Hydrated-electron resonance enhancement of O–H stretching vibration of water hexamer at air–water interface

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Received February 4, 2015; accepted February 21, 2015; posted March 3, 2015 (Doc. ID 233858); published March 25, 2015

Raman scattering of the O–H stretching vibration mode inside water, as well as near and at the air–water interface, was investigated by laser-induced breakdown (LIB). An intense and characteristic higher wavenumber Raman shift of the O–H vibration was observed at the air–water interface, which was attributed to the hydrated-electron resonance enhancement of the O–H stretching vibration mode of water hexamer. The hydrated electron in the water hexamer structure was formed by excess electrons injected into the gas-like phase with low hydrogen bond order under LIB. The electron-phonon coupled mechanism was discussed. © 2015 Optical Society of America

As the most ubiquitous chemical compound on the earth’s surface, water has probably received more scientific and technological attention than any other substance. Much of this interest is because of the role that liquid water plays in physical chemistry of condensed phases, reaction chemistry, biochemistry and biology, atmospheric science, and so on [1]. Raman scattering is an important tool for investigating the structure of water [2], including water cluster analysis, as well as in the calibration for scattering or fluorescence measurements in aqueous solutions or supercritical water [3,4]. The Raman spectrum of liquid water is complex [5]; however, the vibrational spectra in the O–H stretching region from 3000 to 3800 cm⁻¹ sensitively reflect the local hydrogen bond network environment.

Laser-induced breakdown (LIB) is generated when an intense pulsed laser is focused in water, and the accompanying stimulated Raman scattering (SRS) of water molecules arises. LIB is a complex process that produces various optical, electronic, thermal, and structural effects [6]. Excess electrons generated by LIB affect the hydrogen bond network structure of water cluster and change the cluster number and polarizability, resulting in anomalous Raman peak appearances [7]. Simultaneously, excess electrons are injected into the hydrogen bond network of the water cluster [8] and form the hydrated electron ($e_{aq}$), a fundamental species to many areas of physical science, and play a key role in aqueous phase chemistry, upper atmosphere, and organic chemistry [9]. The direct interaction occurs between an excess electron and a solvent via the vibronic coupling. The model proposed for the first time by Abramczyk [10,11] shows that both an excess electron dynamics and an equilibrated cavity structure are determined by the coupling between the electronic states of an excess electron and intramolecular or intermolecular vibrational modes of a solvent [12]. Although the relaxation dynamics of hydrated electrons have been well studied [13], especially, the near-IR absorption spectrum of the solvated electron in alcohols, deuterated water, ammonia, amines and deuterated glasses [14,15], the Raman experiment can often be difficult to manipulate because of convoluted processes.

In this Letter, we study the Raman scattering of O–H stretching vibrations when an intense 8 ns of a full width at half-maximum (FWHM) pulse beam is focused from inside to the surface of water. The Raman peak intensity is sensitive to the dielectric environment, and the Raman shift is strongly related to the hydrogen bond structure in the O–H stretching vibrational region [16,17]. The characteristic SRS spectra obtained inside the water and near the air–water interface were observed at around 5.0 × 10¹¹ W cm⁻² optical power density. At the same time, an FWHM (325 cm⁻¹) and wavenumber shift (3595 cm⁻¹) of Raman peak, which belongs to the O–H stretching vibration of small water cluster, was obtained at the air–water interface. The phenomena of broader FWHM and lower hydrogen bond order are attributed to the hydrated electron resonance enhancement O–H stretching vibration of water hexamer formed by excess electrons injected into water at the air–water interface.

The second harmonic of a neodymium-doped yttrium–aluminum garnet pulsed beam (532 nm wavelength, 1 Hz repetition frequency, 8 ns pulse duration, and energy up to 200 mJ) was used as an excitation laser for the SRS of water; the laser beam was focused inside the water (10 nm from interface), as well as near (2 nm from interface) and at the air–water interface. The laser is coupled to a 50 nm high quartz cell with an 80× magnification objective lens. The output light is focused on the optical fiber spectrometer, and the signals are managed by a computer. The water, which was obtained from Sigma–Aldrich Co., was the high-performance liquid chromatography level. The diagram of the experimental setup is
shown in Fig. 1. All experiments were performed at room temperature and ambient pressure. The maximum irradiance for a Gaussian laser beam with energy of up to 100 mJ at 532 nm could be estimated at approximately $511 \times 10^4$ W cm$^{-2}$ under a focal point at a laser filament diameter of 100 to 200 μm; the diameter of the optical focus is around 50 μm and the pulse duration is 8 ns. The maximum irradiance was sufficient to generate plasma through multiphoton ionization, followed by avalanche ionization [18].

