\omega_e(\text{OH}^-) = 3735 \pm 560 \text{ cm}^{-1}$, and that the OH electron affinity $\text{E.A.}(\text{OH}) = 1.83 \pm 0.04 \text{ eV}$. Thus, the structure of OH^- and OH are remarkably similar, which is consistent with the theoretical predictions of Cade.

INTRODUCTION

THE continuous absorption (or photodetachment) spectrum of a negative molecular ion can under some circumstances be interpreted to yield the structural properties of the molecular ion. These required circumstances were reviewed in a summary of previous work on OH^- photodetachment¹ using crossed beams. In such experiments (including those reported in this paper), negative hydroxyl ions (OH^-), which are created in a suitable electric discharge through appropriate gas mixtures, are extracted and mass analyzed. The resulting beam of ions, the charge to mass ratio of which is accurately known but the internal energy states of which are characteristic of the ion source and must be assumed unknown, is illuminated by modulated optical radiation of known spectral characteristics. The resulting modulated signal of free electrons, which are extracted from the region of intersection of the photon and ion beams, is proportional to the average value of the photodetachment cross section over that spectral interval resulting from the reaction



If sufficient spectral resolution is available, the conditions for determination of the OH affinity and other structural properties such as the equilibrium internuclear separation r_e and the vibrational frequency ω_e would appear to be propitious in the case of OH^- : (a) the electronic absorption spectrum from a particular initial state is predicted² to have infinite slope at threshold, and to rise as $(h\nu - h\nu_0)^{3/2}$, thus providing a clearly demarked threshold for each initial energy state; (b) the vibrational energy levels are sufficiently widely spaced, so that it might be possible to deduce the initial state of the negative ions; (c) the observed cross section is apparently consistent with first-order theoretical expectation—i.e., devoid of complex structure—so that the distinction between vibrational structure and that

due to variations in the electronic cross section can easily be made.

The experimental observations of OH^- photodetachment (by Smith and Branscomb)³ which were available at the time of the last review¹ of this subject were used to deduce a cross section in polynomial form from an integral equation relating signals obtained with optical filters of selected cutoff wavelengths near the OH^- threshold to the transmission curves of these filters. These measurements³ showed clearly an abrupt threshold which had an apparent onset at 1.78 eV ($\sim \lambda 7000 \text{ \AA}$) for OH^- . The cross section at longer wavelengths was less than 10^{-3} of the peak observed value at shorter wavelengths.¹ But the basic ambiguity in interpretation of data obtained with cutoff filters made it impossible to deduce a unique cross-section curve for the region near threshold. Indeed, there were indications of additional structure in the curve for which no ready explanation was at hand [in violation of condition (c) above]. Thus no conclusion could at that time be drawn concerning the electron affinity of OH, since it was not possible to make a convincing argument that the threshold near 1.78 eV does correspond to the vertical detachment energy from the ground state, and that this in turn is equal to the electron affinity.

These problems were largely removed by the use of an optical monochromator to improve the spectral resolution of the experiment. The wavelength can be scanned continuously, and the exit beam spectral form is approximately triangular with a base width of about 100 $\text{\AA}/\text{mm}$ slit width. (The entrance and exit slits are coupled.) Thus when 1-mm slits are used, the resolution is about 50 \AA —a tenfold improvement over the earlier work^{1,3} using band-pass filters. Since the vibrational quanta in OH are about 0.4 eV, and since 100 \AA resolution near 7000 \AA corresponds to about 0.025 eV, it is clear that the resolution is sufficient to discern thresholds due to different vibrational states, but not those due to individual rotational levels.

The procedure adopted in this investigation relies heavily on comparisons between the spectra of OH^- ions and OD^- ions. We make the assumption that the electronic potential functions of OH^- and OD^- are

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¹ L. M. Branscomb, in *Atomic and Molecular Processes*, edited by D. R. Bates, (Academic Press Inc., New York, 1962) p. 100 ff.

² S. Geltman, *Phys. Rev.* **112**, 176 (1958).

³ S. J. Smith and L. M. Branscomb, *Phys. Rev.* **99**, 1657 (A) (1955).

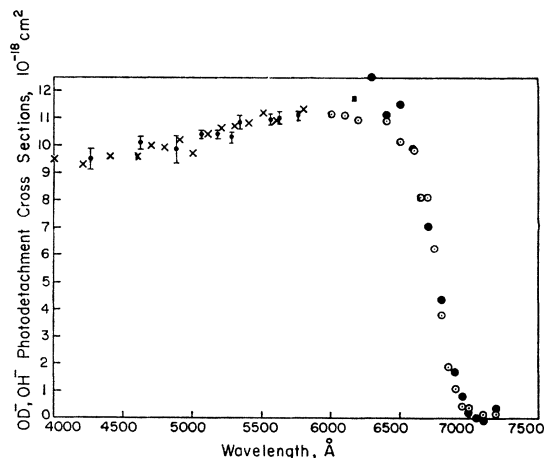


FIG. 1. Cross-section curves for photodetachment of OH^- and OD^- . The solid points refer to OH^- , crosses and circles to OD^- . The small solid dots with error bars are data obtained in 1958 by the author and S. J. Smith (unpublished) using band-pass filters at low ($\sim 500 \text{ \AA}$) resolution. All other data were obtained in the recent work at a resolution of 100 \AA . The recent data were placed on an absolute cross-section scale by comparison with H^- , the cross section of which is known [L. M. Branscomb and S. J. Smith, *Phys. Rev.* **98**, 1028 (1955); see also the discussion in Ref. 1.]; they are in good agreement with the 1958 data.

identical (as indeed they will be if the potential curves—calculated in the Born-Oppenheimer approximation—are to have any meaning). Our interpretations depend on several sequential arguments.

