

Photoelectron imaging of large anionic methanol clusters: $(\text{MeOH})_n^-$ ($n \sim 70\text{--}460$)

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Electron solvation in methanol anion clusters, $(\text{MeOH})_n^-$ ($n \sim 70\text{--}460$), is studied by photoelectron imaging. Two isomers are observed: methanol I, with vertical binding energies (VBE) ranging from 2–2.5 eV, and methanol II, with much lower VBE's between 0.2 and 0.5 eV. The VBE's of the two isomers depend linearly on $n^{-1/3}$ with nearly identical slopes. We propose that the excess electron is internally solvated in methanol I clusters, whereas in methanol II it resides in a dipole-bound surface-state. Evidence of an excited state accessible at 1.55 eV is observed for methanol I. © 2006 American Institute of Physics. [DOI: 10.1063/1.2355484]

The solvated electron has long attracted interest owing to its importance in fundamental chemical and biological processes and its role as the simplest quantum solute. Numerous studies have been made of the hydrated electron,¹ and to a lesser extent, of electrons solvated in ammonia,² acetonitrile,³ and the simpler alcohols.⁴ In the case of water, ammonia and acetonitrile, condensed phase experiments are complemented by work on gas phase cluster anions in which an excess electron is bound to a known number of solvent molecules.^{5–7} For example, recent time-resolved studies of $(\text{H}_2\text{O})_n^-$ cluster anions have provided new insights into electron relaxation dynamics in bulk water.^{8–10} However, extrapolation from the cluster to bulk size regime is complicated by the presence of multiple water cluster anion isomers,^{11,12} and the elucidation of the electron binding motifs in these isomers has become an interesting topic in its own right.^{13–18} These considerations have motivated us to investigate the spectroscopy and dynamics of methanol cluster anions, the first results of which are reported here.

Methanol, the simplest alcohol, may be considered as “methylated water” and is logically the next solvent to study in order to gain a more complete understanding not only of the solvated electron in alcohols, but also the hydrated electron. Several experiments have focused on the solvated electron in bulk methanol,^{4,19–21} but its cluster analog has so far received little attention.^{22,23} Here we present experimental observation and characterization of methanol cluster anions, reporting photoelectron (PE) spectra of $(\text{MeOH})_n^-$ in the size range of $n \sim 70\text{--}460$ taken at photon energies of 4.7, 3.1, and 1.55 eV. We examine the effect of colder and warmer source conditions, and we recover evidence of a bound excited state.

The PE imaging apparatus used in this experiment has been described elsewhere.⁹ Methanol cluster anions were produced by passing argon through a reservoir of methanol

and expanding the gas mixture through a piezoelectrically actuated valve with a pulsed electron impact ionizer mounted on its faceplate. Ions were mass-selected by time-of-flight mass spectrometry and photodetached in a PE velocity-map imaging analyzer by a ~ 100 fs laser pulse, typically the fundamental (800 nm/1.55 eV) or one of the first two harmonics of an amplified Ti:Sapphire laser system. Raw PE images were transformed using the pBasex method of Garcia *et al.*²⁴ to obtain PE kinetic energy and angular distributions.

The mass spectrum was bimodal. At low mass, we observed a distribution of $\text{MeO}^-(\text{MeOH})_n$ clusters extending to a size range of ~ 2200 amu ($n \sim 0\text{--}70$). For $n > 3$, these clusters bind the excess electron too tightly to photodetach at 3.1 eV, although attempts were made to observe photodetachment at larger cluster sizes up to $n \sim 70$. Starting at ~ 2200 amu and extending to very high mass, we observed a second group of cluster anions that did photodetach at 3.1 eV (see below) and were therefore assigned to pure methanol cluster anions. The size of the clusters in this mass range ($n=300$ has a mass of $\sim 10,000$ amu) prevented complete mass resolution between adjacent clusters in our mass spectrometer. Hence, all cluster sizes are reported as average values $n \pm 4\%$, with the spread in cluster sizes $\Delta n \sim 2\%$.

Figure 1(a) shows the PE spectrum of $(\text{MeOH})_{190}^-$ under varying source conditions. At low backing pressure the spectrum is dominated by a tightly bound isomer, labeled methanol I. As the pressure is increased a more loosely bound isomer, methanol II, appears and becomes dominant, with methanol I virtually disappearing by 35 psia. In addition, the binding energy of methanol II is observed to shift by ~ 100 meV to lower binding energy as the pressure is raised from 25 to 35 psia.