The SRS spectra of the O–H stretching vibrations inside the water and near the air–water interface were observed in forward directions of the pumping beam under a similar optical power density of $5.0 \times 10^{11}$ W cm$^{-2}$ (Fig. 2). An SRS peak was observed inside the water at around 3400 cm$^{-1}$, with corresponding anti-Stokes at $-3400$ cm$^{-1}$. Two SRS peaks were observed near the air–water interface at around 3400 and 3000 cm$^{-1}$, with corresponding anti-Stokes at $-3400$ and $-3000$ cm$^{-1}$. The wavenumber of the former peak near the air–water interface was close to that observed inside the water, indicating that the peak was derived from the water molecules inside water [18]. The former peak demonstrated a low hydrogen bond order structure. By contrast, the latter peak observed at $\pm 3000$ cm$^{-1}$ was not observed inside the water, indicating that this peak has a strong hydrogen bond structure. Excess electrons in water were detected when the LIB was generated near the air–water interface. The static electric field (> MV cm$^{-1}$) [19] formed by excess electrons intensified the hydrogen bond strength of the water cluster near the surface environment, which led to O–H bond lengthening and a red shift of the SRS peak of O–H stretching vibration. This phenomenon is consistent with the vibration of hydrogen-bonded water networks on a metal surface [20]. Raman shift at 3000 cm$^{-1}$ near the water surface has been studied in our latest research.

At the air–water interface, a 325 cm$^{-1}$ broader Raman peak of the O–H stretching vibration, in which the Raman shift was approximately 3595 cm$^{-1}$, and plasma spectra were observed under an optical power density of $5.0 \times 10^{11}$ W cm$^{-2}$, as shown in Fig. 3 (a curve). The air plasma spectrum was obtained over the air–water interface (10 mm form interface) with rich atomic and ionic spectral lines under similar optical power density [21] (b curve). An intense O–H stretching vibration line was observed between the a and b curves. However, the air plasma spectrum had a weak hydrogen emission line of 656 nm (Hα). The spectrum intensity of O I: 777.42 nm in the a and b curves was similar, indicating that the oxygen atom spectral line is derived from the air molecules, not the water molecules [22]. Hence, the contribution of the Hα spectral line for the O–H stretching vibration intensity of 3595 cm$^{-1}$ is weak.

The remarkably higher wavenumber shift of the Raman peak is related to a low hydrogen bond order of the water cluster [23]. This Raman peak of broader FWHM and higher wavenumber shift is attributed to the result of hydrated electron resonance enhancement O–H stretching vibration of the water hexamer. The vertical electron–detachment energy of $e_{aq}$ in water hexamer is consistent with the O–H stretching frequency. Therefore, the O–H stretching vibration mode could be easily excited by the $e_{aq}$ detachment mode [24].

Fig. 1. Schematic illustration of (a) the experimental setup and (b) the laser-induced breakdown and SRS formation inside water (1), near the air–water interface (2), at the air–water interface (3), and in air (4).

Fig. 3. Raman and plasma spectrum of (a) the air–water interface and (b) the plasma spectrum of air.
The mechanism of the hydrated electron in the formation of the water hexamer structure and the coupled electron-phonon involves two steps. First, the LIB produces a plasma cloud in the excitation beam focused at the air–water interface by the rising edge of the laser pulse. During the initial LIB formation, which took approximately 10000 ns [25], excess electron content in the air drastically increased (\( \sim 10^{18} \) cm\(^{-3} \)) by multiphoton ionization, followed by avalanche ionization [4]. The duration of the rising edge of the laser pulse is approximately 10 ns, in which the energy causes the inverse Bremsstrahlung and multiphoton absorption processes [26], maintaining the existence of the excess electrons. Simultaneously, the surface water transitions from the liquid to gas-like phases at low hydrogen bond order, low density, and high temperature [4,27]. Molecular dynamics simulations have shown that gas-like phase average densities are fewer than 0.2 g cm\(^{-3} \) at a microscopic level [28], which is similar to the vacuum condition. The average number of hydrogen bonds per molecule and cluster size is reduced with increasing temperature and decreasing density, resulting in water hexamer and heptamer generation.  

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In addition, the photoelectron spectrum main peak of (H\(_2\)O)\(_6\) corresponds with our experimental result [29]. The excess electrons are injected into the gas-like phase, where the electron is stabilized predominantly by \( e^- \cdots HO \) interactions with the six water molecules [24–26] forming the hydrated electron in the water hexamer structure [8,9,24,33,37]:

\[
e^- + (H_2O)_6 \rightarrow (H_2O)_6^e. \tag{1}
\]

In the past few decades, mass spectrometer experiments with various gas-phase water cluster anions were observed [38–40]; an important question regarding water cluster anions concerns whether they are gas-phase counterparts to condensed-phase hydrated electrons [41]. The excess electrons cross askinned pulse supersonic beam of water clusters obtained by expanding water vapor with the laser pulsed [42]. The collision region is on the water surface, in which the water cluster anion was formed, but in the case of \( n < 10 \), clusters with only \( n = 2,6,7 \) were identified with certainty. Of particular interest is the case of \( n = 6 \) (water hexamer anion), since the solvated electron is also coordinated to six water molecules [43].

