

Dipole-bound anions of highly polar molecules: Ethylene carbonate and vinylene carbonate

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Results of experimental and theoretical studies of dipole-bound negative ions of the highly polar molecules ethylene carbonate (EC, $C_3H_4O_3$, $\mu = 5.35$ D) and vinylene carbonate (VC, $C_3H_2O_3$, $\mu = 4.55$ D) are presented. These negative ions are prepared in Rydberg electron transfer (RET) reactions in which rubidium (Rb) atoms, excited to ns or nd Rydberg states, collide with EC or VC molecules to produce EC^- or VC^- ions. In both cases ions are produced only when the Rb atoms are excited to states described by a relatively narrow range of effective principal quantum numbers, n^* ; the greatest yields of EC^- and VC^- are obtained for $n_{\max}^* = 9.0 \pm 0.5$ and 11.6 ± 0.5 , respectively. Charge transfer from low-lying Rydberg states of Rb is characteristic of a large excess electron binding energy (E_b) of the neutral parent; employing the previously derived empirical relationship $E_b = 23/n_{\max}^{*2.8}$ eV, the electron binding energies are estimated to be 49 ± 8 meV for EC and 24 ± 3 meV for VC. Electron photodetachment studies of EC^- show that the excess electron is bound by 49 ± 5 meV, in excellent agreement with the RET results, lending credibility to the empirical relationship between E_b and n_{\max}^* . Vertical electron affinities for EC and VC are computed employing aug-cc-pVDZ atom-centered basis sets supplemented with a ($5s5p$) set of diffuse Gaussian primitives to support the dipole-bound electron; at the CCSD(T) level of theory the computed electron affinities are 40.9 and 20.1 meV for EC and VC, respectively. © 2004 American Institute of Physics. [DOI: 10.1063/1.1629669]

I. INTRODUCTION

Many recent experimental studies have confirmed previous theoretical predictions^{1–6} that molecules with dipole moments above 2.5 D may form what are generally described as dipole-bound anions. Three recent review articles^{7–9} summarize the considerable experimental progress in this field. The first dipole-bound anion to be observed was CH_3CN^- , which was produced by charge transfer from a rare gas atom in a Rydberg state to the neutral CH_3CN parent.¹⁰ Later work adapted this technique, termed Rydberg electron transfer (RET), to produce dipole-bound anions of several neutral parent species.^{7–9,11} RET typically occurs over a narrow range of effective principal quantum numbers n^* of the Rydberg atom; by contrast, electron transfer from Rydberg atoms to produce “normal” valence-bound molecular anions occurs over a wide range of n^* .

Brauman¹² and Lineberger¹³ observed narrow intense resonances in the photodetachment spectra of the valence-bound anions of several polar molecules; these resonances were located slightly above the photodetachment threshold, and were attributed to rotational autodetachment via dipole-

bound molecular anion states lying in the photodetachment continuum. The experiments showed that molecules which support valence-bound anion states may also exhibit features characteristic of dipole-bound anions. In some cases a dipole-bound anionic state may act as a “doorway” for the formation of a more tightly bound valence anion;^{14,15} in this context, Sommerfeld¹⁶ has recently considered the diabatic coupling terms between dipole-bound and valence-bound negative ion states of nitromethane.

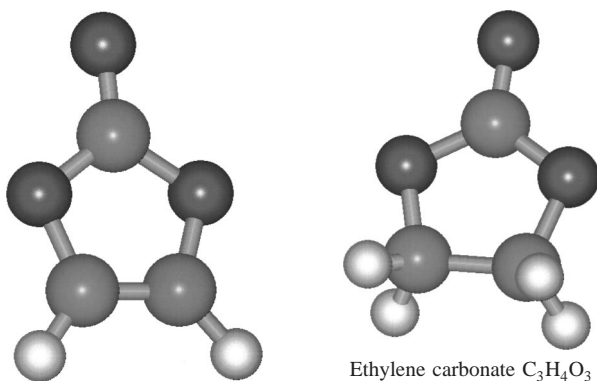
Electron binding energies of both dipole-bound and valence-bound molecular anions can be measured via anion photoelectron spectroscopy; Bowen *et al.*¹⁷ have recorded the photodetachment spectra of ground-state dipole-bound molecular anions that are prepared by crossing a molecular jet expansion with an electron beam. Dipole-bound anion photoelectron spectra exhibit a distinctive spectral signature, with a single narrow peak at low electron binding energy. Excess electron binding energies of dipole-bound anions can also be inferred by detaching the excess electron via application of an electric field,^{7,11} although the possibility that electrons may tunnel through the potential barrier created by an external electric field makes it somewhat complicated to determine accurate electron binding energies via field detachment experiments.

