Direct Measurement of Vertical Electron Binding Energies of Solvated Electrons in Methanol and Ethanol

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Time-resolved photoelectron spectroscopy at ultralow kinetic energy was applied to liquid beams of NaI solutions in methanol and ethanol. Solvated electrons were formed from I$^-$ ions in these solutions by charge transfer to solvent reactions. The vertical electron binding energies of the solvated electrons were determined for the first time. Both of the binding energies were found to be 3.10 ± 0.1 eV. This is in reasonable agreement with the dielectric continuum model of solvated electrons using the previously measured vertical binding energy of a hydrated electron. This indicates that the cavity radii of solvated electrons in water, methanol, and ethanol are approximately the same (0.33–0.35 nm).

The energetics and dynamics of solvated electrons are extremely important in chemistry, biology, and many other areas. However, until recently, there has been no direct measurement of the electron binding energy of a solvated electron in any liquid. The first measurement of vertical electron binding energy (VBE) was performed for a solvated electron in water (hydrated electron) by time-resolved photoelectron spectroscopy (TR-PES) with a liquid beam.[1–3]

Prior to this direct measurement, the VBE of a hydrated electron was estimated by extrapolation of the VBEs of negatively charged water clusters.[4] However, this method is controversial as these clusters may hold excess electrons inside or on their surfaces.[5–11] Three types of isomers (water I–III, Figure 1) have been identified for negatively charged water clusters from the magnitudes of their VBEs and the dependence of their yields on molecular beam conditions.[5] Experimentalists speculated that the type I isomer holds an excess electron inside the cluster, while theoretical simulations suggested that all of the isomers I–III have excess electrons on their surfaces.[8,9] The bulk VBE of a hydrated electron established by TR-PES[1–3] (red square at $n^{-1/3} = 0$ in Figure 1) is consistent with the VBEs of the type I isomer,[4] although it does not rigorously prove that the type I isomer is in the internal state.

In the present study, we investigated the VBEs of solvated electrons in methanol and ethanol. There were several motivating factors behind this. First, the VBEs of negatively charged methanol clusters have been measured by Kammrath et al. for (MeOH)$_n^-$ ($n \approx 70$–460),[12] which provides a point of comparison for the VBE of the solvated electron in bulk methanol. This comparison is very useful for obtaining further insights into the correlation between the properties of the bulk liquids and large molecular clusters. Two types of isomers have been identified for negatively charged methanol clusters (methanol I and II, Figure 1).[12] Type I methanol, which has been speculated to be in the internal state, exhibits a large VBE of 2–2.5 eV and a low
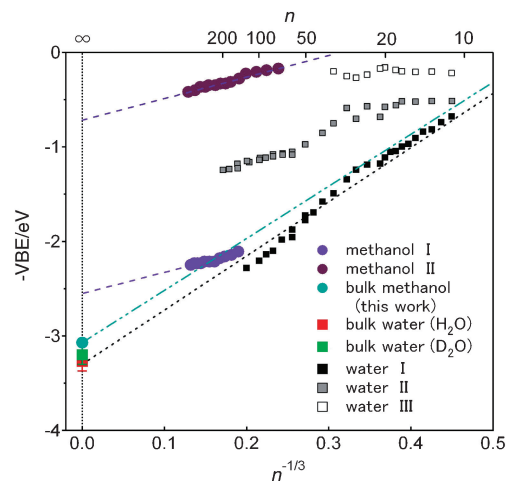

Figure 1. Vertical binding energies of negatively charged water clusters[5] and methanol clusters[12] and those of solvated electrons in bulk water[1] and methanol (this work). The dotted[4] and broken[12] lines are linear extrapolations of the cluster values. The long dashed double-dotted line is the least squares fit to our bulk value and the cluster values of the methanol isomer I: VBE = $3.10 - 5.51 \times n^{-1/3}$.