First we will argue that all of the signals observed arise from ions in the ground vibrational state because of our failure to observe a $\Delta v = -1$ sequence⁴ at longer wavelengths than threshold.

Secondly, we search (unsuccessfully) for evidence of a $\Delta v = +1$ sequence and attempt to put an upper limit on the ratio of intensity of this sequence to that of the $\Delta v = 0$ sequence (to which the only threshold observed is presumed to correspond). From this limit we find—assuming simple-harmonic vibrational wave functions—that $r_e(\text{OH}^-)$ must be very closely equal to $r_e(\text{OH})$ (and similarly for OD^-). This not only confirms the $\Delta v = 0$ identification of the main threshold but shows that the rotational energy constant $B(\text{OH}^-) \simeq B(\text{OH})$. Thus the continua associated with individual rotational levels will occur at wavelengths which do not show “degrading” and band-head formation except at very large rotational quantum numbers. This permits us (if we can assign reasonable rotational temperatures) to construct model spectra for the threshold region.

⁴ We use the standard nomenclature for band spectroscopy, ignoring the fact that “initial” and “final” states contain different numbers of bound electrons. Thus the “(0,0) band” refers to transitions from $\text{OH}^-(^1\Sigma^+, v=0)$ to $\text{OH}(X^2\Pi_i, v=0)$ plus a free electron, and “ $\Delta v = 0$ sequence” is the sum of such transitions with no change in vibrational quantum number v . The (1,0) continuum refers to $v=1$ in the upper (final) state. Since all transitions discussed in this paper are in absorption, the vibrational transitions are given as (v_f, v_i) .

Finally, by comparison of OH^- and OD^- thresholds we can look for differences in the zero-point vibrational energies of the isotopes, and from this make an inference as to the vibrational structure of OH^- and hence the vibrational force constant.

The conclusions which will be drawn are that the negative ions appear to have structures which are remarkably similar to those of the corresponding neutral radicals, that the threshold behavior is actually dominated by the rotational development and OH fine structure splitting (which can fully account for the observed difference in onset of OH^- and OD^- photodetachment), and finally, that the OH affinity is about 1.83 eV.

1. STATE OF EXCITATION OF OH^- BEAM

A fundamental difficulty in the use of discharge ion sources for the generation of molecular ions (which plagues both positive and negative molecular ion crossed-beam experiments) is the unpredictability of the internal-state distribution of the ions. In our previous work⁵ on O_2^- , this question precluded an unambiguous determination of the vertical detachment energy. Our only recourse was to vary, as much as possible, conditions in the ion source—a cold cathode discharge—subject to the requirement for a stable, noise-free ion beam. The data appeared quite reproducible. The ion source in use in this experiment is a hot cathode arc,⁶ which is quite different in character from the cold cathode glow. The O_2^- cross section was not restudied, except for a single measurement at $\lambda 4200$, where the O_2^- cross section (determined relative to O^-) was found to be $2.3 \times 10^{-17} \text{ cm}^2$, in excellent agreement with the earlier report.⁵ Of course, this does not necessarily test the effect of ion excitation; the critical spectral range for O_2^- lies near threshold in the infrared.

In the analysis which follows we rely on the fact that we observe in OH^- (Fig. 1) only one threshold (near 7000 \AA), and a careful search for signals at longer wavelengths permits us to assign an upper limit of 10^{-3} to the ratio of such signals to the strength of the signal near $\lambda 6000$. It therefore seems likely that the $\lambda 7000$ threshold corresponds to the (0,0) band; if $v=1$ of OH^- is appreciably populated, and if the $\lambda 7000$ threshold corresponds to absorption from the $v=1$ state, the intensity of the (0,1) transition causing absorption at longer wavelengths would surely exceed 10^{-3} of the (1,1) continuum. Similarly, if the $\lambda 7000$ edge is the (1,0) continuum, the (0,0) absorption would fall at longer wavelengths and would surely be stronger than 10^{-3} of (1,0). The only assignment for the $\lambda 7000 \text{ \AA}$ edge which permits *no* absorption at longer wavelengths is

⁵ D. S. Burch, S. J. Smith, and L. M. Branscomb, *Phys. Rev.* **112**, 171 (1958); **114**, 1652 (E) (1959).

⁶ M. L. Seman, B. W. Steiner, and L. M. Branscomb, *J. Chem. Phys.* **37**, 6 (1962).

(0,0) absorption from OH⁻ ions, all of which are in the $v=0$ state.