Desfrancois *et al.*⁷ showed that the excess electron bind-

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TABLE I. Dipole moments of vinylene carbonate and ethylene carbonate.



| Vinylene carbonate C ₃ H ₂ O ₃ | | Ethylene carbonate C ₃ H ₄ O ₃ | |
|---|------------------------|---|------------------------|
| Dipole moment (D) | Method | Dipole moment (D) | Method |
| 4.59 | MP2 ^a | 5.39 | MP2 ^a |
| 4.51 ± 0.05 | Microwave ^b | 5.35 ± 0.15 | Microwave ^c |
| 4.45 ± 0.01 | Microwave ^c | | |
| 4.57 ± 0.05 | Microwave ^d | | |

^aThe theoretical dipole moments are from MP2/aug-cc-pVDZ calculations (Refs. 18, 19) using geometries optimized at this level of theory.

^bReference 20.

^cReference 21.

^dReference 22.

^eReference 23.

ing energy E_b of a dipole-bound molecular anion produced via RET can be estimated using the empirical relationship

$$E_b(\text{eV}) = \frac{23}{n_{\text{max}}^* 2.8}, \quad (1)$$

where n_{max}^* is the effective principal quantum number of the Rydberg atom that produces the greatest yield of dipole-bound anions. This method has been recently applied to a large number (27) of molecules possessing dipole moments between 2.5 and 4.3 D.¹¹ The applicability of this relationship to highly polar molecules such as ethylene carbonate (EC, C₃H₄O₃, $\mu = 5.35$ D) and vinylene carbonate (VC, C₃H₂O₃, $\mu = 4.55$ D) is investigated herein. Measured and calculated values of the dipole moments of VC and EC^{18–23} are presented in Table I. The validity of Eq. (1) is confirmed for EC by measuring the electron affinity via anion photoelectron spectroscopy. Theoretical calculations of the electron affinities of EC and VC based on highly correlated electronic structure calculations employing a coupled cluster approach that includes single and double excitations (CCSD)²⁴ and a perturbative estimate of triple excitations, or CCSD(T),^{25,26} and a moderately large atom-centered basis set (aug-cc-pVDZ)¹⁹ supplemented with a (5s5p) set of diffuse Gaussian primitives to support binding of a dipole-bound electron are also presented. All calculations presented in this work were carried out using the GAUSSIAN 98 program.²⁷

Neither EC nor VC appears to support a stable valence-bound anion state. If these molecules are exposed to a low-energy electron beam, they do not form long-lived (lifetimes $t > 1 \mu\text{s}$) valence-bound anions, but rather undergo dissociative electron attachment at electron energies above roughly

0.5 eV.^{28,29} For example, electron attachment to VC generates primarily C₂H₂O[−] and C₂H₂O₂[−] via broad (full width at half maximum roughly 1 eV) dissociative resonances peaking at electron energies of 1.5 ± 0.1 and 3.0 ± 0.2 eV, respectively. Furthermore, studies of fast alkali atom electron transfer to VC show no evidence of a stable parent anion.²⁸ Younkin *et al.*^{30,31} have presented semi-empirical calculations indicating that the ²A₂ and ²B₁ π^* states of VC[−] are unbound by 2.0 and 2.1 eV, respectively; they find no evidence of valence-bound anion states for EC or VC. Since valence-bound molecular anions most likely do not exist for EC and VC the anions produced in the experiments presented herein are true dipole-bound anions.

