OH\(^-\) and OD\(^-\) threshold photodetachment

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Threshold photodetachment cross sections for OH\(^-\) and OD\(^-\) at photon energies close to their electron binding energies have been obtained using a crossed tunable laser-negative ion beam apparatus at a resolution of 25 \(\mu\)eV. The data reveal many clear features associated with photodetachment of single rotational levels of the negative ion, producing single rotational levels of the neutral and a near zero energy electron. From the frequencies of the observed thresholds, the spectroscopic constants of OH\(^-\) and OD\(^-\) are found. The rotational constants of the vibrational ground state are \(B_0 = 18.7409(45) \text{ cm}^{-1}\) and \(D_0 = 2.052(45) \times 10^{-3}\) \text{ cm}^{-1} for OH\(^-\) and \(B_0 = 9.9852(48) \text{ cm}^{-1}\) and \(D_0 = 0.553(33) \times 10^{-2}\) \text{ cm}^{-1} for OD\(^-\). The electron affinities of OH and OD are measured to be 14 741.03(17) \text{ cm}^{-1} and 14 723.92(30) \text{ cm}^{-1}, respectively. The observed bound-free transitions satisfy selection rules only slightly different from the selection rules observed in bound-bound spectroscopy. The relative intensities of the transitions show the transition from Hund's case (a) to case (b) as the rotation in OH increases. The intensities are in agreement with a theory based on an intermediate complex which dissociates into \(J\)-coupled constituents. The shape of the cross section near threshold, a probe of the long range electron–OH interaction, is found to depend on the final rotational state of the OH neutral. This dependence is studied in detail. Analogous studies on photodetachment of OD\(^-\) confirm our deductions.

I. INTRODUCTION

Negative ion threshold photodetachment spectroscopy is a technique for obtaining three different types of information: (1) energy levels of negative ion and neutral, (2) the shape of the photodetachment cross section near threshold, which probes the longest range interaction between electron and neutral, and (3) the relative intensities of different channels which reveal the relative population in the negative ion states and the photodetachment mechanism. Many species studied by negative ion photodetachment have provided these types of information.\(^{1-6}\)

Although molecular negative ion photodetachment studies yield the same types of information available from atomic ion photodetachment, the existence of rotations and vibrations in molecules implies a need for much higher resolution and better instrumental stability than necessary for atomic negative ion photodetachment studies. This paper describes photodetachment cross section measurements for OH\(^-\) and OD\(^-\) in which transitions between individual rotational states of the negative ion and neutral are resolved.

The photodetachment of OH\(^-\) has a rich history beginning with the pioneering work of Smith and Branscomb in 1955.\(^7\) They measured the photodetachment cross section through the visible with a resolution of 1000 \text{ cm}^{-1}. The energy dependence was obtained by deducing a cross section from the photodetachment signal measured using an arc lamp light source and various filters with different spectral bandpasses. They showed that OH\(^-\) has an onset for photodetachment near 1.78 eV.\(^{7}\)

The spectral resolution was improved to 200 \text{ cm}^{-1} by Branscomb\(^8\) using a monochromator instead of filters. The sharp onset of photodetachment is associated with the electron affinity of OH. The absence of a vibrational progression in the cross section and the near zero isotope shift in the onset for photodetachment lead to the conclusion that the bond distances and vibrational frequencies in the negative ion and neutral are nearly identical. These conclusions were confirmed by Celotta \etal\(^9\) and recently extended by Breyer \etal\(^{10}\) both of whom measured the OH\(^-\) photoelectron kinetic energy distribution when illuminated by light \(-0.6 \text{ eV above threshold}.\)

Threshold photodetachment spectra of OH\(^-\) and OD\(^-\) were obtained with a resolution of 25 \text{ cm}^{-1} by Hotop \etal\(^{11}\). They could not discern structure caused by individual rotational levels, but rather observed structure caused by the piling up of many channel openings. The OH\(^-\) photodetachment spectrum was modeled assuming (1) a thermal rotational population distribution characterized by a temperature of 1500 K, (2) a rotational constant for OH\(^-\) equal to the rotational constant of OH, and (3) the intensity of transitions being proportional to the Hön–London factors. The assumption of a cross section that rises as \(\sigma \sim (E - E_{thr})^{1/4}\) at each new channel opening provided a better fit than \(\sigma \sim (E - E_{thr})^{1/2}\), where \(E = \nu h\) is the photon energy and \(E_{thr}\) is the threshold energy for the photodetachment. This observation suggested that the long range interaction of the detached electron and the OH dipole affects the behavior of the cross section above the threshold. A 100-fold improvement in resolution provided the impetus for this new study of OH\(^-\) threshold photodetachment.

Wigner\(^{12}\) has shown that the shape of the cross section near threshold depends only on the long range interaction between the two final particles, in this case, between the electron and the OH neutral. If such an in-
teraction has an $r^m$ dependence, where $r$ is the electron–neutral separation and $m > 2$, then the photodetachment cross section is dominated by the effect of the $r^m$ centrifugal barrier. Wigner\textsuperscript{12} derived and examined with $m = 2$ that the cross section near threshold then has the form $\sigma = (E - E_{\text{th}})^{1/2}$, where $l$ is the orbital angular momentum of the electron in the continuum. Gaifitis and Damburg\textsuperscript{14,15} extended this work to include a long-range potential $V(r) = -e^2/r^2$, where $e$ is the electron charge and $d$ is the coefficient of the $r^2$ potential. The cross section near threshold then has the form

\begin{equation}
\sigma - (E - E_{\text{th}})^{1/2}, \quad \text{for} \quad (l + 1/2)^2 - 2d > 0, \quad (1a)
\end{equation}

\begin{equation}
\sigma = [\sinh^2(\pi l/2) + \cos(\pi/2) \ln(E - E_{\text{th}}) + \delta]^2, \\
\text{for} \quad (l + 1/2)^2 - 2d \geq -\delta^2 < 0, \quad (1b)
\end{equation}

where $\delta$ is a phase factor sensitive to the short range behavior of the potential. The major question is whether the interaction between the departing electron and the dipolar molecule can be represented by a central $r^2$ attractive potential. Engelsing\textsuperscript{16} has extended this approach and applied it to OH photodetachment. All of these studies\textsuperscript{1,3,6-16} suggest that the cross section near threshold might rise more sharply than $\sigma - (E - E_{\text{th}})^{1/2}$ and the exact shape should depend on the rotational quantum number of the resulting OH molecule.