photoelectron angular anisotropy parameter (β_2) of 0.16–0.25.[12] In contrast, the type II isomer exhibits a narrow photoelectron kinetic energy distribution (PKED), a small VBE of 0.2–0.5 eV, and high β_2 of 0.72–0.90.[12] These characteristics of the type II isomer are typical of a dipole-bound surface state. Our second motivation to study methanol and ethanol arose from the interesting similarities and differences their solvated electrons have to those in water. Electron spin echo envelope modulation (SPEEM) study has suggested that the first solvation shell of a solvated electron in methanol consists of four methanol molecules, which is in contrast to the six water molecules in a hydrated electron.[13] In both cases, the OH bonds of water and methanol in the first solvation shell are pointing toward an excess electron cloud.[14] However, in ethanol, a solvated electron orients the dipole moments, instead of the OH bonds, of four ethanol molecules toward an excess electron cloud.[15] These results were supported by resonance Raman spectroscopy.[16]

In the present study, we create solvated electrons in methanol and ethanol by charge transfer to solvent (CTTS) from I$^-$. A 0.14 M NaI solution in methanol or ethanol was introduced into a photoelectron spectrometer as a laminar flow from a glass capillary nozzle with an inner diameter of 25 μm. The liquid flow rate was 0.5 mL min^{-1}. Pressure in the chamber was maintained at 0.8–1.0×10^{-4} Torr by trapping the liquid
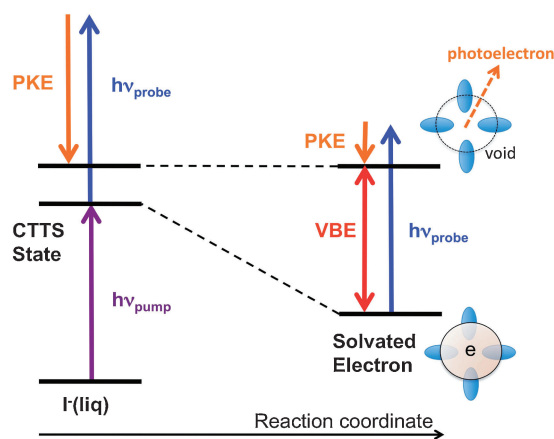
Figure 2. Schematic energy diagram of our experiment.

Figure 3. Photoelectron kinetic energy observed for NO as a function of the distance (l) between the ionization point of NO and a liquid beam of 0.14 M NaI solution in methanol. Gaseous NO was ionized by one-color two-photon ionization via the A state at 226 nm. The solid line is the least-squares fit of eq 1. $L = 11$ mm in our apparatus.[2]

beam with a liquid-N_2-cooled cold finger placed downstream. A 1 kHz regeneratively amplified Ti:sapphire laser excited two optical parametric amplifiers to generate pump and probe pulses. These pulses were attenuated and focused onto the liquid beam at a point 1 mm downstream from the nozzle. Typical laser powers were <20 nJ (pump) and <120 nJ (probe). The CTTS absorption spectra of I^- in alcohols are similar to that in water, with a peak at around 220 nm. Our pump pulse (226 nm) excited I^- in alcohol to the CTTS manifold near the absorption maximum, and the probe pulse (260 nm) was used to interrogate the subsequent electron dynamics by inducing its photoemission from the liquid (Figure 2). These photoelectrons were sampled through a skimmer (5 mm ϕ) located 11 mm from the liquid and were measured with a hemispherical electron energy analyzer. Both the pump and probe laser pulses were linearly polarized, and the cross-correlation was 365 fs. The probe laser polarization was parallel to the electron flight axis, whereas the pump laser polarization was set at the magic angle with respect to the axis in two-color experiment. A strong photoelectron signal was detected only when the laser beams overlapped with the liquid beam. The energy resolution of our experiment was determined to be 40 meV from the line width of the photoelectron spectrum of gaseous NO.

