Time-resolved vibrational and hyper-Raman studies on short-lived chemical species in condensed phase

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Chapter 1

Introduction
One of the universal purposes of chemistry is to see a molecule. Because molecules exist in a micro space, it is impossible to see them directly by our eyes. However, we can see molecules with use of light as a tool. Light interacts with the molecule. This interaction gives rise to a variety of phenomena such as the absorption, emission, scattering, refraction, and ionization. A science which elucidates a true nature of molecules through these phenomena is molecular spectroscopy.

When we see molecules, it is very important to clarify the molecular structure. Vibrational spectroscopy, namely, Raman spectroscopy and infrared spectroscopy, is a science that we observe a light signal arising from the motion of the nuclei in the molecule. It has been widely used as a powerful tool for the structural analysis of the molecule and has given a crucial cue to characterize the molecular structure.

Raman spectroscopy is a method to observe very weak nonelastic light scattering from molecules, whose cross section is over ten orders of magnitude smaller than that of absorption. Nevertheless, Raman spectroscopy is utilized in various fields, e.g., chemistry, biology, medical science, industrial analysis, etc. This is because the sample preparation is easy and the nondestructive measurement is possible. The most characteristic feature of Raman spectroscopy is the resonance Raman effect: the scattering light intensity is enhanced when the energy of the incident light is resonant with that of the electronic transition of the molecule. The intensity of the resonance Raman scattering strongly depends on the nature of the electronic state(s) in resonance and only Raman bands due to the active vibrational modes to the resonance electronic transition are enhanced. Such high-sensitivity and high-selectivity are key characters of resonance Raman spectroscopy. The mechanism of the resonance Raman effect is explained by the vibronic theory introduced by Albrecht, which covers most of the results of the resonance Raman studies reported so far.

Infrared spectroscopy is complementary to Raman spectroscopy. The optical processes of infrared absorption and Raman scattering consist of one- and two-photon transitions, respectively. As a result, the selection rule for vibrational modes observed in infrared spectra is different from that in Raman spectra. Generally, the vibrational bands
attributable to the polar functional groups are observed with high intensities in the infrared spectra, whereas those due to the skeletal vibrations giving rise to high polarizability changes appear strongly in Raman spectra. In the case of the molecule having an inversion center, especially, the mutual exclusion rule between the infrared and Raman spectra appears. Measurements of both the infrared absorption and Raman scattering can provide the complete vibrational spectrum for the first time, and hence the further information on the molecular structure will be acquired more precisely.

For elucidation of the nature of the molecule, it is also essential to see the change of the molecule in chemical reactions. By subdividing a chemical reaction into simple elementary processes in time, we can see how the molecule changes in each process by using molecular spectroscopy, as if we take snapshots of the molecule. The reconstruction of the information of each process provides the understanding of the whole picture of the chemical reaction.

Time-resolved spectroscopy is a suitable method to observe the change of the molecule. The idea of time-resolved spectroscopy was first introduced by Porter and Norrish more than half a century ago. At that time, the time resolution was restricted in the millisecond (~10^{-3} s) region. Owing to the technical development of pulse lasers, the time resolution has progressed remarkably and now it has reached as fast as the femtosecond (~10^{-15} s) region. In such temporal region, crucial processes which dominate the following reaction take place. Especially, in the fields of absorption and luminescence spectroscopy in the UV-visible region, a number of studies have succeeded in the observation of the ultrafast molecular dynamics.

For the observation of the vibrational spectra by using the time-resolved method, picosecond time resolution can be regarded as a limit to obtain a valuable well-energy-resolved spectrum because of the uncertainty relation between the time and energy (the time of 1 ps corresponds to the energy of ~10 cm^{-1}). Most of the dynamic structural change in the molecule, such as the cleavage and recombination between the chemical bonding, occurs after the picosecond region, so that time-resolved vibrational
spectroscopy enables us to directly observe the structural change of various short-lived species. In other words, when the vibrational spectrum of each process is measured, we can see the molecular structure changing in time.

To study the molecular structure of the transient species during chemical reactions, we can also use other time-resolved spectroscopy such as time-resolved X-ray crystallography. Recently, it is performed with the subpicosecond time resolution\textsuperscript{3,4}. However, the application of X-ray diffraction is limited to crystalline materials, whereas vibrational spectroscopy is applied on the sample of various conditions (crystal, liquid, and gas phase). This advantage makes time-resolved vibrational spectroscopy quite unique and applicable for the observation and characterization of the very short-lived chemical species that appear in a variety of conditions. Therefore, time-resolved vibrational spectroscopy is playing an important role in the progress of structural chemistry.

Nonlinear spectroscopy is carried out by using a high peak-power pulse laser. In the case of Raman spectroscopy, the use of pulse lasers allows us to observe nonlinear Raman scattering. Hyper-Raman scattering is well-known as one of the oldest nonlinear Raman processes. Traditionally, the Raman cross section originates from the dipole moment induced by the electric field of incident light, which is given by

\[ \mu = \alpha \cdot E + \frac{1}{2} \beta : E \cdot E + \cdots, \]  

(1-1)

where, \( \alpha \) and \( \beta \) are the polarizability and hyperpolarizability tensors, respectively\textsuperscript{5}. The second-term of the induced dipole gives rise to hyper-Raman scattering, whereas the linear response to the incident electric field (first-term) corresponds to ordinary spontaneous Raman scattering. Because the hyper-Raman process consists of two-photon upward and one-photon downward transitions, the selection rule is different from that of ordinary Raman process. Similarly to ordinary Raman scattering, the resonance effect on hyper-Raman scattering is also observed when double the energy of the incident light is resonant with the
electronic transition of the molecule. In more general treatments about the light-matter interaction for molecular spectroscopy, hyper-Raman cross section is given through the polarization due to the fifth-order electrical susceptibility ($\chi^5$), and, correspondingly, spontaneous Raman scattering and so-called nonlinear coherent Raman scattering, such as coherent anti-Stokes Raman scattering (CARS), arise from the third-order susceptibility ($\chi^3$). Consequently, hyper-Raman scattering is a unique Raman spectroscopy and enables us to observe an aspect of the molecule different from that seen by other Raman spectroscopy.

Most chemical reactions take place in solutions. Thus, the observation of the short-lived chemical species in the condensed phase is essential not only to elucidate the nature of the molecule but also to control the chemical reaction. In this thesis, the time-resolved vibrational and nonlinear Raman studies on the following three interesting photochemical systems in the condensed phase are described.

(a) **Vibrational analysis and structure of the excited-state benzil** (Chapter 2)

![Molecular structure of benzil](image)

**Figure 1-1** Molecular structure of benzil.

Benzil (Figure 1-1) is one of the most basic organic molecules having two carbonyl groups. In its excited states, it exhibits various photochemical and photophysical characters. Therefore, it is very important to elucidate the molecular structure in the excited states as well as in the ground state. In Chapter 2, time-resolved infrared and resonance Raman studies of the excited-state benzil are described. The infrared spectrum of $T_1$ benzil in a
nonpolar solvent was measured by using nanosecond time-resolved infrared spectroscopy. The infrared bands of $T_1$ benzil are assigned on the basis of the frequency shifts on the spectra of isotopically substituted analogues. The transient resonance Raman spectrum of $S_1$ benzil was also measured with use of picosecond time-resolved resonance Raman spectroscopy. Based on the comparison between Raman and infrared spectra of the $S_0$, $S_1$ and $T_1$ states of benzil, the structural change of the excited-state benzil is discussed.

(b) Picosecond and femtosecond time-resolved resonance Raman studies of the hydrated electron (Chapter 3)

(b-1) Observation of the resonance Raman scattering from the hydrated electron\textsuperscript{7,8} (Section 3-2)

![Figure 1-2](image)

Figure 1-2 Local structure around the hydrated electron.

When an electron is ejected into water by electron radiation or photoionization, the electron is solvated by surrounding water molecules and forms the hydrated electron (Figure 1-2). The author wondered what is seen in the “vibrational” spectrum of the electron in water, and tried to measure it. In Section 3-2, the measurement of picosecond time-resolved resonance Raman spectra under the resonance condition with the electronic transition of the hydrated electron is described. It was found that the intensity of the
vibrational Raman bands attributable to the water molecules around the electron is strongly enhanced. This novel resonance enhancement suggests that the hydrated electron, along with the local solvation structure, should be considered as a “quasi-molecule”. On the basis of the results of resonance Raman spectroscopy, the solvation structure around the electron and the nature of the electronic transition of the hydrated electron is discussed.

(b-2) Ultrafast energy relaxation dynamics of the hydrated electron

The electron ejected into water via photoionization is relaxed in energy within a few picoseconds before forming the equilibrated hydrated electron. Although a number of time-resolved absorption studies have been done so far, there is still intense discussion about the relaxation process of the hydrated electron. In Section 3-3, the application of femtosecond time-resolved resonance Raman spectroscopy for the observation to the electron relaxation dynamics in water is presented. From the viewpoint of vibrational spectroscopy, the nature of the electronic transition from the unrelaxed hydrated electron is discussed.

(c) Observation of hyper-Raman scattering of all-trans-retinal

All-trans-retinal (Figure 1-3) is a very important conjugated polyene not only in chemistry but in biology. For this molecule, the character of low-lying electronic states can be considered as the electronic states of the polyene chain, but they are mixed with each
other to some extent because of lowering the molecular symmetry. In Chapter 4, the first observation of the strong resonance hyper-Raman scattering from an all-trans-retinal diluted solution is reported. Based on the hyper-Raman excitation profiles, the character of the electronic transition to the low-lying singlet excited states is discussed. The resonance mechanism of the hyper-Raman scattering of all-trans-retinal is also discussed.

Finally, all the studies in this thesis are summarized in Chapter 5.
References

(9) Mizuno, M.; Yamaguchi S.; Tahara, T. in preparation
Chapter 2

Vibrational analysis and structure of the excited-state benzil: Time-resolved infrared and Raman study
Abstract

Structures of the S1 and T1 states of benzil are examined based on the experimental results from nanosecond time-resolved infrared spectroscopy and picosecond time-resolved Raman spectroscopy. Nanosecond time-resolved infrared spectra of the T1 state of benzil as well as its three isotopically substituted analogues were measured in carbon tetrachloride. The observed infrared bands of T1 benzil were assigned based on the frequency shifts on isotopic (18O, 13C, and deuteration) substitutions. The infrared band at 1312 cm⁻¹ is assigned to the C=O anti-symmetric stretch vibration. An infrared band that has large contribution from the central C–C stretch is not observed. Picosecond time-resolved resonance Raman spectra of the S1 state of benzil were also measured. It has been reported that, after the photoexcitation, the benzil molecule shows ultrafast conformational change in the S1 state. The observed resonance Raman bands are attributable to the vibrations of the relaxed form of the S1 state. By comparing the Raman and infrared spectra of the S0, S1, and T1 states of benzil, the structures of benzil in the excited states are discussed. On going from the S0 state to the S1 or T1 state, the bond order of the C=O bond decreases while that of the central C–C bond increases. Although several ground-state bands appear in both the infrared and Raman spectra, there is no band observed simultaneously in the infrared and Raman spectra of the T1 state, except for bands attributable to the phenyl ring vibrations. We conclude that T1 benzil has the inversion center that arises from the trans-planar structure. The spectral pattern of the resonance Raman scattering of the relaxed S1 state is very similar to that of the T1 state. This implies that the molecular structure of the relaxed S1 state is similar to that of the T1 state. The structure of the relaxed form of the S1 state is also considered to be the trans-planar structure.
2-1 Introduction

Benzil is one of the most familiar α-dicarbonyl molecules. There are many investigations published on its excited states of benzil, because it represents a variety of absorbing photochemical and photophysical properties such as the photoreduction by amines or alcohols\textsuperscript{1-3}. The structure of the excited states of benzil has also been the great interest, in particular, compared with other α-carbonyl systems, e.g., benzophenone\textsuperscript{4}.

It has been reported that benzil in the ground ($S_0$) state has skewed structures around the central C–C bond. The two carbonyl planes make the dihedral angles of 98 degrees in solution\textsuperscript{5}, and approximately 111 degrees in the crystal\textsuperscript{6}. For the first excited singlet ($S_1$) state and the first excited triplet ($T_1$) state, however, both the skewed structure and the trans-planar structure have been assumed. (Figure 2-1) In the trans-planar structure, the dihedral angle between the two carbonyl groups is 180 degrees. Dual fluorescence and phosphorescence, attributable to these two structures, are observed in the glass matrices\textsuperscript{7,8}. The emission spectra measured at low temperatures are strongly blue-shifted compared with those at the room temperature while the absorption spectrum does not change with the temperature.

![Figure 2-1](image) Two expected molecular structures of benzil.
Time-resolved absorption studies strongly suggest the ultrafast conformational change in the S\(_1\) state\(^9,10\). In cyclohexane, an absorption band around 580 nm appears immediately after photoexcitation and decays with a time constant of less than 500 fs. On the contrary, another band located at around 530 nm decays with the fluorescence lifetime. The former has been assigned to the unrelaxed form of the S\(_1\) state and the latter to the relaxed form. Theoretical investigation shows that the n-\(\pi^*\) excited states is the most stable in the \textit{trans}-planar conformation, although the skewed form possesses a local minimum on the potential surface\(^{11}\).

Vibrational spectroscopy is a powerful tool for determining the structure of a molecule not only in the excited states but in the ground state. Resonance Raman spectra of the T\(_1\) state of benzil as well as Raman spectra of the S\(_0\) state were measured for studying their structure (Figure 2-2)\(^{12,13}\). Vibrational assignments of the S\(_0\) and T\(_1\) states were carried out.

![Figure 2-2](image-url)  

**Figure 2-2**  
Raman spectrum of the S\(_0\) state (top) and resonance Raman spectrum of the T\(_1\) state (bottom) of benzil. The assignments are indicated in parentheses based on ref. 12.
based on the frequency shifts on the isotopically substituted analogues whose structure are
described in Figure 2-3.  The bands at 1685 and 1050 cm\(^{-1}\) in the S\(_0\) spectrum and those at
1426 and 1160 cm\(^{-1}\) in the T\(_1\) spectrum are assigned to the C\(=\)O symmetric stretch of the
carbonyl group and the C–C stretch of the central C–C bond, respectively, which is
considered as the key bands to verify the predicted structural change in the excited states.
Vibrational analysis shows that the bond-order of the C\(=\)O and C–C bonds changes on going
from the S\(_0\) to the T\(_1\) state.  It was suggested that the T\(_1\) state had the trans-planar structure
in solution.  However, there are no experimental results available for infrared spectra of T\(_1\)
benzil.  As is well known, if we have both the infrared and Raman spectroscopic data, we
can determine the structure of benzil in the excited states more precisely.

In this chapter, time-resolved infrared spectra of benzil as well as its three isotopically
substituted analogues in the T\(_1\) state are reported.  The infrared bands of the T\(_1\) state are
assigned based on the observed isotope shifts.  Picosecond time-resolved resonance Raman
spectra of the $S_1$ state of benzil are also measured. By comparing the infrared and Raman spectra of the $S_0$, $S_1$ and $T_1$ states, the molecular structure of the excited states of benzil is discussed by taking advantage of the vibrational spectroscopy.

2-2 Experimental

The experimental setup of our dispersive time-resolved infrared spectrometer has been described in detail elsewhere$^{14,15}$, and is shown in Figure 2-4. The forth harmonic of a Q-switched Nd:YLF laser (Spectra-Physics, TFR, wavelength 262 nm, pulse width 5 ns, pulse energy 20 $\mu$J, repetition rate 190 Hz) was used for photoexcitation. Infrared white light generated by a MoSi$_2$ infrared source is focused on the same position of the sample where the excitation beam irradiates, and dispersed by a grating infrared spectrometer, and

![Diagram](image)

Figure 2-4 Nanosecond time-resolved infrared apparatus with a dispersive infrared spectrometer. EM: ellipsoidal mirror, PA: preamplifier.
then detected by a photovoltaic MCT detector. The frequency resolution of measurements is 16 cm⁻¹. The sample solution (5 × 10⁻³ mol dm⁻³) was circulated through a BaF₂ cell (optical path length 50 μm) under the argon atmosphere.

