

Observation of Dipole-Bound States of Negative Ions

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High-resolution threshold photodetachment of $\text{H}_2\text{C-CHO}^-$ has resulted in the observation of ~ 50 narrow resonances (some < 20 MHz full width at half maximum). These resonances are due to autodetachment from a diffuse negative-ion complex consisting of an electron weakly bound ($\sim 5 \text{ cm}^{-1}$) by the dipolar electric field of the neutral. Electric fields of $< 70 \text{ V/cm}$ are adequate to detach the electron from the lower (bound) levels where autodetachment is not possible. Such states should exist for all neutrals with dipole moments greater than about 2 D.

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An electron bound by the dipolar field of a molecule has been discussed many times in the past few decades. The first theoretical study¹ dealt with the binding of an electron by a proton and negative meson. It was found that the minimum dipole field required to bind an electron was $0.639ea_0$ (1.625 D). The energy levels in this field were calculated by Wallis, Herman, and Milnes² and subsequently rediscovered³⁻⁷ by others. Later calculations showed that inclusion of rotation⁸⁻¹⁰ increases the dipole moment required to bind an electron, and reduces the number of bound states (infinite in the nonrotating model) to only a few. Using pseudopotential techniques, Garrett^{11,12} has calculated binding energies for real molecules. He finds that all molecules with sufficient dipole moments (≥ 2 D) exhibit states bound by less than 100 cm^{-1} . The electron is bound in a diffuse orbital ($\sim 100 \text{ \AA}$) and only weakly perturbs the core, much like ordinary Rydberg states.

Experimental evidence for either this critical dipole moment or such diffuse states has been indirect. While electron scattering experiments have shown strong resonances^{13,14} related to negative-ion states, the best evidence concerning dipole-bound states of negative ions arises from photodetachment studies. For a dipolar molecule whose strength is *less* than the critical value (e.g., OH), the shape of the OH^- threshold photodetachment cross section is modified¹⁵ by the OH dipole field, but dipole bound states are not found, nor are they expected. The best evidence for dipole bound states comes from experiments of Brauman and co-workers, who have seen¹⁶⁻¹⁸ broad ($\sim 50 \text{ cm}^{-1}$) resonances in photodetachment in a class of highly polar organic molecules called enolates. Because these resonances appear near the threshold for direct photodetachment, they attribute them to a slightly unbound dipole-supported state, although

they could not eliminate the possibility that it was slightly bound. They also carried out electronic structure calculations¹⁹ which support their characterization of the resonances as arising from dipole-supported states. With an effective experimental resolution¹⁸ of $\sim 10 \text{ cm}^{-1}$, the properties of the state producing the resonances were largely inferred.

The expected properties of dipole bound states of negative ions can thus be summarized as follows: (1) The electron should be in diffuse orbital, only weakly perturbing the neutral core. (2) There should be at least one (perhaps several) such states bound by $0-100 \text{ cm}^{-1}$ for molecules with $\mu \geq 2$ D. (3) There should be no such states for $\mu \leq 2$ D.

While many molecules are expected to support dipole-bound states, the straightforward study of dipole-bound states with optical resolution requires a few fortuitous circumstances. The dipole-bound state must be optically accessible from a bound negative-ion state, and the excitation energy should allow the use of convenient tunable laser technology. Acetaldehyde enolate ($\text{H}_2\text{C-CHO}^-$) fulfills these requirements, with an electron affinity of 1.8 eV^{18,20} and a dipole moment greater than 3 D.^{19,21}

In this Letter, we report a high-resolution (< 20 MHz) study of threshold photodetachment resonances of the acetaldehyde enolate negative ion. From these measurements, we show that the resonances are due to autodetachment from a weakly bound (5 cm^{-1}) state. The bound levels are readily electric field detached, indicating that the electron is in a diffuse orbital. The structure of the upper state is found to be very similar to the structure of the neutral radical.²²

The photodetachment apparatus has been described in detail in an earlier paper²³ and is reviewed here only briefly. An ~ 2 -nA beam of acetaldehyde enolate negative ions is formed by ex-

traction of the ions from a hot cathode electric discharge containing acetaldehyde ($\text{H}_3\text{O}-\text{CHO}$) and carbon monoxide, mass selection with a 90° sector magnet, and acceleration to 3 keV. The ion beam is then merged with the laser beam (200 mW cw, single mode) over a 30-cm path by means of electrostatic quadrupole deflectors. Following the interaction region, the remaining ions and photodetached neutrals are separated in a transverse electric field. The fast neutrals that are produced in the photodetachment process strike a glass plate and produce secondary electrons, which are then detected by an electron multiplier and counted. This neutral signal is related to the total photodetachment cross section. Simultaneous measurement of the ion beam current, laser power, and laser wavelength permit determination of the relative photodetachment cross section.