II. EXPERIMENT

A. Rydberg electron transfer

Crossed beam reactions of excited rubidium atoms with nozzle jet expanded EC and VC were carried out in the source region of a time-of-flight mass spectrometer chamber pumped by a (200 L/s) turbomolecular pump. The background pressure in the chamber was 1×10^{-7} Torr. The alkali atom source was housed in a separate chamber and was also pumped by a separate (75 L/s) turbomolecular pump. The pressure in the flight tube during operation of the experiment was 1×10^{-6} Torr. The output of a tunable OPO laser (Continuum Sunlite) pumped by the third harmonic ($\lambda = 355$ nm) of the fundamental ($\lambda = 1064$ nm) of a Nd:YAG laser (Continuum Powerlite) was used to excite the beam of rubidium atoms to various Rydberg $ns \ ^2S_{1/2}$ and $nd \ ^2D_{5/2,3/2}$ levels via two-photon excitation. The rubidium beam source was held at approximately 180 °C. The absolute wavelength of the pulsed laser was determined to within 0.001 nm with a Burleigh Wavemeter model WA-4500-0. An RM Jordan PSV Pulsed Supersonic Valve (model C-211) was used to pulse a seeded jet of the molecules under study into the region of excited rubidium atoms. The valve was heated to ~ 40 °C in order to minimize clogging the low vapor pressure of EC and VC. The samples were also slightly heated to increase their vapor pressures and the molecules were entrained in ~ 200 Torr of He. After a reaction time of approximately 2 μs the resulting negative ions were extracted with a pulsed electric field of ~ 1000 V/cm and analyzed with a 0.65 m time-of-flight mass spectrometer. The ions were detected using a dual-microchannel plate detector and were displayed on a digital oscilloscope, averaged by a boxcar integrator (Stanford Research Systems model SR250), and recorded by a data acquisition computer program.

B. Anion photoelectron spectroscopy

Negative ion photoelectron spectroscopy was conducted by crossing a mass-selected beam of anions with a fixed-frequency laser beam and energy-analyzing the resultant photodetached electrons. This method is governed by the energy-conserving relationship: $h\nu = \text{EBE} + \text{EKE}$, where $h\nu$ is the photon energy, EBE is the electron binding energy, and EKE is the electron kinetic energy. One knows the photon energy of the experiment, one measures the electron kinetic energy, and then by subtraction, one obtains electron binding

energies, which in effect are the transition energies from the anion to the energetically accessible states of its corresponding neutral. The apparatus employed here has been described elsewhere.³² To prepare EC^- , ethylene carbonate was placed in the stagnation chamber of the nozzle-ion source, heated to a temperature between 70 and 120 °C, and expanded with $\sim 1\text{--}2$ atm of argon through a 23 μm diam nozzle into the high vacuum. There it was intercepted with 30–50 V electrons from a biased Th/Ir filament in the presence of magnetic fields. The resulting negative ions were extracted, and EC^- was then mass-selected with a magnetic sector mass spectrometer having a resolution of ~ 400 . The resulting EC^- beam intensity was $\sim 10 \times 10^{-12}$ A. Electrons were next photodetached from EC^- with visible light from an argon ion laser operating intracavity with a power of ~ 100 circulating watts. During these experiments, EC^- spectra were recorded using the following three photon energies: $h\nu = 2.41, 2.54,$ and 2.71 eV. Lastly, the electrons were energy-analyzed with a magnetically shielded, hemispherical electron energy analyzer having a resolution of ~ 25 meV. Given the goal of making a comparison between the electron affinity predicted by Eq. (1) and that determined by anion photoelectron spectroscopy, it was especially important to obtain a reliable value from the latter. For this reason, we calibrated numerous times with the photoelectron spectra of three different calibrants. These included O^- , whose transitions are unfortunately not close to the peak of the EC^- spectrum; the origin peak ($v''=0 \rightarrow v'=0$) of NO^- , which is extremely close to the EC^- peak, but because it is a molecular transition is broadened by several underlying effects; and Cr^- , whose atomic transitions are not close to the EC^- peak, but which are very narrow and precisely located. Together, these three calibrants gave us our best possible determination for the peak location of EC^- and thus the electron affinity of EC.

III. RESULTS AND DISCUSSION

Using the above-described RET technique, dipole-bound anions of EC and VC were produced via collisions between the neutral precursors and excited $nd\ ^2D_{5/2}$ or $^2D_{3/2}$ Rb atoms. Figure 1 shows how the relative intensities of the dipole-bound product anions depend on the effective principal quantum number n^* of the Rb atom. Similar behavior is observed for collisions with Rb atoms excited to ns states, although the absolute signal intensity is much weaker in this case. For dipole-bound anions with excess electron binding energies below 10 meV, the Rb effective quantum numbers n^* that lead to significant RET typically range from 15 to 50. Because the corresponding Rb excited states are closely spaced in energy, the effective quantum number n_{max}^* that leads to maximum anion production can usually be estimated with little uncertainty. This is not the case for EC and VC, however; in these molecules, RET takes place at lower effective quantum numbers, where the Rydberg levels of Rb are much more widely spaced.