Picosecond time-resolved resonance Raman spectra were obtained by a spectrometer with a cw mode-locked Nd:YAG laser (Spectra-Physics 3800S) and a regenerative amplifier. For this study, the laser system was modified for chirped pulse amplification. The apparatus is described in Figure 2-5. The output of the mode-locked Nd:YAG laser was coupled into an optical fiber and was chirped in the fiber. The cw Nd:YAG regenerative amplifier was seeded with this chirped pulse. After the amplification, the pulse was temporally compressed by a grating pair. The energy, pulse width, wavelength, and repetition rate of the amplified output were ~ 300 μJ, ~ 10 ps, 1064 nm, and 2 kHz, respectively. The second harmonic (532 nm) was used to probe resonance Raman scattering from the photoexcited transient. The forth harmonic (266 nm) was utilized as the

**Figure 2-5** Picosecond time-resolved resonance Raman apparatus with a chirped pulse regenerative amplification.
pump pulse. Typical energy of the pump and probe pulses were ~ 3 µJ and ~ 3.2 µJ at the sample point. The scattered light was collected by fused silica lens and introduced into a polychromator (Instruments SA, HR320). Both the Rayleigh scattering light and fluorescence component were eliminated by optical filters. The dispersed light was detected by a liquid-nitrogen cooled CCD detector (Princeton Instruments LN/CCD-1024 TKB). The sample solution (2 × 10⁻³ mol dm⁻³) was flowed as a thin film-like jet stream under an aerated atmosphere.

Benzil (Bz-h₁₀) was purchased from Tokyo Chemical Industry Co., Ltd., and was recrystallized from ethanol. Isotopically substituted analogues of benzil (Figure 2-3(b)–(d)), Bz-¹⁸O (C₆H₅C¹⁸OC¹⁸OC₆H₅), Bz-d₁₀ (C₆D₅COCOC₆D₅), and Bz-d₅ (C₆H₅COCOC₆D₅), were synthesized with the method described previously¹². The net content of ¹⁸O in the Bz-¹⁸O analogue was approximately 50 %. Carbon tetrachloride and cyclohexane (special grade) were purchased from Kanto Chemical Co., Inc. and were used as received.

2-3 Results and discussion

2-3-1 Time-resolved infrared spectra of benzil

Benzil was photoexcited in deoxygenated carbon tetrachloride and the subsequent changes were recorded with the time-resolved infrared spectrometer. The results are shown in Figure 2-6 as difference spectra. Both the negative and positive bands are observed in the figure. The negative bands at 1680, 1596, 1452, 1208, and 1176 cm⁻¹ represent the depletion of the S₀ molecule due to the photoexcitation. The positive bands at 1564, 1480, 1432, 1308, 1096, and 1064 cm⁻¹ are infrared bands of the transient species generated by the photoexcitation. The temporal intensity change of the observed transient infrared bands is shown in Figure 2-7. As seen in Figure 2-7(a), all the infrared bands disappear within 10 µs, following the same kinetics. The lifetime of the observed transient species is shortened in
the presence of oxygen. (Figure 2-7(b)) Judging from the observed lifetime and the effect of oxygen, the transient species observed in the time-resolved infrared spectra is attributable to the T₁ state of benzil. The depleted ground state is directly recovered from the T₁ state in this photoinduced reaction.

The lifetime of the observed T₁ benzil is shorter than the reported value of 20 µs\textsuperscript{18}. It is most likely that this shortening of the T₁-state lifetime is caused by the T–T annihilation. Under the deoxygenated condition that we employed for the time-resolved infrared
measurements, a single exponential decay is expected for the $T_1$ state. However, the observed decay kinetics was not explained by the single exponential decay function. This is probably because the second-order reaction, reflecting the T–T annihilation process, also contributes to the decay process of $T_1$ benzil.

**Figure 2-7** Temporal intensity change of the transient infrared bands of benzil in carbon tetra chloride in (a) the deoxygenated and (b) the oxygenated atmosphere. Fitted curve is calculated as the single exponential decay. The obtained time constants are 2.4 µs and 230 ns in the deoxygenated and oxygenated atmosphere, respectively.
2-3-2 Vibrational assignments of the T₁ state of benzil

Assignments of the vibrational bands of the T₁ state of benzil are discussed on the basis of the observed frequency shifts in the time-resolved infrared spectra of isotopically substituted analogues. Time-resolved infrared difference spectra of the isotopically substituted analogues of benzil (Bz-\textsubscript{H₁₀}, Bz-\textsuperscript{18}O, Bz-d₅, and Bz-d₁₀) in deoxygenated carbon tetrachloride were measured. The results are shown in Figure 2-8. The infrared spectrum of the S₀ state of each analogue was also measured under the same experimental condition. The results are also shown in the figure. The frequency shifts among the ground-state spectra are in agreement with the reported value\textsuperscript{13,19}. From the observed time-resolved difference spectra and the ground-state spectra, the infrared spectra of T₁ benzil and its three analogues were obtained from the difference spectra. The negative bands in the difference spectra were compensated by adding the ground-state spectra. The results are also shown in Figure 2-8. In Figure 2-8(a), the bands at 1564, 1480, 1440, 1312, 1288, 1096, and 1064 cm\textsuperscript{-1} are clearly observed as the infrared bands of the T₁ state of benzil.

The infrared spectrum of the T₁ state of benzil in carbon tetrachloride is compared with the spectra of three isotopically substituted analogues in Figure 2-9. The infrared bands of the T₁ state of benzil are analyzed based on the frequency shifts observed on these isotopic substitutions. The position of the infrared bands of benzil and the three isotopically substituted analogues, together with their assignment, are summarized in Table 2-1, both for the ground state and for the T₁ state.

The strong band at 1312 cm\textsuperscript{-1} shifts to 1280 cm\textsuperscript{-1} on the \textsuperscript{18}O-substitution of the two carbonyl groups. Because it is the only band that shows a frequency downshift on the \textsuperscript{18}O-substitution, this band is assigned to the C=O stretch. However, this band also exhibits a downshift to 1284 cm\textsuperscript{-1} on deuteration of the two phenyl groups. Therefore, the band at 1312 cm\textsuperscript{-1} is not the pure C=O stretch but it is mixed with the phenyl ring vibrations.

Most of the observed infrared bands except for the band at 1312 cm\textsuperscript{-1} are sensitive to the deuteration of the phenyl groups. Therefore, these vibrational modes have contribution
Figure 2-8  Time-resolved infrared difference spectra (0 - 1.6 µs after photoexcitation) and infrared spectra of the S₀ and T₁ states of benzil and its isotopically substituted analogues in carbon tetrachloride: (a) Bz-h₁₀ (Normal), (b) Bz-¹⁸O (the net content of ¹⁸O is approximately 50 %), (c) Bz-d₁₀, and (d) Bz-d₅. Concentration of the sample is $5 \times 10^{-3}$ mol dm⁻³ for the time-resolved measurements and $2.5 \times 10^{-2}$ mol dm⁻³ for the measurements of the S₀ state. The pump wavelength is 262 nm. The infrared spectrum of the T₁ benzil was constructed from the time-resolved spectrum and the spectrum of the S₀ benzil. In the spectrum (b), the spectrum due to the normal species (Bz-h₁₀) has already been subtracted.
from the phenyl ring vibrations. These transient infrared bands are assigned not only on the basis of the isotope shifts of the infrared bands, but also by taking into consideration the assignments of the Raman bands of the T₁ state. The bands at 1564, 1480, and 1440 cm⁻¹ are assigned to the 8b, 19a, and 19b phenyl C–C stretch modes, respectively, because these bands show isotope shifts similar to those observed in the Raman spectra. The bands at 1096 and 1064 cm⁻¹ are attributable to the 18b and 18a phenyl C–H bend vibrations. These infrared active bands are not observed in the resonance Raman spectrum of the T₁ state of benzil. The band at 1288 cm⁻¹ shifts to 1280 cm⁻¹ on the ¹⁸O-substitution, and vanishes on the deuteration. There are two probable assignments for this band; the C–H

![Infrared spectra](image-url)
Finally, it is notable that, in the infrared spectrum of the T₁ state of benzil, there is no band observed assignable to the central C–C stretching vibration at around 1160 cm⁻¹. This result is an important key when discussing the structure of the T₁ state of benzil, as shown below.

Table 2-1  Infrared frequencies and vibrational assignment of the S₀ and T₁ states of benzil and its isotopically substituted analogues

<table>
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<th>BZ-d₁₀</th>
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</tbody>
</table>

² From Refs. 12, 13.
³ Since the spectral resolution of the system is not high, these bands seem to be overlapped.
⁴ The band is buried under nearby bands or noise.
⁵ This frequency coincides with that if transient resonance Raman spectrum.

in-plane bend (phenyl 3 mode) or the C–phenyl stretch. It cannot be assigned this band from the present experimental results.
2-3-3  Resonance Raman spectrum of the $S_1$ state of benzil

It is considered that benzil exhibits an ultrafast conformational change in the $S_1$ state. Porter et al. observed that the spectral evolution of the $S_0 \leftrightarrow S_1$ absorption of benzil in cyclohexane was completed within a few picoseconds after photoexcitation\textsuperscript{10}. The transient absorption spectrum immediately after the photoexcitation showed a broad band with a peak at $\sim 570$ nm. As the time delay increased, the absorption maximum was shifted to $\sim 530$ nm. They proposed that this spectral change corresponded to the structural change in the $S_1$ state. The fast component has been attributed to the unrelaxed form of benzil, which has the same structure as that of the ground state (skewed structure\textsuperscript{5,6}).

![Figure 2-10](image)

**Figure 2-10** Picosecond time-resolved resonance Raman spectra of benzil in cyclohexane ($2 \times 10^{-3}$ mol dm$^{-3}$, pump 266 nm, probe 532 nm). The spectrum taken with only pump pulse irradiation and that of the solvent Raman scattering have been subtracted from each time-resolved spectrum.
Picosecond time-resolved resonance Raman spectra of benzil in cyclohexane were measured with the 266-nm pumping and the 532-nm probing and shown in Figure 2-10. The probe wavelength was chosen because it was close to the absorption maximum of the S1 state\textsuperscript{9,10}. The resonance Raman spectrum measured at 50 ps after the photoexcitation is shown in Figure 2-11. The spectra are acquired by subtracting both the quite strong luminescence background and solvent Raman bands from the spectrum taken with the pump and probe pulses. As seen in Figure 2-10, no spectral change was observed between 0 ps and 100 ps after the pump pulse irradiation. Therefore, the observed bands at 1580, 1543, 1195, 1140, and 995 cm\textsuperscript{-1} should represent the Raman bands of the relaxed S1 state\textsuperscript{20}.

The spectral pattern shown in Figure 2-11 is quite similar to that of the resonance Raman spectrum of the T1 state (Figure 2-2)\textsuperscript{12,13}. The two spectra are compared in details in the next section. This similarity suggests strongly that the structure of S1 benzil resembles that of the T1 state. It is noteworthy that the band at 1140 cm\textsuperscript{-1} in Figure 2-11 is broader and is more intense than any other observed bands. In the T1 state, the Raman band at 1160 cm\textsuperscript{-1} shows the same characteristics. Because the T1 Raman spectrum is quite similar to that of the S1 spectrum and because the corresponding T1 band at 1160 cm\textsuperscript{-1} is the central
C–C stretch, it is most probable that the band at 1140 cm\(^{-1}\) is the central C–C stretch of \(S_1\) benzil. A Raman band due to the C=O stretch is observed at 1426 cm\(^{-1}\) in the \(T_1\) state spectrum, while there is no band observed in this spectral region in the \(S_1\) state. It is likely that the C=O stretch band is buried under the noise in the \(S_1\)-state spectrum.

**2-3-4 Structures of the excited states of benzil**

In order to discuss the molecular structure of the excited states of benzil, Raman and infrared spectra of the \(S_0\), \(S_1\), and \(T_1\) states are compared in Figure 2-12. There are two key bands that characterize the molecular structure in the excited states of benzil; the C=O stretch and the central C–C stretch.

In the present infrared study, it is found that the C=O anti-symmetric stretch is downshifted from 1676 to 1312 cm\(^{-1}\) on going from the \(S_0\) state to the \(T_1\) state. Previously, it was reported that the C=O symmetric stretch in the Raman spectra was downshifted from 1685 to 1426 cm\(^{-1}\) when going from the \(S_0\) state to the \(T_1\) state\(^{12,13}\). The large downshift of the C=O stretch vibrations indicates the decrease of the C=O bond orders in the excited state. It is also noticed that the absorbance of the band attributable to the \(T_1\)-state C=O stretch is about four times weaker than the \(S_0\) state (in Figure 2-6, the negative band at 1680 cm\(^{-1}\) is assigned to the C=O stretch). Both the decrease of the bond orders and the decrease of infrared absorption in the \(T_1\) state indicate that the dipole moments of the C=O bonds are smaller in the \(T_1\) state than in the \(S_0\) state.

The central C–C stretch, however, shows the frequency shift to the opposite direction to that of the C=O stretch. In the observed Raman spectra, it is upshifted from 1050 to 1140 cm\(^{-1}\) on going from the \(S_0\) state to the \(S_1\) state, and further to 1160 cm\(^{-1}\) in the \(T_1\) state. This indicates that the bond order of the C–C bond increases from the \(S_0\) state to the \(S_1\) state and further to the \(T_1\) state, in contrast to the C=O bond. Since both of the resonance Raman bands of the \(S_1\) state and the \(T_1\) state are strongly enhanced, it is highly likely that the central
C–C bond participates in the conjugation system, as a result of the conformational change in the excited states.

By comparing the infrared and Raman spectra of a molecular species, the molecular symmetry can be discussed. We now have both the infrared and Raman spectra of the T₁
and $S_0$ states of benzil, which enables us to examine the structure in the $T_1$ state, as well as in the $S_0$ state, in further details. There is a noticeable difference between the structures of the $S_0$ state and the $T_1$ state. In the $S_0$ state, benzil is twisted around the central C–C bond with the dihedral angle between the two carbonyl groups being 98 degrees in solution (skewed structure)\textsuperscript{5}. Therefore, the $S_0$-state benzil does not possess an inversion center. This is in good accordance with several bands appearing in both the infrared and Raman spectra of the $S_0$ state as seen in Figure 2-12. Especially, the infrared bands at 1685 cm\textsuperscript{-1}, 1286 cm\textsuperscript{-1}, and 1209 cm\textsuperscript{-1} and the Raman bands at 1685 cm\textsuperscript{-1}, 1284 cm\textsuperscript{-1}, and 1208 cm\textsuperscript{-1} are observed. It should be noted that these infrared or Raman bands are not from the phenyl ring vibrations. In the $T_1$ state, on the contrary, there are no bands commonly observed in the infrared and Raman spectra, except for the ring vibrations. In other words, the mutual exclusion rule between the infrared and Raman spectra holds for the $T_1$ state. The $T_1$ state of benzil has a center of symmetry. It is concluded that the molecular structure of the $T_1$ state of benzil is trans-planar. The decrease of the C=O bond order and the simultaneous increase of the central C–C bond order, mentioned above, provide a good support for our conclusion that benzil is trans-planar in the $T_1$ state.

In the previous section, the structure of the $S_1$ state of benzil is discussed. Because the observed Raman spectra from the relaxed $S_1$ state are quite similar to those from the $T_1$ state, it is considered that the structure of the $S_1$ state is similar to that of the $T_1$ state. It seems probable that the molecular structure changes in the $S_1$ state and benzil has a trans-planar structure in the relaxed $S_1$ state as well.

2-4 Conclusion

By analyzing the experimental results from the time-resolved infrared spectroscopy and time-resolved Raman spectroscopy, the photoinduced conformational change of benzil in the excited states is examined. The photochemistry of benzil is summarized in Figure 2-13.
In the $S_0$ state, benzil is in a skewed structure. With the UV photoirradiation, it is excited to
the unrelaxed $S_1$ state, still holding the skewed structure. Within a few picoseconds, the
ultrafast relaxation in the $S_1$ state changes the structure to trans-planar. The relaxed $S_1$ state
then undergoes the intersystem crossing with a time constant of a few nanoseconds to form
the trans-planar $T_1$ state. The $T_1$ state of benzil directly recovers back to the skewed $S_0$
state.