The liquid beam ejected from a nozzle is electrically charged by dynamic separation of electrical double layers formed around the inner wall of the nozzle. The streaming current creates an electric potential that accelerates or decelerates a photoelectron ejected from the liquid. In our previous work[1,2] on aqueous NaI, we minimized the streaming potential (Φ_{str}) by optimizing the concentration to 0.14 M. In the present work, we simply used the same concentration for the alcohol solution. The observed PKE was calibrated using $(1 + 1)$ one-color two-photon ionization of NO at 226 nm in the presence of the liquid beam near the ionization point of NO. The detailed procedure is described in our previous paper.[2] Nitric oxide was introduced from a gas nozzle as a continuous effusive beam into the chamber. Figure 3 shows an example of the PKE shift measured for different distances (l) between the ionization point of NO and the liquid beam. The experimental geometry is shown as an inset in Figure 3. The results show that the PKE of NO diminished when the liquid beam was closer to the ionization point, implying that the liquid beam was positively charged.
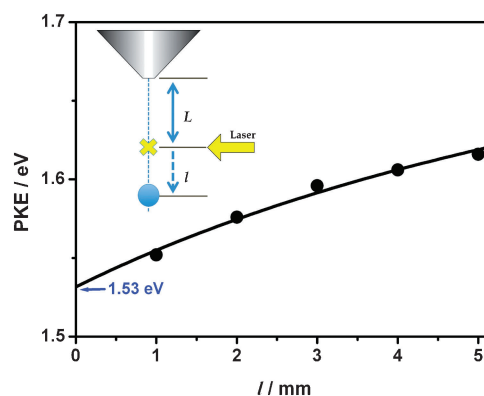
The PKE observed for NO in the presence of the liquid beam is expressed as:

$$PKE(l) = PKE(NO) - L/(L + l)\Phi_{str} + V \qquad (1)$$

where PKE(NO) is the known value (1.71 eV) for two-photon ionization of NO at 226 nm, V is an additional PKE shift that depends on the condition of the photoelectron spectrometer, and $L = 11$ mm in our apparatus.[2] Figure 3 indicates that PKE(0) = 1.53 eV in this particular case, which provides $-\Phi_{str} + V = -0.18$ eV. The VBE of a solvated electron, VBE(e), is obtained from the observed PKE(e) as follows:

$$VBE(e) = h\nu_{probe} - PKE(e) - \Phi_{str} + V \qquad (2)$$

A typical streaming potential of 0.14 M NaI solution in methanol was 210–280 meV.

A liquid beam injected into a vacuum is cooled by evaporation of solvents from the surface. The temperature reduction is less than 10 K in a liquid beam of water[1,2] 1 mm downstream from the nozzle, whereas the reduction is estimated[17] to be 70 K for methanol. Since the melting point of methanol is 175 K, the beam is not frozen at 230 K. The liquid laminar flow was stable at the excitation position and exhibited clear Fraunhofer diffractions of the UV laser beams.

As we demonstrated in our previous study, the bulk sensitivity of TR-PES is ensured by generation of photoelectrons at ultralow kinetic energy (ULKE: <5 eV).[1,2] At this energy, the inelastic mean free path of an electron exceeds the electron attenuation length determined by elastic scattering of an electron in solution. Therefore, photoelectrons are observed almost free from inelastic scattering with phonons in liquids.