The relative intensities of different photodetachment channels are predicted\textsuperscript{17} using a model in which the negative ion absorbs a photon producing an LS-coupled excited negative ion complex that subsequently dissociates into its jj-coupled electron and neutral constituents. This theory is in agreement with atomic photodetachment experiments.\textsuperscript{3,6,16} The theory has been extended by Walker\textsuperscript{18} to the photodetachment of molecules initially in a $^1S$ state and in a final state described by the Hund's case (a), case (b), or intermediate case coupling scheme. Walker\textsuperscript{18} made predictions of the photoelectron spectra for HF, OH, SH, and SeH. Janousek and Brauman\textsuperscript{19} found that their threshold photodetachment spectrum of SH could be accurately modeled using Walker's predictions.\textsuperscript{15} Breyer et al.\textsuperscript{20} obtained the photoelectron spectra of SH and OH, both of which are in qualitative agreement with Walker's predictions.

This paper describes the OH and OD photodetachment spectroscopy experiment in which transitions between rotational states of the negative ion and neutral are resolved. Modifications to the apparatus important for obtaining the high resolution spectra are described in the experimental section. A spectroscopy section is included as a guide to the energy levels of OH(OD) and OH(OD). The photodetachment spectra are presented in the results and analysis section. The analysis consists of associating the observed transitions with the rotational states of the negative ion and neutral and obtaining electron affinities and rotational constants from the frequencies of the observed transitions. The discussion is divided into three sections: the first on the energy levels of OH and OD, the second on selection rules in photodetachment and the relative intensities of new channel openings in the photodetachment, and the third on the shape of the cross section above threshold.

![FIG. 1. Schematic of the OH(OD) ion beam source. Electron impact on 0.5 Torr H$_2$O$_2$(D$_2$O) produced ~100 pA of the negative ion.](image)

II. EXPERIMENT

The threshold photodetachment apparatus has been described in detail previously.\textsuperscript{17,21} Only a brief description emphasizing the differences from previous experiments is given here. The OH$^-$ ions are produced in a hot cathode discharge source and accelerated to 420 eV. The ions are mass selected using a 90° sector magnet with a resolution of 40 and focused into the interaction region. There they are crossed at 90° by tunable laser light. Only a small fraction ($< 10^3$) of the ions photodetach. Those ions which are not photodetached are deflected by an electrostatic analyzer and enter a Faraday cup. The ion beam current is measured and used for normalization of the signal. The electrons produced in the photodetachment, if they have less than ~50 meV of kinetic energy in the laboratory frame, are collected and counted. The number of electrons divided by the laser power and the ion beam current is called the electron signal. The experiment is controlled from a PDP-8 computer, which also collects the data.

The hot cathode discharge source used to produce OH$^-$ and OD$^-$ is shown schematically in Fig. 1. It consists of a discharge region and a drift region from which ions are extracted into a 10$^4$ Torr vacuum. In the discharge region, 1 mA of electrons from a thoriated iridium filament impinges on 0.5 Torr of H$_2$O$_2$, producing OH by dissociative attachment. Two grids and a differential pumping wall with an aperture have potentials applied such that an electric field of ~15 V/cm causes OH$^-$ to drift toward the 0.5 mm aperture while being cooled by collisions. A 70 V/cm field is used to extract the negative ions from the source. This source produces a stable, relatively cool 50–100 pA beam of OH$^-$.

The laser is a modified Spectra-Physics model 375 dye laser with rhodamine 640 dye pumped by 2.5 W of 514 nm light from an argon-ion laser. The cavity of the dye laser is extended to approximately 1 m long\textsuperscript{22} and includes the interaction region. The circulating laser power in the cavity is ~30 W. A relative measurement of the laser power is made by measuring the amount of light transmitted through the reflector at one end of the cavity. To account for the frequency dependence of the reflector transmission, the apparent O$^-$ photodetachment spectrum is obtained. Dividing the
OH$^-$ signal by the O$^+$ signal (the O$^+$ cross section is known to be constant$^{24}$) gives an OH$^-$ photodetachment cross section corrected for any frequency dependence in the reflector transmission. Since we are only interested in small energy intervals near threshold, this procedure is adequate and produces only a small correction. The frequency of the dye laser light is determined with an absolute accuracy of about half the linewidth using a traveling interferometer developed by Lee and Hall. $^{25}$

The major improvements over previous OH$^-$ photodetachment experiments are the cooler, more stable ion source, and the cw intracavity laser which result in higher signal to noise and higher resolution. The signal-to-noise ratio is limited by shot noise, errors in ion current and laser power measurements, and changes in the ion beam–laser overlap. Typically, a signal to noise of 200 is obtained for 15 s integration periods. The laser linewidth is set to either 0.35 or 0.1 cm$^{-1}$ by placing different etalons in the laser cavity. The resolution of the apparatus is also limited by Doppler width coming from angular divergence of the ion beam ($\approx 2, 5^\circ$). The Doppler width is expected to be 0.13 cm$^{-1}$. The overall resolution has been measured in experiments on C$_2$H$_2$ photodetachment$^{22}$ to be 0.4 and 0.2 cm$^{-1}$ for the two different etalons, consistent with the above estimates.

III. OH AND OH$^-$ SPECTROSCOPY

In this section, energy level diagrams for OH and OH$^-$ ground states are given and expectations for OH$^-$ photodetachment are discussed. Similar considerations apply to OD$^-$ photodetachment. OH$^-$ photodetachment in the past has provided approximate values for the spectroscopic constants. $^{8-11}$ On the other hand, OH spectroscopy has been studied at high resolution in the visible, infrared, and microwave regions of the spectrum. Coxon$^{23}$ has merged the results from the different spectra in order to obtain the energy levels and accurate spectroscopic constants for OH.

Figure 2 shows energy level diagrams for the ground vibrational states of OH and OH$^-$.