Figure 2-13  Photochemistry of benzil.
References and notes


(20) The probe wavelength agrees with the absorption band assigned to the unrelaxed form of the $S_1$ state of benzil. It may seem possible that the Raman bands of the unrelaxed
$S_1$ state are resonantly Raman enhanced. However, the observed intensity of the $S_n \leftrightarrow S_1$ absorption of the unrelaxed form is much smaller than that of the relaxed form. Therefore, we do not think that the unrelaxed form contributes to the observed resonance Raman spectrum to a large extent.
Chapter 3

*Picosecond and femtosecond time-resolved resonance Raman studies of the hydrated electron*
Abstract

Picosecond time-resolved Raman spectra of water were measured under the resonance condition with the electronic transition of the hydrated electron. Transient Raman bands were observed in the bend and the stretch regions in accordance with the generation of the hydrated electron. The lifetime of the transient Raman bands were shortened by the addition of the electron scavenger, in exactly the same manner as the hydrated-electron absorption. It was concluded that the observed transient Raman bands are attributed to the water molecules that directly interact with the electron in the first solvation shell. The resonance enhancement factors were estimated as high as $\sim 10^5$ (bend) and $\sim 10^3$ (stretch) when the probe wavelength was tuned to the absorption maximum of the $s \rightarrow p$ transition of the hydrated electron. The observed very high resonance enhancement indicated that the vibrational state of the solvating water molecules is strongly coupled with the electronic state of the electron. This implied that we should consider the electron and the solvating water molecules together (as a “quasi-molecule”) when we discuss the vibronic state of the local solvation structure. The probe wavelength dependence of the transient Raman intensity was examined in a wide range from 410 nm to 800 nm. The obtained excitation profiles suggested that the $s \rightarrow$ conduction band transition does not significantly contribute to the resonance Raman enhancement. The polarized Raman measurement was also undertaken for the bend band. A non-zero depolarization ratio was observed, which showed that the nondegeneracy of the three sublevels in the excited p state can be observed on the time scale of the Raman process. The bending and stretching frequencies of the solvating water molecule are down-shifted compared with the frequencies of the bulk water, indicating that a structural change is induced by the strong interaction with the electron.

Femtosecond time-resolved resonance Raman spectra of the nonequilibrated hydrated electron were measured. The temporal intensity change of the intra- and intermolecular vibrational Raman bands, the luminescence band, and the transient absorption signals was investigated. The Raman and luminescence signals exhibited the same temporal behavior. The rise-up time of the Raman bands was reproduced neither by the equilibrated-electron
population nor by the transient absorption at the probe wavelength. This result leads us to
conclude that the electronic state of the so-called “wet” electron is the ground s state, and that
not only the $s \rightarrow p$ transition but the $s \rightarrow$ conduction band transition contributes to the
transient absorption at 800 nm during the wet-electron equilibration. To confirm this
conclusion, we measured the probe wavelength dependence of the temporal behavior of the
Raman signal, and found that the signal measured under the higher-energy probe condition
rose up slower. It indicates that the effective resonance condition changes with time. The
resonance anti-Stokes Raman spectra from the nonequilibrated hydrated electron were
measured, but no anti-Stokes band was observed. On the basis of the present Raman results,
the nature of the electronic states of the nonequilibrated hydrated electron was discussed.
3-1 Introduction

When the electron is ejected into water, it is solvated by surrounding water molecules and forms the hydrated electron. The hydrated electron has been attracting much interest in wide fields in chemistry, physics and biology because of its fundamental importance. Large number of spectroscopic studies has been carried out. First optical properties of a characteristic absorption spectrum peaked around 720 nm (Figure 3-1) were reported by pulse radiolysis about 40 years ago\(^1\). The pressure, temperature and isotopic dependence of the absorption spectrum shape of the fully-relaxed hydrated electron have been investigated in detail\(^2,3\). The absorption spectrum has an asymmetric shape that is well fitted with a combination of the Gaussian (\(\lambda > \lambda_{\text{max}}\)) and Lorentzian (\(\lambda < \lambda_{\text{max}}\)) functions. The hydrated electron is generated not only by the electron beam radiation but by photoionization of neat water or organic molecules and by photodetachment from anions such as ferrocyanide and iodide via the charge-transfer-to-solvent state. The absorption spectrum of the hydrated electron generated by photolysis is identical with that created by radiolysis\(^4\). The theoretical calculation indicated that the ground state and the first excited state of the hydrated electron are the s-like and the p-like states, respectively, and that the absorption band is mainly attributed to the \(s \rightarrow p\) transition of the electron in a solvent cavity. The

![Figure 3-1](image)

**Figure 3-1** The absorption spectrum of the hydrated electron at 298 K from ref. 3
excited p-state intrinsically has three sublevels which are mutually perpendicular. These triple p-like excited states are considered to be nondegenerate owing to asymmetrical solvation cavity, which makes the $s \rightarrow p$ absorption very broad. The energy of the excited p-state is located just below the conduction band (CB) and the higher-energy side of the p-state distribution is lower-energy side of the conduction band (Figure 3-2)\textsuperscript{5,6}.

In order to understand the physicochemical properties of the hydrated electron, the information about the local solvation structure is obviously indispensable. For hydrated electron trapped in low temperature glass matrices, ESR spectroscopy revealed that equivalent six water molecules solvate the electron octahedrally in the first solvation shell, in which one of the OH bonds of each water molecule is oriented towards the electron (Figure 3-3). The distance between the center of the electron and the closest hydrogen atom was evaluated to be 0.21 nm\textsuperscript{7}. A molecular dynamics simulation indicated that the orbital radii of the hydrated electron in the ground s-state and the excited p-state are ~ 0.2 nm and ~ 0.3 nm, respectively\textsuperscript{5}, and the electron is localized in a solvent cavity\textsuperscript{8}. The structure of the water cluster anions in the gas phase has also been studied experimentally and theoretically, as a model of the hydrated electron\textsuperscript{9-13}. These works provided important information about the local solvation structure as well as the interaction between the electron and the water molecule. However, direct information about the local solvation structure is still scarce in
the condensed phase, especially for the hydrated electron at room temperature.

For the observation of the ultrafast generation dynamics of the hydrated electron, a large number of time-resolved absorption studies have been carried out\textsuperscript{14-36}. Because the electron ejected into water is fully relaxed within a few picoseconds, femtosecond pump-probe spectroscopy is essential and has been performed with use of two-\textsuperscript{14-26,36} or three-pulse sequences\textsuperscript{27-35} (Figure 3-4). The absorption signal of a precursor to the fully hydrated electron after photoionization was first observed in 1987\textsuperscript{14}, whereas its existence had been predicted based on the picosecond time-resolved experiments in alcohols\textsuperscript{37-40}. This precursor was named the “wet” electron\textsuperscript{16}. To investigate the generation process of the hydrated electron, the assignment of the wet electron is still under hot discussion that is classified into following three groups: (1) The wet electron is assigned to the excited p state\textsuperscript{14-17,19,20}; (2) Both the p and s states contribute the wet-electron absorption band\textsuperscript{18,21,27,28}; (3) The wet electron is attributable solely to the s state\textsuperscript{22-26,31,34,35}. The wet electron shows a broad absorption band in the near-infrared region just after photoionization, and the band subsequently shifts the higher-energy side until it becomes identical with the fully-relaxed
band centered at 720 nm. This dynamic peak shift has been given following three different explanations: (i) the internal conversion from the p state to the s state\textsuperscript{14-17,19,20}; (ii) both the stepwise transition between the two states and the spectral shift due to the solvation\textsuperscript{18,21,27,28}; (iii) the continuous shift attributable to either thermalization\textsuperscript{25,34,35} or solvation\textsuperscript{22-24,26,31} in the ground state. Recently an optical absorption spectrum of the precursor to the wet electron has been discovered in mid-infrared region\textsuperscript{36}. So far, ultrafast time-resolved absorption spectroscopy has played an important role to investigate the generation dynamics of the hydrated electron. However, it is still difficult to give a clear-cut answer to the above problems only on the basis of the time-resolved absorption studies.

In this chapter, from a viewpoint of the vibrational spectroscopy, the study for the structure, electronic states, and relaxation dynamics of the hydrated electron is reported. First, in Section 3-2, the novel resonance Raman enhancement of the local solvation structure around the hydrated electron is discussed based on picosecond time-resolved resonance Raman spectroscopy. Second, in Section 3-3, the energy relaxation dynamics of the electron photoejected into water is investigated by femtosecond time-resolved resonance Raman spectroscopy.
3-2 Observation of the resonance Raman scattering from the hydrated electron:
Picosecond time-resolved resonance Raman study

3-2-1 Introduction

Although many spectroscopic studies have been carried out, direct information about solvation structure is scarce especially for the solvated electron in the condensed phase at room temperature. To determine its structure, it is very desirable to measure vibrational spectra of the solvating water molecules. However, it is not an easy task because the signal from the bulk solvent dominates spectra in ordinary circumstances. Resonance Raman spectroscopy can overcome this problem owing to its high-sensitivity and high-selectivity.

In this section, the picosecond time-resolved Raman study of the hydrated electron is presented. The transient Raman bands are observed in the bend and stretch regions in accordance with the presence of the hydrated electron. The mechanism of this novel resonance enhancement is considered on the basis of the vibronic theory of the resonance Raman scattering. The probe wavelength dependence of the transient Raman intensity and the data of the polarization measurements are examined. The down-shifted bending and stretching frequencies of the solvating water molecules are discussed in relation to the local structure around the electron.

3-2-2 Experimental

The experimental setup for picosecond time-resolved Raman measurements has been already described elsewhere\textsuperscript{41,42}, and is shown in Figure 3-5. Briefly, a picosecond mode-locked Ti:sapphire laser (Spectra-Physics, Tsunami) pumped by an Ar\textsuperscript{+} ion laser (Spectra-Physics, Beamlok 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). The pulse width, energy, and repetition rate of the amplified pulse were 2 ps, 600 µJ, and 1 kHz, respectively. The wavelength was changed from 770 to 840 nm by tuning the color of the oscillator laser.
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. Six wavelengths, 410, 494, 620, 770, 800, and 810 nm, were used for probing transient resonance Raman scattering. The 770-nm, 800-nm and 810-nm pulses were the fundamental output of the Ti:sapphire laser. The 410-nm pulse is the second harmonic of the laser output. The 494-nm (the first Stokes line) and 620-nm (the second Stokes line) pulses were generated from a H₂ Raman shifter that was excited by the second harmonic (410 nm). The third harmonic pulses (273 nm for the 410, 494, and 620 nm probe, 257 nm for the 770 nm probe, 267 nm for the 800 nm probe, and 270 nm for 810 nm probe) of the amplified pulse were used for the photoexcitation to generate hydrated electrons. The pump and probe pulses were focused by a quartz lens (f = 50 mm) onto a thin film-like jet stream (thickness ~ 300 µm) of the sample solution. Typical pulse energy is 20 ~ 25 µJ (pump) and 1 ~ 10 µJ (probe) at the sample point. 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) using a camera lens. A holographic notch filter (Kaiser Optical Systems, Inc.) or sharp-cut colored glass filters (HOYA) were used to eliminate Rayleigh scattering. A liquid nitrogen cooled CCD camera (Princeton Instruments, LN/CCD-1100PB) was used for the detection of Raman scattering in the visible region, whereas a liquid nitrogen cooled InGaAs detector (Jobin-Yvon, IGA-512×1-1) was used for the near-infrared Raman detection. Time-resolved absorption was measured by monitoring the intensity of the probe pulse that passed through the sample.

Indole (special grade) was purchased from Tokyo Chemical Industry Co., Ltd. and sublimated in vacuo. Potassium ferrocyanide trihydrate (special grade) was purchased from Wako Pure Chemical Industries and used without purification. Water was distilled and deionized before use. Acetonitrile (HPLC grade) and acetone (special grade) were purchased from Wako Pure Chemical Industries and used as received.
3-2-3 Results and discussion

3-2-3-1 Observation of the resonance Raman scattering from the hydrated electron

**Bend mode.**

Figure 3-6(a) 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 hydrated electron, since indole injects electrons much more easily than neat water owing to its low ionization potential (indole 4.35 eV\textsuperscript{43}; water 8.8 eV\textsuperscript{20}). As clearly seen in this figure, a transient absorption signal appeared immediately after photoexcitation. The intensity maximum of the $s \rightarrow p$ transition of the hydrated electron is located around 720 nm, so that the observed transient absorption is attributable to the hydrated 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\textsuperscript{44}. The lifetime of the hydrated electron is as long as a few hundreds nanoseconds in the absence of the electron scavenger\textsuperscript{4}. 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 within a few picoseconds\textsuperscript{14-36}.

Figure 3-6(b) shows picosecond time-resolved resonance Raman spectra of water in the bend region measured with 800-nm probe. This probe wavelength is close to the maximum of the transient absorption of the hydrated electron. The spectrum taken with pump pulse irradiation has been already subtracted from the time-resolved spectra shown in this figure. In the spectrum taken before the pump irradiation (-10 ps), as well as in the spectrum measured with only probe pulse irradiation, only a weak Raman band due to the bending vibration of the bulk water was observed at $\sim$ 1640 cm$^{-1}$. After the pump irradiation, a strong transient Raman band appeared on a featureless luminescence signal in accordance with the generation of the hydrated electron. The peak frequency of the transient Raman
Picosecond time-resolved Raman spectra from neat water as well as water in the presence of other seed molecules (KI, etc.) were also measured, and the same transient Raman band was observed in all cases. In addition, it was 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.

Figure 3-6  (a) Time-resolved absorption trace, and (b) picosecond time-resolved resonance Raman spectra in the bend region of water in the presence of indole (1.7 × 10⁻³ mol dm⁻³; pump laser, 267 nm; probe laser, 800 nm). The spectrum taken with only pump pulse irradiation has been subtracted from each time-resolved spectrum.
compared with those in the indole aqueous solution. This weak transient signal in neat water is ascribable to the low yield of the hydrated 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

Figure 3-7  (a) Time-resolved absorption trace and (b) picosecond time-resolved resonance Raman spectra in the bend region of a water-acetonitrile mixture (4:1) in the presence of indole ($1.7 \times 10^{-3}$ mol dm$^{-3}$; pump laser, 267 nm; probe laser, 800 nm). The Raman intensity at each delay time has been normalized by using the acetonitrile band intensity. The spectrum taken with only pump pulse irradiation and luminescence signal arising from probe pulse irradiation has been subtracted from each time-resolved spectrum. The Raman band of acetonitrile is indicated by an asterisk.
water transient that appears along with the hydrated electron. The featureless luminescence signal observed with the transient Raman band is assigned to the fluorescence of the hydrated electron\(^{45}\).

The time-resolved spectra shown in Figure 3-6(b) indicate that the observed water transient species gains high Raman intensity enhancement under the resonance condition with the electronic transition of the hydrated electron. However, in the time-resolved resonance Raman measurements, it is difficult to quantitatively compare the intensity of Raman band measured at different delay times, because Raman scattering is re-absorbed by the sample that exhibits transient absorption. In the present experiment, it was also necessary to assure that the optical artifacts such as thermal effects did not affect the time-resolved Raman spectra. Thus, picosecond time-resolved Raman spectra of a water-acetonitrile mixture (4:1) were measured. It has been reported that the hydrated electron is not formed in acetonitrile\(^{44}\), so that the Raman bands of acetonitrile do not change with the generation of the hydrated electron. Therefore, the acetonitrile Raman bands can be used as the intensity standard, and the Raman intensity in time-resolved spectra can be quantitatively compared after intensity normalization. (Because of this reason, a water-acetonitrile mixture was often used in the experiments described in the present report.) The intensity-normalized time-resolved Raman spectra obtained from a water-acetonitrile mixture are shown in Figure 3-7. The same transient Raman band was observed at the same position (~ 1610 cm\(^{-1}\)) as observed in the time-resolved spectra of water. The intensity of the transient Raman band was about 4 times larger than that of the bulk water in spite of the low concentration of the transient species (\textit{vide infra}), which confirmed that the water transient Raman band gains very high resonance enhancement through the electronic transition of the hydrated electron.

