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LETTERS

Novel Resonance Raman Enhancement of Local Structure around Solvated Electrons in Water

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Picosecond time-resolved Raman spectra of water were measured under the resonance condition with the s → p electronic transition of the solvated electron for the first time. We found that a strong transient Raman band appears in the frequency region 30 cm^{-1} lower than the OH-bend band of bulk water in accordance with the formation of solvated electrons. The observed transient Raman band was assigned to the vibration of the solvating water molecules that strongly interact with the solvated electron in the first solvation shell. The mechanism of this novel resonance enhancement is discussed on the basis of the vibronic theory.

Introduction

When electrons are injected into polar solvents such as water and alcohols, electrons are solvated and form so-called solvated electrons. This solvated electron is considered the most important basic anionic species in solutions, and it has been extensively studied by variety of experimental and theoretical methods.[1−18] The geometrical structure of the solvated electron in low-temperature matrices has been studied by ESR spectroscopy.[2−4] In the case of water, it was concluded that the solvated electron is surrounded by six equivalent water molecules that are arranged octahedrally in the first solvation shell and that one of the two OH bonds of each water molecule is oriented toward the electron.[2] Concerning the electronic states, it is well-known that the solvated electron exhibits a broad structureless absorption band extending from the visible to near-infrared region. The absorption has been attributed to the strongly allowed electronic transition from the ground state to the three lowest excited states.[5−7] The ground state of the solvated electron has a spherical s-like orbital, while the three excited states have p-like orbitals which are mutually perpendicular. These triple p-like excited states are nondegenerate owing to asymmetrical solvation cavities, which makes the s → p absorption very broad.[5] Ultrafast dynamics of the solvated electron has been studied using picosecond and femtosecond time-resolved visible−infrared absorption spectroscopy.[8−18] The existence of several short-lived precursors, including “wet electron” , have been indicated.[8−14] Time-resolved experiments using a three-pulse sequence were also carried out in order to examine the relaxation process after the s → p photoexcitation.[15−18]

While large number of spectroscopic studies have been carried out, direct information about solvating molecules is scarce, especially for the solvated electron at room temperature. Obviously, it is very desirable to measure vibrational spectra of the solvating molecules in order to understand the local solvation structure around the electron. However, it is not an easy task because the signal from the bulk solvent dominates spectra in ordinary circumstances.

In this letter, we report transient Raman spectra of water that were measured under the condition resonant with the s → p transition of the solvated electron. A transient Raman band

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appeared in accordance with the formation of solvated electrons, and we assigned it to the resonance Raman scattering of the water molecules that directly solvate the electron.

Experimental Section

The experimental setup for picosecond time-resolved Raman measurements has been already described elsewhere.[19,20] Briefly, a picosecond mode-locked Ti:sapphire laser (Spectra-Physics, Tsunami) pumped by an Ar^+ laser (Spectra-Physics, Beam-Lok 2060-10SA) was used as the light source of the apparatus. The output of this oscillator laser was amplified by a regenerative amplifier (Spectra-Physics, Spitfire) with a cw Q-switched Nd:YLF laser (Spectra-Physics, Merlin) and then used for the experiment. The wavelength, pulse width, energy, and repetition rate of the amplified pulse were 800 nm, 2 ps, 600 μJ, and 1 kHz, respectively. The second harmonic of the amplified pulse was generated by a 5 mm LBO crystal, and then the third harmonic was created by a 5 mm BBO crystal. The obtained third harmonic (267 nm, 25 μJ) was used for photoexcitation to generate solvated electrons in water. The residual fundamental pulse (10 μJ) was used for probing Raman scattering under the resonance condition with the s → p transition of the solvated electron. The pump and probe pulses were focused with a quartz lens ($f = 50$ mm) onto a thin film-like jet stream of the sample solution. Typical cross correlation time between the pump and probe pulses was about 5 ps (fwhm). The Raman scattering was collected and introduced into a spectrometer (Jobin-Yvon, HR320) by a camera lens, after Rayleigh scattering was eliminated by a holographic notch filter (Kaiser Optical Systems, Inc.). A liquid nitrogen cooled CCD camera (Princeton Instruments, LN/CCD-1100PB) was used for the detection of Raman scattering. Time-resolved absorption was measured by monitoring the intensity of the probe pulse passing through the sample.

Indole (special grade) was purchased from Tokyo Chemical Industry Co., Ltd. and sublimated in vacuo. Water was distilled and deionized before use. Acetonitrile (special or HPLC grade) was purchased from Wako Pure Chemical Industries and used as received.