The rotational structure in OH$^-$ is simple because the ground state ($^2\Sigma^+$) has no electronic angular momentum. Rotational structure of OH is complicated by orbital and spin angular momentum in the $^2\Pi$ states. The total angular momentum of OH is the sum of rotational and orbital angular momenta and electronic spin. Spin–orbit coupling gives rise to the two fine structure components $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$, each with their own manifold of rotational states. In addition, orbit–rotation (as well as spin–orbit) interactions lift the degeneracy of levels with electronic angular momenta pointing in opposite directions. $^{27}$

These $\Lambda$-doubling splittings in OH are shown in Fig. 2 exaggerated by a factor of 50. For a given rotational level, the $\Lambda$-doubling states have opposite parity. Typically, increasing the angular momentum quantum number $J$ by one exchanges the ordering of the two parity components. In OH this is true except for the $^2\Pi_{1/2}$ state in going from $J = 7/2$ to $J = 9/2$ (see Fig. 2). $^{28}$

The present experiment, obtaining the OH$^-$ photodetachment spectrum, has a resolution much better than the rotational spacings in the negative ion and neutral. Therefore, the photodetachment spectrum is expected to show photodetachment channel openings caused by transitions from individual rotational states of OH$^-$ to rotational states of OH. In order to label these photodetachment transitions, we adopt the notation used previously$^{10,11}$ based on the changes in the angular momentum neglecting spin: $N = J - S$. $N$ is a good quantum number for OH in a high rotational level, where the electron spin decouples from the rest of the angular momentum, namely Hund's case (b). $^{27}$ For $^1\Sigma^+$ OH$^-$, $N$ is identical to $J$. Transitions from OH$^+$ to OH are then identified by giving (1) the rotational branch, that is the change in the quantum number $N$ upon photodetachment, (2) the fine structure state of the OH produced, and (3) the initial rotational quantum number $J^\prime$ of the OH$^+$. Photodetachment transitions producing changes in $N$ [$\Delta N = N(OH) - N(OH^+)$] of $-2, -1, 0, +1, +2$ are labeled as $O, P, Q, R$, and $S$ branches, respectively. The letter identifying the branch is followed by either a 1 or a 3 to indicate that the OH produced is either in the $^2\Pi_{1/2}$ or $^2\Pi_{3/2}$ fine structure manifold, respectively. Following this is a number in parentheses giving the rotational quantum number of the OH$^+$. Photodetachment transitions expected in this study from OH$^-$ in $J = 3$ are shown and labeled in Fig. 2.

The unresolved manifold of these transitions cause the photodetachment cross section to have the shape measured by Holop et al.,$^{11}$ shown in Fig. 3. Their interpretation of the spectrum is that the sharp increase in photodetachment at 14,700 cm$^{-1}$ is caused by the pileup of many different rotational thresholds in the Q3 branch.

![Fig. 2. Energy level diagram for OH+ showing rotational fine structure, and \(\Lambda\)-doubling levels. The \(\Lambda\)-doubling splittings have been exaggerated by a factor of 50 so that they can be discerned. The thresholds expected in photodetachment are labeled. See the text for explanation.](http://jcp.aip.org/jcp/figure.jsp)
As in bound-bound spectroscopy, the pileup of many rotational transitions appears in the Q branch. The monotonically increasing photodetachment cross section at lower energies is caused by P branch transitions and at higher energies by R branch transitions. We have reinvestigated a portion of the region shown in Fig. 3 at much higher resolution. The results are shown in the next section.

IV. RESULTS

Figure 4 shows the observed OH\(^-\) photodetachment spectrum between 14300 and 14950 cm\(^{-1}\) with a point spacing of 0.2 cm\(^{-1}\) and a resolution of 0.4 cm\(^{-1}\). The spectra shown in Fig. 4 plot the normalized electron signal as a function of frequency. Since the present arrangement discriminates against electrons with kinetic energies greater than 50 meV, these data are not directly comparable to the low resolution data of Fig. 3. Rather these data emphasize thresholds. Each abrupt rise is in fact associated with the threshold for detachment from a single rotational state of the negative ion, producing a single rotational state of the neutral molecule. The photon energy at such a threshold is the energy difference between the corresponding states of the negative ion and neutral. The transitions are labeled using the scheme described in the previous sections. The number of thresholds observed is large enough that unique assignments of the individual thresholds are readily obtained. It should be noted that in Fig. 4 (1) the zero of electron signal is suppressed to show more clearly the observed structure, (2) the scale for electron signal changes from one figure to the next, (3) the electron signal is not proportional to the photodetachment cross section, because higher energy electrons are discriminated against, but (4) the rise in signal at the opening of a new channel is proportional to the cross section for that transition, because all low energy electrons are detected and counted.

Table 1 gives a list of the clearly resolved channel openings in OH\(^-\) and OD\(^-\), the measured frequencies for the thresholds of those transitions, and the relative intensities for OH\(^-\). The measured frequencies are found by inspecting the highest resolution data obtained for the appropriate transition. Uncertainties in the frequencies are caused by uncertainty in the measured laser frequency and the signal-to-noise level at the threshold. The relative intensities of the transitions are measured 3.5 cm\(^{-1}\) above the threshold. The uncertainty given is that caused by the electron signal measurements. Other uncertainties in measuring the transition intensities arise from the unknown shape of the cross section near threshold and from changes in the ion source conditions causing changes in the negative ion population distribution. Therefore, the measured intensities should be used only to form qualitative conclusions.

From the measured frequencies the spectroscopic constants of OH\(^-\) and OD\(^-\) and the electron affinities of OH and OD are to be obtained. The energies of the states of OH and OD are found in the work of Coxon and co-workers.\(^{24,21}\) For OH\(^-\) and OD\(^-\), the energies of the rotational states in the vibrational ground state relative to the OH ground state have the following form:\(^{27}\)

\[ E = -E.A. + B_{p0}(J + 1) - D_{p0}(J + 1)^2 + H_{p0}(J + 1)^3, \]

where E.A. is the electron affinity of the neutral species and \(B_p\) and \(D_p\) are the rotational constant and centrifugal distortion constant for the vibrational ground state of the negative ion. \(H_p\), the coefficient of the cubic term in the expansion for the rotational energy levels, is assumed to have the same value in OH\(^-\)(OD\(^-\)) as in OH(OD). The cubic term, though small, slightly changes the values of the other spectroscopic constants. To obtain
E. A., $B_0$, and $D_0$, each frequency given in Table I is subtracted from the frequency (energy) of the appropriate OH (OD) final state found in the tables of Refs. 26 and 28. A least squares fit to a second order polynomial in $J(J+1)$ gives the band molecular constants reported in Table II. The electron affinity is defined as the energy difference from the ground state of the negative ion to the ground state of the neutral and should be equal to the threshold frequency of the $R3(0)$ transition given in Table I. On the other hand, a more accurate value for the E. A. consistent with the $R3(0)$ threshold frequency can be obtained using the fitting procedure described. Note that this procedure allows a measurement of the electron affinity even when the $R3(0)$ transition is not observed (e.g., in OD$^-$).

