Resonance Raman Spectra of Electrons Solvated in Liquid Alcohols

Michael J. Tauber,[†] Christina M. Stuart, and Richard A. Mathies*

Department of Chemistry, University of California, Berkeley, California 94720

Received December 18, 2003; E-mail: rich@zinc.cchem.berkeley.edu

Electrons solvated in polar liquids have drawn widespread interest due to their unusual chemical reactivity, solvation thermodynamics, transport properties, and ultrafast photophysics.[1–8] Recently, resonance Raman spectroscopy was employed to provide valuable experimental data on the ground-state vibrational structure and excited-state nuclear dynamics of the hydrated electron.[9–13] In particular, resonance Raman spectra of mixed H_2O/D_2O solvated electrons support a cavity model in which the nearest water molecules are oriented with a single proton preferentially bound to the solvated electron, consistent with earlier proposals and molecular dynamics (MD) simulations.[11,14,15] Strong resonance Raman enhancement of the water librations and intramolecular vibrations reveal that these modes play a significant role in the excited-state nuclear dynamics after photoexcitation of the solvated electron, consistent with isotope effects on the fastest (35–80 fs) kinetic component in transient absorption experiments, and on the fluorescence quantum yield of the hydrated electron.[7,9]

Electrons solvated in liquid alcohols have also been studied by ultrafast transient absorption and modeled using MD simulations, but little is known about their vibrational structure or excited-state nuclear dynamics.[16–19] We present in this Communication the first resonance Raman spectra of electrons solvated in the primary alcohols. Our spectra reveal enhancements of the downshifted OH stretch, the OH in-plane bend, and the OH out-of-plane bend (torsion), which are analogous to the enhanced modes of the aqueous solvated electron.[11] These vibrational perturbations, relative to spectra of the pure solvent, are different from those caused by halides and show that the electron uniquely forms a strong hydrogen bond with the hydroxyl group of the alcohol. We also observe Franck–Condon (FC) coupling of the electronic excitation to methyl/methylene deformations, demonstrating that the electronic wave function of the solvated electron extends significantly into the alkyl group of the alcohols.

Electrons solvated in alcohols are produced in 0.2–0.6 mM average concentrations across a ~100 μm flowing film by nanosecond 218 nm photolysis of dilute (1–10 mM) KI solutions as described elsewhere.[9,20] After a 20 ns delay, a 683 nm (7 ns) pulse resonantly probes the equilibrated solvated electron. Pump+probe spectra of the KI + alcohol solutions are alternated with pump+probe spectra of the same stock solution with 80 mM acetone added to scavenge the electron during the delay time between pump and probe pulses. Subtraction of the spectra acquired with and without acetone yields a difference spectrum of the solvated electron resonance Raman and fluorescence emission features. The subtraction parameter was optimized here for removal of CH(CD) stretching bands. This procedure leads to quantitative removal of all features from photoproducts not scavenged by acetone, such as the resonantly enhanced vibrational bands of I_2^-. The fluorescence component of the solvated electron emission has
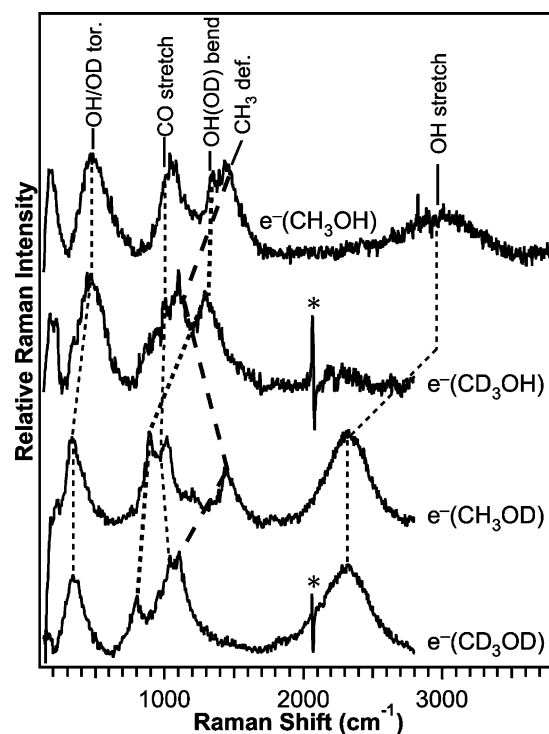
Figure 1. Resonance Raman spectra of electrons solvated in methanol isotopes. The dominant internal coordinates of the main bands are indicated and correlated with dotted or dashed lines. The asterisk marks a residual feature due to a slight frequency shift in the CD stretch region.

been subtracted from the spectra presented here to focus attention on the Raman features.