The observed high resonance enhancement indicates that there exists a strong coupling between the water transient and the electron. In other words, the transient species giving rise to the strong resonance Raman band is attributable to the water molecule that strongly interacts with the electron.
In order to confirm this assignment, the temporal behavior of the observed transient Raman band in the presence of an electron scavenger was investigated. Although the lifetime of the hydrated electron is as long as a few hundreds nanoseconds in pure water\textsuperscript{4}, it is significantly shortened in the presence of the electron scavenger. For example, it is known that acetone efficiently quenches the hydrated electron by the following reaction\textsuperscript{46}:

\[
\begin{array}{c}
\text{acetone} + e_{\text{aq}}^\cdot \rightarrow \text{acetone-H} + e^{-} \\
\text{acetone-H} + H_2O \rightarrow \text{acetone} + H_2O \\
\text{acetone} + H_2O \rightarrow \text{HO-acetone} \\
\text{HO-acetone} + H_2O \rightarrow \text{HO-acetone} + H_2O \\
\text{HO-acetone} + H_2O \rightarrow \text{HO-acetone} + H_2O
\end{array}
\]

Figure 3-8  Picosecond time-resolved resonance Raman spectra in the bend region of a water-acetonitrile mixture (4:1) in the presence of indole (1.7 × 10\textsuperscript{-3} mol dm\textsuperscript{-3}) and 1 % acetone (pump laser, 267 nm; probe laser, 800 nm). The Raman intensity at each delay time has been normalized by using the acetonitrile band intensity. The spectrum taken with only pump pulse irradiation and luminescence signal arising from probe pulse irradiation has been subtracted from each time-resolved spectrum. The Raman band of acetonitrile is indicated by an asterisk.
Thus, acetone was added to the sample, and the effect on the temporal behaviors of the transient Raman and transient absorption intensities was compared.

Time-resolved Raman spectra of a water-acetonitrile mixture in the presence of 1 % acetone were measured. Figure 3-8 shows the obtained picosecond time-resolved resonance Raman spectra in the bend region. The luminescence background has been subtracted from each time-resolved Raman spectrum, and the Raman intensity at each delay time has been normalized with use of the acetonitrile Raman band intensity. As marked by

\[ CH_3COCH_3 + e_{at}^- \rightarrow CH_3\dot{C}OCH_3^- \]  \hspace{1cm} (3-1)

**Figure 3-9** Temporal intensity change of the transient Raman band at 1610 cm\(^{-1}\) and transient absorption trace monitored at 800 nm. (a) A water-acetonitrile mixture (4:1) in the presence of indole and 1 % acetone and (b) water in the presence of indole. Concentration of indole is \(1.7 \times 10^3\) mol dm\(^{-3}\). Temporal intensity change of Raman band have been normalized at the intensity measured at 10 ps. Large black circles indicate the intensity of transient Raman band at 1610 cm\(^{-1}\). Small circles and solid lines exhibit the intensity of transient absorption and the best fitted curves, respectively.
arrows, the transient Raman band was observed. However, in the presence of acetone, the transient Raman band decayed within a few nanoseconds. In Figure 3-9, the temporal change of the intensity of the transient Raman band at \( \sim 1610 \text{ cm}^{-1} \) is compared with the decay of the transient absorption at 800 nm. As clearly seen, the temporal change of the transient Raman band is in very good agreement with that of the transient absorption, and they show a rapid decay with a lifetime of as short as 1.2 ns. For comparison, the temporal behavior in the absence of acetone is also shown in Figure 3-9(b). Reflecting the long lifetime of the hydrated electron without any scavenger, both of the transient Raman and absorption signals did not show any noticeable decay in the time range of the present measurements. These results clearly demonstrated that the transient Raman band is quenched by the electron scavenger in exactly the same manner as the hydrated electron. This shows that the relevant water transient certainly appears and disappears in accordance with the hydrated electron.

**Stretch mode.**

Time-resolved Raman spectra in the stretch region could not be measured with the 800-nm probe using highly sensitive CCD, because the stretch band appears around 1.1 \( \mu \text{m} \) where CCD does not have sensitivity. Therefore, experiments for the stretch region were carried out with use of an InGaAs array detector (Figure 3-5). In contrast to the drastic change observed in the bend region, the spectral change induced by the generation of the hydrated electron was not very large in the stretch region. Actually, we needed to perform careful measurements to confirm the existence of the transient Raman band in this region. Figure 3-10(a) depicts picosecond time-resolved resonance Raman spectra of a water-acetonitrile mixture (4:1) probed at 800 nm. The spectra measured in the presence of acetone are shown here, in order to discuss the temporal behavior of the spectral feature. Figure 3-10(b) shows the time-resolved spectra obtained after spectral subtraction. The spectrum taken with only probe irradiation as well as the featureless luminescence was subtracted. Although the S/N ratio is not high, a weak transient Raman band is clearly
recognized around 3170 cm\(^{-1}\). This transient Raman band decays in a few nanoseconds in the presence of the electron scavenger (acetone), which indicates that this transient band is also attributable to the water molecule that interacts with the hydrated electron. It should be noted that the acetonitrile Raman bands were completely erased in the subtracted spectra. It assured the validity of the subtraction procedure, and hence assured the existence of the transient Raman band observed in the stretch region.

The sensitivity of the InGaAs detector is lower than CCD, which made the S/N ratio of

\[ 49 \]
the spectra in the stretch region much lower. As described in Section 3-2-3-3, picosecond time-resolved Raman measurements using shorter probe wavelengths were also carried out. In such measurements, the stretch band of the water transient was detected with CCD. For comparison, the spectrum measured with the 620-nm probe is depicted in Figure 3-10(c). A transient Raman band is clearly seen at the same position (~ 3170 cm\(^{-1}\)) as observed in the spectra measured with 800-nm probe.

3-2-3-2 Assignment of the transient water and resonance Raman mechanism

The experiments described in the previous section showed that the observed transient Raman bands are attributed to the vibration of the water transient that appears and disappears in accordance with the hydrated electron. The frequencies of the two transient Raman bands (the bend and stretch bands) are lower than the frequencies of the corresponding Raman bands of the bulk water, which indicates that the structure of the water transient is somewhat different from that of water molecules in the bulk. These results strongly suggest that the observed water transient is ascribed to the water molecule that directly interacts with the hydrated electron.

For the local structure around the hydrated electron, Keavan studied the electron trapped in a low-temperature glass matrix\(^7\). On the basis of the ESR data, they concluded that six water molecules solvate the electron in the first solvation shell and that one of the OH bonds of each water molecule is oriented towards the electron. The distance between the center of the electron and the closest hydrogen atom was estimated to be ~ 0.2 nm (Figure 3-3). This local solvation structure was determined for a low-temperature matrix. At room temperature, it is expected that the solvation structure is fluctuated and not solid. Nevertheless, the averaged structure may be considered essentially similar. On the other hand, a molecular dynamics simulation indicated that the orbital radii of the hydrated electron in the ground s-state and the excited p-state are ~ 0.2 nm and ~ 0.3 nm, respectively\(^5\),
and the electron is localized in a solvent cavity. Because the orbital radius of the hydrated electron is almost the same as the distance between the electron and the closest water molecule, it is natural to think that the water molecules in the first solvation shell interact with the electron much more strongly than those in the outer shell. Therefore, it is highly likely that the water transient observed in the time-resolved resonance Raman measurements is the water molecule in the first solvation shell around the electron. This argument is strongly supported by the experiments of water-acetonitrile mixtures described in the previous sections. In the presence of the high concentration of acetonitrile in solutions (which is added as the Raman intensity standard), the outer solvation shell is highly likely perturbed. Nevertheless, the Raman spectra of the water transients observed in the mixture do not show any noticeable change compared with those taken in neat water. Thus, it is concluded that the vibrational spectra of the very local solvation structure around the electron are observed when we measure Raman scattering under the resonance condition with the absorption of the hydrated electron.

It was surprising that the solvating water molecule gains high resonance Raman enhancement through the electronic transition of the electron. However, this intensity enhancement can be treated in the framework of the standard vibronic theory of the resonance Raman scattering, if we deal with the electron and the solvating water molecules as a whole, in other words, as a “cluster” or a “quasi-molecule”.

In the frequency-domain representation, the intensity of the Raman scattering relevant to the \( m \rightarrow n \) vibrational transition is represented as,

\[
I_{mn} = \frac{2^7 \pi^5}{3^2 c^4} I_0 (v_n - v_m)^2 \sum_{\rho, \sigma} \left| \alpha_{\rho \sigma} \right|^2 ,
\]

\[
(\alpha_{\rho \sigma})_{mn} = \sum_r \left[ \frac{\langle n | \mu_\rho | r \rangle \langle r | \mu_\sigma | m \rangle}{E_r - E_n - E_0 - i\Gamma} + \frac{\langle n | \mu_\sigma | r \rangle \langle r | \mu_\rho | m \rangle}{E_r - E_n + E_0 - i\Gamma} \right] .
\]

Here, \( \alpha_{\rho \sigma} \) is the \( \rho \sigma \)th component of the Raman tensor; \( I_0 \) is the intensity of the incident light;
$E_0$ is the photon energy of the incident light; $\nu_{mn}$ is the Raman shift ($= (E_m - E_n)/\hbar$); $m$, $n$, and $r$ are the initial, final, and intermediate states, respectively; $\mu_\rho$ is the $\rho$th component of the electronic dipole moment operator. In the standard vibronic theory of the resonance Raman scattering, each state is expressed as the product of the electronic and vibrational wavefunctions (the Born-Oppenheimer approximation), and then the Raman tensor is expanded using the Herzberg-Teller expansion. The resultant zero-th and first order terms of the vibronic coupling are called as the $A$ (the zero-th order) and $B, C$ (the first-order) terms. It is known that, in usual cases, the intensity enhancement of resonance Raman scattering is attributed to the $A$ term (the Franck-Condon mechanism):

\[
\langle \alpha_{\rho\sigma} \rangle_{\rho\sigma} \approx A + B + C \cdots ,
\]

(3-3)

where

\[
A \propto \sum_{v \neq g} \sum_{\rho} \left[ \frac{\langle g | \mu_\rho | g \rangle \langle e | \mu_\rho | e \rangle}{E_m - E_n - E_0 - i\Gamma} \right] \langle j | v \rangle \langle v | i \rangle .
\]

(3-4)

As seen in this formula, the $A$ term contains the Franck-Condon factor between the vibrational states in the ground and excited states. Therefore, in order that a particular vibrational mode gains high intensity enhancement in the resonance Raman process, the vibrational states having different quantum number in the ground and excited states need to have a significant Franck-Condon factor. Thus, the potential curves of the ground and excited states need to be displaced along the relevant vibrational coordinate.

Concerning the resonance Raman scattering from the hydrated electron, the electron and the surrounding water molecules have to be treated together. (For the sake of convenience, it is called the “hydrated-electron cluster”.) Then, like an ordinary molecule, the vibronic states of the “hydrated-electron cluster” can be expressed as the product of the electronic and vibrational wavefunctions:
Here, $g_{e\text{ - water}}$ and $e_{e\text{ - water}}$ represent the electronic ground and excited states of the “hydrated-electron cluster”, respectively (Figure 3-11). In these formulas, the vibrational wavefunctions represent intra- and inter-molecular vibrations of solvating water molecules. Because the excitation is localized in the electron at the center (and hence the electronic excitation of water molecules are negligible), the ground and excited states of the “hydrated-electron cluster” is essentially the $s$ and $p$ states of the electron at the center. Then, the formula of the $A$-term resonance (3-4) can be rewritten as follows:

$$
|m\rangle = |g_{e\text{ - water}}\rangle |i\rangle \\
|n\rangle = |g_{e\text{ - water}}\rangle |j\rangle \\
|r\rangle = |e_{e\text{ - water}}\rangle |v\rangle 
$$

(3-5)
Because the interaction between the electron and water molecules in the first solvation shell is very strong, it is expected that the vibrational states (or structure) of the solvating water molecules are significantly changed with the change of the electronic state of the hydrated electron. In this case, as the formula (3-6) indicates, a strong resonance Raman effect is expected for the vibrational modes of the solvating water molecules along which the structural change is induced with the electronic excitation of the electron.

The intensity of resonance Raman spectra provides information about the structural change induced with the electronic transition. In the resonance Raman spectra probed at 800 nm, the intensity of the bend band is highly enhanced whereas the stretch band gains only moderate intensity enhancement. This indicates that the structural change, which is induced on the solvating water molecules by the $s \rightarrow p$ transition of the electron, is large along the bend coordinate but relatively small for the stretch coordinate.

3-2-3-3 Excitation profiles: Probe wavelength dependence of resonance Raman intensity

The vibronic theory of resonance Raman scattering indicates that the intensity enhancement of Raman scattering is attributable not solely to the property of the ground state but to the character of the electronic transition in resonance (the structural change induced by the electronic transition). Therefore, the resonance Raman intensity should significantly vary when the electronic transition in resonance is changed. Keeping this point in our mind, the excitation (probe) wavelength dependence of the intensity of resonance Raman scattering
from the hydrated electron was examined.

Picosecond time-resolved Raman spectra with four more probe wavelengths (410, 494, 620, 770 nm) were measured, and they were compared with the spectra taken with 800-nm probe. Five wavelengths, in total, cover almost the entire region of the broad absorption of the hydrated electron. In order to obtain reliable excitation profiles, several notices were paid. First, a water-acetonitrile mixture as the sample was used in order to utilize the acetonitrile bands as the internal standard for the intensity normalization. Second, in the experiments using shorter wavelengths, potassium ferrocyanide (K₄Fe(CN)₆) was used as a seed molecule, in place of indole, because the cation radical of indole exhibits transient absorption around 580 nm. It is known that the ferrocyanide ion and its photo-oxidized products do not show any absorption in the visible wavelength region. Third, the probe intensity was set as low as possible, in order to minimize the photo-bleaching of the ground-state hydrated electron. Actually, a significant bleaching effect was observed in the experiment using the probe wavelength shorter than 500 nm.

The obtained time-resolved Raman spectra are shown in Figure 3-12 (the bend region) and Figure 3-13 (the stretch region). The spectrum in the stretch region measured with the 770-nm probe is not shown, because the S/N ratio was very low. Either of the detectors, CCD or the InGaAs array, did not provide good data for the relevant wavelength region. For quantitative discussion, the enhancement factor of the transient Raman bands (the intensity ratio between the Raman scattering from a transient water molecule and that of a bulk water molecule) at each excitation wavelength was calculated by the following way: First, the time-resolved spectra measured at 20 ps were compared with the spectra taken with only probe irradiation, and the apparent intensity ratio \( R_p = \frac{I_{\text{transient}}}{I_{\text{bulk}}} \) between the water transient Raman band and the bulk water band was evaluated. Second, the concentration of the hydrated electron \( c_{\text{electron}} \) was estimated from the transient absorption intensity. For the estimation, both the absorption coefficient of the hydrated electron \(^3\) and the optical path length of the sample solution (300 µm) were used. The concentration of the hydrated
Figure 3-12  Raman spectra of a water-acetonitrile mixture (4:1) in the bend region. (1) Spectra measured at 20 ps delay time. Featureless luminescence signals were subtracted; (2) Spectra taken with only probe pulse irradiation; (3) Subtracted spectra, (1) – (2). The probe wavelength used for each experiment is indicated in the figure. Potassium ferrocyanide (5 × 10⁻³ mol dm⁻³; 410–770-nm probe), or indole (1.7 × 10⁻³ mol dm⁻³; 800-nm probe) was added as a seed molecule. Raman intensity has been normalized by using the acetonitrile Raman band that is indicated by an asterisk.
electron varied in the range between $1.8 \times 10^{-4}$ and $2.5 \times 10^{-3}$ mol dm$^{-3}$, reflecting the difference in the experimental condition (the energy of the pump pulse, the focus size, etc.).

Then, assuming that the number of the water molecules in the first solvation shell is also $\sim 6$ in water at room temperature ($N_{\text{solvation}} \approx 6$), the concentration of the water molecules that give rise to the transient Raman band was estimated. Since the concentration of the bulk water is readily obtained ($c_{\text{bulk water}} = 44$ mol dm$^{-3}$ in the water-acetonitrile mixture), the resonance enhancement factor, $f_{\text{resonance}}$, was calculated by using the following formula,
\[ f_{\text{resonance}} = R_T \cdot \frac{c_{\text{bulk water}}}{N_{\text{solvation}} \cdot c_{\text{electron}}} \]  

(3-7)

The resonance enhancement factor calculated for each probe wavelength is listed in Table 3-1 with the parameters used in the calculation. The excitation profiles are plotted in Figure 3-14 with the absorption spectrum of the hydrated electron. It is noted that the ambiguity in \( N_{\text{solvation}} \) might cause some error in the absolute value of the evaluated resonance enhancement factor. However, it does not affect relative values, so that it does not change the shape of the excitation profiles shown in Figure 3-14.

