PHOTODETACHMENT THRESHOLD PROCESSES

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INTRODUCTION

The experimental study of the photodetachment process provides an opportunity (via the half-collision concept) to probe low-energy electron-molecule collisions with optical resolution. The experiments described here all measure the interaction of a mass selected negative ion beam with radiation from a tunable laser. Both crossed-beam\(^1\) and colinear-beam\(^2\) geometries are employed with the latter providing a 100-fold increase in resolution to \(10^{-7}\) eV.

In this discussion, we first review earlier studies determining the range of validity of the Wigner\(^3\) threshold laws. We next look at the case of photodetachment from a negative ion, producing a neutral molecule with a permanent dipole moment. Here the molecular dipole moment has the possibility of affecting the ultrahigh (\(10^{-7}\) eV) resolution studies of \(\text{C}_2\)\(_2\) autodetachment lineshapes. In this unusual case, even the hyperfine structure of the \(^{13}\)C species is resolved.

THRESHOLD BEHAVIOR

In 1948, Eugene Wigner derived\(^3\) the form of the photodetachment cross section for energies near threshold. Valid for final states with two particles whose longest range interaction is the centrifugal barrier, his result gives the variation of the cross section with energy as

\[
\sigma \propto k^2 \ell^2 + \frac{1}{2} \alpha E^2 + \frac{1}{2}
\]

where \(\sigma\) is the cross section, \(E\) is the energy of the departing electron (the energy above the minimum required for reaction to occur), and \(k\) and \(\ell\) are the linear and orbital angular momenta of the outgoing electron. The physical origin for this predictable threshold behavior is the variation of the electron's potential energy with distance from the neutral. At threshold, only the longest range potential
matters. Normally, this is simply the \( \ell (\ell + 1)/r^2 \) centrifugal potential. Departures from the law can occur above threshold where shorter range terms in the potential become important, or when forces with the same range as the centrifugal force are active.

The Wigner law is a threshold law, giving the shape of the cross section as the energy of the departing electron approaches zero. A threshold law may be viewed as only the first term of a power series expansion in momentum. The range of validity can be determined only by calculating the next term in the power series or by directly measuring the cross section.

The law is then considered "valid" if the deviation from the law in some energy range is less than some arbitrarily chosen fraction. The effects of a variety of long-range interactions (polarizability, quadrupole moments, resonances) on the range of validity have been investigated both theoretically and experimentally. The Wigner law has been found\(^4\) to hold in Au\(^{17}\) photodetachment over a range of 100 meV with deviations of only a few percent. Extremely rapid breakdown of the law is seen\(^5\) in detachment to the \(^2P_{1/2}\) state of Cs where large deviations from Wigner's are seen only 25 \(\mu\)eV above threshold! This is not to say Wigner's law is incorrect, but rather the condition that \(E\) be taken sufficiently close to zero has not been satisfied. These variations in range of validity complicate the extraction of such constants as electron affinities from data, since the precise functional form of the cross section is not known. One justifiable procedure involves fitting some theoretical form (i.e., the Wigner law) to data sets of successively smaller energy range. For sufficiently small energies, the constants obtained should be invariant to the range of the data. This issue is especially important in cases where the functional form of the threshold law is in doubt, as in OH\(^-\).

**OH\(^-\) THRESHOLD PHOTODETACHMENT**

When potentials with the same range as the \( \ell (\ell + 1)/r^2 \) centrifugal potential are present, the Wigner law may not be valid at all. This result may be of significance for many molecular systems, since the potential between a fixed polar molecule and an electron has a \(1/r^2\) radial dependence. Solution of the radial potential problem provides guidelines for the real system, but it is not completely applicable to molecules because the dipole potential has a \(\cos \theta\) angular dependence and the molecule may be rotating. Gallitis and Damburg\(^6\) and O'Malley\(^7\) extended Wigner's work to include a spherically symmetric long-range potential, \(V(r) = -ed/r^2\),
where $e$ is the electron charge and $d$ is the coefficient of the $r^{-2}$ 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. Engleking has extended this approach and applied it to OH$^-$ photodetachment. All of these studies suggest that the cross section near threshold might rise more sharply than $E^{1/2}$, and the exact shape should depend on the rotational quantum number of the resulting polar molecule.

The most detailed studies of OH$^-$ threshold photodetachment have recently been reported by Schulz et al. This crossed beam study had a resolution (25 $\mu$eV) adequate to resolve individual rotational thresholds and to determine the threshold energy dependence as a function of the product OH rotational state.

From the data, energy levels of the OH$^-$ and OD$^-$ ions are first obtained. The electron affinities of OH and OD were found to be 14741.03 $\pm$ 0.17 cm$^{-1}$ and 14723.92 $\pm$ 0.30 cm$^{-1}$, respectively. In addition, the equilibrium constants from a composite fit of OH$^-$ and OD$^-$ data were found to be: $B_0$(OH$^-$) = 19.127(12) cm$^{-1}$, $D_0$(OH$^-$) = 2.067(38) $\times$ 10$^{-3}$ cm$^{-1}$, $\alpha_0$ = 0.773(24) cm$^{-1}$, and $\omega_0$ = 3680(37) cm$^{-1}$.

With the individual thresholds identified, the shape of an individual rotational threshold could be determined. Close examination of the thresholds shows that the cross-section shape, though independent of the initial OH$^-$ rotational state, depends on the rotational state of the product OH. The energy dependence is sharper for lower rotational states and more like a square root dependence for higher rotational states. These effects take place over an energy interval less than 1 meV. This behavior is qualitatively consistent with the notion of the dipole averaging out for high rotational levels. The classical picture is not completely accurate, however. To appreciate this effect, we must consider the origin of the dipole moment.

Dipole moments are only possible for states of mixed parity, because states of definite parity have equal probability density upon inversion through the origin. A first-order dipole moment requires degeneracy of states of opposite parity, or a field strong enough to mix the non-degenerate levels. For electron energies below 1 meV, there is no possibility for first-order mixing of OH rotational states of opposite parity, because the separation of rotational states is much larger than 1 meV. However, for a molecule such as OH that has orbital angular momentum, the near degeneracy of A-doubled levels with opposite parity produces a dipole moment in an external field. For detached electrons with kinetic energies less than the splitting
between levels of opposite parity, the states are not mixed in first order and there is no long-range $1/r^2$ interaction. The threshold cross-section shape then is expected to follow the Wigner law. On the other hand, for electron kinetic energies larger than the splitting of parity states, the first-order mixing of parity states gives rise to a dipole moment. These ideas have been incorporated by Engleking in a close-coupling calculation of the threshold process. Though the shape of the measured cross section is consistent with his 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 Engleking.

ULTRAlIGH RESOLUTION PHOTODETACHMENT

Fundamental limitations of the crossed-beam photodetachment technique preclude resolution much better that one part in $10^5$. The recent advent of coaxial beam techniques has produced an improvement to one part in $10^7$. In fact, this is one of the few methods where subdoppler resolution is obtainable using single-photon spectroscopic techniques. The first study of negative ions using the coaxial beams technique has been of perturbations and autodetachment in $C_7^-$. These experiments take advantage of the earlier $C_7^-$ studies of Herzberg and Lagerqvist and Jones et al. to provide the approximate locations of the autoionization features to be studied in high resolution. The result is a detailed probe of the autoionization mechanism, with resolution of spin-rotation and hyperfine interactions in the autodetachment profiles. The significance of these results will be briefly discussed in this seminar.

ACKNOWLEDGMENTS

Work reported here was supported by NSF Grants CHE 78-18424 and PHYS 79-04928.

REFERENCES
