Coexistence of Solvated Electrons and Solvent Valence Anions in Negatively Charged Acetonitrile Clusters, $(\mathrm{CH_3CN})_n^-$ (n = 10–100)

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(Received 6 February 2003; published 10 October 2003)

Anion photoelectron spectroscopy of acetonitrile cluster anions, $(\mathrm{CH_3CN})_n^-$ (n = 10–100), successfully demonstrates the competitive coexistence of two different anionic species: a solvated electron and a solvent-bound valence anion. The distinctly different nature of these anions is revealed by hole-burning-type photoelectron spectroscopy and relative photodetachment cross section measurements. This unusual coexistence is attributed to the closely lying nature of their anionic states at just the number of solvent molecules sufficient to almost complete the first solvation layer.

DOI: 10.1103/PhysRevLett.91.153002 PACS numbers: 33.80.Eh, 36.40.Wa

Excess electron localization in dielectric media has attracted widespread interest largely because of its fundamental importance in physics and chemistry. In general, two different localized forms of excess electrons are known for dielectric media. One is a solvated electron, e_s^-, in which an excess electron is cooperatively trapped in a cavity formed by several solvent molecules. The other is a solvent-bound valence anion where the excess electron is fully localized on one (or two) solvent molecule(s), i.e., monomer (or dimer) radical anion. The e_s^- is well known to be exclusively formed in liquids, for instance, water, ammonia, and alcohols. On the other hand, valence anions can be produced permanently or temporarily in many organic liquids. Although equilibria of e_s^- with solute anions in nonpolar liquids have been known for a long time [1], cases of *neat* liquids, in which e_s^- and solvent valence anion stably coexist, are rare.

Like water, acetonitrile ($\mathrm{CH_3CN}$) is highly polar and has a large negative vertical electron affinity (EA) in the gas phase. In very early studies [2], it was considered that solvated electrons are produced in both liquid acetonitrile and water. In 1977, however, Bell *et al.* [3] suggested that the exclusive formation of two kinds of valence anions in *neat* liquid acetonitrile: one absorbing in the IR region at 1–2 μm and the other in the visible at 400–800 nm. They assigned the former and the latter species as the monomer and dimer valence anions of $\mathrm{CH_3CN}$, respectively. Very recently, however, this view has had to be revised. Shkrob and Sauer [4] conducted a definitive study on excess electron localization in liquid acetonitrile using pulse radiolysis-transient absorption and time-resolved photoconductivity methods. A second group, led by Xia [5], also studied this system using femtosecond pump-probe spectroscopy. Although different techniques were used by both groups, each reached the same conclusion, namely, that the IR-absorbing species is e_s^- and the visible-absorbing species is the dimer valence anion of $\mathrm{CH_3CN}$.

In the gas phase, acetonitrile cluster anions, $(\mathrm{CH_3CN})_n^-$, have been also studied by many researchers [6–8]. For small clusters, only the odd numbered $(\mathrm{CH_3CN})_n^-$ (n = 3, 5, 7) species are produced by charge transfer collisions between laser-excited xenon Rydberg atoms and clusters [6,7]. From studies on larger clusters, the continuous formation of $(\mathrm{CH_3CN})_n^-$ is reported to begin at $n = 13$ [8]. To our knowledge, however, their excess electron states have not yet been experimentally elucidated. Currently, it is therefore not clear how the excess electron states in finite acetonitrile systems evolve into the two different bulk anionic forms, i.e., e_s^- and dimer valence anion. Elucidation of this point could provide a rationale for the unusual coexistence of e_s^- and valence anion in neat liquid acetonitrile.

In this Letter, anion photoelectron spectroscopy of $(\mathrm{CH_3CN})_n^-$ clusters was used to reveal the binding forms of excess electrons over the range (n = 10–100). Coexistence between solvated electron and valence anion states was discovered for the first time via hole-burning-type photoelectron spectroscopy and relative photodetachment cross section measurements.