The error bars on $B_0$ and $D_0$ given are two standard deviations based on the statistics of the fit. These
TABLE I. OH$^-$ and OD$^-$ photodetachment threshold assignments, frequencies, and intensities. Numbers in parenthesis are two standard deviation uncertainties in the last digits. All the frequencies are used in the fit to obtain the spectroscopic constants given in Table II. Relative intensities are measured 3.5 cm$^{-1}$ above threshold. Intensities for OD$^-$ were not measured as the quality of the data was not as high as for OH$^-$.  

<table>
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<th>Assignment</th>
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<th>OD$^-$ thresholds</th>
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<tr>
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<td>frequency (cm$^{-1}$)</td>
<td>Relative intensity</td>
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<td>O3(4)</td>
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<td>R3(3)</td>
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represent 95% confidence limits. Offset errors in the absolute wavelength measured by the traveling interferometer or in the determination of the threshold frequency from the cross section do not affect the values for the rotational constants, but do affect the values of the electron affinities. Therefore, we have added our estimate of possible systematic errors (0.1 cm$^{-1}$ for OH and 0.2 cm$^{-1}$ for OD) to the error bars on the electron affinities. The difference in electron affinities of OH and OD is 17.11 ± 0.23 cm$^{-1}$. The uncertainty is two standard deviations plus possible systematic errors in the absolute wavelength calibration that did not cancel.

TABLE II. Band rotational constants for OH, OH$^-$, OD, and OD$^-$ and the corresponding electron affinities. These values (in cm$^{-1}$) are obtained from a least squares fit to the frequencies given in Table I as described in the text. Errors are 95% confidence limits. Bracketed parameters have been constrained to these values.

<table>
<thead>
<tr>
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<th>OH</th>
<th>OH$^-$</th>
<th>OD</th>
<th>OD$^-$</th>
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<tr>
<td>E.A.</td>
<td>14741.03(17)$^a$</td>
<td>14723.92(30)$^a$</td>
<td>14723.92(30)$^a$</td>
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<td>$B_3$</td>
<td>18.5310$^b$</td>
<td>18.7409(45)$^a$</td>
<td>9.8831$^c$</td>
<td>9.8832(48)$^a$</td>
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<tr>
<td>$D_3$</td>
<td>1.908×10$^{-4}$</td>
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<tr>
<td>$E_3$</td>
<td>1.4×10$^{-7}$</td>
<td>(1.4×10$^{-7}$)</td>
<td>2×10$^{-7}$</td>
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</table>

$^a$This work.  $^b$Reference 26.  $^c$Reference 28.

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FIG. 5. Detail of the OH$^-$ photodetachment spectrum showing the $P3(2)$ threshold for 12 cm$^{-3}$ above threshold. A linearly rising background arising from photodetachment transitions with thresholds at lower energies has been subtracted from the data. Thus, these data give the relative cross section for the transition $OH^+(J''=2)+h\nu \rightarrow OH (X^1\Sigma_g^+, J'=3/2)+e^-$ as a function of photon energy.

In addition to these two separate fits for OH$^-$ and OD$^-$, the results of a composite fit performed to obtain the equilibrium spectroscopic constants are presented in the discussion section.

With the resolution available in this experiment, we can observe the shape of the photodetachment cross section for an individual rotational threshold. To do this, the cross section arising from all the already open, lower energy channels must be subtracted from the observed cross section. This can be done if we assume that the cross section for the open channels does not change abruptly near the new threshold. The cross section for already open channels in the region of threshold for a new channel could change abruptly if (1) there was a resonance in the region of the new channel opening or (2) a Wigner cusp appeared in the already open channels. Resonances have been observed near the threshold for photodetachment of other negative ions. However, there is no indication of any similar structure in this OH$^-$ photodetachment study, nor are resonances expected. OH$^-$ excited states which would cause resonances in the energy region studied are not expected, because (1) unlike negative ions, the negative ions do not have a series of Rydberg states converging on the ionization limits, (2) HF, which is isoelectronic with OH$^-$, has no low lying excited states, and (3) although OH has an appreciable dipole moment, it is not large enough to support a dipole bound state. Wigner cusps have been observed in negative ion photodetachment only when enhanced by a nearby resonance, so cusps are not expected in the photodetachment of OH$^-$. In addition, cusps cannot occur in the lowest energy channel from a given initial state. In OH$^-$ the $O3$ branch, the $P3(2)$, $Q3(1)$, and $R3(0)$ thresholds cannot have Wigner cusps. Thus, the simple procedure of subtracting a linearly rising cross section from the data should be adequate to obtain a state-selected partial cross section.

Figure 5 shows the $P3(2)$ threshold so derived from Fig. 4(c), with scales expanded to show the threshold more clearly. The measured cross section is compared with a function corresponding to the Wigner threshold law $\sigma = (E - E_{th})^{1/2}$ convolved with the resolution of the apparatus. By comparison, the actual cross section looks almost like a step function and is showing the influence of a long range electron–dipole interaction. With twice the resolution (0.2 cm$^{-3}$), some of the rise of the $P3(2)$ threshold can be resolved (see Fig. 6). The cross section is distinctly different from both the Wigner threshold law and a step function at this resolution. The implications of this measurement will be discussed in the next section.

V. DISCUSSION

The three types of information to be extracted from the OH$^-$ and OD$^-$ photodetachment spectra are: (1) energy levels and spectroscopic constants of the ions, (2) photodetachment selection and propensity rules, and (3) electron–polar molecule dynamics. The spectroscopic analysis gives directly the values for the electron affinities of OH and OD and the rotational parameters $B_r$ and $D_0$ of the $v=0$ level of OH$^-$ and OD$^-$. Then, a model must be employed to obtain the vibrational frequency of the negative ion. This model and the isotope shift of the electron affinity are discussed. Second, many possible thresholds do not appear in the spectra. The absence of those thresholds reveals selection rules for photodetachment that arise from conservation of angular momentum and parity. Other thresholds appear only weakly and the strength of the thresholds depends on rotational state. This is a result of the angular momentum coupling in OH changing from Hund’s case (a) to case (b) with increasing rotation. Third, the shape of the cross section probes the longest range interaction between the electron and the neutral. By investigating the shape as a function of OH rotational state, the dynamics is probed.