Anticipating the conclusion of this paper, we will find that the equilibrium internuclear separations for OH⁻ and OH are so similar that the off-diagonal vibrational intensities are less than a few percent of the (0,0) sequence. Thus, a population of perhaps 10% of the ions in ($v=1$) would probably have escaped detection. This does not contribute an appreciable error in the conclusions, since $\Delta v = -1$ is not detected and the $v=1$ state of OH⁻ merely contributes a weak (1,1) continuum to the (0,0) absorption, both of which start from approximately the same band origin near 7000 Å.

2. SEARCH FOR THE $\Delta v = 1$ SEQUENCE

Next we will attempt to deduce the relative values of the equilibrium internuclear separation (r_e) of OH⁻ and OH by searching for the (1,0) band.

Assume that the ground states of OH⁻ and OH, in the harmonic-oscillator approximation, have equal force constants (to be justified later), and define the distance β as the difference in equilibrium internuclear separation of OH⁻ and OH:

$$\beta = r_e(\text{OH}^-) - r_e(\text{OH}).$$

The intensity of the (0,0) band is proportional to the square of the vibrational matrix element between $\Psi_0^-(r)$ and $\Psi_0^0(r+\beta)$:

$$\begin{aligned} I_{0,0}(\beta) &= \left| \int_{-\infty}^{\infty} \Psi_0^-(r) \Psi_0^0(r+\beta) dr \right|^2 \\ &= \left| \left(\frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha(r+\beta)^2/2} e^{-\alpha r^2/2} dr \right|^2 = e^{-\alpha\beta^2/2}, \end{aligned} \quad (2)$$

where the superscripts $(-, 0)$ refer to OH⁻ and OH, and $\alpha = (4\pi^2\mu c/h)\omega_e$. Similarly,

$$\begin{aligned} I_{1,0}(\beta) &= \left| \alpha \left(\frac{2}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} r e^{-\alpha r^2/2} e^{-\alpha(r+\beta)^2/2} dr \right|^2 \\ &= \frac{1}{2} \alpha \beta^2 e^{-\alpha\beta^2/2}. \end{aligned} \quad (3)$$

Thus, the ratio of intensity of the (1,0) continuum to the (0,0) continuum, as a function of the shift in r_e is

$$I_{(1,0)}/I_{(0,0)} = \frac{1}{2} \alpha \beta^2, \quad (4)$$

or

$$\beta = ((2/\alpha)(I_{(1,0)}/I_{(0,0)}))^{1/2}. \quad (5)$$

Now from Herzberg⁷ we find that for OH,

$$(\alpha_{\text{OH}}/2)^{-1/2} = 0.0138 \text{ \AA}$$

and for OD,

$$(\alpha_{\text{OD}}/2)^{-1/2} = 0.0117 \text{ \AA}.$$

⁷ G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Inc., New York, 1950), p. 171.

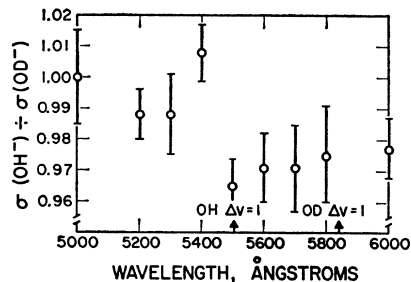


FIG. 2. Ratios of relative cross sections for OH⁻ and OD⁻ as a function of wavelength with a resolution of about 50 Å. The increase in the ratio for wavelengths shorter than 5500 Å suggests the possibility of a weak (2%) contribution from the continuum associated with vibrational transitions from $v=0$ of OH⁻ to $v=1$ of OH. This small magnitude is not, however, statistically significant, and the data are interpreted as applying a limit to the strength of such a continuum relative to the (0,0) continuum which begins at 7000 Å.

Thus

$$\begin{aligned} \beta_{\text{OH}} &= 0.0138 (I_{(0,1)}/I_{(0,0)})^{1/2} \text{ \AA}, \\ \beta_{\text{OD}} &= 0.0117 (I_{(0,1)}/I_{(0,0)})^{1/2} \text{ \AA}. \end{aligned} \quad (6)$$

Now, let us look at the experimental evidence. The vibrational constants ω_e for hydroxyl are⁷

$$\omega_e(\text{OH}) = 3735 \text{ cm}^{-1}$$

and

$$\omega_e(\text{OD}) = 2721 \text{ cm}^{-1}.$$

Thus, if the (0,0) threshold is near $\lambda 7000$ Å (for both OH⁻ and OD⁻), we should look for the (1,0) threshold at

$$\lambda_{(1,0)} = 5830 \text{ \AA} \text{ for OD}^-$$

and

$$\lambda_{(1,0)} = 5500 \text{ \AA} \text{ for OH}^-.$$

Let us now examine Fig. 1. Plotted here are OD⁻ cross-section data (crosses and open circles) obtained with the monochromator at about 100 Å resolution; some earlier low-resolution OD⁻ data obtained by Branscomb and Smith in 1958 (but unpublished) shown as solid points with error bars, and OH⁻ data near threshold (solid points) with 50 Å resolution. Inspection of the region near $\lambda 5830$ fails to show evidence of a second absorption threshold, nor does one see structure at shorter wavelengths which might be ascribed to a (2,0) continuum.