The photodetached electrons that are produced with very low energy relative to the neutral (threshold electrons) are collected²⁴ with a weak solenoidal magnetic field (approximately 2 G), and counted with a particle counter, giving rise to the threshold electron signal. Electrons that are produced with more than approximately 20 cm^{-1} excess energy spiral out of the solenoidal field and are not collected. For these experiments, the laser frequency was scanned, and its wavelength was monitored with a λ meter.²⁵ The sub-Doppler resolution of 20 MHz was limited by the residual velocity spread in the ion beam. Data shown here were obtained with an

integration time of 1 s per point, with a typical count rate of $\sim 10^5$ Hz.

Figure 1 is a low-resolution ($\sim 1\text{ cm}^{-1}$) view of a 200-cm^{-1} segment of the acetaldehyde enolate threshold electron signal in the vicinity of threshold. The peak near 14725 cm^{-1} in the *threshold* cross section is related to the broad resonance in the *total* cross section reported by Brauman and co-workers.¹⁶⁻¹⁸ The gross structural features arise from the superposition of some 10^4 unresolved individual rotational cross sections, each contributing to the cross section above its respective threshold. Detailed analysis of this structure and structure at other excited vibrational state thresholds will be the subject of a subsequent publication.²⁴ Of importance in this Letter is a series of small "spikes" in the cross section near 14700 cm^{-1} . These spikes are confirmed dramatically in $1000\times$ higher resolution, a typical example being shown in Fig. 2. There are approximately 50 such spikes in the entire spectrum, contained within a 20 cm^{-1} range. The paucity of features, coupled with the fact that the varying widths of the peaks enables one to pick out common upper levels, allows a straightforward assignment of quantum states. The features displayed in the upper trace of Fig. 2 (from the essentially electric-field-free electron collection system) correspond to a series of transitions to an excited state of the negative ion with $N' = 3, 4, 5, 6$ and $K' = 1$, followed by autodetachment to states of the neutral plus continuum electron. This two-step

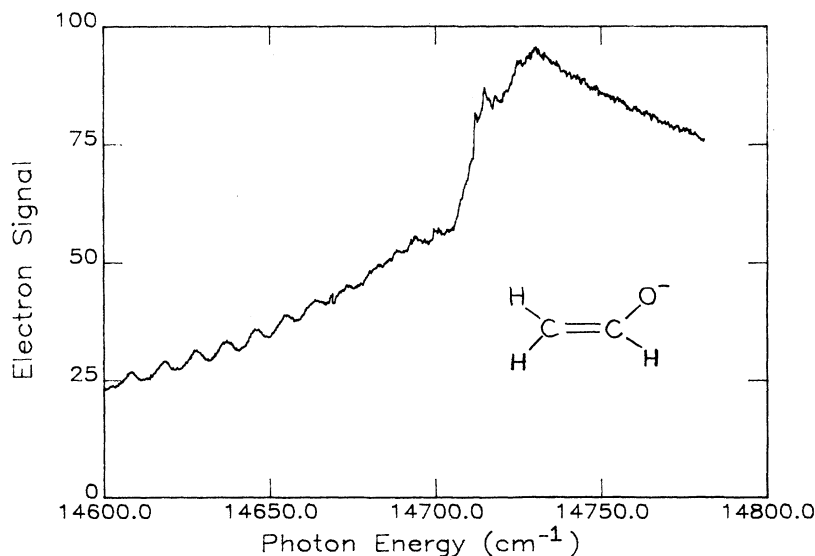


FIG. 1. Low-resolution scan ($\sim 1\text{ cm}^{-1}$) of the threshold photodetachment spectrum of acetaldehyde enolate anion. Only about 20 cm^{-1} centered around 14700 cm^{-1} contains unresolved structure. The structure of the anion is shown at the right.