The obtained excitation profiles show that both of the vibrational bands, the bend and stretch bands, gain high intensity enhancement when the probe wavelength is tuned around the maximum of the hydrated electron absorption. The enhancement factor of the bend band becomes as large as \( \sim 2 \times 10^5 \). This enhancement factor is fairly large, even compared with the resonance Raman scattering from ordinary molecules. The enhancement factor of the stretch band is much smaller, but it is still as large as \( \sim 4 \times 10^3 \). A characteristic feature seen in the excitation profiles of the bend and stretch bands is that the resonance enhancement factor sharply decreases in the blue side of the absorption (< 500 nm). Especially, the enhancement factor becomes very little at 400 nm, although the hydrated electron still exhibits significant absorption.

The very small resonance enhancement in the blue side of the absorption is highly likely to reflect the difference in the nature of the electronic transition. The electronic state of the hydrated electron was theoretically studied by Schnitker et al (Figure 3-2)\(^5\). Their calculation showed that the energy of the p-type excited state is located just below the continuum (the conduction band, CB) and that the high energy side of the p-state distribution is overlapped with the low energy side of the conduction band. It implies that the blue side of the absorption of the hydrated electron has a nature of the \( s \rightarrow \text{CB} \) transition, although the major part of the absorption is attributable to the \( s \rightarrow p \) transition. This conclusion of the
theoretical calculation has been supported experimentally, for example, by recent femtosecond time-resolved absorption experiments of Barbara and coworkers\textsuperscript{32,33}. They photoexcited the s state to the CB band with the 400-nm pulse and observed that geminate 

\begin{table}[h]
\centering
\caption{Table 3-1 Resonance enhancement factor of the bend and stretch bands}
\begin{tabular}{cccccc}
\hline
\textbf{Excitation profiles of the bend (a) and stretch (b) bands.} The absorption spectrum reported by ref. 3 is also shown with solid lines.
\end{tabular}
\end{table}
recombination is suppressed owing to the detrapping of the electron. Therefore, very small resonance Raman enhancement in the blue side of the absorption implies that the Raman scattering from the solvating water molecules are enhanced under the resonance condition with the $s \rightarrow p$ transition, but not with the $s \rightarrow CB$ transition. This conclusion is very consistent with the standard vibronic theory discussed in the previous section, because it is expected that the structural change induced by the $s \rightarrow CB$ transition is significantly different from that caused by the $s \rightarrow p$ transition.

3-2-3-4 Polarized Raman measurements: Nondegeneracy of the sublevels of the $p$ state of the hydrated electron

The present Raman study demonstrates that we should consider the electron and the solvating water molecules together as a “hydrated-electron cluster” when we discuss the vibronic state of the local solvation structure. Nevertheless, the ground and excited states of the “hydrated-electron cluster” is essentially the $s$ and $p$ states of the electron at the center. It is expected that the properties of the excited $p$ state are strongly affected by the symmetry of local solvation structure, and it has been an issue of intense discussion.

The excited $p$ state intrinsically has three sublevels, $p_x$, $p_y$, and $p_z$. If the system is isotropic, these three sublevels are degenerate, as the case of the $2p$ state of the hydrogen atom. However, a theoretical calculation based on the cavity model indicated that the $p_x$, $p_y$ and $p_z$ states of the hydrated electron are not degenerate because of the non-spherical nature of the solvent cavity. The energy splitting of the three sublevels was estimated as large as 0.8 eV. This argument from the theory is widely accepted, but it has not been well supported by the experiment. For example, Assel et al. measured femtosecond time-resolved absorption following the $s \rightarrow p$ photoexcitation but did not detect either anisotropy or hole burning in the absorption signal.

The polarization measurement of Raman scattering (the Raman depolarization ratio)
affords decisive information about the symmetry of the molecular vibration: In non-resonant case, the totally symmetric vibration gives the depolarization ratio between 0 and 0.75 \( (0 \leq \rho < 0.75) \) whereas the non-totally symmetric vibrations give the value of 0.75 \( (\rho = 0.75) \). Moreover, in the case of resonance Raman scattering, the Raman depolarization ratio provides information about the symmetry and degeneracy of the excited state in resonance. For example, when the resonant excited state is nondegenerate and only one component of the transition moment from the ground state is non-zero, the depolarization ratio is known to become 1/3, because only one diagonal component of the Raman tensor \( (\alpha_{xx}, \alpha_{yy}, \text{or} \alpha_{zz}) \) can have a non-zero value. Therefore, the polarization measurement of resonance Raman scattering can provide unique information about the excited p state of the hydrated electron.

Polarized time-resolved resonance Raman spectra of the bend region were measured at the delay time of 20 ps and they are shown in Figure 3-15. Although the quality of the obtained spectra is not good, the transient Raman band due to the bending vibration of the solvating water molecules was clearly seen as marked by arrows. It is obvious that the transient Raman band was observed also in the perpendicular spectrum, although the quite low S/N ratio hindered us from determining the depolarization ratio quantitatively. This demonstrates that the depolarization ratio of the transient resonance Raman band is definitely not zero.

If the local environment around the electron is isotropic, the three sublevels of the excited p state are degenerate. Then, the \( p_x, p_y \) and \( p_z \) states equivalently contribute to the resonance Raman process and the three diagonal components of the Raman tensor \( (\alpha_{xx}, \alpha_{yy}, \text{or} \alpha_{zz}) \) have the same value. (The Raman tensor becomes isotropic.) This type of the isotropic Raman tensor gives the Raman depolarization ratio of zero \( (\rho = 0) \). However, the observed Raman depolarization ratio is not zero, which sharply contradicts the above argument based on the degeneracy of the three sublevels. Therefore, the observed non-zero depolarization ratio strongly implies that the three sublevels of the p state do not equally contribute the resonance Raman process. In other words, the resonance Raman process
seems to “feel” the nondegeneracy of the $p_x$, $p_y$, and $p_z$ states, within a time scale of its optical process.

The time scale of the resonance Raman process is equivalent to the dephasing time of the electronic transition. Therefore, it can be estimated from the width of the absorption band. The absorption of the hydrated electron is asymmetric and is considered to be broadened due to the nondegeneracy of the three sublevels of the p-state (inhomogeneous broadening). Nevertheless, the apparent band width of the absorption gives the shortest limit of the time scale of the resonance Raman process. The band width of the hydrated electron absorption is approximately $\sim 6700 \text{ cm}^{-1}$, which corresponds to a time scale (a dephasing time) of $2 \sim 3$ fs. The observed non-zero value of the depolarization ratio suggests that the nondegeneracy of the three sublevels is “observable” in this short time scale of the Raman process. Assel et al. did not observe any hole burning in their femtosecond absorption experiments, and they concluded that the relaxation among the three sublevels

---

Figure 3-15  Polarized transient resonance Raman spectra in the bend region of a water-acetonitrile mixture (4:1) in the presence of ferrocyanide ion ($5 \times 10^{-3}$ mol dm$^{-3}$; pump laser, 270 nm; probe laser, 810nm; delay time, 20 ps). (a) Parallel and (b) perpendicular polarized Raman scattering. The spectrum taken with only pump pulse irradiation and luminescence signal arising from probe pulse irradiation has been subtracted. The Raman bands of acetonitrile are indicated by an asterisk.
occurs within 80 fs\textsuperscript{35}. If their value is adopted as the upper limit, the redistribution time of the three sublevels of the p state can be considered to be in the range of \(2 \sim 3 \text{ fs} < \tau < 80 \text{ fs}\).

### 3-2-3-5 Raman spectra of the local solvation structure around the hydrated electron

As described in the present study, we can obtain Raman spectrum of the water molecules that solvate the electron, when we measure Raman scattering under the resonance condition with the \(s \rightarrow p\) transition of the hydrated electron. In Figure 3-16, the resonance Raman spectrum of the “hydrated electron” is compared with the spectrum of the bulk water. (To show the Raman spectrum measured with a single detector, the “hydrated electron” spectrum taken with the 620-nm probe is shown.) Some similarity seen between the two spectra indicates that the “hydrated electron” spectrum is basically the spectrum of water. However, the Raman spectrum of the “hydrated electron” is significantly different from the spectrum of the ordinary water in several points. First, the intensity of the bend band is much higher than that of the stretch band, reflecting the resonance condition. Second, the vibrational frequencies are down-shifted compared with the corresponding frequencies of the bulk water. The bending frequency is \(~ 30 \text{ cm}^{-1}\) lower than that of the bulk water, whereas the stretching frequency is downshifted by \(~ 150 \text{ cm}^{-1}\) from the average of the anti-symmetric and symmetric stretching frequencies of the bulk water. Third, most strikingly, the intensity of the Raman scattering is highly enhanced under this resonance condition. For example, the bend band of the solvating water molecules gains the intensity enhancement in the order of \(10^5\) when the probe wavelength is tuned to the intensity maximum of the absorption band of the hydrated electron.

The resonance enhancement as large as \(~ 2 \times 10^5\) is quite large, even compared with the resonance Raman enhancement of ordinary molecules. In fact, it is comparable to the resonance enhancement of \(\beta\)-carotene\textsuperscript{50}. This fact strongly suggests very strong interaction between the electron and the water molecules in the first solvation shell. The observed very
high resonance enhancement of the solvating water molecules claims that the picture of “an electron in a cavity” is too simple when we consider the vibronic state of the “hydrated electron”, because the electronic state of the electron and the vibrational state of the solvating molecules are strongly coupled. We should treat the hydrated electron as a “water cluster anion” in the condensed phase. This is the most important implication of the results of the present resonance Raman study.

The water cluster anion has been intensively studied in the gas phase, in relation to the interest in the hydrated electron. Therefore, it is worth comparing the vibrational frequency of the water cluster anion in the gas phase with the frequency of the water transient observed in the present time-resolved Raman study. Johnson and co-workers reported autodetachment spectra of the mass-selected water cluster anions in the gas phase, which
correspond to the IR spectra in the stretch region. They compared the obtained vibrational spectra with the result of theoretical calculations, and claimed that the water cluster anion has a linear chain-like structure, and the electron is attached at one end of the chain (Figure 3-17(a)). According to their assignment based on a density functional calculation, the stretch frequency of the water molecule that is directly attached to the electron is lower than the stretching frequency of the free OH, but it is higher than the stretching frequency of the hydrogen-bonded OH which makes the backbone of the chain-like structure. It seems that this order of the stretching frequency, $\nu_{\text{free OH}} > \nu_{\text{OH...e}} > \nu_{\text{hydrogen-bonded OH}}$, is not specific to the water cluster anion having a chain-like structure. Actually, other structures have also been suggested by theoretical calculations of the other groups, and the vibrational spectra of the several possible conformers have been calculated. In any calculated cluster anion in the gas phase, the stretching frequency of the water molecule attached to the electron is higher than that of the hydrogen-bonded OH. This is a sharp contrast to the present observation for the hydrated electron in the condensed phase. In the observed resonance Raman spectra, the stretching frequency of the solvating water molecules is lower than the frequency of the bulk water molecules which are hydrogen-bonded. This means that the electron-water interaction in the condensed phase is much stronger than that in the cluster in the gas phase. Although the structure of the water cluster anions in the gas phase is still controversial, it has been agreed that the stable water cluster anion is the surface state, in which the electron is trapped on the surface of the cluster and it is exposed to the vacuum. In such a surface state, the electron is much more delocalized, compared with the internal state. Undoubtedly, in the condensed phase, the electron is surrounded by the water molecules and hence the “water cluster anion in water” (or the “hydrated-electron cluster”), is the internal state. Naturally, the electron is more localized, which results in much stronger interaction between the electron and the water molecules in the first solvation shell (Figure 3-17(b)). It is noteworthy that theoretical calculations indicated that the stretching frequency can be a good indicator of the strength of the O-H...e$^-$ interaction. It is highly likely that the difference in the
delocalization of the electron between the gas phase and the condensed phase is reflected on the stretching frequency.

Finally, the uniqueness of the frequency shift was discussed for the bend and stretch vibrations observed in the present study. In ordinary hydrogen bonding systems, it is known that the frequency shift of the stretching vibration is opposite to that of the bending vibration\textsuperscript{51}. For example, as the hydrogen bonding strength increases, in usual cases, the stretching frequency decreases whereas the bending frequency increases. However, both of the bending and stretching frequencies of the observed water transient are lower than those of the bulk water, which means that the strong interaction with the electron causes downshifts of both of the bending and stretching frequencies. This unique frequency shifts looked puzzling for us at the beginning. However, it can be considered that these frequency shifts are also consistent with the assignment that the observed transient species is the water molecule that directly solvates the electron.

A simple explanation about the ordinary opposite frequency shift of the stretch and bend vibrations, and is described as follows, for a simplified case that an O–H bond is hydrogen-bonded to the neighboring X atom (O–H…X). Concerning the O–H stretching frequency, as the strength of the H…X hydrogen bond increases, the O–H bond strength decreases (and the bond length increases), which causes a downshift of the O–H(…X)
stretching frequency. On the other hand, for the H–O–H bending motion, the hydrogen bond between H and X atoms provides additional restoring force because the bending motion is off-axial motion for the linear O–H…X structure. In other words, the H…X hydrogen bonding acts as “the second spring” for the H–O–H bending vibration. Thus, even if the O–H bond strength decreases, as the hydrogen bonding strength increases, the force constant for the H–O–H(…X) bending motion increases with the help of the H…X hydrogen bond. As a result, the H–O–H(…X) bending frequency shows an upshift. Although this explanation is very simple, it describes the physical background of the opposite shifts of the OH stretching and HOH bending frequencies in ordinary hydrogen-bonded systems. Here, we should note that this discussion, especially for the bending vibration, assumes that the X atom is much heavier than hydrogen. It is because the end of “the second spring” needs to be fixed in a space in order that the H…X bonding acts as a restoring force. Obviously, this assumption is not valid for the case of the OH bond that interacts with the electron. In this case, X corresponds to the electron which is very light. Therefore, even if the interaction between the OH bond and the electron is strong, the O–H…e⁻ interaction does not afford any practical restoring force for the O–H(…e⁻) bending motion owing to the lightness of the electron. Thus, it seems that the HOH bending frequency does not necessarily show an upshift although the OH stretching frequency exhibits a significant downshift due to the strong O–H…e⁻ interaction. On the basis of this discussion, it is considered that the observed unique frequency shifts is consistent with the assignment that the observed water transient is the water molecule in the first solvation shell, and also it is consistent with the Keavan’s type local structure around the electron in which one of the OH bond of the water molecule is oriented toward the center of the electron. It is considered that the electron is stabilized by the electrostatic interaction between the electron and OH bond dipole in this type of the solvation structure.7
3-3 Relaxation dynamics of the hydrated electron: Femtosecond time-resolved resonance Raman study

3-3-1 Introduction

As described in Section 3-2, resonance Raman scattering from the equilibrated hydrated electron was recently discovered by two groups, our group and Mathies’ group, independently.\textsuperscript{45,52-55} Raman spectroscopy has proved to be a powerful tool to study both the local solvation structure and the nature of the resonant electronic transition of the hydrated electron.

Here time-resolved Raman measurements are applied to the study of the ultrafast dynamics of the hydrated electron that is still controversy. Picosecond time-resolved Raman spectroscopy, which has been carried out for the equilibrated electron, does not have sufficient time resolution for the dynamics of interest, because the relaxation of the hydrated electron is complete in a few picoseconds. Then, the measurement of femtosecond time-resolved resonance Raman spectra was tried. Because of the uncertainty principle, however, femtosecond time-resolved spontaneous Raman measurements are not general. Figure 3-18 shows the time traces (response time between pump and probe pulses) and spectra measured by using femtosecond and picosecond laser pulses. When we used the femtosecond pulse, though the time resolution is drastically improved (Figure 3-18(a)), the spectral width of the laser pulse is much wider than that measured by the picosecond pulse (Figure 3-18(b)). In such a case, observed Raman bands are also wider and hence overlap each other, so that the characteristic advantage of the Raman spectroscopy that we can obtain detailed information on molecular structure will be lost (Figure 3-18(c)). In the case of the water Raman bands, however, the advantage of Raman spectroscopy is preserved even with the femtosecond time resolution, because the bands are isolated and intrinsically broad (Figure 3-18(d)). This allows us to consider that femtosecond time-resolved resonance Raman spectroscopy is suitable to observe the ultrafast relaxation dynamics of the electron.
Figure 3-18  Time traces and spectra of femtosecond and picosecond laser pulses. The top of each figure is measured by a femtosecond pulse, and the bottom is monitored by a picosecond pulse.  (a) Response time traces between the pump and probe pulses. (b) Spectra of the probe laser.  (c) Raman spectra of cyclohexane.  (d) Raman spectra of water.
injected into water after photoionization.