We now turn to a more careful examination of the region from $\lambda 5000$ to $\lambda 6000$ in a search for the (1,0) threshold. Taking data at 50 Å resolution with the best signal to noise available to us (statistical probable errors of about 2%), relative-cross-section curves for OH⁻ and OD⁻ were obtained. In Fig. 2 we display the ratio of the OH⁻ to OD⁻ signals, thus dividing out any wavelength-dependent systematic errors (especially in the radiometry) which might otherwise have led to spurious "bumps" in the curve. Since both sets of data are relative, we normalized the ratio to unity at $\lambda 5000$.

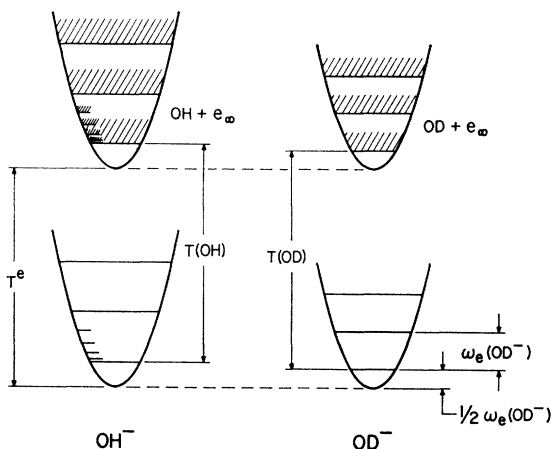


FIG. 3. Schematic potential curves to illustrate the method by which the vibrational constant for OH^- could, in principle, be deduced from an observation of the difference in the photodetachment thresholds for OH^- and OD^- .

The tendency of the points for $\lambda < 5500$ to lie about 2% higher than those for $\lambda \geq 5500$ is suggestive of a weak onset of (1,0) continuum. But we will only conclude that

$$I_{(1,0)}/I_{(0,0)} \leq 0.02$$

because of the size of the statistical errors and because the discontinuity seen in Fig. 2 is clearly in part accidental. The transition is too abrupt to be consistent either with the instrumental resolution or the rotational development which we find near $\lambda 7000$. In addition, although we have only one point ($\lambda 6000$) at $\lambda > 5830 \text{ \AA}$, we fail to see evidence of the onset of another continuum in the OD^- data.

Referring back to Eq. (6),

$$\begin{aligned} \beta_{\text{OH}} &\leq 0.0020 \text{ \AA}, \\ \beta_{\text{OD}} &\leq 0.0017 \text{ \AA}. \end{aligned}$$

Thus, we conclude

$$\begin{aligned} r_e(\text{OH}^-) &= r_e(\text{OH}) \pm \beta \\ &= 0.9706 \pm 0.002 \text{ \AA} = 1.834 \pm 0.004 a_0, \\ r_e(\text{OD}^-) &= r_e(\text{OD}) \pm \beta \\ &= 0.9699 \pm 0.0017 \text{ \AA} = 1.832 \pm 0.003 a_0. \end{aligned}$$

3. OH^- AND OD^- ROTATIONAL CONSTANTS

Since the rotational constant B is proportional to the reciprocal moment of inertia

$$B_e \propto (\mu r_e)^{-2},$$

where μ is the molecular reduced mass, it follows from the previous section that

$$B_e(\text{OH}^-)/B_e(\text{OH}) = B_e(\text{OD}^-)/B_e(\text{OD}) = 1 \pm 0.004. \quad (7)$$

The nature of the rotational development—the distribution in frequency of the onset of the continua associated with each rotational transition—is deter-

mined by this ratio of B_e values in the two electronic states. In systems in which the $B_e' = B_e''$, that is when no changes in rotational level spacings occur in the transition, the band head is not formed; and the rotational lines (or origins of continua in our case) are equally spaced. In degraded electronic band systems with $B_e' \neq B_e''$ the vertex of the Fortrat parabola identifies the rotational quantum number m at which the band head is formed. (For P and R branches $m = -J$ and $m = +J+1$, respectively.) Since⁷

$$m_{\text{vertex}} = -(B_e' + B_e'')/2(B_e' - B_e''), \quad (8)$$

and since we found for the largest value

$$B_e'/B_e'' = 1.004, \quad m_{\text{vertex}} = 250.$$

For rotational states populated in a Boltzmann distribution, the most populated level is at $J_{\text{max}} = (kT/2B)^{1/2}$. We find, for OH ($B = 18.87 \text{ cm}^{-1}$) at 3000°K , $J_{\text{max}} = 7$. Thus, for all practical purposes we can ignore the infinitesimal band degrading which is permitted by the small changes in internuclear separation between OH^- and OH . We will also ignore the rotational stretching.

4. DETERMINATION OF $\omega_e(\text{OH}^-)$

If possible, we would like to determine the vibrational constant ω_e for OH^- and OD^- . The absence of apparent vibrational structure need not prevent such a determination. We can look for evidence of an inequality of $\omega_e(\text{OH}^-)$ and $\omega_e(\text{OH})$ by comparing in detail the threshold regions for photodetachment of OH^- and OD^- . This analysis is based on the existence of zero-point vibrational energy and on the assumption that the electronic potential functions at their minima show the same electronic potential-energy difference (T^e) between OH^- and OH , and between OD^- and OD .