The RET profiles observed in Fig. 1 could be fitted experimentally more exactly by employing an alternative alkali metal, such as cesium, as the electron donor, or by employ-

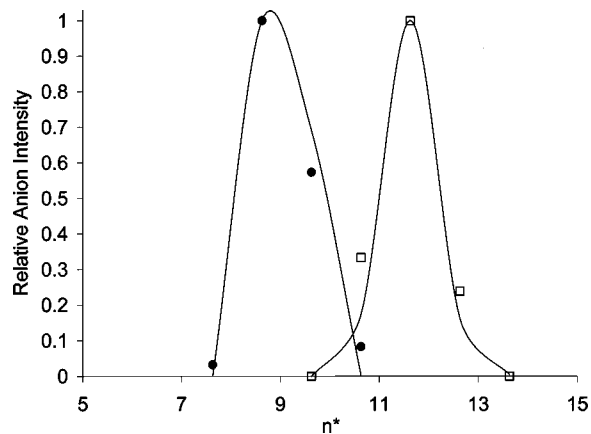


FIG. 1. Relative anion signal for ethylene carbonate (left) and vinylene carbonate (right) as a function of effective Rydberg quantum number n^* (from nd states) of rubidium. The lines through the data are calculated using a previously described curve crossing model.

ing other angular momentum states of Rb. In this study, however, n_{max}^* for EC and VC is estimated by fitting the available data points in Fig. 1 to the curve-crossing model proposed by Desfrancois;³³ the solid lines shown in Fig. 1 are the predictions of this model. The best fit to the experimental data is given by $n_{\text{max}}^* = 9.0$ for EC and 11.6 for VC; from these n_{max}^* values and Eq. (1), the excess electron binding energies of EC^- and VC^- are estimated to be 49 and 24 meV, respectively. An uncertainty of 0.5 in n_{max}^* would correspond to respective uncertainties of 8 and 3 meV in the EC^- and VC^- excess electron binding energies.

Figure 2 depicts the photoelectron spectrum of EC^- . The spectrum is clearly that of a dipole-bound anion: such spectra are typically dominated by a single narrow peak at low electron binding energy. The peak shown in Fig. 2 is very narrow because the structures of EC and EC^- are very similar, so that the Franck–Condon factor for the underlying transition is close to unity. The electron binding energy is therefore obtained from the maximum of this peak (which is very close to the peak centroid) as the adiabatic electron affinity of EC. Using the calibration techniques described previously, the adiabatic electron affinity of EC is determined to be 49 ± 5 meV, in excellent agreement with the

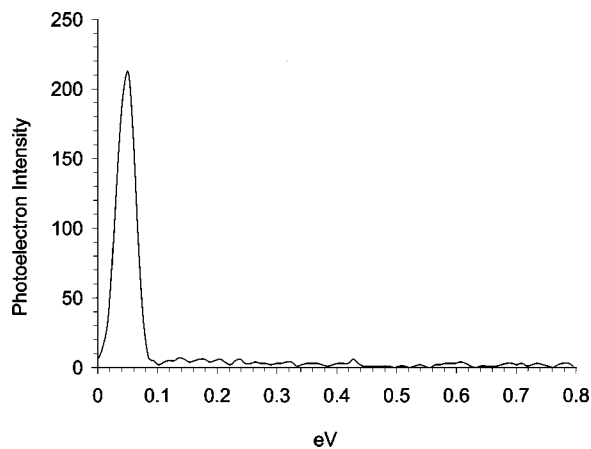


FIG. 2. Photoelectron spectrum of ethylene carbonate negative ion.

TABLE II. Calculated vertical electron affinities (meV) of vinylene carbonate and ethylene carbonate.

| | Vinylene carbonate | Ethylene carbonate |
|--------------------|--------------------|--------------------|
| KT | 11.97 | 23.95 |
| HF | 12.94 | 26.36 |
| MP2 | 15.58 | 31.70 |
| CCSD | 20.43 | 40.43 |
| CCSD(T) | 20.11 | 40.88 |
| Expt. ^a | 24 | 49 |
| Expt. ^b | | 49 |

^aPresent work, using RET method.