The high-pressure pulsed valve described in Ref. [9] was used as a cluster source. Acetonitrile vapors in He carrier gas at 90–110 atm were expanded into vacuum. Cluster anions were produced by the electron impact ionization method. The cluster anions thus formed continue through a skimmer to a linear time-of-flight spectrometer, where a pulsed electric field directs the cluster anions toward a magnetic bottle photoelectron spectrometer [10]. When the target anions reach the magnetic bottle, they are photodetached with 532 nm (2.331 eV) or 355 nm (3.496 eV) of a Nd:YAG laser. In some measurements, the anions were impulsively decelerated so as to minimize the degradation in energy resolution arising from the velocity of the ion beam. The resultant energy resolution was about 50 meV for 1 eV photodetached electrons. The relative photodetachment cross sections were determined by monitoring the fast photoneutral intensities at each photon energy, e.g., 355 nm (3.496 eV) and 266 nm (4.658 eV), versus that at 1.165 eV (or 2.331 eV) for the same ion beam. Note that the fast neutral signal reflects the total electron detachment yield at each wavelength, since photodetachment is the only photoprocess at all wavelengths. In fact, no photofragments such as CH_3 and CN^- were observed in this study. The intensity ratios thus obtained were collected for the relative fluence in each laser beam.

Figure 1 shows photoelectron spectra of $(CH_3CN)_n^-$ with $n = 10$–13, 30, and 100, taken using a photodetachment laser at 355 nm, together with the spectra of $n = 10$–12 taken at 532 nm with deceleration of parent ions. In the 532 nm photodetachment spectra of $n = 10$, a strong narrow peak is observed around 0.43 eV, following a much weaker peak at ~0.8 eV, which is not resolved in the lower energy-resolution spectra at 355 nm. Since the energy spacing between these two peaks is very close to the energy of CH stretching vibrations, we have tentatively assigned the two peaks to the origin-containing peak and to the excitation of C-H stretching modes. A similar assignment is also found in the spectra of $n = 11$ and 12. As shown in Fig. 1, we hereafter denote the two peaks as "band I."

A noticeable change is found in the spectra as the cluster size increases. In $n = 10$, *only* band I is observed. Interestingly, in $n = 11$, another very weak band (denoted by "II") suddenly emerges at much higher energy (~2.4 eV). The relative peak intensities between bands I and II are completely reversed in $n = 13$, and the peak intensity of band II is increased preferentially with the size n. However, band I does *not* completely disappear in much larger clusters, and band I surprisingly survives even to $n > 100$. Indeed, the relative intensities of band I to band II do not change markedly on moving to $n \geq \sim 30$. The vertical detachment energies (VDE)—the energy required to remove the excess electron vertically—of band I shift gradually with increasing cluster size, as do those of band II. Another remarkable feature is the large energy difference between bands I and II. Thus far, the coexistence of two anionic isomers has been reported for several cluster anions such as $(uracil)^-Xe$ [11], $(pyridine)_4^-$ [12], and $(HF)_3^-$ [13], in which the differences between VDEs of the isomers were reported to be ~0.2 eV. For the $(CH_3CN)_n^-$ clusters, however, the differences between VDEs of bands I and II (~1.8 eV at $n = 11$–100) are much larger than in these species. These results illustrate the following three points: (1) Two different anionic forms exist in $(CH_3CN)_n^-$ with $n \geq 11$ and their relative abundances switch drastically in the very narrow size region of $n = 10$–13. (2) A significant energy barrier seemingly exists between the two anion states. (3) The nuclear rearrangement from the corresponding neutral is much larger in the anion state of band II than that of band I.