Figure 3 shows schematically potential curves drawn under this assumption. The energy differences between the potential-curve minima (called T^e) are assumed

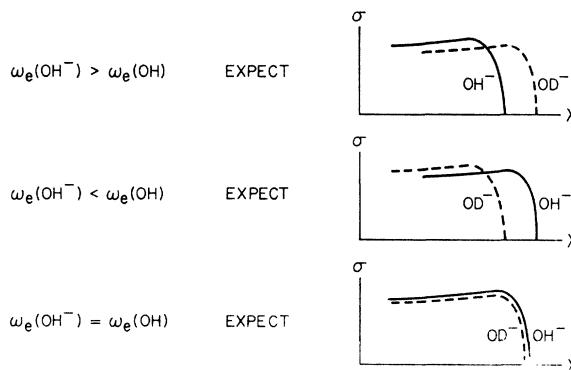


FIG. 4. Illustration of the influence on the wavelength of the photodetachment threshold of OH^- and OD^- of the relative values of the vibrational constants of OH^- and OH . The curves are sketched without taking into account the influence of the rotational distribution of the negative ions. The effect arises solely from the differences in zero-point energy between OH^- and OD^- .

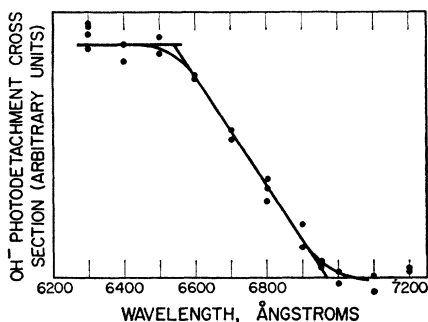


FIG. 5. Relative cross section for photodetachment of OH^- in the region near threshold. Resolution is 100 Å. Solid lines are artificial constructions.

equal. The values $T(\text{OH})$ and $T(\text{OD})$ need not be equal and are the energy differences appropriate to the electron affinities of OH and OD, respectively.

For simplicity, let us consider only $v''=v'=0$ and $J'=J''-1$. From the figures, and from the fact that the zero-point energy for the harmonic oscillator is $\frac{1}{2}\omega_e$, we see that

$$\begin{aligned} \Delta T &= T(\text{OH}) - T(\text{OD}) \\ &= \frac{1}{2}\{[\omega_e(\text{OH}) - \omega_e(\text{OD})] - [\omega_e(\text{OH}^-) - \omega_e(\text{OD}^-)]\} \\ T(\text{OH}) &= T^*(\text{OH}) + \frac{1}{2}[\omega_e(\text{OH}) - \omega_e(\text{OH}^-)], \\ T(\text{OD}) &= T^*(\text{OD}) + \frac{1}{2}[\omega_e(\text{OD}) - \omega_e(\text{OD}^-)]. \end{aligned} \quad (9)$$

Therefore,

$$\Delta T = T(\text{OH}) - T(\text{OD}) = \frac{1}{2}\{[\omega_e(\text{OH}) - \omega_e(\text{OD})] - [\omega_e(\text{OH}^-) - \omega_e(\text{OD}^-)]\}. \quad (10)$$

We can relate the vibrational constants for OH^- and OD^- by assuming again that the force constants k are the same and that the molecules are simple harmonic oscillators. Then since

$$\begin{aligned} \omega_e &\propto (k/\mu)^{1/2}, \\ \omega_e(\text{OH}^-) - \omega_e(\text{OD}^-) &= 0.272\omega_e(\text{OH}^-), \end{aligned} \quad (11)$$

and similarly for the corresponding neutral molecules. Substituting, we find

$$\Delta T = 0.136\{\omega_e(\text{OH}) - \omega_e(\text{OH}^-)\}. \quad (12)$$

Thus the quantity ΔT tells us the energy (and hence wavelength) difference of the thresholds for absorption between OH^- (in state $v=0, J=1$) and OD^- (in same states). In Fig. 4 we see a diagram of the expected qualitative behavior.

Data taken in the threshold regions are shown in Fig. 5 for OH^- and in Fig. 6 for OD^- . Here, the instrumental resolution is about 100 Å and can explain much of the curvature, although data taken at 50-Å resolution did not show appreciably less curvature. We note that the thresholds, as determined by the straight-line extrapolations in the figures, are different, and are

$$\begin{aligned} \lambda_0(\text{OH}^-) &= 6970 \text{ Å}, \\ \lambda_0(\text{OD}^-) &= 6890 \text{ Å}. \end{aligned}$$

In Fig. 7 these curves are superposed, and we see that they have markedly different slopes near the threshold. In order to relate this data to the relation given in Eq. 12, we must reconstruct this threshold region taking the rotational and spin-rotation splitting structure into account, for Eq. (12) refers to transitions in the $\Delta J=0$ or Q branch only.