FIG. 6. More detailed view of the P3(2) threshold than that shown in Fig. 5. Point spacing is 0.06 cm$^{-3}$ at a resolution of 0.2 cm$^{-3}$. The solid line shows a $\sigma = (E - E_{th})^{1/2}$ threshold law convolved with our resolution. It is seen that for an energy range as small as 3 cm$^{-3}$, the cross section rises much more sharply than the Wigner (square root) threshold law.
A. Energy levels

In the past, energy levels for OH and OD have been inferred from modeling of the experimental photodetachment or photoelectron spectra. The absence of the photodetachment process into vibrationally excited product;
\[ \text{OH}^+(X^1\Sigma^+, v = 0) + h\nu \rightarrow \text{OH}(X^2\Pi, v = 1) + e^- \]  
(3)
both in photoelectron and threshold photodetachment studies led to the conclusion of a vertical photodetachment; i.e., the equilibrium bond distances are the same in OH and OH. Recently, Breyer et al. used photoelectron spectroscopy to observe Reaction (3) as a very weak process, indicative of a small change in the equilibrium bond distance. The rotational constant \( B_e \) measured in their experiment is 18.74(15) cm\(^{-1}\), in good agreement with the value we have measured (see Table II). The similarity in bond distance between OH and OH is expected because the highest lying orbital in the molecular negative ion is for the most part an atomic oxygen nonbonding orbital. A calculation at the Hartree–Fock level by Cadé gives nearly identical internuclear separations in OH and OH. A more recent coupled electron pair approximation calculation by Rossmus and Meyer gives a slightly shorter bond distance in OH than in OH and is consistent both in sign and magnitude with the measured values of \( B_e \) in the negative ion and neutral.

In order to obtain more spectroscopic information than given in Table II, a model is used which simultaneously fits the OH and OD photodetachment spectra. The model assumes that the rotational levels of the OH state relative to the OH ground state are given by the formula
\[ E = -E.A.(\text{OH}) + \left( B_e + \frac{1}{2} \alpha_e \right) J(J + 1) - \left( D_e + \frac{1}{2} \beta_e \right) J(J + 1)^2 + \frac{1}{2} \mu_i J(J + 1)^2, \]  
(4)
where the constants are described by Herzberg. Briefly, \( B_e \) is the rotational constant for OH at the minimum of the potential well, \( \alpha_e \) is the first vibrational correction for \( B_e \), \( D_e \) is the equilibrium centrifugal distortion constant, \( \beta_e \) is the first vibrational correction term for \( D_e \), and \( H_e \) is the third term in the expansion for the rotational energy levels. The constants \( B_e \), \( \alpha_e \), \( D_e \), \( \beta_e \), and \( H_e \) for OD can be obtained from the corresponding OH constants by multiplying by the reduced mass ratio \( \left( \mu(\text{OH})/\mu(\text{OD}) \right) \) to some power. The powers for the constants \( B_e \), \( \alpha_e \), \( D_e \), \( \beta_e \), and \( H_e \) are 1, 3/2, 2, 5/2, and 3 respectively. These relationships are remarkably accurate. For instance, the ratio \( B_e(\text{OH})/B_e(\text{OD}) \) is equal to the reduced mass ratio within three parts in 10\(^4\). One also expects approximately this accuracy in the negative ion and therefore can proceed with a fitting routine similar to that described in the previous section. Because the potential curves of OH and OH are similar, it was assumed that \( \beta_e \) and \( H_e \) had the same values in OH and OH, namely, \( \beta_e = -4.2 \times 10^{-4} \) and \( H_e = 1.4 \times 10^{-1} \) cm\(^{-1}\). The results of the fit are five constants, \( B_e(\text{OH}) = 19.127(12), D_e(\text{OH}) = 2.067(38) \times 10^{-3}, \alpha_e(\text{OH}) = 0.773(24), E.A. (\text{OH}) = 14741.02(20) \) cm\(^{-1}\), and the difference in electron affinity of OH and OD, \( \Delta E.A. = E.A.(\text{OH}) - E.A.(\text{OD}) = 17.05(21) \) cm\(^{-1}\). The error bars represent 95% confidence limits. The error bars are twice the statistical standard deviation obtained in the fits, with the exception of E.A.(OH) and \( \Delta E.A. \) to which our estimate of possible systematic errors in the frequency measurement has been added. The spectroscopic constants obtained from this model reproduce the spectroscopic constants found in the individual fits of OH and OD threshold frequencies (see Table II). The larger error bars obtained in this analysis show that the preferred values of E.A.(OH), E.A.(OD), \( \Delta E.A. \), and the rotational constants are those obtained directly from the band analysis.

From the constants \( B_e \) and \( D_e \) one can obtain the equilibrium vibrational frequency \( \omega_e = 2(B_e/D_e)^{1/2} \). This expression is exact for a rotating harmonic oscillator and is found to be accurate to 1 cm\(^{-1}\) for a wide variety of diatomic molecules, including OH and HF (isoelectronic with OH). The value one obtains for OH is \( \omega_e(\text{OH}) = 3600(37) \) cm\(^{-1}\) with the 37 cm\(^{-1}\) error bar being two standard deviations (95% confidence limits). This shows that the OH vibrational frequency is larger than the OH vibrational frequency \( \omega_e(\text{OH}) = 3738 \) cm\(^{-1}\). It is interesting that the bond length is shorter and the vibrational frequency is smaller in the negative ion, though the changes in both bond length and frequency are very small. The equilibrium vibrational frequency found here agrees with \( \omega_e(\text{OH}) = 3604(74) \) obtained by Hotop et al.

This latter determination is based on the measured \( \Delta E.A. \) and assumes no electronic isotopic shift. A value for \( \omega_e(\text{OH}) = 3770(44) \) cm\(^{-1}\) is obtained from a Hartree–Fock SCF calculation, but an \( \omega_e = 3809 \) cm\(^{-1}\) is calculated using a coupled electron pair approximation. Both of these calculations provide much better estimates of the internuclear separation \( r_e \) than of the force constant in the potential well.