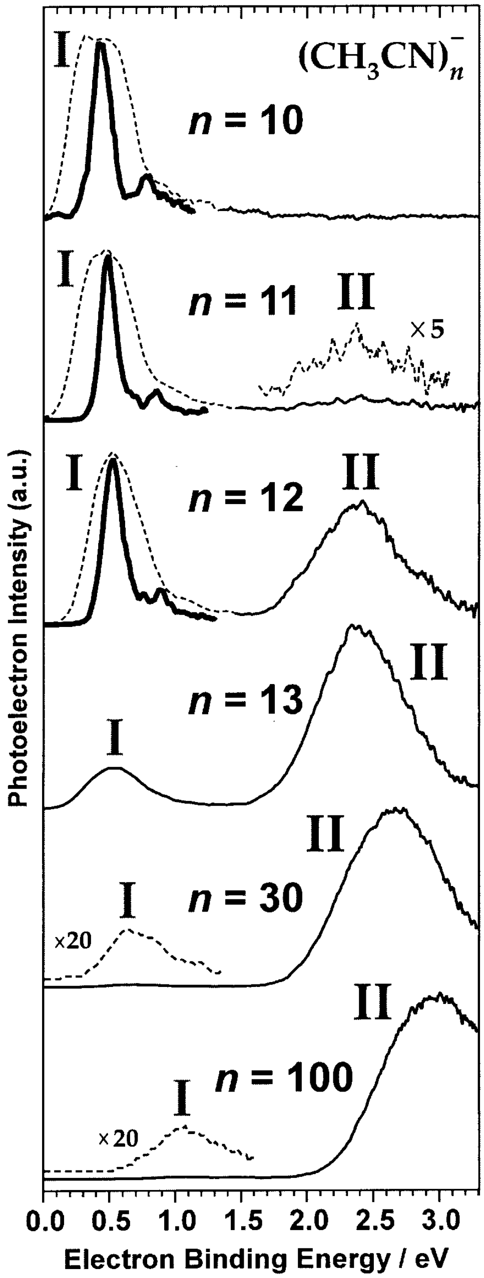

FIG. 1. Photoelectron spectra of $(CH_3CN)_n^-$ ($n = 11$–13, 30, and 100) measured at 355 nm (3.496 eV) without deceleration of parent ions, together with the spectra of $n = 10$–12 taken at 532 nm (2.331 eV) with deceleration of parent ions (thick solid lines). The two anionic forms are labeled as I and II.

To verify these facts experimentally, we performed hole-burning-type photoelectron spectroscopy (HB-PES). Band I (e.g., VDE of $n = 12$ is 0.53 eV) is so widely separated from band II (e.g., VDE of $n = 12$ is 2.38 eV) that the anions yielding band I are selectively photodetached by 1064 nm (1.165 eV). After the photodetachment by 1064 nm, they enter the magnetic bottle and the photoelectron spectrum is measured at 355 nm. The two laser pulses were temporally separated by 5 μs.

Figure 2 shows typical results of HB-PES for $n = 12$ and 13. Complete depletions of band I (only) can be identified for all the cluster anions examined here ($n = 11$–30); a result which decisively confirms that bands I and II originate from different anionic isomers. Besides, it manifests no transformation between two anion isomers *within* 5 μs, which is due to relatively low internal temperatures of cluster anions examined in the current study.

To gain further insight into these two species, we conducted relative photodetachment cross section (PDCS) measurements for bands I and II in the clusters $n = 11$ and 30, respectively. At $n = 11$, band II is almost absent so that only the relative PDCS for band I could be measured. In contrast, at $n = 30$ (see Fig. 1), band II is much more dominant and only the relative PDCS for band II could be measured at $n = 30$. The results are shown in Fig. 3. Even though the threshold detachment region of band I was not examined, it is apparent that the PDCS of band I in $n = 11$ sharply decreases with increasing photon energy. This is clear evidence for diffuse spatial distribution of the excess electron in a cluster. The diffuse spatial distribution is characteristic of a dipole-bound anion [14] and solvated electron clusters [15]. In the case of the dipole-bound anion, for example, the PDCS is evaluated by the dipole matrix element between the wave functions of the dipole-bound electron and the free electron. The wave function of the dipole-bound electron in the ground state spans a much larger volume than that of the neutral core, and has no node. On the other hand, the free electron wave function has nodes which become dense with increasing kinetic energy. Thus, the magnitude of the dipole matrix element has a maximum around the threshold detachment energy and decreases with the photon energy, since the overlap integral is canceled out by the fast oscillation of the free electron wave function [14,15]. Thus, the anion state of band I is assigned to either dipole-bound anion or solvated electron state. In contrast to band I, for $n = 30$, a rapid increase of PDCS with photon energy is found for band II. This dependence is often observed for anions in which the excess electron occupies a valence orbital, that is valence anion [16]. In common with the photoionization cross sections of neutral molecules, this can be attributed to a substantial geometric change between anion and neutral states. Thus, we can expect that the anionic state of band II is a valence anion.