The final state in this photodetachment process is split, by interaction of the electron spin with the molecular rotation, into two states $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ with energies differing by

$$T_e = T_0 + A\Lambda\Sigma,$$

where $A = -139.7 \text{ cm}^{-1}$, (0.0173 eV) and the notation is that of Herzberg.⁸ We will assume that the relative strength of the continua leading to their final states are in proportion to $(2\Omega+1)$, i.e., 2:1.

The spacing of the rotational lines, in the absence of degrading and ignoring vibration-rotation interaction, is $2B$. If we assume that the OH^- and OD^- ions are distributed in thermal equilibrium in their rotational states, then we can construct synthetic continua by adding all the continua associated with the three main branches $\Delta J=0, \pm 1$.

Because we could not possibly resolve the rotational thresholds, we will ignore the rotational quantization. The total intensity of the Q branch is approximately equal to the sum of the intensities in the P and R branches (which in turn are equal).

Unfortunately, we have no *a priori* knowledge of the temperature of the plasma from which the ions come. But it is reasonable to assume that this hot cathode arc at about 0.05 Torr pressure is at a few thousand degrees K. We will illustrate what is expected at 1000°K. In any event we shall show that the deductions as to the value of $\omega_e(\text{OH}^-)$ are weakly dependent on the assumed temperatures. Figure 8 shows, by a dotted line, such a synthetic spectrum for OH^- , in which we have taken a step function for the electronic cross section for OH^- photodetachment. This assumption is surely not correct. We

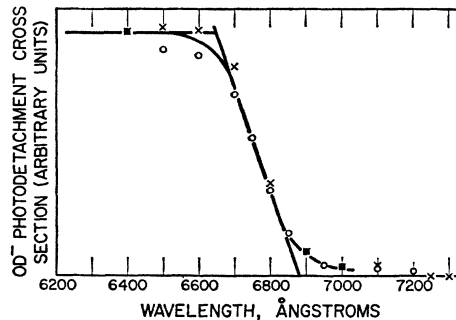


FIG. 6. Relative cross section for photodetachment of OD^- in the region near threshold. Resolution is 100 Å. Solid lines are artificial constructions.

⁸ G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Inc., New York, 1950), p. 215.

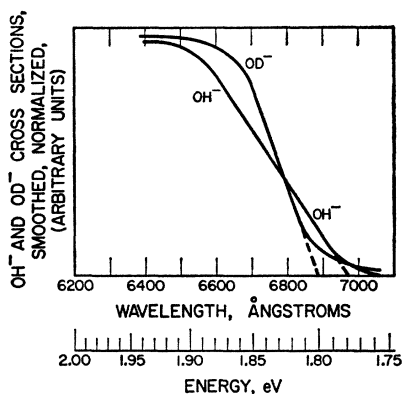


FIG. 7. The cross-section curves of Figs. 5 and 6 are smoothed and superposed to illustrate that the extrapolated thresholds differ, but that the two curves have different slopes in the threshold region. The explanation lies in the more extensive rotational development of the OH^- cross section if the OH^- and OD^- are obtained from an ion source at a single temperature.

expect, from experience with atomic ions^{9,10} a shape somewhere between a parabola and a step function.

In Fig. 9 the composite curves for OH^- and OD^- are

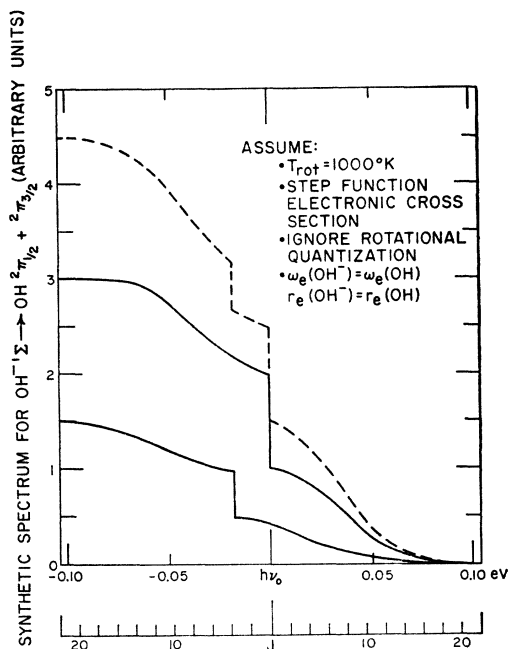


FIG. 8. A hypothetical synthetic OH^- photodetachment cross section, which assumes that the electronic transition probability can be characterized as a step function [theoretical expectation makes the lead term $(h\nu - h\nu_0)^{3/2}$], taking the rotational temperature at 1000°K , and including the two fine structure states of the OH molecule. Positions of the rotational levels in the OH^- molecule are indicated by the quantum number J , but rotational quantization is ignored in the construction.

⁹ B. W. Steiner, M. L. Seman, and L. M. Branscomb, in *Atomic Collision Processes*, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964) p. 537.

¹⁰ L. M. Branscomb, S. J. Smith, and G. Tisone, *J. Chem. Phys.* 43, 2906 (1965).

compared with the smoothed experimental data of Fig. 7. The synthetic spectra have been drawn with the Q -branch origin at 1.83 eV to get best agreement with experiments. Both the synthetic curves and the data, for OH^- and OD^- , respectively, cross at this point. The agreement is reasonably satisfactory if one makes allowance for experimental resolution and for the step-function cross-section assumption.