In this section, femtosecond time-resolved resonance Raman spectra of the nonequilibrated hydrated electron are reported. The temporal intensity changes of the resonance Raman bands attributable to the intra- and intermolecular vibrations is discussed by comparing with those of the luminescence and the transient absorption signals for the hydrated-electron relaxation process. Anti-Stokes Raman scattering from the hydrated electron is also investigated. Taking advantage of the resonance Raman spectroscopy, the nature of the electronic transition of the nonequilibrated hydrated electron is examined from a viewpoint different from the absorption studies reported previously.

3-3-2 Experimental

The experimental setup for femtosecond time-resolved Raman measurements consist of a typical time-resolved resonance Raman apparatus and is shown in Figure 3-19. The light source of the apparatus was a femtosecond mode-locked Ti:sapphire oscillator (Spectra-Physics, Tsunami) pumped by the frequency-doubled output of a cw diode-pumped Nd:YVO₄ laser (Spectra-Physics, Millennia-Vs). The output of the oscillator laser was amplified with a Ti:sapphire regenerative amplifier (Spectra-Physics, Spitfire) that was pumped by a cw Q-switched, diode-pumped Nd:YLF laser (Spectra-Physics, Evolution-X). The wavelength, pulse energy, pulse width, and repetition rate of the amplified output are 800 nm, 950 µJ, 150 fs, and 1 kHz, respectively. A part of the amplified output was frequency-doubled by a 1-mm BBO crystal and then tripled by a 0.3-mm BBO crystal. The generated third harmonic (267 nm) was used as the pump pulse to photoionize water molecules. The residual fundamental output was used as the probe light source. Two probe wavelengths, 800 and 600 nm, were used to obtain the transient Raman signal under the resonant condition with the electronic transition of the hydrated electron. The 800-nm probe pulse was the fundamental output of the Ti:sapphire laser. The 600-nm probe pulse
was the second harmonic of the signal output of an optical parametric amplifier (Quantronix, Topas) which was pumped by the fundamental output of the regenerative amplifier, by a 1-mm BBO crystal. The pump and probe pulses were collinearly focused onto a thin film-like jet stream of water (thickness ~300 µm) with a quartz lens (f = 400 mm). To minimize the chromatic aberration, the beam radius of the probe pulse is expanded by a lens pair (f = – 250, 350 mm) before the superimposition of the two pulses. Typical pulse energy was 10 µJ (pump), 2 µJ (800-nm probe), and 0.5 µJ (600-nm probe) at the sample point. The beam radii of the pump and probe pulses were about 200 µm and 30 µm, respectively. The linear polarizations of the pump and probe pulses were set perpendicular. The spectral width of the probe pulse (fwhm) was about 160 cm\(^{-1}\) (800 nm) and 350 cm\(^{-1}\) (600 nm). The response time (fwhm) between the pump and probe pulses was about 250 fs. The zero-delay time was precisely determined by measuring the optical Kerr signal of n-hexane. The Raman scattering light was collected and introduced into a spectrometer.
(Jobin-Yvon, HR320) by a camera lens. A holographic notch filter (Kaiser Optical Systems, Inc.), sharp-cut colored glass filters (HOYA), and a short wave pass dielectric filter (Asahi Spectra Co., Ltd.) were placed before the entrance slit of the spectrometer in order to eliminate unwanted light, such as strong Rayleigh scattering or the emitted light arising from the pump pulse irradiation. A liquid nitrogen cooled CCD camera (Princeton Instruments, LN/CCD-1100PB) was used to detect the Raman scattering. The obtained signal intensity, which was distorted by the optics such as a camera lens and filters and by the sensitivity of each pixel on the CCD camera, was corrected by a calibrated halogen lamp (Ushio Inc.). The intensity correction for the reabsorption effect was carried out by using the correction curve that was made on the basis of femtosecond time-resolved absorption spectra of the hydrated electron and the evaluation of the optical path length in the present experimental configuration. All the spectra described in Section 3-3 have been already corrected. Time-resolved absorption trace was measured by monitoring the intensity of the probe pulse that passed through the sample solution. This measurement was carried out under the same experimental apparatus of the time-resolved Raman measurement. Under the present experimental condition, the obtained data was free from the undesired higher-order nonlinear optical effects (e.g. distortion of the temporal behavior of the transient absorption) that could be potentially induced by the high peak-power laser pulses.

Distilled water (HPLC grade) was purchased from Wako Pure Chemical Industries and used as received. All measurements were performed at room temperature in the aerated atmosphere.

3-3-3 Results and discussion

Figure 3-20 shows time-resolved spectra from the hydrated electron with the 267-nm pumping and the 800-nm probing. The two-photon energy of the 267-nm light is larger than the ionization threshold of the water molecule (~8.0 eV)\textsuperscript{56}. The 800-nm light for
Figure 3-20  Femtosecond time-resolved spectra of the hydrated electron in the delay time range from -1.9 to 5.1 ps (pump laser, 267 nm; probe laser 800 nm). The intensity at each delay time has been normalized by the correction curve. The spectrum taken with either pump or probe pulse irradiation has been subtracted from each spectrum.
probing is resonant with the electronic transition from the nonequilibrated state of the hydrated electron (wet electron) as well as that from the equilibrated state, so that it is expected that the transient signals from the either states can be observed\textsuperscript{14-26}. In both the lower- and higher-energy region of the probing light (12500 cm\textsuperscript{-1}), the Stokes and the anti-Stokes Raman region, respectively, signals inherent in the hydrated electron appeared within a few hundreds of femtosecond after the photoionization. The signal was divided into two components: transient Raman scattering and luminescence background (Figure 3-21)\textsuperscript{57}. Femtosecond time-resolved resonance Stokes Raman spectra are shown in Figure 3-22. The bands around 1600 cm\textsuperscript{-1} and 600 cm\textsuperscript{-1} are assigned to the intramolecular bending vibration and the intermolecular libration of the water molecule surrounding the electron, respectively, which were previously reported\textsuperscript{45,52,53,55}. Under this experimental condition, the transient Raman band due to the stretch vibration located around 3200 cm\textsuperscript{-1} could not be observed because of lack of the CCD sensitivity. The broad structureless luminescence signal was observed in the whole spectral region (Figure 3-21). This signal is assignable to the hydrated-electron luminescence. The anti-Stokes Raman bands were not observed within the present S/N ratio even at early delay time before the full equilibration (Figure 3-21).
The temporal intensity change of the observed Stokes Raman and luminescence signals was analyzed. Figure 3-23 shows the temporal intensity change of the two Stokes Raman
bands (bend and libration) and luminescence signals. It was found that all the Raman and
luminescence signals exhibited the same temporal behavior not only in the early stage during
the relaxation process of the hydrated electron but in the later delay time after the electron is
fully relaxed. It indicates that the Raman and luminescence signals originate from the same
electronic transition. Because the resonance Raman enhancement of the water molecule
around the electron is induced by the electronic transition between the s and p states, the
observed luminescence signal is considered to be attributable to the fluorescence from the p
state in the whole temporal region.

The temporal behavior of the Raman band due to the bending vibration is compared
with the time-resolved absorption trace monitored at 800 nm as shown in Figure 3-24(a).
Because the temporal intensity change of the Raman band due to the libration and the
luminescence signal was identical with that of the bend Raman band, only the result of the
bend Raman band is shown here. In the same figure, the best-fitted curves for the temporal
intensity change of the observed signals and the calculated rise curve corresponding to the
appearance of the equilibrated electron are also shown in the same figure. The fitting and
calculation methods of these curves are described in the Appendix (Section 3-5-1). As seen
in the Figure 3-24(a), it was found that the temporal behavior of the Raman signal was
reproduced neither by the transient absorption nor by the equilibrated-electron population.
To confirm the deviation of the Raman intensity either from the transient absorption or from
the equilibrated-electron population in the time region of 0 – 1.5 ps, the decay of the bend
Raman band was compared with that of the transient absorption in long time range 3 – 300
ps (Figure 3-24(b)). In this long time range, the trace of the transient absorption is identical
with that of the equilibrated-electron population. The Raman intensity data were in good
agreement with the transient absorption in the long time range, which indicates that the
deviation at early delay time is not an artifact but inherent in the electron equilibration
process.

According to Figure 3-24, the resonance Raman and luminescence signals rose up faster
than the population of the equilibrated hydrated electron at 0 – 1.5 ps. It indicates that the
Figure 3-23 Temporal intensity change of the Stokes Raman bands (bend and libration) and luminescence signals (pump laser, 267 nm; probe laser, 800 nm). Temporal behavior in the early time region of -2.5 – 5.5 ps for (a) – (d), and that in the later time region up to 300 ps for (e) – (f). (a) and (e): Raman band due to the intramolecular bend mode (area intensity from 1450 to 1750 cm⁻¹ for Raman shift). (b): Raman band due to the intermolecular libration (area intensity from 600 to 800 cm⁻¹ for Raman shift). (c) and (f): Luminescence signal observed in the Stokes (lower-energy) side (area intensity from 1000 to 1200 cm⁻¹ for Raman shift). (d): Luminescence signal observed in the anti-Stokes (higher-energy) side (area intensity from -800 to -400 cm⁻¹ for Raman shift). Filled circles indicate the observed intensity of each signal. Error bars are settled by the S/N ratio of the obtained spectra. Thick lines are the best-fit curve. (See Section 3-5-1.)
resonance Raman and luminescence signals are observed from the nonequilibrated state of the hydrated electron as well as from the equilibrated state. Because the Raman intensity of the water molecules surrounding the electron is enhanced under the resonance condition with the $s \rightarrow p$ transition\textsuperscript{53}, the electronic transition from the nonequilibrated electron has to be of the $s \rightarrow p$ nature. It is concluded that the nonequilibrated hydrated electron (wet electron) is assigned to the ground-state electron. The present conclusion supports the previous studies mentioned in Section 3-1 as (3) and (iii) that the nonequilibrated hydrated electron is attributable to the ground-state electron with higher energy than the fully relaxed state and the spectral change of the time-resolved absorption spectra is described as the continuous

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig3-24.png}
\caption{Comparison of the temporal intensity change between Raman band due to the bend mode (black circles) and transient absorption (dark gray dots). (a) Temporal behavior in the early time region of -1 – 3 ps. Black and gray lines indicate the best-fit curve of the temporal behavior of the Raman and absorption intensity, respectively. Gray dashed line represents the rise curve corresponding to the appearance of the equilibrated hydrated electron. (b) Temporal behavior in the later time region up to 300 ps. Gray line indicates the population of the hydrate electron. Fitting and calculation methods are described in Section 3-5-1.}
\end{figure}
blue shift\textsuperscript{22-26,31,34,35}.

It was also found in Figure 3-24 that the rise of the Raman intensity was slower than that of the transient absorption. It implies that the nonequilibrated hydrated electron absorbs the probe light but does not give rise to the resonance Raman and luminescence signals at 0 – 1.5 ps as much as expected from the transient absorption. It is concluded that the transient absorption signal at 800 nm in this time region is not solely due to the $s \rightarrow p$ transition that is supposed to induce the Raman and luminescence signals but partly due to the $s \rightarrow$ conduction band (CB) transition. It indicates that there exists a time when the 800-nm probe light is in resonance with the transition between the $s$ state and conduction band, and that the rise-up time of the Raman signal corresponds to the appearance of the $s \rightarrow p$ transition. In the equilibrated state, both the theoretical\textsuperscript{5} and experimental\textsuperscript{53} studies reported that the major contribution to the absorption intensity arises from the $s \rightarrow p$ transition, and that a nature of the electronic transition to the conduction band contributes to the blue side of the absorption band. Similarly, even in the nonequilibrated state, it is expected that the contribution of the $s \rightarrow$ CB transition is located in higher energy region than that of the $s \rightarrow p$ transition. The present observation suggests that the transition energy between the $s$ state and the conduction band as well as that between the $s$ and $p$ states increases with time and the effective resonance condition changes in accordance with the relaxation of the hydrated electron. It is considered that the present femtosecond time-resolved Raman measurements allow us to detect the $s \rightarrow$ CB transition energy in the early delay time, which is beyond the other spectroscopic methods.

The luminescence intensity displayed the same temporal behavior as the Raman intensity: in other words, the luminescence is not detected through the $s \rightarrow$ CB transition. This observation leads us to conclude that the luminescence as well as the Raman scattering has the transition-specific intensity. It is probably due to the detrapping of the electron from the solvent cavity in the conduction band\textsuperscript{31-33}.

To reverify the dynamic energy-level shift of the hydrated electron, femtosecond time-resolved Raman and luminescence spectra and absorption trace probed at 600 nm were
measured. Time-resolved resonance Raman spectra with the 800-nm and 600-nm probing are compared in Figure 3-25. The temporal intensity change of the transient absorption and the resonance Raman band due to the bend mode measured at two probe wavelengths (800 nm and 600 nm) is shown in Figure 3-26. (Because the temporal behavior of the luminescence signal was identical with that of the resonance Raman signal, only the resonance Raman result is shown here.) The absorption signal monitored at 600 nm rose up slower than that at 800 nm (Figure 3-26(a)). It is consistent with the continuous blue shift of the hydrated-electron absorption peak in accordance with the relaxation of the hydrated electron. For the resonance Raman band, the rise-up time measured under the

Figure 3-25  Femtosecond time-resolved resonance Raman spectra of the hydrated electron in the bend region in the delay time range from -0.1 to 1 ps with 267-nm pumping. Probe wavelength is (a) 800 nm and (b) 600 nm. The Raman intensity at each delay time has been normalized by the correction curve. The spectrum taken with either pump or probe pulse irradiation has been subtracted from each spectrum. The luminescence spectrum measured at each delay time has also been subtracted.
800-nm and 600-nm probe conditions was approximately 400 fs and 500 fs, respectively (Figure 3-26(b)). It implies that the contribution from the s → CB transition persists until the later delay time under the higher-energy probe condition. The measurement of the probe wavelength dependence of the temporal behavior of the observed signal supports the conclusion that the transition energy between the s state and conduction band increases with time.

Time-resolved anti-Stokes Raman spectroscopy is a good probe to measure the local temperature change, because the intensity ratio between the Stokes and anti-Stokes bands is equal to the Boltzmann factor. Keeping this advantage of the vibrational spectroscopy in our mind, the investigation of the thermal relaxation dynamics of the hydrated electron was tried. As shown in Figure 3-20, the signal corresponding to the anti-Stokes Raman band attributable to the intramolecular bending vibration or the intermolecular libration was not observed significantly at early delay time. Taking the S/N ratio of the observed spectra into
consideration, when the intensity ratio between the Stokes and anti-Stokes bands is less than 10 %, it is expected that an anti-Stokes signal is buried in the luminescence signal or the noise. If the intensity ratio between the Stokes and anti-Stokes bands measured at 0.3 ps is assumed to be 10 %, the temperature rise from room temperature is estimated at ~ 100 K for the libration band, and ~ 700 K for the bend band. Because it is natural to think that the intensity of the anti-Stokes Raman band with the lower frequency is stronger than that with higher frequency, the detected temperature rise of the local solvation structure around the electron at 0.3 ps is about 100 K at most. This suggests that the electron ejected into water does not have sufficient energy to excite the water molecule to the vibrational hot state that can give rise to the anti-Stokes Raman bands due to the libration as well as the bend mode.