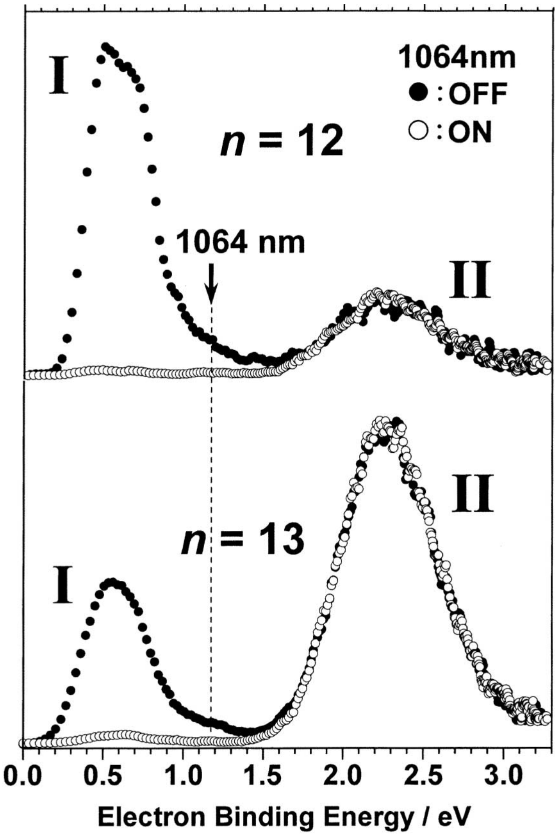

FIG. 2. Photoelectron spectra of $(CH_3CN)_n^-$ with $n = 12$ and 13 measured with (○) and without (●) 1064 nm (1.165 eV) photodetachment prior to the photoelectron measurements at 355 nm. The arrow indicates the maximum electron binding energy accessible with 1064 nm photodetachment.

A very important observation is that band I exists throughout the broad range from $n = 10$–100 and gradually shifts to higher energy with increasing size. This behavior indicates that the anionic state of band I is a

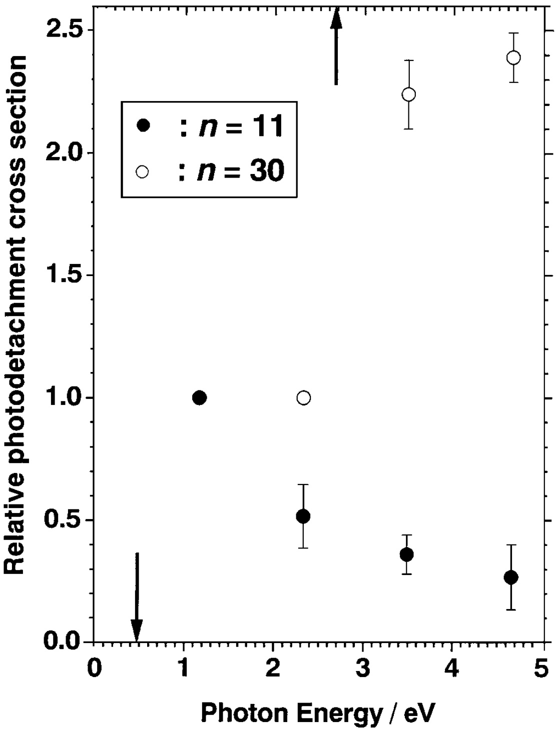

FIG. 3. Relative photodetachment cross sections of $(CH_3CN)_n^-$ with (●) $n = 11$ and (○) 30. The down and up arrows indicate the vertical detachment energies of the band I in $n = 11$ and of the band II in $n = 30$, respectively.

solvated electron state, since dipole-bound anions having very small binding energies can survive only at low n. Besides, the VDEs of band I (0.5–1.0 eV for $n = 10$–100) are higher than those of dipole-bound anions, which are typically much lower than ~0.2 eV [11–14]. Consistently, the formation of e_s^- was experimentally confirmed in liquid acetonitrile [4,5]. In the solvated electron state, the excess electron is trapped in a cavity formed by CH_3CN molecules. Based on our observation of excitation of CH stretching modes by electron detachment, we anticipate that the CH_3 group of CH_3CN will be orientated towards the excess electron and may involve strong interaction with its H atoms.

As mentioned earlier, the dimer anion is the most stable anionic form in liquid acetonitrile [4,5]. Since band II becomes the more abundant and stable species with increasing cluster size, it can be expected that the anion state of band II will be the dimer anion. As shown in Fig. 1, band II exhibits bell-shaped broad envelopes with very large VDEs. We note that the spectral shape of band II is intrinsically broad even in higher energy-resolution measurements. Both the broad envelopes and the large VDEs of band II indicate the considerable intramolecular and intermolecular rearrangements by electron detachment. Consistently, recent computational studies [4,5] have suggested that the acetonitrile dimer anion has a largely bent structure with a CCN angle of ~130°, which is far from the neutral, and a large positive VDE (1.4 eV) [5]. Therefore, the Franck-Condon effect occurring on photodetachment should result in the broad envelope and the very large VDE of band II.