Figure 4a shows the time profile of the photoelectron signal intensity observed for the CTTS reaction in methanol. The photoelectron signal intensity diminished rapidly within several picoseconds and exhibited a long-lived component. This is similar to that of CTTS from I^- to water.[1,2] The photoelectron signal intensity is approximately proportional to the population in the excited electronic state and of solvated electrons. The result suggests that the quantum yield (QE) of solvated electrons in methanol is less than 0.3, which is considerably smaller than the previous estimate (0.7) by Vilchiz et al.[18] at room temper-
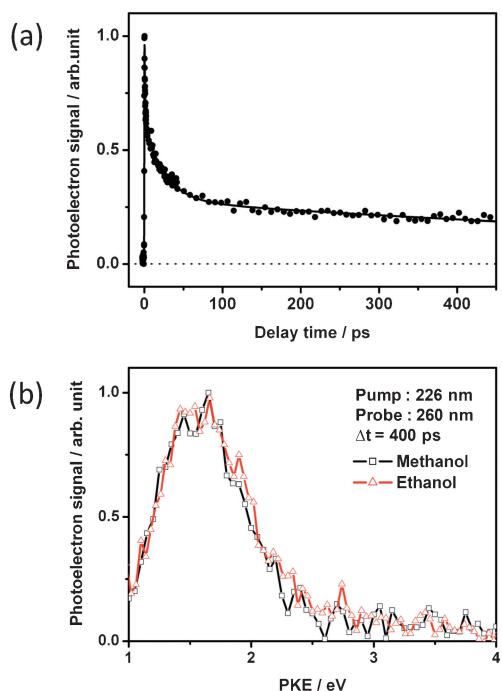
Figure 4. (a) Time profile of photoelectron signal intensity in $(1 + 1')$ ionization of 0.14 M NaI in methanol. The pump and probe wavelengths were 226 and 260 nm, respectively. Plotted points are the integrated areas (PKE = 0–4.5 eV) of the photoelectron spectra measured at each time delay. (b) Representative photoelectron kinetic energy distributions observed at a time delay of 400 ps.

ature. The difference in QE may be partly ascribed to different viscosity coefficients at 300 K (533 μPa s) and at 230 K (1889 μPa s). However, the population rapidly diminishes in a very short time as shown in Figure 4a, which cannot be explained by the increased viscosity at low temperature. We will discuss the details of the CTTS reaction dynamics in methanol elsewhere and focus on the measurement of VBE in this study. The VBE of a solvated electron can be determined from the PKED measured at the pump–probe delay time of 400 ps when the solvated electron is relaxed to the thermal equilibrium. The observed PKED is shown in Figure 4b. From the peak energy of this distribution, the VBE of the solvated electron in methanol was determined to be 3.1 ± 0.1 eV (blue-green dot at $n^{-1/3} = 0$ in Figure 1). This value is close to the VBE (3.27 eV) of a hydrated electron determined in our previous study (Figure 1).[1,2]

Previously, Kammrath et al. indicated that extrapolation of the VBEs of negatively charged methanol clusters leads to 2.6 eV at the limit of $n = \infty$ (dashed line in Figure 1), although they did not infer this value was a prediction for the bulk VBE.[12] This extrapolation line is indeed problematic in that the slope of VBE against $n^{-1/3}$ is too small and that the VBE does not become zero at small n. Our bulk VBE clearly indicates that the actual slope is much greater than the previous estimate. The overall dependence on $n^{-1/3}$ (long dashed double-dotted line in Figure 1) is similar to that of water isomer I (dotted line).

The dielectric continuum model (DCM) predicts the VBE of a solvated electron as:[19]

$$\text{VBE} = (1 + 1/\varepsilon_{op} - 2/\varepsilon_s)e^2/2a \qquad (3)$$

where a is the cavity radius for an excess electron, and ε_{op} and ε_s are the optical and static dielectric constants, respectively, of a solvent. If we assume that the cavity radius in methanol is the same as that in water, the VBE of the solvated electron in methanol is predicted to be 3.2 eV using $\varepsilon_{op}(1.8)$ and $\varepsilon_s(80)$ of water,[20] $\varepsilon_{op}(1.8)$ and $\varepsilon_s(34)$ of methanol at 293 K,[21] and the VBE of a hydrated electron $(3.27 \pm 0.1 \text{ eV})$.[1] The dependence of dielectric constants on temperature and ion concentration is not important. The VBE (3.2 eV) estimated for a solvated electron in methanol is reasonably close to the observed VBE $(3.1 \pm 0.1 \text{ eV})$. We can estimate the cavity radii from the observed VBEs using DCM to be 0.33 and 0.35 nm for water and methanol, respectively. Previously, ESEEM study has estimated the distance from the centers of electron clouds to the H atoms of OH bonds to be 0.21–0.23 nm in solvated electrons in water, methanol, and ethanol.[12–14] The estimated cavity radii are slightly larger than these values and, therefore, seem reasonable.