It is of interest to consider the reasons for the difference in electron affinities of OH and OD. The important contributions to this difference are (1) rotational energy differences in OH and OD, (2) vibrational zero-point energy differences, (3) an electronic isotope shift arising from the difference in reduced mass of OH and OD, and (4) coupling of electronic and vibrational motion. Many of the expressions for these contributions cannot be evaluated without more theoretical work. For instance, in the Mulliken and Christy Hamiltonian for a \( ^3\Pi \) state energy levels are obtained by ignoring a constant term \( B(L^2) \), where \( \langle L^2 \rangle \) is the average value of the square of the orbital angular momentum. Since the orbital angular momentum quantum number in a molecule is not a good quantum number, the value of \( \langle L^2 \rangle \) can be obtained only by a calculation. Without such a calculation, the difference in electron affinities cannot be accurately predicted, because the unknown terms are approximately the same size as the difference in electron affinities. Some contributions to \( \Delta E.A. \) are easily calculated. A rotational contribution to \( \Delta E.A. \) ignoring the \( B(L^2) \) term was found to be 11.3 cm\(^{-1}\). The vibrational contribution to \( \Delta E.A. \) is another 7.7 ± 5.0 cm\(^{-1}\). These two contributions (21 ± 5 cm\(^{-1}\)) give a \( \Delta E.A. \) in agreement with the measured value of
17.11(23) cm\(^{-1}\). Thus, the other contributions to $\Delta E_A$ cancel to a remarkable extent.

**B. Selection rules and intensities**

Selection rules appear in threshold photodetachment because both angular momentum and parity are conserved. A photon incident on a negative ion produces an intermediate state of opposite parity and with angular momentum which is different by $\pm 1$ or 0. At threshold, the lowest angular momentum barrier appears for an electron that departs in an $s$ wave, which has even parity and 1/2 unit of total (spin) angular momentum. The only photodetachment transitions observed are those expected for an $s$ electron and which conserve both angular momentum and parity, as shown in Fig. 2.

Figure 2 shows transitions occurring only with changes in the angular momentum quantum number of 3/2, 1/2, -1/2, or -3/2 (i.e., $|\Delta J| < 3/2$). In Table I, it is seen that four different branches with four different values of $\Delta J$ are observed, namely O3 branch with $\Delta J = -3/2$, P3 branch with $\Delta J = -1/2$, Q3 branch with $\Delta J = 1/2$, and R3 branch with $\Delta J = 3/2$. (See Sec. III for the labeling scheme.) All of these transitions leave OH in its $^3\Pi_{\delta \gamma}$ state. The corresponding transitions leaving OH in the $^3\Pi_{\delta \gamma}$ state are the P1, Q1, R1, and S1 branches. All except the S1 branch are observed. The threshold frequency of the S1(0) transition is marked in Fig. 4(e), but the large backgrounds in that frequency range and the relative weakness of the S1 branch are two contributing factors for this threshold not being observed. This experiment provides the first observation of the O3 branch and confirms our expectations for the allowed transitions in OH photodetachment.

Parity is conserved in the photodetachment process. As illustrated in Fig. 2, the parity of the OH (or OD) product is the opposite of the parity in the negative ion. Since the two $\Lambda$ doubling states of OH (or OD) have opposite parity, only one of these states is an allowed final state for any particular transition. This is confirmed for the higher rotational states where the $\Lambda$ doubling is larger than the resolution by taking differences of the threshold frequencies given in Table I. Differences in the threshold frequencies for transitions starting in the same OH rotational state give energy differences in the OH molecule. These measured differences can be compared with already known\(^{25}\) energy differences in order to find which of the two $\Lambda$ doubling states is the final state of the photodetachment transition. The only transitions observed both in OH and OD photodetachment are those for which the parity of the initial and final state differ.

The above selection rules are obeyed rigorously only in the region of threshold. As the energy is increased, partial waves other than the lowest angular momentum waves can contribute to the photodetachment process. For what energies the other partial waves become important depends on the system. Photoelectron angular distributions of OH at energies 0.7 eV above the threshold show\(^{25,16}\) a substantial $d$-wave contribution. However, there is no substantial $d$-wave contribution over the range of these data.

The absence of thresholds revealed the selection rules described above. The relative intensity of thresholds can provide additional information on the photodetachment process.\(^{2,13}\) In atomic negative ion photodetachment, the relative intensities are determined by the probability that a negative ion absorbs a photon into an LS-coupled excited negative ion complex which dissociates into its jj-coupled electron–neutral atom state constituents.\(^{5,11}\) The process of resolving the LS-coupled complex into its jj-coupled constituents is called a frame transformation.\(^{17}\)

A similar analysis has been performed on electron detachment from diatomic molecules by Walker and co-workers.\(^{19}\) They assumed that the photoabsorption occurs as a $^2\Sigma - ^1\Pi$ transition, so its intensity is given by the Hön–London factors. The detachment of an electron from the $^1\Pi$ complex gives rise to four possible final states. This was indicated schematically by Janousek and Brauman,\(^{25}\) who modeled their SH\(^+\) photodetachment spectrum. This frame transformation\(^{13,32}\) is valid for Hund’s cases (a), (b), or intermediate between (a) and (b).\(^{24}\) The OH\(^+\) photodetachment spectrum was modeled by Hotop et al.,\(^{15}\) assuming that the angular momenta in OH are described by Hund’s case (b) coupling. Since OH is described better by the intermediate coupling case, we compare the intensities based on the theory of Walker\(^{15}\) with the observed OH\(^+\) photodetachment intensities.

Our method for calculating the intensities of the photodetachment transitions is the same as that used previously.\(^{19,30}\) Explicitly, the intensity of the transition can be written as\(^{35}\)

$$I_{03}(J', J, \Omega') = \left| \sum_{J_1} \langle \Omega_{4\mu'4}, J' | ^1\Pi_{\delta}, J_1 \rangle \langle ^1\Pi_{\delta}, J_1 | ^1\Sigma, J'' \rangle \right|^2. \tag{5}$$

The bra $\langle \Omega_{4\mu'4}, J' |$ is the eigenstate of the final OH + e\(^-\) system and is determined by the quantum numbers $\Omega_{4\mu'4}$, the projection of the OH angular momentum onto the internuclear axis,\(^{35}\) and $J'$, the total angular momentum of the OH. The ket $| ^1\Pi_{\delta}, J'' \rangle$ is the initial state of the OH with rotational quantum number $J''$. The intermediate state $| ^1\Pi_{\delta}, J_1 \rangle$ is allowed by a dipole transition from the ground state and can be projected onto the final OH + e\(^-\) state for $J_1 = J' \pm 1/2$. The first bracket can be calculated by diagonalizing the Hamiltonian for the e\(^-\) + OH system and is just the projection of the e\(^-\) + OH eigenstates onto the $^1\Pi_{\delta}$ basis state (see Table I of Ref. 19). The second bracket is simply the square root of the Hön–London factor.\(^{27}\) One then obtains relative values for the intensities of transitions. It can be shown\(^{28}\) that in this particular case, taking the sum of the squared amplitudes gives the correct result.