The comparison of experiment and theoretical reconstruction shown in Fig. 9 is somewhat confused by the fact that we have not introduced the experimental resolution into the reconstructed curves. With 2 mm slits in the monochromator, the slit function is approximated by a triangle with 100 \AA width at half-maximum. If we smooth the theoretical curves of Fig. 9 with such a function, we find the curves in Fig. 10 (solid line for OD^- , dashed line for OH^-). All evidence of the Q -branch step has been washed out. For comparison the averaged experimental data of Figs. 5 and 6 (represented by a single point at each energy) are plotted in Fig. 10. In view of statistical uncertainties of about 10% in the data, the agreement is quite satisfactory.

Thus, we see that the point at which ΔT should be measured is approximately (i.e., for step-function cross sections) the point at half-maximum absorption. At the half-maximum point we find

$$\Delta T = 0 \pm 0.01 \text{ eV.}$$

From this value and Eq. (12)

$$\omega_e(\text{OH}^-) - \omega_e(\text{OH}) \leq 0.07 \text{ eV or } 560 \text{ cm}^{-1};$$

hence,

$$\omega_e(\text{OH}^-) = 3735 \pm 560 \text{ cm}^{-1}.$$

5. DETERMINATION OF THE ELECTRON AFFINITY (E.A.) OF OH

This crossing point ($\lambda 6780$) is also the value which should be identified with the electron affinity

$$\text{E.A.}(\text{OH}) = 1.83 \pm 0.01 \text{ eV.}$$

This error of 0.01 eV refers to the statistical confidence in the positions of the curves as measured. The larger number of assumptions which underlie the analysis make it difficult to assign a limit to possible systematic errors, i.e., to define the accuracy of the result. A conservative assignment (which is large enough to cover most of the region of rapid variation near threshold) is

$$\text{E.A.}(\text{OH}) = 1.83 \pm 0.04 \text{ eV.}$$

The most important conclusion is none the less surely valid: for molecules one cannot take the vertical detachment energy from the wavelength of the onset of continuous absorption. Furthermore, one notes that the minimum detachment energy for a molecular ion will depend on temperature as well as on the rotational constants.

TABLE I. Cade's calculations^a of potential-curve data for OH⁻(¹Σ⁺) compared with this experiment.

	Molecule	r_e (a_0)	B_e (cm^{-1})	ω_e (cm^{-1})
OH X ² Π _i	Known values ^b	1.8342	18.871	3735.2
	Calculation	1.795	19.712	4062.0
	Error	-2.14%	+4.46%	+8.75
HF(¹ Σ ⁺)	Known values ^b	1.7328	20.949	4139.0
	Calculation	1.6960	21.868	4469.0
	Error	-2.12%	+4.39	+7.97
OH ⁻ (¹ Σ ⁺)	Calculation	1.781	20.023	4087.9
	(Averaged) error	(-2.13%)	(+4.4%)	(+8.4%)
	Predicted	1.82	19.2	3770
	This experiment ^c	1.834±0.004	18.87±0.075	3735±0.560
Ratio	Predicted	0.992	1.016	1.009
OH ⁻ /OH	This experiment	1.000±0.002	1.000±0.004	1.00±0.15

^a Reference 11.^b Reference 7.^c This experiment only bounds the difference between OH⁻ and OH properties and thus provides only the error in these figures. The absolute values are from Herzberg (Ref. 7).

6. COMPARISON WITH THEORY

The most detailed calculations of the potential function for OH⁻ are contained in the unpublished work of Cade.¹¹ These LCAO-MO-SCF calculations, which are believed to yield wave functions of Hartree-Fock accuracy, were carried out for OH⁻ in concert with the extensive Hartree-Fock calculations made by Cade and Huo for the ground states of the first row hydrides, AH. The electron affinity of OH is not determined by these calculations, and except at large and small internuclear separations, the total energy curve for OH⁻ lies very slightly above that for OH. This former result is to be expected, since in going from OH

($1\sigma^2 2\sigma^2 3\sigma^2 1\pi^3, X^2\Pi_i$) to OH⁻($1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4, ^1\Sigma^+$), one new electron pair is formed; and hence the "correlation" energy error of OH⁻ is greater than that for OH. The detailed effects that correlation error introduces into derived results of potential curves, such as the spectroscopic constants, is unknown; but extensive related studies on the neutral hydrides indicate they are small for this group of molecules.