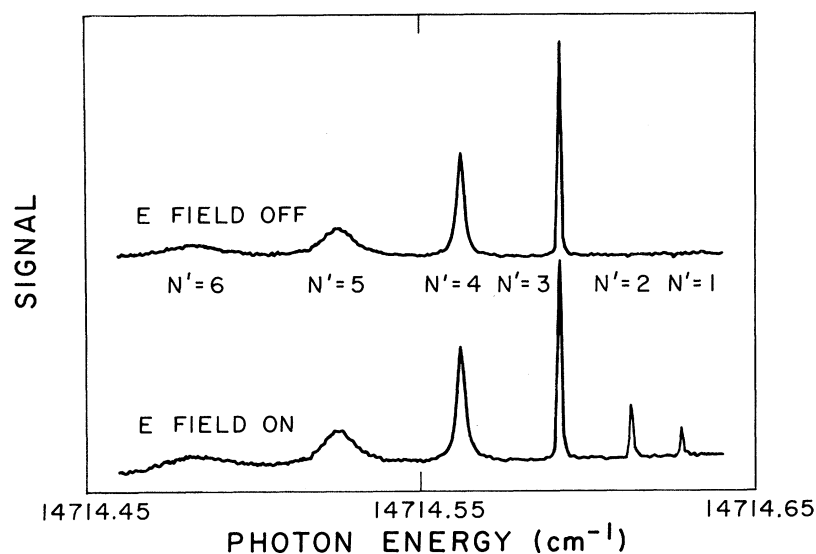


FIG. 2. High-resolution scans of a small part of the spectrum shown in Fig. 1. The upper trace (electron collector) has no field applied before the detector, while the lower trace (neutral detector) shows data where a 70 V/cm electric field was applied between excitation and detection. The numbers near each peak correspond to the rotational quantum number of the dipole-bound state. The peaks corresponding to $N' = 1, 2, 3$ are machine-resolution limited.

process is shown schematically in Fig. 3. Rotational levels higher than $N' = 7$ are too broad to be distinguished from the background, and $N' = 2$ and $N' = 1$ are not observed because they are bound. The rotational angular momentum of the molecule is designated by N , while K is the component of the angular momentum along the axis with the smallest moment of inertia.

Application of a transverse electric field to separate the ions and neutrals after excitation to the dipole-bound state causes the $N' = 1$ and $N' = 2$ levels to field detach, and so transitions to these levels may be seen in the neutral-detector signal shown in the lower trace of Fig. 2. Similarly, levels with $K' = 0$ and $N' = 0, 1, 2, 3$ are observable only with field detachment, but higher levels may be seen without an external field. The fields required to detach electrons from the dipole-bound state are quite weak; an upper bound of 70 V/cm was established for the lowest ($N' = 0, K' = 0$) state. The rapid detachment of these levels in weak electric fields conclusively demonstrates the diffuse nature of this state.

The positions of all of the resonances are fitted to within 0.01 cm^{-1} (the random error in wavelength measurement) by a model²⁴ of a ${}^2A'' \leftarrow {}^2A'$ transition for a near-prolate asymmetric top. The electronic term energy is found to be $14712.74(5) \text{ cm}^{-1}$ and the rotational constants of both states are determined²⁴ to better than 0.006 cm^{-1} . The rotational constants yield the moments of inertia of the upper (negative-ion) state. They are essentially

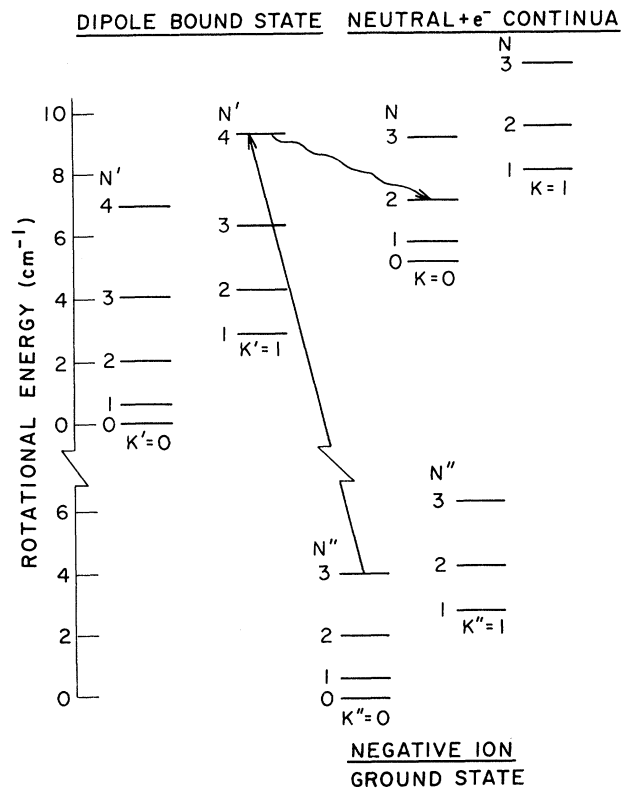


FIG. 3. Simplified energy-level diagram for the system studied. The straight vertical line corresponds to absorption of one photon and optical selection rules (Ref. 26) are in effect. The wavy line corresponds to autodetachment from the dipole-bound state. The asymmetry doublings for this near-prolate symmetric top are not shown in this figure.

identical to those known²² for the neutral molecule, confirming the weakly interacting nature of the extra electron. Finally, lack of autodetachment²⁴ from some low-rotational levels of the upper state shows that it is bound by about 5 cm^{-1} . Thus the upper $^2A''$ state meets all of the tests for a dipole-bound state.

We have now observed similar threshold resonances in several other molecules (e.g., FeO) with large dipole moments. Taken together with the detailed investigation of the CH_2CHO^- excited state reported here, there can be no doubt that this excited state is in fact a dipole-bound state. Such states are to be expected for all neutrals with dipole moments $\geq 2 \text{ D}$.

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