Resonance Raman spectra of solvated electrons in methanol isotopes are presented in Figure 1. The OH(OD) stretch is enhanced and downshifted 350 (160) cm⁻¹ relative to the pure solvent. The OH(OD) torsion is peaked at 475 (340) cm⁻¹ and is clearly a 180 (140) cm⁻¹ downshifted version of the strong and broad IR bands of pure liquid methanol.[21] A band near 1330 (800–890) cm⁻¹ is slightly downshifted from bands of the pure liquids that are assigned primarily to the OH(OD) in-plane bending motion.[21–23] Most notably, we also observe the $CH_3(CD_3)$ deformation at ~1440 cm⁻¹ (1100 cm⁻¹), and a predominantly CO stretch at 950–1020 cm⁻¹ which shifts only slightly among the different isotopomers. Both bands are close to the frequencies of the pure liquid, but are broader and cannot be removed by any choice of subtraction parameters.[21]

Spectra of electrons solvated in longer primary alcohols (Figure 2) reveal that the photoexcitation of the electron is significantly FC coupled to the alkyl chain. Enhanced solvated electron bands at 1075 cm⁻¹ (EtOH) and at 1057/1130 cm⁻¹ (EtOD) are primarily CC/CO stretch in character.[24] Electrons solvated in n-propanol (n-PrOH) display enhanced vibrations in the 800–1100 cm⁻¹ spectral range, which includes possible contributions from CC/CO stretches as well as CH_2/CH_3 rocks and twists.[25] Last, the CH_2/CH_3
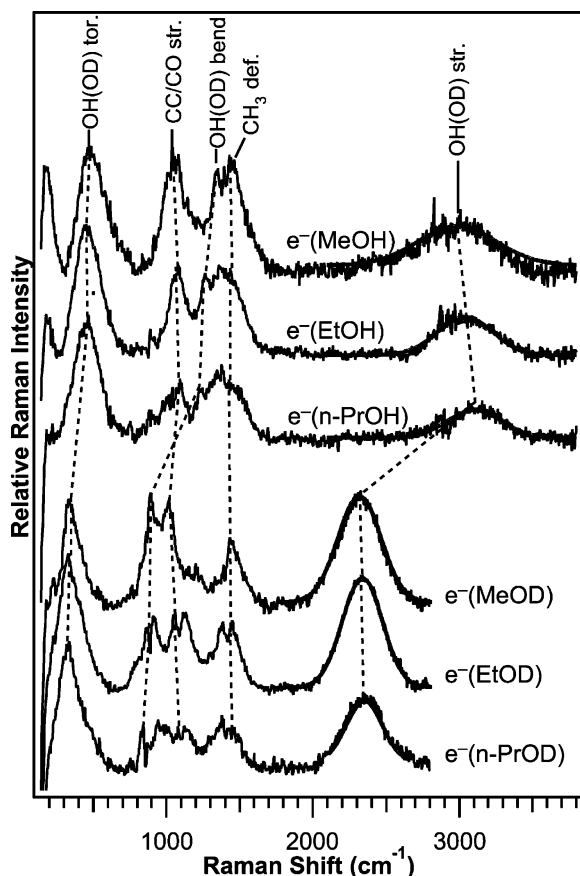
Figure 2. Resonance Raman spectra of electrons solvated in methyl, ethyl, and propyl primary alcohols. Gaussian fits to the OH and OD stretch regions are shown as bold lines. Dotted lines link assignments of correlated peaks.

deformation bands of both ethanol and *n*-propanol are enhanced across a broad region spanning from 1300 to >1500 cm^{-1}. As a whole, the FC couplings provide a unique fingerprint of the extended solvated electron wavefunctions.

The strong downshifts of the OH(OD) stretch and low-frequency OH(OD) torsion for electrons solvated in the primary alcohols parallel similar observations for solvated electrons in liquid water.[11] The results reveal strong hydrogen bonding between the electron and the hydroxyl group[26] and a reduction of torsional forces on alcohol molecules in the immediate vicinity of the electron.[11] One trend apparent in Figure 2 is that the magnitude of the OH stretch downshift, relative to $\tilde{\nu}_{max}$ of the pure solvent, increases in the order *n*-PrOH (200 cm^{-1}) < EtOH (270 cm^{-1}) < MeOH (350 cm^{-1}). We attribute this trend to stronger interaction between the electron and hydoxyl group of the smaller alcohols, possibly due to decreased steric hindrance of the smaller alkyl chain. We note that the downshifted OH stretch observed here is in contrast to IR/Raman studies of concentrated anions dissolved in the alcohols, which cause a strong upshift in the OH stretching frequency.[27,28]

Resonance Raman frequencies and intensities are a critical part of a full multimode FC analysis of the alcohol-electron optical absorption band.[10,29] Our spectra reveal strong vibronic coupling of the solvated electron in liquid alcohols to at least five normal modes of the solvent. This unexpected observation contrasts with the theoretical prediction that the vibronic coupling in e$^-$(MeOH) is dominated by a single OH bend.[30] Moreover, our data imply that the energy gap between the ground and excited states of the

solvated electron must be modulated at the frequencies of the solvent librations and intramolecular modes. In contrast, MD simulations emphasize the role of solvent translations.[31] This difference is possibly due to the choice of electron−solvent pseudopotential, in view of the known sensitivity of simulated results on these functions.[32,33]

Our resonance Raman study of the alcoholic electron is a novel counterpart to burgeoning experimental and theoretical studies of alcohol solvent dynamics which employ traditional molecular solutes.[34−39] Spectra of electrons solvated in other alcohols, as well as analysis of their fluorescence and FC absorption profiles, will be reported separately.

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