The low-lying energy structures of water hexamer are hybrid (partially internal and partially surface) excess electron states [24]. The three-dimensional highest-occupied molecular orbital (HOMO) electron density distribution of the hybrid state is shown in Fig. 4(a). Kim and co-workers [24] have carried out density functional theory calculations by Becke–Lee–Yang–Parr type nonlocal density functional using the 6-311++G** basis set. This structure (Y42) has the maximum vertical electron-detachment (VDE) and dipole moment in the water hexamer. At the same time, Y42 is the lowest energy conformer. VDE could be defined by the following equation:

\[
VDE = h\nu - eKE_{\text{max}},
\]

where VDE is the energy needed to detach an electron to form a particular neutral state with no geometric relaxation of the neutral, and eKE is the photoelectron kinetic energy [9]. Second, the falling edge of the laser pulse excites the hydrated electron in the water hexamer; the hydrated electrons are photodetached by the absorption of one or more photons from the laser pulse:

\[
(H_2O)_6^{eKE_{\text{falling}}} \rightarrow (H_2O)_6^e + e^-.
\tag{2}
\]

The charge-transfer-to-solvent (CTTS) process [Fig. 4(b)] reveals the hydrated electron dynamics characteristic in water [8]. Bailey and co-workers observed [29] the strong vibrational resonances in the photodetachment spectra of (H\(_2\)O)\(_n\) \( n = 6,7 \) clusters in the mid-infrared region. The resonances occur in the spectral region corresponding to O–H bonding (\( \sim 3400 \) cm\(^{-1} \)). They assigned the features to “free” O–H groups interacting with the excess electron on the basis of the calculations by Kim and co-workers [43]. Their assignment was supported by the fact that excitation of the free O–H vibration is observed in the photodetachment of (H\(_2\)O)\(_6\) [41]. However, they did not obtain the structure of the water hexamer anion like Y42 or Y51, and the free O–H vibrational frequency is at around 3680 cm\(^{-1} \) [23]. The lower the energy conformer of the water hexamer anion, the higher is the VED. Y42 is the lowest-energy conformer with the VED 0.46 eV. The O–H stretching frequency (3595 cm\(^{-1} \approx 0.45 \) eV) mode of water hexamer could be easily coupled with the vertical electron-detachment (0.46 eV) mode because once an excess electron is detached from the cluster, the H\(_{\text{ex}}\) act as electrophilic sites attracting the excess electron, which are no longer involved in the \( e^- \cdots \cdot HO \) interaction. Hence, the O–H stretching mode corresponding to 0.46 eV could be easily excited [24,29]. The vertical electron-detachment energy of the water heptamer is higher than the 0.46 eV, so that it does not meet the resonance condition [33]. These processes show that the hydrated-electron resonance enhances the O–H stretching vibration of water hexamer.

The hydrated-electron resonance-enhancement Raman scattering, whose intensity is similar to the intensity of stimulated Raman scattering from Figs. 2–3, is intense Raman scattering, and belongs to one type of resonance
Raman effect [44]. The estimated Raman enhancement factor was about 200 times larger than that of neutral species when an $\varepsilon_{aq}$ was detached [7].

Three reasons affirm that the Raman peak at 3595 cm$^{-1}$ belongs to $\varepsilon_{aq}$ resonance enhancement O–H stretching vibration of the water hexamer. (1) H$_2$ spectral intensity is very weak; hence, its influence on the Raman bandwidth and intensity at 3580 cm$^{-1}$ is nonexistent. (2) The water hexamer is easily formed at the air–water interface under LIB, because of the low density, low hydrogen bond order, and high temperature water environment. (3) The VDE of 0.46 eV from the hydrated electron in the water hexamer corresponds to the O–H stretching frequency (3595 cm$^{-1}$) of the water hexamer, easily exciting the O–H stretching mode by excess electron-detachment mode.

In conclusion, we observed the SRS of O–H stretching vibrations inside the water and near the air–water interface when the LIB was generated. At the air–water interface, the hydrated electron in the water hexamer structure was formed by the LIB. The O–H stretching frequency mode could be excited by the hydrated electron-detachment mode, which results in direct electron-phonon coupling. This study provides a new insight into hydrated electron effects, which are fundamental for understanding electron–phonon coupling and aqueous solvation reactions, and useful for controlling electron-driven chemical reactions.

The authors acknowledge the financial contribution from the National Nature Science Foundation of China (Nos. 11104106, 11374123), the Science and Technology Planning Project of Jilin Province (Nos. 201201030, 20130101017JC, 20140101173JC, and 20140204077GX), and the National Fund for Fostering Talents of Basic Science (No. J1103202).

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