Results and Discussion

Figure 1a shows the time-resolved absorption trace of an indole aqueous solution monitored at 800 nm. The indole molecule was added in water for efficient generation of the solvated electron, since indole injects electrons much more easily than neat water owing to its low ionization potential (indole, 4.35 eV;[21] water, 8.8 eV[8]). As clearly seen in this figure, a transient absorption signal appeared immediately after photoexcitation. The intensity maximum of the s → p transition of the solvated electron is located around 720 nm in water[1] so that the observed transient absorption is attributable to the solvated electron. Although the cation radical of indole is also generated with photoexcitation, it does not contribute to the signal at 800 nm since its absorption is located around 580 nm.[12] The lifetime of the solvated electron in water is as long as a few hundreds nanoseconds in the absence of the electron scavenger.[22] Therefore, the decay of the transient absorption was not recognized in the time range of the present measurement. The absorption change due to the early solvation process of electrons was not observed in the present experiment because it is finished in the subpicosecond time region.[8−11,15−18]

Figure 1b shows picosecond time-resolved Raman spectra measured under the same condition as that of the transient absorption measurement. Before the pump pulse irradiation, only a weak Raman band due to the OH-bending vibration of bulk water was observed. After photoexcitation, however, a strong transient Raman band appeared in the frequency region about 30 cm^{-1} lower than the Raman band of bulk water (indicated by arrows in the figure). The observed spectra showed that a transient species of water was created with the generation of the solvated electron.

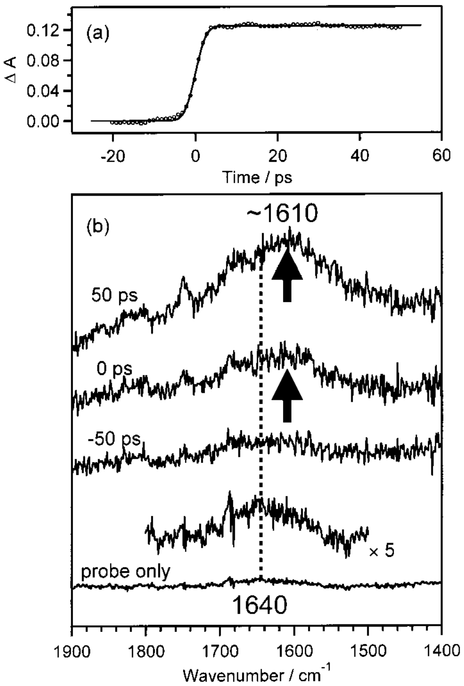

Figure 1. Time-resolved absorption trace monitored at 800 nm (a) and picosecond time-resolved resonance Raman spectra (b) of water in the presence of indole (1.7×10^{-3} mol dm^{-3}; pump laser, 267 nm; probe laser, 800 nm). The luminescence background has been subtracted from each time-resolved Raman spectrum.

We also measured picosecond time-resolved Raman spectra of neat water as well as a potassium iodide aqueous solution under the same experimental condition. The same transient Raman band was observed as the case of the indole aqueous solution. In addition, we found that the intensity of the transient Raman band coincided with the intensity of transient absorption signal. For example, both of the transient Raman and transient absorption signals were significantly weak in neat water compared with those in the indole aqueous solution. This weak transient signal in neat water is ascribable to the low yield of the solvated electron in the absence of the electron seed molecule. These experimental results assured that the observed transient Raman signal is not due to the cation radical of the seed molecule but certainly attributable to the water transient that appears along with the solvated electron.

The intensity of the observed transient Raman band was obviously enhanced under the probing condition resonant with the s → p transition of the solvated electron. In addition, the OH-bending frequency of the transient is 30 cm^{-1} lower than that of bulk water, which implies that the structure of the relevant water transient is somewhat different from that of the ordinary water molecule. These facts strongly indicate that the water molecule giving rise to the transient Raman band directly interacts with the solvated electron.

For solvated electron trapped in low-temperature glass matrices, ESR spectroscopy revealed that six water molecules solvate the electron in the first solvation shell. The distance between the center of the electron and the closest hydrogen atom was evaluated to be 0.21 nm[2]. A molecular dynamics simulation, on the other hand, indicated that the orbital radius of the s-like

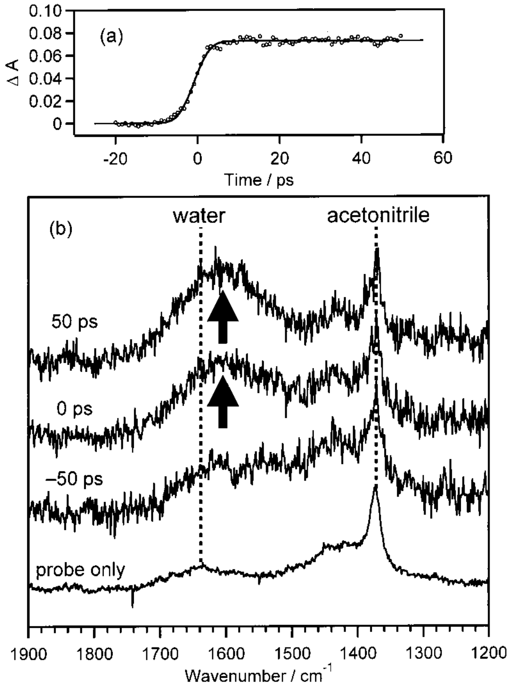

Figure 2. Time-resolved absorption trace monitored at 800 nm (a) and picosecond time-resolved resonance Raman spectra (b) of a water−acetonitrile mixture (4:1) in the presence of indole (1.7×10^{-3} mol dm^{-3}; pump laser, 267 nm; probe laser, 800 nm). Raman intensity at each delay time has been normalized by using the solvent band intensity. The luminescence background has been subtracted from each time-resolved Raman spectrum.