From a viewpoint of resonance Raman spectroscopy, the ultrafast relaxation process of the hydrated electron is summarized in Figure 3-27. After the photoionization of water, the nonequilibrated hydrated electron (wet electron) in the ground s state is formed within the present time resolution. For the wet electron, the $s \rightarrow CB$ transition contributes to the absorption signal even at 800 nm so that there exists a time when only the transient absorption signal is observed around 800 nm (Figure 3-27(a)). It implies that the energy difference between the s state and conduction band is considered to be approximately half compared with that in the equilibrated state. A theoretical work predicted the energy stabilization of the s-state hydrated electron as the snowballing effect. According to the theoretical work, the increase of the solvation structure radius makes the s-state energy decrease and only one bound state (the s state) exits when the solvation structure radius is smaller than a critical value. Based on both the present experimental results and the theoretical prediction, it is likely that the nonequilibrated s-state electron is relaxed in energy following the solvation of the surrounding water molecules (conformation change), and that the p state does not exhibit a significant contribution to the transient absorption. In accordance with the energy relaxation of the nonequilibrated electron due to the solvation, the transition energy between the s state and the conduction band increases (Figure 3-27(b)). The energy relaxation of the electron progresses further, and then the electron is fully
equilibrated in energy (Figure 3-27(c)). In the equilibrated state, the $s \rightarrow CB$ transition mainly contributes to the blue-side of the absorption band around 400 nm according to the previous reports.$^{5,33}$

Figure 3-27  Schematic picture of the temporal changes of the absorption band shape and the electronic transition of the hydrated electron in the relaxation process. Left side represents the absorption spectra of the hydrated electron, in which gray area indicates the contribution of the $s \rightarrow$ conduction band (CB) transition. Right side indicates the energy level of the hydrated electron during the equilibration. (a) Nonequilibrated state immediately after the appearance of the wet electron. (b) Nonequilibrated state. (c) Equilibrated state. Probe wavelengths exhibit in the figure, that is, $\lambda_1: 800 \text{ nm}$, $\lambda_2: 600 \text{ nm}$, $\lambda_3: 400 \text{ nm}$.
3-4 Conclusion

Time-resolved Raman spectroscopy has afforded important data that shed new light on the property of the hydrated electron. With use of picosecond time-resolved resonance Raman spectroscopy, the novel observation of the Raman scattering from the local structure around the hydrated electron was found for the first time. This observation strongly suggests that the interaction between the electron and the water molecules is so strong that we should consider them together, at least, from the viewpoint of the vibronic state of the local structure. The observed vibrational frequencies suggest a significant structural change induced by the interaction with the electron in the ground state, and the resonance Raman intensity affords information about the structural change induced by the $s \rightarrow p$ electronic excitation. The polarization measurements provide a clue for discussing the nondegeneracy of the excited $p$ state as well as the time scale of the relaxation. The downshifts of observed Raman frequencies of the solvating water molecule are explained by the structural change which is induced by the strong interaction with the electron.

Femtosecond time-resolved resonance Raman spectroscopy of the hydrated electron was performed to discuss the energy relaxation dynamics of the hydrated electron. It was found that the observed Raman and luminescence signals show the same temporal change. The rise-up time of these signals is faster than the equilibration of the hydrated electron, and is slower than the appearance of the transient absorption. From this observation, it was concluded that the contribution of the $s \rightarrow CB$ transition is located at 800 nm in the blue side of the nonequilibrated absorption band, and that the transition energy increases with time. For transient absorption spectroscopy, it is difficult to distinguish the contribution of the $s \rightarrow CB$ transition from the whole absorption band. In the present study, this contribution was clarified by monitoring the temporal change of the effective resonance condition of Raman bands attributable to the nonequilibrated hydrated electron.
Femtosecond time-resolved absorption traces were measured at 15 probe wavelengths by using the same experimental apparatus. The pump wavelength is 267 nm and the probe light was tuned in the range of 600 – 950 nm that was the second harmonic of the signal (600 – 800 nm) and idler (825 – 950 nm) outputs of the optical parametric amplifier. Temporal intensity change of transient absorption monitored at each probe wavelength is shown in Figure 3-28. The average intensity measured at 20 – 40 ps for each time-resolved absorption trace has been matched to the extinction coefficient of the equilibrated hydrated-electron as shown in Figure 3-1.

The fitting-analysis method for the kinetics of the time-resolved absorption trace is described. We assumed the following model for the hydrated-electron dynamics:

\[
\text{precursor} \xrightarrow{r_1} e_{\text{NE}} \xrightarrow{r_1} e_{\text{eq}}^{\prime} \xrightarrow{\alpha} e_{\text{eq}}^{\text{geminate recombination}} \xrightarrow{(1-\alpha)} e_{\text{eq}}^\text{long} \quad \text{(long lived species, \sim 300 ns)}
\]

where \(e_{\text{NE}}\) represents the nonequilibrated hydrated electron, \(e_{\text{eq}}^{\prime}\) stands for the equilibrated electron that is going to recombine geminately, \(e_{\text{eq}}^\text{long}\) denotes the equilibrated electron that escapes from the geminate recombination, and \(\alpha\) is the probability of the geminate recombination. When the electron is ejected into water, \(e_{\text{NE}}\) is generated with the time constant \(\tau_1\) from the precursor. For the sake of convenience, it was assumed that the relaxation process from the nonequilibrated state to the equilibrated state is reproduced as the exponential decay or rise with the time constant of \(\tau_2\) in the present case\(^{59}\). A part of the equilibrated electron decays in accordance with the geminate recombination in the picosecond region. The population decay of the equilibrated electron due to the geminate recombination is represented by the diffusive model. Based on the model (3-8), the
The differential equation for the population change of each state of the hydrated electron is as follows,

\[
\frac{dN}{dt} = \text{Absorption coefficient} \times C_0 \times e^{-t/\tau}
\]

\text{Absorption coefficient} (25000 \text{ M}^{-1} \text{ cm}^{-1} / 1 \text{ div.})

\text{Time / ps}

\begin{tabular}{c}
600 nm \\
625 nm \\
650 nm \\
675 nm \\
700 nm \\
725 nm \\
750 nm \\
775 nm \\
800 nm \\
825 nm \\
850 nm \\
875 nm \\
900 nm \\
925 nm \\
950 nm \\
\end{tabular}

\text{Figure 3-28}  Femtosecond time-resolved absorption traces of the hydrated electron in neat water (gray dots). Black solid line denotes the response time between pump and probe pulses. Gray solid, dashed and dotted lines represent the best fitted curves of the transient absorption trace and the population of the nonequilibrated \((e_{\text{NE}})\) and equilibrated \((e_{\text{eq}})\) electron, respectively, which are calculated based on formula (3-9). Pump wavelength is 267 nm. Probe wavelength of each trace is indicated in the figure.
precursor: \( \frac{d[\text{precursor}]}{dt} = \frac{-[\text{precursor}]}{\tau_1} \), \hspace{1cm} (3-9A) 

e_{\text{NE}}: \quad \frac{d[e_{\text{NE}}]}{dt} = \frac{[\text{precursor}]}{\tau_1} \cdot \frac{[e_{\text{NE}}]}{\tau_2} \), \hspace{1cm} (3-9B) 

\[ [e_{\text{eq}}] = [e_{\text{eq}}^{\text{long}}] + [e_{\text{eq}}^{p}]. \hspace{1cm} (3-9C) \]

Here, \( T \) indicates the jump rate of the one-dimensional random walk model, which is often utilized to numerically describe the recombination between the radical pair in the framework of the diffusion controlled model\(^{50}\). Only \( e_{\text{NE}} \) and the equilibrated electron \( e_{\text{eq}} \) give rise to the transient absorption signal in the observed wavelength region. For these two species, the global fitting over the obtained 15 transient-absorption traces was carried out with use of formula (3-9). We fixed the parameter \( \tau_1 \) to 200 fs, which was reported by the time-resolved absorption measurement with 50-fs time resolution\(^{22}\). The best fit parameters were \( \tau_2 = 540 \) fs, \( \alpha = 0.41 \), and \( T = 3.1 \) ps. The obtained value for \( \tau_2 \) is consistent with the correlation time reported by the previous time-resolved absorption study\(^{22}\).

Because of the different pulse duration of each probe pulse, the response time of each time-resolved absorption trace was not equal. Based on both the calculated parameters and response time, time-resolved absorption spectra when measuring time-resolved Raman spectra were reconstructed. The spectra are shown in Figure 3-29. From these spectra, the reabsorption correction curve was made. The reconstructed spectra exhibit the similar spectral evolution which was reported previously\(^{22}\).

As is analyzed the time-resolved absorption, the temporal behavior of the resonance Raman band was fitted based on formula (3-9). During the fitting procedure, the parameter \( \tau_2 \), \( \alpha \) and \( T \) were fixed at the calculated value obtained by the time-resolved absorption data in Section 3-3-3.
3-5-2 Spectral shift of the transient Raman band: Femtosecond time-resolved resonance Raman spectra of the hydrated electron in the stretch region

The Raman frequency sharply reflects the structural change of molecules. This feature is the large advantage of the vibrational spectroscopy. For the equilibrated hydrated...
electron, the stretch band is downshifted by ~150 cm\(^{-1}\) from the average of the two stretching frequency of bulk water band owing to the structural change, whereas the bend Raman band due to the transient water is located around 30 cm\(^{-1}\) lower than that due to bulk (Section 3-2). If the shift of Raman band due to the transient water is observed during the relaxation, crucial information on the dynamics of the hydrated electron can be obtained.

In Figure 3-30, femtosecond time-resolved resonance Raman spectra of the hydrated electron in the stretch region are shown. These spectra were measured under the 600-nm probe condition. The reabsorption correction has been carried out for the spectra. The temporal behavior of the stretch Raman band was identical with that of the bend Raman and luminescence signals. It was found that the stretch band of the transient water exhibits the
~ 100 cm$^{-1}$ downshift in the time region up to 2 ps. Observed spectral shift was not ascribed to the undesired optical effect on the time-resolved Raman spectra arising from the use of the downchirped laser pulse$^{61}$. The downshift of the stretch band of the nonequilibrated hydrated electron was similarly observed in the time-resolved Raman spectra measured with 680-nm probing. Therefore, it is concluded that the structure of the water molecule surrounding the electron changes in accordance with the solvation. It is expected that this conclusion can make a final solution to the discussion of the relaxation dynamics of the hydrated electron, in other words, the energy of the hydrated electron is relaxed following the structural change due to the conformation change.

The intensity of the stretch Raman band attributable to the transient water is very weak, which is 10 times smaller than that due to bulk water under the present experimental condition, because of the small resonance enhancement factor of the stretch band. The subtraction of the bulk water spectrum from the obtained raw spectrum seriously affects the shape of the transient stretch Raman band. Even if the subtraction factor was changed, the downshift of the stretch band was observed. However, further quantitative discussion about the dynamics, such as the correlation time, based on the Raman results was not performed.
References and notes


(48) The frequency resolution of the spectra taken with 494-nm probe pulse is worse than that taken with the other probe wavelength owing to the broadness.

(49) In an earlier femtosecond time-resolved absorption measurement, Barbara and coworkers reported that the anisotropy was observed. See the following paper: Reid, P. J.; Silva, C.; Walhaut, P. K.; Barbara, P. F. Chem. Phys. Lett. 1994, 228, 658.


(57) To separate the Raman band from the luminescence background, we had to know the spectral shape of the luminescence signal. When the probe wavelength is changed within the small energy deviation, the Raman band moves correspondingly but the luminescence band does not. The spectrum probed at 780 nm in the presence of the hydrated electron was measured to determine the band shape of the luminescence background. The luminescence signal was subtracted from each time-resolved spectrum to obtain the transient Raman spectrum.


(59) Even if the dynamic peak shift of the hydrated-electron absorption is reproduced by the continuous blue shift, it is considered that the solvation time is closely associated with the time constant described as the stepwise transition model (3-8). Here, it is considered that the calculated rise-up time \( \tau_2 \) regards as the appearance of the nonequilibrated hydrated electron.


Chapter 4

Observation of resonance hyper-Raman scattering from all-trans-retinal
Abstract

Hyper-Raman scattering of all-trans-retinal was measured for the first time in solution at room temperature. Under the two-photon resonance condition, the intensity of hyper-Raman scattering was so strong that it could be measured from a diluted solution at a concentration as low as $1 \times 10^{-3}$ mol dm$^{-3}$. Hyper-Raman excitation profiles were examined in the excitation wavelength range from 770 to 840 nm ($\lambda_{ex}/2$, 385 – 420 nm). In this excitation range, the intensity of all the hyper-Raman bands monotonically increased with shortening excitation wavelength, and the hyper-Raman spectral feature was very similar to that of resonance Raman spectra excited with double the excitation energy ($\lambda_{ex}/2$). The resonance mechanism of hyper-Raman scattering was discussed, and it was concluded that hyper-Raman scattering gains intensity enhancement from two-photon resonance with the "$1B_u$" state, not with the "$1A_g$" state, through the Franck-Condon (the $A$ term) mechanism.
4-1 Introduction

4-1-1 Resonance hyper-Raman scattering

When intense laser light at frequency \( \nu_0 \) is irradiated onto a sample, very weak scattering is generated at a frequency of \( 2\nu_0 \pm \nu \) besides the ordinary Raman scattering at \( \nu_0 \pm \nu \). This weak scattering is hyper-Raman scattering, which is well-known as one of the oldest nonlinear Raman processes. This process originates from the second-order nonlinear induced dipole \( \mu \) given by

\[
\mu^{(2)} = \frac{1}{2} \beta : E \cdot E ,
\]

where \( \beta \) is the hyperpolarizability of the molecule which dominates the intensity of the hyper-Raman scattering. Hyper-Raman scattering is the three-photon process: two-photon upward and one-photon downward transitions (Figure 4-1). In nonresonance case, the intensity of hyper-Raman scattering is estimated to be smaller than that of ordinary Raman scattering by a factor of \( 10^5 \sim 10^6 \) under typical excitation condition (~ \( 10^{10} \) W/cm\(^2\)). When there exists an electronic state that is resonant with double the excitation energy (\( 2h\nu_0 \)), the intensity of the hyper-Raman scattering is highly enhanced. This intensity enhancement is due to the two-photon resonance, which is analogous to the one-photon resonance effect of Raman scattering.

When there exists an electronic state that is resonant with double the excitation energy (\( 2h\nu_0 \)), the intensity of the hyper-Raman scattering is highly enhanced. This intensity enhancement is due to the two-photon resonance, which is analogous to the one-photon resonance effect of Raman scattering. Ziegler and co-workers investigated resonance hyper-Raman scattering and constructed a theoretical framework on the basis of the vibronic theory. By using the Born-Oppenheimer approximation as shown in Figure 4-1(c), the
The hyperpolarizability $\beta_{\mu\nu}$ is given by

$$
\beta_{\mu\nu} = \sum_n \frac{\langle f \mid (M_\lambda)_{ge} \mid m \rangle \langle m \mid (M_\mu)_{nf} \mid n \rangle \langle n \mid (M_\nu)_{nf} \mid g \rangle}{(v_{\nu',go} - v_0)(v_{\nu,go} - 2v_0 - i\Gamma_{\nu,go}/2)}, \tag{4-2}
$$

where $(M_\lambda)_{ge}$ is the $g \leftarrow e$ electronic transition moment. With use if the Herzberg-Teller expansion around the nuclear equilibrium configuration, this electronic transition moment is described as

$$
(M_\lambda)_{ge} = (M_\lambda)_{ge}^0 + \sum_a (M_\lambda)_{ge}^{\alpha} Q_a + \cdots, \tag{4-3}
$$

$(M_\lambda)_{ge}^{\alpha} Q_a$ is the part of the electronic transition moment which linearly depends on the nuclear coordinate $Q_a$. When the magnitude of the higher-order nuclear coordinate dependence of $(M_\lambda)_{ge}$ is neglected, the hyperpolarizability $\beta_{\mu\nu}$ is expanded into three terms.
(the $A$, $B$, and $C$ terms) according to the order of the vibronic interaction as follows:

$$\beta_{\omega, \omega} = A + B + C,$$

(4-4)

$$A = \sum_{\sigma, \tau, \nu, \mu} \left( M_{\mu} \right) \left( M_{\nu} \right) \left( M_{\sigma} \right) \left< f \left| v \right| r \right> \left< r \left| o \right) \right. \left( \nu - \nu_{0} - 2\nu_{0} - i\Gamma_{\nu, \omega} \right),$$

(4-5A)

$$B = \sum_{a} \sum_{\sigma, \tau, \nu, \mu} \left[ \left( M_{\mu} \right) \left( M_{\nu} \right) \left( M_{\sigma} \right) \left< f \left| v \right| r \right> \left< r \left| o \right) \right. \left( \nu - \nu_{0} - 2\nu_{0} - i\Gamma_{\nu, \omega} \right),$$

(4-5B)

$$= \sum_{a} \sum_{\sigma, \tau, \nu, \mu} \left[ \left( M_{\mu} \right) \left( M_{\nu} \right) \left( M_{\sigma} \right) \left< f \left| v \right| r \right> \left< r \left| o \right) \right. \left( \nu - \nu_{0} - 2\nu_{0} - i\Gamma_{\nu, \omega} \right),$$

(4-5C)

$$C = \sum_{a, \sigma, \tau, \nu, \mu} \left[ \left( M_{\mu} \right) \left( M_{\nu} \right) \left( M_{\sigma} \right) \left< f \left| v \right| r \right> \left< r \left| o \right) \right. \left( \nu - \nu_{0} - 2\nu_{0} - i\Gamma_{\nu, \omega} \right),$$

In the above formulas, the $A$ term arises from two-photon allowed upward and one-photon allowed downward transition. No vibronic transition moment is required for this Frank-Condon type of resonance enhancement. The resonant electronic state must have both intrinsic one-photon and two-photon allowedness, so that only noncentrosymmetric molecules can acquire the resonance hyper-Raman intensity for this term. The $B$ term arises from the first-order vibronic coupling and it is the leading term of the resonance hyper-Raman activity of centrosymmetric molecules. The resonant electronic state of the $B$ term is either two-photon allowed (upward) and vibronic one-photon allowed (downward), or vibronic two-photon allowed (upward) and one-photon allowed (downward). The higher-order terms, namely, the $C$ term in the theory are not important in the present case because these terms become significant only when the resonant state is both one-photon and two-photon forbidden.
Ziegler and co-workers studied several fundamental molecules such as CH$_3$I and CS$_2$ in the gas phase and clarified their resonance hyper-Raman activity on the basis of the vibronic theory$^{2,3}$. Bonang and Cameron extended resonance hyper-Raman studies to the solution-phase molecules$^{4-6}$. They constructed a unique apparatus that takes advantage of the high intracavity and high repetition rate of a synchronously pumped dye laser, and succeeded in measuring resonance hyper-Raman spectra of benzene, monosubstituted benzenes, and naphthalene in ethylene glycol. These works demonstrated that resonance hyper-Raman spectroscopy provides unique information about the excited states, which are often not accessible by linear spectroscopy such as resonance Raman spectroscopy. However, despite the unique status of resonance hyper-Raman scattering in molecular spectroscopy, the number of the reports is very limited because of the extremely weak signal intensity.