Figure 1(b) shows size-dependent PE spectra of $(\text{MeOH})_n^-$ taken at 3.1 eV with backing pressures of 20 psia ($n \sim 143\text{--}458$) and (c) 30 psia ($n \sim 73\text{--}458$). At low backing pressure, methanol I is observed only for clusters larger than $n \sim 140$. Though suppressed relative to methanol II at the higher backing pressure (colder source conditions), methanol I is still observed for $n > 140$ and becomes increasingly

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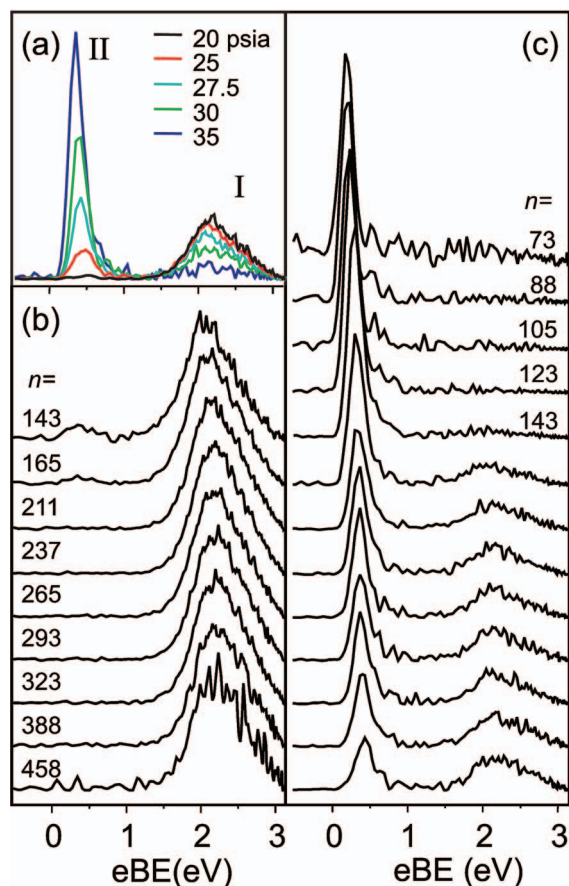


FIG. 1. (Color) (a) PE spectrum of $(\text{MeOH})_{190}^-$ taken at 3.1 eV with Ar backing pressures of 20 (black), 25 (red), 27.5 (light blue), 30 (green) and 35 psia (dark blue). (b) PE spectra of $(\text{MeOH})_n^-$, $n \sim 140\text{--}460$, at 3.1 eV with 20 psi backing pressure compared to (c) $n \sim 70\text{--}460$ with 30 psia backing pressure.

prominent at larger cluster sizes. At high pressures, methanol II persists out to the largest cluster sizes studied ($n \sim 460$), but at low pressure it is not observed at all above $n \sim 190$. Clusters throughout this size range were also examined at 4.7 eV. No additional isomers were observed, while the binding energies and size-dependent behavior of methanol I and II showed no change at the higher photon energy.

Figure 2 plots the vertical binding energies (VBEs) of both methanol isomers (stars) versus $n^{-1/3}$. VBEs were obtained by fitting each PE spectrum to a Gaussian-Lorentzian function, as was used for anionic water clusters.²⁵ The VBEs for methanol II are shown for a backing pressure of 30 psia. The choice of axes is prompted by dielectric continuum theory²⁶ (DC theory) according to which, for an internally solvated electron or an electron on a flat surface (i.e., small electron on the surface of a large cluster):

$$\text{VBE}(n) = \text{VBE}(\infty) - (e^2/2r)(1 + D_o^{-1} - 2D_s^{-1})n^{-1/3} \quad (1)$$

where $\text{VBE}(\infty)$ is the photoelectric threshold, D_o and D_s are the optical and static dielectric constant, respectively, and r is the average radius of a single solvent molecule. Figure 2 also shows previously determined VBEs for Isomers I-III of water cluster anions (squares).^{9,12}

The measured VBEs for methanol I and II show good qualitative agreement with DC theory, both depending lin-