Since the strength of specific photodetachment channels is proportional to the unknown population in the initial rotational state, the best method to compare threshold photodetachment intensities is to study the intensity ratios of pairs of channels sharing a common initial state, so that the observed strength is independent of the
initial populations. Table III compares the observed intensity ratios with those predicted by the theory described above. There is reasonably good agreement between the observed and theoretical intensities. One of the more interesting results from the theory is that the $^2\Pi_{1/2}$ final state is favored over the $^2\Pi_{3/2}$ final state by a factor of between about 1 and 2.5, depending on the specific transition. This is in good qualitative agreement\textsuperscript{11} with the ratio of 1.6 observed in the OH\textsuperscript{-} photoelectron spectra of Breyer \textit{et al.}\textsuperscript{16} and is in good qualitative agreement with the present data. Another expectation is that high rotational levels with the OH molecule in Hund's case (b) the ratio of $^2\Pi_{1/2}$ to $^2\Pi_{3/2}$ intensities should approach one. This appears to be the case in our experiment (see Table III) despite some discrepancies with the theory. Discrepancies between the experiment and theory can be caused by a dependence of the shape of the photodetachment cross section near threshold on rotational state. A discussion of the shapes of the threshold cross section is postponed to the next section.

Walker's theory,\textsuperscript{19} which agrees with our experiment, can be used to calculate the OH\textsuperscript{-} rotational population distribution. The experimental photodetachment transition intensities are proportional to the initial state population with a proportionality constant given by Eq. (5). The relative populations can be derived by comparing the intensities of transitions with different initial rotational quantum numbers. If one assumes that the rotational population distribution is a Boltzmann distribution, then a plot of $\ln(I_{\exp}/I_{th}(2J'+1))$ vs $J(J+1)$ should give a straight line with a slope of $-B_J/kT$, where $I_{\exp}$ is the experimentally observed transition intensity, $J'$ is the rotational state of the OH\textsuperscript{-}, $B_J$ is the OH\textsuperscript{-} rotational constant, and $T$ is the rotational temperature of the ions. Such a plot is given in Fig. 7 using the intensities given in Table I for the P3 branch of OH\textsuperscript{-}. This plot shows that the rotational distribution of OH\textsuperscript{-} in the beam is described adequately by a Boltzmann distribution with a temperature of $\sim$ 600 K. Such a temperature is completely consistent with our expectations for this ion source.

C. Electron-OH \textsuperscript{−} dynamics

As mentioned in the Introduction, the longest range forces between the products determine the shape of the threshold cross section.\textsuperscript{11,12} In the absence of potentials falling off as $r^{-2}$ or more slowly (other than the centrifugal potential) the angular momentum of the outgoing electron determines the shape of the cross section. In OH\textsuperscript{+}, the highest occupied orbital is a $\pi$ orbital that looks like an atomic $p$ orbital. An electric dipole transition can occur to the $s$ wave continuum, which in the absence of a molecular dipole gives a cross section of the form $\sigma \sim (E - E_{th})^{1/2}$. Shapes different from this may be expected in OH\textsuperscript{+} photodetachment because there is an anisotropic $r^{-2}$ potential arising from the electron-dipole interaction in the final state.

Since the shape of the cross section depends only on the long-range forces, photodetachment transitions with the same final state should give the same threshold energy dependence.\textsuperscript{12} Figure 8 presents a plot of the P3(2), P3(1), and P3(0) threshold cross sections, showing that the shape of the cross section is the same within experimental error when the final state is OH\textsuperscript{+} $^2\Pi_{3/2}$, $J = 3/2$. This result demonstrates that the initial state of OH\textsuperscript{−} does not influence the shape of the photodetachment cross section in the first 0.3 meV above threshold, insuring that we are observing threshold behavior, and allowing us to use the threshold cross section as a probe for the long range interactions.

It is of interest to consider the time scales, distances, and energies being probed in this OH\textsuperscript{−} photodetachment experiment. The resolution in this experiment is 0.2 cm\textsuperscript{-1} = 25 \mu eV, so this experiment cannot probe potential energies of interaction less than 25 \mu eV. Assuming an interaction caused by an aligned dipole with a moment of 1 D gives a potential energy of 25 \mu eV at a distance
of 300 Å. Thus, distances larger than 300 Å are not probed in this experiment. The amount of time it takes an electron with 25 μeV final kinetic energy to reach 300 Å in a 1 D dipole field is \( 5 \times 10^{-12} \) s. This is slow compared with the period of rotation of OH \( T = 2 \times 10^{-13} \) s/J, where J is the OH rotational quantum number. A 1 meV (8 cm\(^{-1}\)) electron takes \( 10^{-13} \) s to travel 45 Å, where the potential energy is equal to the electron’s excess kinetic energy of 1 meV. Thus, by examining the shape of the threshold cross section for the first few wave numbers above the threshold, the interaction being probed is between an electron and a dipole rotating rapidly on the timescale in which the electron leaves.

Another physically meaningful method of viewing the charge–dipole interactions is by considering the energy levels in the OH molecule and how they are affected by the detached electron. For electron energies below 1 meV, there is no possibility for first order mixing of OH rotational states, because the separation of rotational states is much larger than 1 meV. For a \( ^{1}\Sigma \) ground state this would imply an expectation value for the dipole moment of zero. However, for a molecule that has orbital angular momentum, the near degeneracy of \( \Lambda \) doubling levels with opposite parity produces a dipole moment in an external field in a manner similar to the manner in which the degeneracy of the 2S and 2P states of atomic hydrogen produces a dipole moment. In OH the dipole comes about because the molecule rotates about an axis not perpendicular to the internuclear axis. However, this axis of rotation slowly precesses and the dipole vanishes when averaged over long observation times. This precession causes the two \( \Lambda \) doubling states to be nondegenerate. Therefore, for detached electrons with kinetic energies less than the \( \Lambda \) doubling splitting, the \( \Lambda \) doubling states are not mixed in first order and there is no long range electron–dipole interaction. The threshold cross section shape then is expected to be \( \sigma \sim (E - E_{th})^{1/2} \). On the other hand, for electron kinetic energies larger than the \( \Lambda \) doubling splitting, the first order mixing of \( \Lambda \) doubling states gives rise to a dipole. If the electron kinetic energies are still small enough that mixing of rotational states is unimportant, the threshold cross section shape may be solved using a time independent potential in a close coupling calculation. This approach has been taken by Engeling to derive the threshold law. Since his theory makes a specific prediction on the behavior of the threshold law, a comparison with this experiment can be made.