Finally, our initial objective was to arrive at a reason for why e_s^- and dimer valence anion coexist in liquid acetonitrile. One of our most interesting findings is that band II starts to appear at $n = 11$. This result indicates that the solvation of (at least) *nine* CH_3CN molecules is necessary to turn the adiabatic EA of the acetonitrile dimer valence anion into a positive value. Because of the large width of band II, this value cannot be determined from the photoelectron spectrum. However, it is likely to be very small and positive, since the EAs of clusters change only gradually with increasing size. On the other hand, the photoelectron spectrum of the same size indicates that the adiabatic EA of the excess electron solvated by 11 CH_3CN molecules is also low, 0.3–0.5 eV (see the onset and vertical detachment energy of band I of $n = 11$ in Fig. 1). Therefore, the adiabatic levels of the solvated electron and the dimer valence anion states are probably very closely located in energy (which may be within 0.5 eV) at $n = 11$. We note that experimental and theoretical studies have shown that 9–11 CH_3CN molecules can nearly complete the first solvation layer for halide ions [17,18]. In the first solvation layer, the strong direct ion-(or excess electron-)solvent interaction results in efficient anion (or excess electron) stabilization. In contrast, in the second (and larger) layer(s), solvent molecules do not directly interact with the core charge and, hence, provide no further substantial stabilization for the anion or excess electron. Hence, it is expected that solvation beyond the first layer will *not* modify the relative energy levels between the solvated electron and dimer valence anion states greatly. Consequently, the close vicinity of these two anionic states is maintained in very large clusters and even in bulk, resulting in the unusual coexistence of e_s^- and dimer valence anion in liquid acetonitrile.

We are grateful to Professor U. Even and Mr. N. Lavie for a newly designed pulsed valve. This work is supported by RFTF (Research for the Future) of the Japan Society for the Promotion of Science (JSPS), by the 21st Century COE program "KEIO LCC" from the Ministry of Education, Culture, Sports, Science, and Technology, and by CREST (Core Research for Evolutional Science and Technology) of Japan Science and Technology corporation (JST).

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[1] See, for example, R. A. Holroyd, T. E. Gangwer, and A. O. Allen, Chem. Phys. Lett. **31**, 520 (1975); R. A. Holroyd, Ber. Bunsen-Ges. Phys. Chem. **81**, 298 (1977).

[2] A. Singh, H. D. Gesser, and A. R. Scott, Chem. Phys. Lett. **2**, 271 (1968).

[3] I. P. Bell, M. A. Rodgers, and H. D. Burrows, J. Chem. Soc., Faraday Trans. 1 **73**, 315 (1977).

[4] I. A. Shkrob and M. C. Sauer, Jr., J. Phys. Chem. A **106**, 9120 (2002).

[5] C. Xia, J. Peon, and B. Kohler, J. Chem. Phys. **117**, 8855 (2002).

[6] C. Desfrançois *et al.*, Europhys. Lett. **26**, 25 (1994).

[7] C. Desfrançois *et al.*, J. Chem. Phys. **102**, 4952 (1995).

[8] T. Kondow, J. Phys. Chem. **91**, 1307 (1987).

[9] U. Even *et al.*, J. Chem. Phys. **112**, 8068 (2000).

[10] A. Nakajima *et al.*, Chem. Phys. Lett. **214**, 22 (1993).

[11] J. H. Hendricks, S. A. Lyapustina, H. L. de Clercq, and K. H. Bowen, J. Chem. Phys. **108**, 8 (1998).

[12] S. Y. Han, J. H. Kim, J. K. Song, and S. K. Kim, J. Chem. Phys. **109**, 9656 (1998).

[13] M. Gutowski *et al.*, Phys. Rev. Lett. **88**, 143001 (2002).

[14] C. G. Bailey, C. E. H. Dessent, M. A. Johnson, and K. H. Bowen, J. Chem. Phys. **104**, 6976 (1996).

[15] T. Maeyama, T. Tsumura, A. Fujii, and N. Mikami, Chem. Phys. Lett. **264**, 292 (1997).

[16] L. G. Christophorou, P. G. Datskos, and H. Faidas, J. Chem. Phys. **101**, 6728 (1994).

[17] G. Markovich, L. Perera, M. L. Berkowitz, and O. Cheshnovsky, J. Chem. Phys. **105**, 2675 (1996).

[18] R. Ayala, J. M. Martinez, R. R. Pappalardo, and E. S. Marcos, J. Phys. Chem. A **104**, 2799 (2000).