We performed a similar measurement on NaI in ethanol (Figure 4b) and obtained the VBE $(3.10 \pm 0.1 \text{ eV})$ of a solvated electron in ethanol, which is again close to the predicted VBE (3.2 eV) using DCM.

In conclusion, we have determined the VBEs of solvated electrons in methanol and ethanol for the first time. The VBEs of solvated electrons in water,[1,2] methanol, and ethanol indicate that their effective cavity radii are approximately the same (0.33–0.35 nm).

References
1 Y. Tang, H. Shen, K. Sekiguchi, N. Kurahashi, T. Mizuno, Y. Suzuki, T. Suzuki, *Phys. Chem. Chem. Phys.* **2010**, *12*, 3653.
2 Y. Tang, Y. Suzuki, H. Shen, K. Sekiguchi, N. Kurahashi, K. Nishizawa, P. Zuo, T. Suzuki, *Chem. Phys. Lett.*, submitted.
3 K. R. Siefermann, Y. Liu, E. Lugovoy, O. Link, M. Faubel, U. Buck, B. Winter, B. Abel, *Nat. Chem.* **2010**, *2*, 274.
4 a) J. V. Coe, G. H. Lee, J. G. Eaton, S. T. Arnold, H. W. Sarkas, K. H. Bowen, C. Ludewigt, H. Haberland, D. R. Worsnop, *J. Chem. Phys.* **1990**, *92*, 3980. b) J. V. Coe, *Int. Rev. Phys. Chem.* **2001**, *20*, 33.
5 A. E. Bragg, J. R. R. Verlet, A. Kammrath, O. Cheshnovsky, D. M. Neumark, *Science* **2004**, *306*, 669.
6 D. H. Paik, I.-R. Lee, D.-S. Yang, J. S. Baskin, A. H. Zewail, *Science* **2004**, *306*, 672.
7 N. I. Hammer, J.-W. Shin, J. M. Headrick, E. G. Diken, J. R. Roscioli, G. H. Weddle, M. A. Johnson, *Science* **2004**, *306*, 675.
8 L. Turi, W.-S. Sheu, P. J. Rossky, *Science* **2005**, *309*, 914.
9 A. Madarász, P. J. Rossky, L. Turi, *J. Phys. Chem. A* **2010**, *114*, 2331.
10 J. V. Coe, S. M. Williams, K. H. Bowen, *Int. Rev. Phys. Chem.* **2008**, *27*, 27.
11 D. M. Neumark, *Mol. Phys.* **2008**, *106*, 2183.
12 A. Kammrath, J. R. R. Verlet, G. B. Griffin, D. M. Neumark, *J. Chem. Phys.* **2006**, *125*, 171102.
13 S. Schlick, P. A. Narayana, L. Kevan, *J. Chem. Phys.* **1976**, *64*, 3153.
14 L. Kevan, *Chem. Phys. Lett.* **1979**, *66*, 578.
15 M. Narayana, L. Kevan, *J. Chem. Phys.* **1980**, *72*, 2891.
16 M. J. Tauber, C. M. Stuart, R. A. Mathies, *J. Am. Chem. Soc.* **2004**, *126*, 3414.
17 M. Faubel, S. Schlemmer, J. P. Toennies, *Z. Phys. D* **1988**, *10*, 269.
18 V. H. Vilchiz, X. C. Jeremiah, A. Kloepfer, S. E. Bradforth, *Radiat. Phys. Chem.* **2005**, *72*, 159.
19 J. Jortner, *Mol. Phys.* **1962**, *5*, 257.
20 W. J. Ellison, *J. Phys. Chem. Ref. Data* **2007**, *36*, 1.
21 Y. Marcus, *The Properties of Solvents*, John Wily and Sons, **1998**.