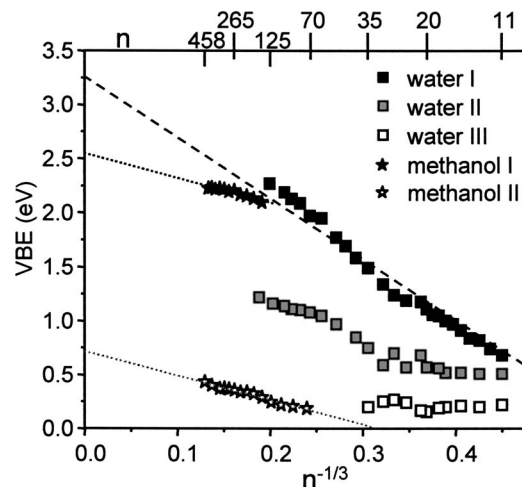


FIG. 2. Vertical binding energy (VBE) plotted vs inverse cluster radius ($n^{-1/3}$) for both methanol isomers and the three isomers of water, as shown in legend. The dotted lines are linear fits of the experimental data, and the dashed line is taken from Ref. 5.

early on $n^{-1/3}$ with similar slope, 2.25 ± 0.04 eV and 2.41 ± 0.04 eV for methanol I and II respectively. However, a rough calculation using the values for bulk methanol of $D_o = 1.76$, $D_s = 33.6$, and $r = 2.5$ Å yields a slope of ~ 4.3 eV, considerably larger than that obtained by an empirical fit of the data. Interestingly, the experimental slope is very similar not only to that for large water II ($n > 50$), but also to that obtained for ammonia clusters,⁶ which show a similar discrepancy between predicted and experimentally obtained slope.

The photoelectron angular distributions (PADs) are also analyzed for methanol I and II in the size ranges of $n \sim 140\text{--}400$ and $n \sim 70\text{--}400$, respectively. For a single-photon process, the PAD is described by:²⁷

$$I(\theta) = (\sigma/4\pi)[1 + \beta_2 P_2(\cos \theta)] \quad (2)$$

where β_2 is the anisotropy parameter and θ the lab-frame angle to the z -axis in the plane of the detector. For both isomers, the anisotropy parameter decreases slightly with increasing cluster size, from $\beta_2 \sim 0.25$ to 0.16 for methanol I and from $\beta_2 \sim 0.90$ to 0.72 for methanol II. The large anisotropy of methanol II relative to I indicates a different solvent environment around the excess electron.

Methanol II clusters, in addition to their low VBE's, show remarkably narrow PE spectra, less than 0.25 eV wide even for the largest clusters shown in Fig. 2 ($n = 458$). This suggests a state in which the excess electron is bound by the collective dipole moment of the solvent network.²⁸ The electron wavefunction in this case is expected to be a diffuse surface state. Theory and experiment indicate that the methyl groups tend to orient outwards in neutral methanol clusters²⁹ and at the surface of bulk methanol,^{30,31} allowing maximal hydrogen bonding among the interior OH groups. These results suggest that in methanol II a dipole-bound electron is delocalized over multiple external methyl groups. Because the dipole moments of the surface monomers tend to lie parallel to the surface,³⁰ some re-orientation of the surface

MeOH molecules in the vicinity of the excess electron may be required to bind it. This would be consistent with the shift towards lower VBE observed for methanol II under colder conditions—the neutral cluster is restricted and generates a collective dipole somewhat smaller than when more intermolecular freedom is present.

Methanol I is a promising candidate for the cluster analog of an electron solvated in bulk methanol. Experimental data and quantum molecular dynamics simulations indicate the solvated electron in methanol resides in a cavity of 2.5 Å radius surrounded by methanol hydroxyl groups.³² The cluster analog would be an internally solvated electron, similar to what has been calculated for large water cluster anions.^{11,14} Based on these calculations, we expect methanol clusters with internally solvated electrons to have higher VBEs than those with surface-bound electrons. Internal solvation should be favored at larger cluster size, and we see in Fig. 1 that methanol I is increasingly prominent above $n \sim 140$. The assignment of methanol I to internally solvated clusters and methanol II to surface-bound clusters is thus consistent with both of these trends. Moreover, the size of the clusters under consideration (radius ~ 17 Å at $n=300$, from bulk density) is sufficiently large that, based on spatial considerations alone, an electron may be easily accommodated inside.

Although these are compelling arguments, recent theoretical work on water cluster anions suggest that assignments to internal and surface states based on VBE values and trends merit caution. However, several factors suggest that such an assignment is more straightforward for methanol clusters. For instance, in small water clusters, both hydrogen atoms of a single water molecule can bind the excess electron,^{13,33} providing a mechanism for high VBE that is not accessible in methanol. Additionally, as mentioned above, the CH₃ groups tend to lie on the surface of a methanol cluster, implying OH groups are not available on the surface to bind the electron without major cluster rearrangement. Finally, in water cluster anions, an internally solvated electron disrupts the tetrahedral hydrogen bonding network favored by water molecules, an effect which may destabilize internal states versus surface states. In methanol, hydrogen-bonding results in a mixture of open chains and rings,³⁴ a more porous network that should be less perturbed by the incorporation of an excess electron. These considerations support the assignment of methanol I to an internalized state, particularly since there appears to be no obvious means of forming a surface-bound state with a high VBE.