^bPresent work, from photodetachment method.

value obtained via RET studies. To provide additional confidence in this value, the photoelectron spectrum was measured using the three photon energies listed earlier in order to guard against possible complications arising from resonant phenomena;³⁴ the same photoelectron spectrum and the same electron binding energy was obtained using all three excitation wavelengths. Repeated efforts were made to obtain the photoelectron spectrum of VC^- , but the VC^- parent ion was never observed in the mass spectrometer. This is not entirely surprising given the relatively low electron binding energy of VC^- ; dipole-bound anions with electron binding energies below 40 meV have never been observed in this particular instrument. This is most likely due to field detachment of weakly bound electrons as the dipole-bound anions traverse the numerous electric fields associated with the ion optics in the apparatus. The absence of weakly bound anions may also be attributed to the process of formation. The dipole-bound anions in these experiments may result from RET from Rydberg states of Ar^{**} atoms excited by electron impact. The highly excited atoms necessary to produce anions of molecules with small dipole moments may not survive the harsh conditions of the discharge.

The vertical electron affinities of EC and VC were computed at various levels of theory: Koopman's theorem (KT), Hartree-Fock (HF), second-order Møller-Plesset (MP2),¹⁸ coupled cluster with single and double excitations (CCSD),²⁴ and CCSD with a perturbative estimate of triple excitations [CCSD(T)].^{25,26} These calculations were performed using the MP2/aug-cc-pVDZ equilibrium geometries of the neutral parent molecules; the HF and post-HF calculations for the anions employed unrestricted HF wave functions. The computed vertical electron affinities are defined as the difference between the total energies of the parent neutral and the anion; the total energies of both species are computed using the aug-cc-pVDZ atom-centered basis set¹⁹ augmented with a (5s5p) set of diffuse Gaussian primitive functions located at a point removed from the molecule, but on the twofold rotational symmetry axis of the molecule. The location of this point was determined by maximizing the electron binding energy at the HF level. The exponents for the (5s5p) primitives were chosen to be 0.000 25, 0.001, 0.004, 0.016, and 0.064 a.u. No significant change in the excess electron binding energies was observed when larger (5s5p1d), (5s5p3d), or (7s7p3d) sets of diffuse functions were used.

The computed excess electron binding energies for EC^-

and VC^- are summarized in Table II. At the highest level of theory employed, CCSD(T), the computed electron binding energies are in reasonably good agreement with experiment. Note that the electron binding energies increase dramatically on going from the KT level of theory to the CCSD(T) level of theory, with a substantial portion of the increase arising from the inclusion of high-order electron correlation effects beyond the MP2 level of theory. This behavior is similar to that observed for several other molecules,^{1,2,11,35-41} and reflects the importance of dispersion-like interactions between the excess electron and the electrons of the neutral parent. Figure 3 shows the charge densities of the molecular orbitals occupied by the excess electron in EC^- and VC^- . The excess electron density for VC^- is nearly spherically symmetric while that for EC^- is more irregular in shape.

The computed excess electron binding energies are roughly 20% lower than the experimentally measured binding energies. A similar discrepancy is observed between the electron affinities computed^{11,35} using techniques similar to those described here and measured¹¹ using RET techniques for a series of alkylnitriles with dipole moments between 3.9 and 4.3 D. The theoretical binding energies presented in