ground-state electron is ~0.2 nm while that of p-like excited state is ~0.3 nm.[5] Since the radius of the orbital of the solvated electron is almost the same as the distance to the water molecules in the first solvation shell, the interaction between the electron and the molecules in the first solvation shell should be much stronger than that with molecules in the outer shell. Therefore, we assigned the observed water transient, which strongly interacts with the solvated electron, to the water molecules that solvate the electron in the first solvation shell.

Since it was a little surprising to us that the water molecule gains high resonance Raman enhancement through the electronic transition of the electron, we evaluated the magnitude of this novel resonance enhancement. The time-resolved Raman spectra in Figure 1b, however, are not very suitable for quantitative discussion about the intensity because the Raman intensity measured at the positive delay time is affected by the self-absorption effect due to the transient absorption. Therefore, we carried out picosecond time-resolved Raman measurements for a water−acetonitrile mixture. It is known that the solvated electron is not formed in acetonitrile.[12] Thus, in the experiment for the mixed solvent, the Raman intensity of acetonitrile is expected not to change with the generation of the solvated electron so that the intensity of the Raman bands of acetonitrile can be used as the internal intensity standard for time-resolved Raman spectra.

Figure 2 shows the time-resolved absorption trace and time-resolved resonance Raman spectra of a water−acetonitrile mixture (4:1) in the presence of indole. With photoexcitation, the same spectral change, i.e., the appearance of the transient Raman band in the OH-bend region, was observed also for the mixed solvent. By comparing the time-resolved spectrum at 50 ps with the spectrum taken with only probe irradiation, we evaluated the intensity of transient Raman band is about 4 times larger than that of the Raman band of bulk water. On the other hand, the transient absorption intensity (ΔA) measured under the same condition was 0.073, which means that the concentration of solvated electron in water is $\sim 1.7 \times 10^{-4}$ mol dm^{-3}. (The extinction coefficient of the solvated electron in water is $\sim 1.5 \times 10^{4}$ mol^{-1} dm^{3} cm^{-1} at 800 nm,[22] and the optical path length of the jet stream of the sample solution is ~300 μm.) Since we can consider that six water molecules directly solvate the electron also in solution at room temperature (by referring to the study in low-temperature matrices[2]), the concentration of the water molecule that solvates the electron is estimated to be 1.0×10^{-3} mol dm^{-3}. It implies that the number of the water molecules giving rise to the strong transient Raman band is just 2.3×10^{-5} of the number of the water molecule in the bulk (44 mol dm^{-3}). Consequently, on the basis of the concentration and the Raman intensity between the solvating water and the bulk water, we estimate the factor of the resonance Raman enhancement is as large as 2×10^{5}.

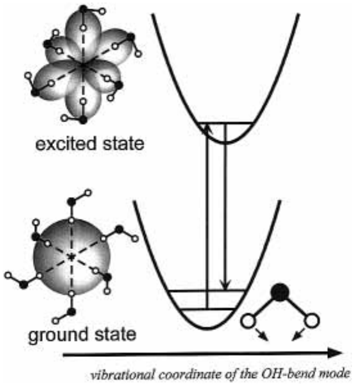

Figure 3. Sketch of the vibronic states of the local solvation structure around the solvated electron.

Although the resonance enhancement of the Raman band due to the solvating water molecule was unexpected, we now consider that this phenomenon is explainable in the framework of the vibronic theory.[23] Since the water molecules in the first solvation shell strongly interacts with the electron at the center, it is highly likely that the vibrational states of the surrounding water molecules are affected with the change of the electronic state of the solvated electron. In other words, a significant structural change of solvating water molecules is expected to occur with the s → p electronic transition of the solvated electron. It is well-known that those vibrational modes along which the structural change occurs with the electronic transition give rise to strong Raman bands in resonance Raman spectra (the A-term mechanism). Therefore, if we consider the local solvation structure as a whole, it is natural to expect that the Raman band of the solvating water molecules gains high-intensity enhancement under the probe condition resonant with the s → p transition of the solvated electron. The present result suggests that we need to theoretically treat the vibronic states of the local solvation structure as a “supermolecule” or a “cluster” (Figure 3).

Obviously, it is highly desirable to examine the OH-stretch region of water under the same experimental condition. With the probe at 800 nm, the Raman scattering due to the OH stretching vibration appears around 1100 nm. Since our detector (CCD) has no sensitivity for this wavelength region, we could not perform any measurements at the present moment. We are now planning picosecond time-resolved Raman measurements with use of an InGaAs array detector that has sensitivity for near-infrared region.

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