Figure 2 shows that methanol II and water III have VBEs in the same energy range, while VBE's for methanol I are close to those for the largest water I clusters. At first glance, the results in Fig. 2 suggest that weakly-bound surface states are present for both methanol and water cluster anions (isomers II and III, respectively), while the more strongly bound surface state, water II, is absent in methanol cluster anions. Other factors, however, indicate that methanol II may correspond more closely to water II than water III. First, water III is observed only for very small clusters ($n \leq 35$), while extrapolation of VBE(n) versus $n^{-1/3}$ for methanol II shows that its VBE is negative for clusters smaller than $n \sim 35$. Second, the slope of VBE(n) versus $n^{-1/3}$ is very

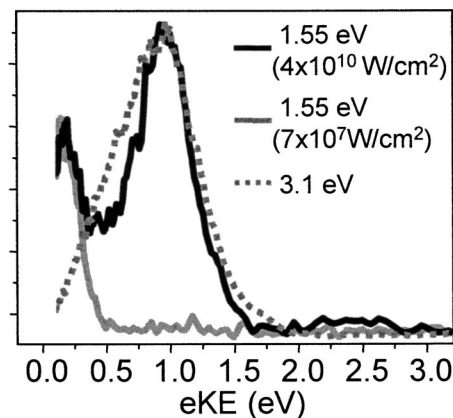


FIG. 3. PE spectra of $(\text{MeOH})_{190}^-$ at backing pressure of 20 psia at different photon energies and intensities. Dotted gray line shows single-photon detachment at 3.1 eV. Black and solid gray lines correspond to laser intensities of 4×10^{10} and 7×10^7 W/cm², respectively, at 1.55 eV.

similar for methanol II and water II above $n \sim 50$. Methanol II and water II are favored under colder source conditions,¹² suggesting similar binding and formation mechanisms. On the other hand, while the detachment feature for methanol II is extremely narrow, that of water II is of comparable width to water I and methanol I. Overall, the correlations between methanol and water cluster anions implied by inspection of Fig. 2 are more suggestive than definitive, and are worthy of further experimental and theoretical study.

In considering the formation mechanisms for these cluster anions, we note that (a) the less tightly bound methanol II is favored under conditions that would normally produce colder species in the ion beam and (b) methanol II starts at much smaller cluster sizes than methanol I. The first observation was attributed in our recent study of water cluster anions¹² to the formation of metastable structures, in which electrons injected into the expansion were trapped on the surface of pre-formed, cold neutral clusters. The striking similarity of Fig. 1(a) to Fig. 1 of Ref. 12 implies that the same mechanism is operative with methanol cluster anions. The much larger minimum size for methanol II clusters ($n \sim 70$ versus $n=2$ in water³⁵) would then reflect the nature of neutral methanol clusters, with their outward pointing CH₃ groups that have considerably less ability to attract electrons than the OH groups in water clusters.

In closing, one motivation for studying $(\text{MeOH})_n^-$ was to investigate their excited state spectroscopy and dynamics, and to compare these with previous results on water cluster anions^{9,10} as well as solvated electrons in bulk methanol.^{19,21} The first step is to determine whether $(\text{MeOH})_n^-$ clusters have a low-lying excited state near the broad feature in bulk methanol centered at 1.9 eV.⁴ Figure 3 shows the PE spectrum obtained for $n \sim 190$ (backing pressure 20 psia) at 3.1 eV (dotted gray line) superimposed with spectra obtained at 1.55 eV with power densities of 4×10^{10} W/cm² (black line) and 7×10^7 W/cm² (solid gray line) at the interaction region. Higher laser intensity at 1.55 eV results in a strong detachment feature at ~ 1.0 eV electron kinetic energy that is absent at the lower intensity. This feature signifies resonant two-photon detachment through an excited state, bearing a

notable similarity to observations by Weber *et al.*³⁶ for anionic water clusters. Such an excited state is, of course, expected for methanol I if it is indeed analogous to the solvated electron in liquid methanol.

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