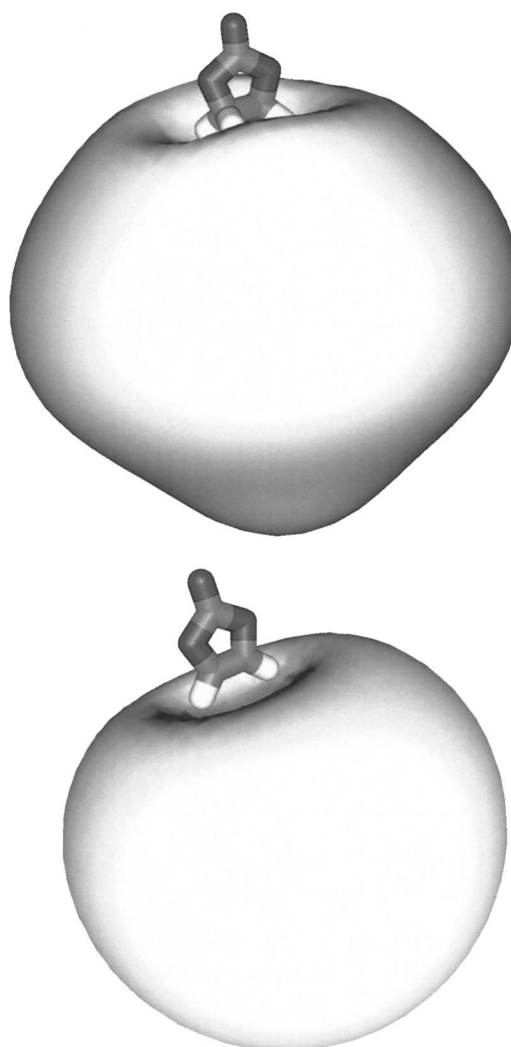


FIG. 3. Charge densities of the dipole-bound molecular orbitals of vinylene carbonate (bottom) and ethylene carbonate (top) using an isosurface of 0.003.

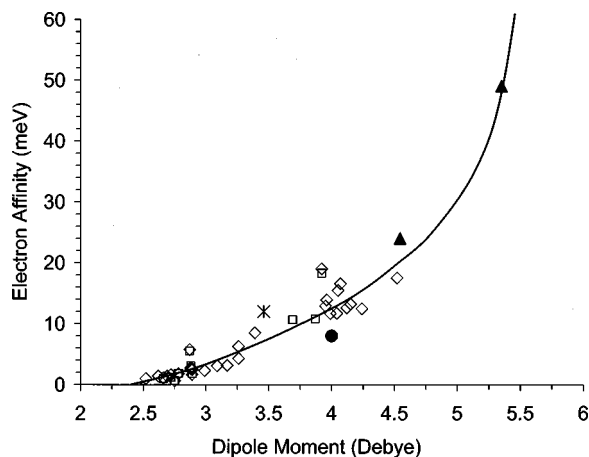


FIG. 4. Electron affinities of a number of dipole-bound anions. The various shapes indicate the source of the measurements: squares (Ref. 7), diamonds (Ref. 11), asterisk (Ref. 14), circle (Ref. 41), and triangles (current work).

Table II are vertical electron affinities, while the RET and photodetachment experiments give adiabatic electron affinities and vertical detachment energies, respectively. A substantial change in molecular geometry following attachment of the dipole-bound electron could thus lead to discrepancies between the computed and measured excess electron binding energies. However, the good agreement between the two experimental measurements for EC, and the structure of the photodetachment spectrum shown in Fig. 2, suggests that the equilibrium geometries of EC and EC^- are very similar, so that nuclear framework relaxation is probably not the source of the discrepancy between the computed and measured electron affinities. Furthermore, framework relaxation effects were explicitly considered in Ref. 34 for CH_3CN and were found to be negligible. It is possible that for highly polar molecules electron correlation effects beyond those recovered at the CCSD(T) level of theory make significant contributions to the excess electron binding energies.

Figure 4 displays a plot of electron affinity as a function of dipole moment for EC and VC in comparison to that for a number of dipole-bound anions^{7,11,14,42} that do not contain stable valence negative ion states. All of the electron affinities were determined by RET and in some cases the RET values were also determined by electric field detachment thresholds. For the most part, the electron affinity (EA) values for the compounds are seen to follow a general trend of increasing EA with dipole moment. We include an arbitrary line which attempts to best describe the general trend of all of the data points for discussion purposes. However, EA values for a number of molecules lie well outside this general trend. Part of this scatter could be due to the fact that the experimental dipole moments for some of these molecules are not accurately known. Other factors that could contribute to the scatter include the importance of permanent moments other than the dipole, contributions from dispersion interactions between the excess electron and the electrons of the molecules, and variations in the “excluded volume” effect from molecule to molecule. The overall trend in the observed EA versus dipole moment lends support for this correlation as a means to estimate the unknown dipole moments of mol-

ecules. As a test of this idea, we have applied this method to estimate the dipole moment of camphor ($C_{10}H_{16}O$). The n_{max}^* for the formation of $C_{10}H_{16}O^-$ is 20.6 ± 0.2 , which gives an electron affinity of 4.8 ± 0.1 meV. Using the very approximate general relationship in Fig. 4 as expressed by the arbitrary line fitting the data, we estimate the dipole moment for camphor to be 3.1 ± 0.3 D. A recent value of the dipole moment for camphor determined from microwave spectroscopy was reported to be 3.08 D.⁴³

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