Using the potential curve for OH⁻ obtained at 14 R values, Cade calculated the spectroscopic constants with the Dunham analysis, and these results are given in Table I. Also in Table I are previous results for R_e , B_e , and ω_e obtained by Cade and Huo for HF (isoelectronic with OH⁻) and OH (the parent molecule) together with the same constants from band spectra. The percentage error between the theoretical and experimental values are also given for HF and OH. Using

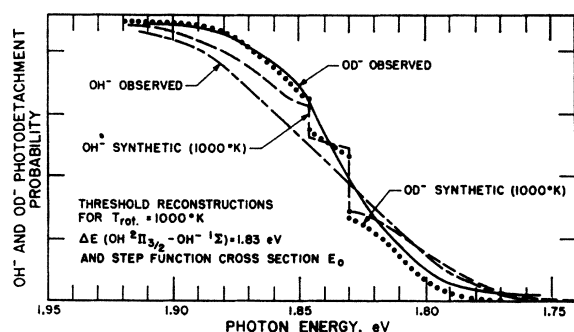


FIG. 9. Using synthetic spectra like that illustrated in Fig. 8, the experimental data of Fig. 7 are approximately reconstructed. The experimental resolution has not been added to the synthetic curves and will account for the failure to observe the structure near the band origins, as well as account for the extended "tail" on the curves at threshold. The inadequacy of the step function approximation to the electronic part of the cross section is not as serious as might have been expected, and the crossing point for the OH⁻ and OD⁻ curves is very similar to that predicted on the basis of equal vibrational constants for OH⁻ and OH. The synthetic curves are placed with the Q branch origins at 1.83 eV, the value selected as the OH electron affinity by the quality of this fit with the data.

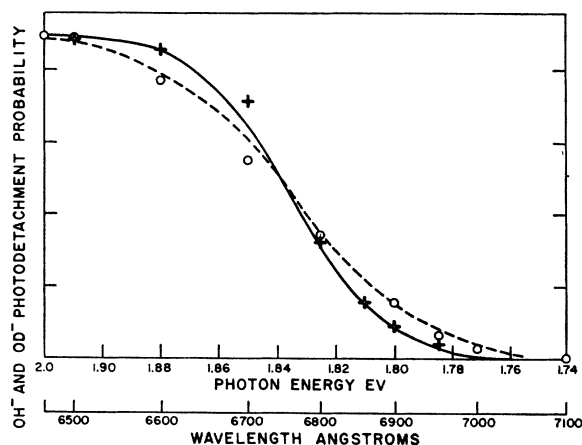
¹¹ P. E. Cade (to be published).¹² L. M. Branscomb and S. J. Smith, Phys. Rev. **98**, 1028 (1955). See also the discussion in Ref. 1, above.

FIG. 10. The synthetic curves of Fig. 9 have been smoothed by a triangular slit function representing the 100 Å resolution typical of most of the data. The solid line refers to OD⁻, the dashed line to OH⁻. For comparison the data of Figs. 5 and 6 are shown averaged—open crosses representing OD⁻ and open circles OH⁻.

these results and the knowledge gained earlier that the calculated spectroscopic constants for all the ground states of the first- and second-row hydrides have a small and systematic trend of percentage errors, Cade has made estimates of the percentage errors for the theoretical OH^- spectroscopic constants. These estimates (in parentheses) are then employed to give "predicted" experimental values for $\text{OH}^- (^1\Sigma^+)$ which are internally consistent with the other hydride calculations and which may be compared with the results of experimental analysis given in this paper. Qualitatively our experiment is in agreement with Cade's prediction that the OH and OH^- ground-state functions are very similar indeed in shape. Both in the case of r_e and ω_e the uncertainties associated with the two methods overlap.

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Electric Dipole Hyperpolarizabilities for S-State Atoms and Ions*

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Electric dipole hyperpolarizabilities are calculated for a large number of 2- to 20-electron *S*-state atoms and ions. The calculations are carried out within the framework of a Hartree-Fock perturbation procedure. This approximation is developed to high order and it is shown explicitly that the total Hartree-Fock energy is obtained to fifth-order from a knowledge of the Fock orbitals to second-order. The first- and second-order coupled Hartree-Fock orbital equations are "uncoupled" in a direct manner and the resulting approximate equations solved by minimizing associated one-electron functionals. The resulting hyperpolarizabilities for the He, Ne, and Ar series are all positive. The calculated values for the inert gases agree with experiment within a factor of two. Some of the high *Z* hyperpolarizabilities for the Na, Mg, and K series are negative, while for the Li and Be series the values are large and positive. These interesting signs are discussed. Finally, it is shown that the hyperpolarizabilities are quite sensitive to the choice of zeroth-order Hartree-Fock function used in the calculation.

I. INTRODUCTION

IN the past, considerable theoretical and experimental effort has been directed toward an understanding of the behavior of atomic systems in external electrostatic fields. In virtually all of this previous work it has been customary to assume a linear dependence relating induced moments to external field strengths and gradients. Thus, for example, in the linear approximation the dipole moment μ induced in an *S*-state atom or ion by an external field of strength F is given by the familiar expression

$$\mu = \alpha F, \quad (1.1)$$

where α is the well-known dipole polarizability. The energy associated with the induction of the moment is

$$\Delta E = -\frac{1}{2}\alpha F^2. \quad (1.2)$$

The linear microscopic relationship Eq. (1.1) leads to the macroscopic Clausius-Mossotti law for the dielectric constant of a nonpolar gas. The validity of this law over a wide range of experimental conditions has been adequately substantiated, a success which may be attributed to the usually small ratio of externally applied field strength to average internal atomic field strength. This small ratio apparently gives rise to a microscopic behavior adequately described by Eq. (1.1). An excellent review article dealing with the calculation of dipole polarizabilities, as well as higher order linear multipole

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