Figure 6 shows the P3(2) threshold at a resolution (0.2 cm\(^{-1}\)) much larger than the \( \Lambda \) doubling splitting of 0.055 cm\(^{-1}\). The cross section shows clearly the effects of a strong electron–dipole interaction in that it is definitely different from \( \sigma \sim (E - E_{th})^{1/2} \) Wigner behavior and is consistent with the predicted \( \sigma \sim (E - E_{th})^{3/2} \). Though the shape of the cross section is consistent with the dipole theory, the signal-to-noise ratio does not allow a definite conclusion to be made concerning the range of validity of the threshold law. Still, the agreement should be considered support for the close coupling approach used by Engeling.

We now wish to consider the behavior of the threshold cross section when the \( \Lambda \) doubling is well resolved. The P3(9) threshold has a \( \Lambda \) doubling splitting of 3 cm\(^{-1}\), 15 times larger than our resolution. Figure 9 shows the P3(9) threshold with 0.2 cm\(^{-1}\) resolution and a point spacing of 0.05 cm\(^{-1}\). The shape of the threshold, up to the \( \Lambda \) doubling splitting, appears to be in good agreement with a \( (E - E_{th})^{3/2} \) threshold law. This figure should be contrasted with the P3(2) threshold in Fig. 6 where \( \Lambda \) doubling is much smaller than the resolution. With resolution of the \( \Lambda \) doubling states, the longest range interaction between the electron and the OH is a \( 1/r^2 \) interaction that causes the threshold law to be the same as that predicted by Wigner.

The OH molecule

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**FIG. 8.** Threshold cross section shapes for P3(2) (x), Q3 (1) (o), and R3 (0) (a). While starting from different initial states, these transitions all terminate in OH(\( ^{2}\)H\(_{2}\), J = 3/2). Their similarity demonstrates the exclusive importance of final state interactions over this energy range.

**FIG. 9.** Detailed view of the P3(9) threshold showing the threshold energies corresponding to the thresholds for production of the parity allowed and parity forbidden \( \Lambda \) doubling states. A Wigner (square root) threshold law is seen to describe adequately the photodetachment cross section for photon energies such that only one \( \Lambda \) doubling component is accessible.
in the final state of the $P(9)$ transition has a small effective dipole moment,\textsuperscript{39} so only a weak effect of the electron dipole interaction should be expected. This would also lead to a threshold cross section with a square root dependence. The detailed understanding of these two effects awaits experiments at higher resolution and better sensitivity.

VI. CONCLUSION

We have studied the photodetachment of OH$^-$ and OD$^-$ at high resolution in order to understand better the mechanism for molecular negative ion photodetachment. Analysis of the data provides the negative ion energy levels, the relative intensities near each of the many photodetachment transitions, and the shape of the cross section as a function of frequency above threshold.

From the data, energy levels of the OH$^-$ and OD$^-$ ions are obtained. The isotope modeling described in this paper is used to obtain more information than if photodetachment spectra of only OH$^-$ were obtained. From the analysis, the electron affinities of OH and OD are found to be $14.741, 0.05 \pm 0.17$ and $14.723, 0.92 \pm 0.30 \text{ cm}^{-1}$, respectively. The band molecular constants for the negative ions are obtained. In addition, the equilibrium constants from a composite fit of OH$^-$ and OD$^-$ data are found; $B_{e}(\text{OH}^-) = 19.127(12)$, $D_{e}(\text{OH}^-) = 2.067(38) \times 10^{-3}$, $\alpha_e = 0.773(24)$, and $\omega_e = 3860(37) \text{ cm}^{-1}$. Thus, OH$^-(\text{OD}^-)$ has a slightly shorter bond than OH(OD), in agreement with calculations.\textsuperscript{33,34} The negative ion has a slightly smaller vibrational frequency than the neutral. This is an unexpected result because calculations\textsuperscript{33,34} suggested that the reverse was true.

The thresholds appearing in the photodetachment show that the photodetachment selection rules are simply derived from the conservation of angular momentum and parity. The conservation of angular momentum requires that the change in angular momentum quantum number for an $s$-electron detachment is restricted to $\Delta \ell = \pm 3/2$ or $\pm 1/2$. Conservation of parity in OH$^-$ photodetachment restricts the final state to a parity opposite the initial negative ion parity. Intensities of the observed thresholds have been measured and show behavior in accord with the view that the photodetachment process proceeds through an intermediate $\pi^+ \psi$ neutral complex. The agreement between the theory as developed by Walker\textsuperscript{19} and the observed intensity ratios confirm that threshold channel strengths in molecular photodetachment are governed by the same mechanism as in atomic photodetachment. The theory has then been used to determine the rotational population distribution of OH$^-$ emanating from our ion source.

Finally, we have attempted to understand the shape of the photodetachment cross section near threshold. For the charge--dipole interaction with a long-range $1/r^2$ potential, the threshold cross section is definitely sharper than the Wigner threshold law on a $1 \text{ cm}^{-1}$ energy scale. The shape of the cross section predicted using an effective model dipole\textsuperscript{16} is consistent with this experiment. The cross section shape, though independent of the OH$^-$ rotational state, depends on the rotational state of the OH. It is sharper for lower rotational states and more like a square root dependence for higher rotational states. This is in part caused by the resolving of $\Delta$-doubling splitting for higher rotational states. When $\Delta$ doubling is resolved, there is no long-range $1/r^2$ potential and the cross section rises with the Wigner threshold behavior $\sigma \sim (E-E_{th})^{-1/2}$.

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21. There is some confusion because Fig. 1 in the Walker paper (first of Ref. 19) appears to be misdrawn. The two large Q branch peaks should be interchanged.
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