4-1-2 Electronic excited states of all-trans-retinal

*All-trans*-retinal is a very important polyene not only in chemistry but also biology$^7$. The excited singlet states linear polyenes have been intensively studied, and it is now well established that there are two singlet excited states, that is, the one-photon allowed $^1$Bu$^*$ state and the two-photon allowed $^1$Ag$^*$ state, in the low-energy region$^{8,9}$. Although the symmetry of *all-trans*-retinal is low, it is known that there exist singlet excited states that can be directly correlated to the $^1$Ag$^*$ and $^1$Bu$^*$ states of linear polyenes. Nevertheless, lowering symmetry causes mixing of the character of the $^1$Bu$^*$ and $^1$Ag$^*$ states to some extent$^{10}$. The $^1$Bu$^*$ state of retinal shows a very strong one-photon absorption but it also exhibits some two-photon absorptivity. On the other hand, the $^1$Ag$^*$ state has a clear doubly excited nature and exhibits strong two-photon absorption while it has a small one-photon oscillator strength$^{11}$. In addition to these two excited states, retinal has a carbonyl group that gives rise to an nπ$^*$ state. Consequently, there are three low-lying excited singlet states, namely, the $^1$Bu$^*$,
“^1A_g”*, and ^1nπ* states, in the low energy region of all-trans-retinal. In nonpolar solvents, the state ordering of these states was reported “^1B_u*” > “^1A_g*” > ^1nπ* in energy. The photochemical properties as well as dynamics of these three excited states have been subjects of intensive spectroscopic studies\textsuperscript{10,12-14}.

For the resonance hyper-Raman measurement, however, the ^1nπ* state is not important, because of its small one-photon and two-photon electronic transition probabilities. The “^1B_u*” and “^1A_g*” states have both one-photon and two-photon allowedness, reflecting the low symmetry of the molecule as well as conformational distortion. Thus, in principle, these two excited states can contribute to the resonance enhancement of hyper-Raman scattering observed in the present study.

In this chapter, the first resonance hyper-Raman spectra of all-trans-retinal in solution are reported. It was found that resonance hyper-Raman scattering from this molecule is quite strong, so that it can be measured even from a diluted solution. The hyper-Raman excitation profiles are examined. Based on the vibronic theory, the resonance hyper-Raman mechanism and the character of the resonant excited states of all-trans-retinal are discussed.

\textbf{4-2 Experimental}

For the measurements of hyper-Raman scattering of all-trans-retinal, the following experimental setup was used\textsuperscript{15}. A picosecond mode-locked Ti:sapphire laser (Spectra-Physics, Tsunami) pumped by an Ar\textsuperscript{+} ion laser (Spectra-physics, Beamlok 2060-10SA) was utilized as the light source. The output of this oscillator laser was amplified by a regenerative amplifier (Spectra-Physics, Spitfire) with a Q-switched Nd:YLF laser Spectra-Physics, Merlin) and then used for excitation. The energy, the pulse width, and the repetition rate of the amplified pulse are 650 – 850 \textmu J, 1.7 – 2.5 ps, and 1 kHz, respectively, and its color was changed from 770 to 840 nm in the tuning range of the laser.
system. The excitation pulses were focused with a quartz lens \((f = 50 \text{ mm})\) onto a thin film-like jet stream \((\sim 300 \mu \text{m})\) of the sample solution. A typical beam radius at the sample position was about 20 \(\mu\text{m}\), and the energy of the sample pulse was adjusted in the range of 2 – 10 \(\mu\text{J}\) by a variable neutral density filter. The hyper-Raman scattering was collected and introduced into a spectrometer (Jobin-Yvon, HR-320) by a camera lens. A colored glass filter (HOYA, CM-500) was used to eliminate the strong scattering of the excitation laser. A liquid-nitrogen cooled CCD camera (Princeton Instruments, LN/CCD-110PB) was utilized for the detection. A typical exposure time to obtain one resonance hyper-Raman spectrum was 20 min.

For the measurements of the Raman scattering of all-trans-retinal, the second harmonic of the output from a picosecond mode-locked Ti:sapphire laser was used for excitation \((385 – 420 \text{ nm}, \sim 50 \text{ mW}, 90\text{MHz})\). The incident laser power was reduced to 5 mW by a variable neutral density filter. The detection system was essentially the same as that used for hyper-Raman measurements although no optical filter was used in the Raman measurements. A typical exposure time to measure one Raman spectrum was 2 min.

All-trans-retinal was purchased from Sigma Chemical Co. and was used without further purification. Cyclohexane (special grade) was purchased from Wako Pure Chemical Industries and was used as received. The sample solution was prepared under deep red light.

### 4-3 Results and discussion

#### 4-3-1 Observation of resonance hyper-Raman scattering

Figure 4-2 shows the hyper-Raman spectrum of all-trans-retinal in cyclohexane, excited at 800 nm. All the observed hyper-Raman signals in this spectrum are attributed to all-trans-retinal, and no signal ascribable to the solvent was observed. This indicates that
the intensity of the hyper-Raman scattering of all-trans-retinal is highly enhanced by the two-photon resonance effect. In the fingerprint region of the spectrum, eight hyper-Raman bands due to fundamental vibrations are observed at 1672, 1579, 1332, 1270, 1196, 1163, 1008 and 966 cm\(^{-1}\). These vibrations have already been observed in spontaneous Raman spectroscopy, and the vibrational assignments have been made on the basis of the normal coordinate analysis\(^{16,17}\). All the bands are ascribed to the in-plane vibrations of the polyene backbone except for the 966 cm\(^{-1}\). The strongest hyper-Raman band at 1579 cm\(^{-1}\) is attributed to the C=C stretch vibration. This vibration gives rise to a series of overtone and

Figure 4-2  
(a) Resonance hyper-Raman spectra of all-trans-retinal in cyclohexane.  
Excitation wavelength is 800 nm. Laser energy is 10 \(\mu\)J. A spectrum in overtone region is also shown in the inset. Concentrations of all-trans-retinal are \(1 \times 10^{-3}\) and \(3 \times 10^{-3}\) mol dm\(^{-3}\) for measuring the frequency region from \(-200\) cm\(^{-1}\) to 1900 cm\(^{-1}\) and that from 2500 to 3400 cm\(^{-1}\), respectively.  
(b) A signal from neat cyclohexane solvent measured under the same excitation condition.
combination bands in the frequency region from 2500 to 3400 cm\(^{-1}\), as shown in the inset of the figure.

It is noted that hyper-Raman scattering was measured with a high S/N ratio even from a diluted solution of concentration as low as \(1 \times 10^{-3}\) mol dm\(^{-3}\). This concentration is very low, compared with the concentration adopted in the measurements reported previously\(^4,6\). Bonang and Cameron used about \(10^3\) times higher concentration (0.5 – 1 mol dm\(^{-3}\)) in their experiments but obtained spectra with much lower S/N ratio. This clearly demonstrates that resonance hyper-Raman scattering of \textit{all-trans}-retinal is quite strong. In fact, the hyper-Raman scattering of \textit{all-trans}-retinal was first observed unexpectedly, and detected as the second-order light in the spectrometer, whose intensity was comparable to the spontaneous Raman signal that was detected as the first order light. Quantitative comparison of hyper-Raman intensity measured by different apparatus is not easy because the intensity of the nonlinear hyper-Raman signal depends on the excitation condition. However, our estimation indicated that the high hyper-Raman intensity observed in the present measurements is not merely due to the difference in the excitation laser intensity\(^{18}\).

The molecular hyperpolarizability (\(\beta\)) of \textit{all-trans}-retinal has been evaluated by the measurement of hyper-Rayleigh scattering\(^{19,20}\) and it was reported to be \(730 \times 10^{-30}\) esu in methanol at 1064 nm. This value is much higher than the hyperpolarizability of \textit{p}-nitroaniline (34.5 \(\times\) \(10^{-30}\) esu) that is known as a typical molecule showing a large optical nonlinearity\(^{19,21}\). The hyperpolarizability value was determined under the nonresonance condition, whereas hyper-Raman scattering was measured under the resonance condition. Nevertheless, very large hyperpolarizability value in the literature suggests that the hyper-Raman scattering of \textit{all-trans}-retinal is exceptionally strong not only because of the two-photon resonance enhancement but also owing to the intrinsic high optical nonlinearity of this molecule.

It may worth mentioning the hyper-Rayleigh scattering observed in the present measurement. The observed hyper-Rayleigh scattering is also attributed solely to \textit{all-trans}-retinal because no hyper-Rayleigh scattering was recognized from neat cyclohexane
Actually, hyper-Rayleigh scattering is not observed from isotropic systems theoretically, because the second-order susceptibility ($\chi^{(2)}$) is zero when the system has the inversion symmetry. The fact that the hyper-Rayleigh scattering was observed from the retinal solution implies that the solution is not completely isotropic. It is known that the instantaneous fluctuation of the local density in the solution can temporally break the isotropic nature of the system. In other words, even though the solution is isotropic in the time average, it can be non-isotropic in the dynamic sense. Because of this reason, hyper-Rayleigh scattering is observed from liquids of noncentrosymmetric molecules. In fact, when hyper-Raman spectra of all-trans-retinal in methanol were measured, it was found that hyper-Rayleigh scattering of noncentrosymmetric methanol also contributed to the signal. Even in this case, the hyper-Rayleigh intensity of all-trans-retinal was much stronger than that of methanol owing to the resonance enhancement.

### 4-3-2 Excitation profiles of resonance hyper-Raman scattering

Because the $^{1}B_u^{-}$ and $^{1}A_g^{-}$ states have both one-photon and two-photon allowedness, these two excited states is expected to contribute to the resonance enhancement of hyper-Raman scattering. The excitation energy of hyper-Raman scattering (the excitation profile) affords information about the relevant resonant electronic state as well as the mechanism of resonance enhancement. Therefore, the excitation profiles of the resonance hyper-Raman scattering of all-trans-retinal were examined.

To compare quantitatively the hyper-Raman spectra taken with different excitation wavelength, the laser power dependence of hyper-Raman intensity of all-trans-retinal was checked first. The observed hyper-Raman intensity showed a good quadratic dependence on the incident pulse energy for the energies below 3 µJ under the present focusing condition, but started showing deviation in the higher energy region. This saturation effect is probably due to the bleaching of the ground-state molecule. High-energy laser pulses pump the
molecules to the excited state and significantly reduce the ground-state population, so that the hyper-Raman intensity of the ground-state molecule can not show good square dependence any more. Thus, the laser pulse energy was set at ~ 2 µJ to avoid this saturation effect when measuring the probe wavelength dependence of the hyper-Raman intensity.

Resonance hyper-Raman spectra were measured with eight different excitation wavelengths in the range from 770 nm to 840 nm. The obtained raw spectra were normalized and corrected in the following way. First, the hyper-Raman intensity measured with different excitation wavelengths has to be normalized, by taking account of difference in the excitation condition. The hyper-Raman process is a nonlinear optical process so that its intensity is very sensitive not only to the total pulse energy but also to the focusing condition. For the normalization procedure, hyper-Rayleigh scattering of methanol was measured under the same experimental condition at each excitation wavelength and its intensity was used as the external intensity standard23. Second, the self-absorption effect has to be also corrected. Since the wavelength region of hyper-Raman scattering is overlapped with the one-photon absorption band due to the $1^1B_u^→S_0$ transition, the generated hyper-Raman scattering is reabsorbed by the solution, and the spectral feature is severely distorted. In order to correct this spectral distortion, a correction curve was used, which was produced as follows. By using the second harmonic of the excitation pulse of each hyper-Raman measurement, resonance Raman spectra of the sample solution and Raman spectra of neat solvent were measured. Based on the comparison of the solvent band intensity between these two spectra, the magnitude of the self-absorption effect was evaluated. Three solvent Raman bands were used in each Raman spectrum so that 24 experimental data points, in total, were obtained in the wavelength region from 397 nm to 447 nm. These experimental data points were fitted by a suitable model function and a calculated correction curve was used for all the observed hyper-Raman spectra.

The hyper-Raman spectra obtained after the intensity normalization and the reabsorption correction are shown in Figure 4-3. The spectral feature (relative intensity of
the hyper-Raman bands in each spectrum) does not show any noticeable change with the change of the excitation wavelength. It means that the excitation profiles of the all the observed hyper-Raman bands are very similar to each other. The hyper-Raman excitation profiles of the C=C stretch band (1575 cm⁻¹) and the two C–C stretch bands (1189 cm⁻¹ and 1157 cm⁻¹) are plotted in Figure 4-4. The one-photon absorption spectra, which exhibit the strong “1B_u” ← S_0 transition, are also shown. As clearly seen, the intensity of the observed hyper-Raman bands increases monotonically with shortening excitation wavelength, within experimental error in the range of the present study. The sharp increases of the hyper-Raman intensity assumed that the hyper-Raman scattering gains intensity...
enhancement from two-photon resonance, not from one-photon preresonance, because there is no excited state that can be resonant at the energy of one photon. The hyper-Raman
intensities seem to increase rapidly double the excitation energy approaches the intensity maximum of the one-photon absorption.

4-3-3 Resonance mechanism of hyper-Raman scattering of all-trans-retinal

When there are no excited singlet states that can be one-photon resonant in the two-photon upward transition process (the intermediate state must be the virtual state), we can sum over vibrational level $r$ of the intermediate state $s$ in formula (4-5A). Then, the $A$ term of the hyperpolarizability can be written as

$$A = \sum_{\nu,\mu} \frac{(M_s)^r}{\nu} \left( \nu_0 - \nu \right) \left( \nu_0 - 2\nu_0 - i\Gamma_{\nu_0,\nu} / 2 \right).$$

(4-6)

The Franck-Condon overlap integrals in this formula are the same as those of the $A$-term mechanism of spontaneous Raman scattering resonant with the electronic state $e$. Therefore, the $A$-term active resonance hyper-Raman spectrum can have the same appearance (frequencies and relative intensities) as the $A$-term active spontaneous resonance Raman spectrum excited with double the photon energy$^{2,3}$, when the resonant electronic state of the hyper-Raman process is the same as that of the Raman process.

In order to consider the resonance mechanism of hyper-Raman scattering of all-trans-retinal, it is important to compare two-photon resonance hyper-Raman spectra with one-photon resonance Raman spectra taken with double the excitation energy. In Figure 4-5, the resonance hyper-Raman spectrum taken with 800-nm excitation is compared with the resonance Raman spectrum measured with 400-nm excitation. As clearly seen, the spectral features of the one-photon resonance Raman spectrum are almost identical with those of the two-photon resonance hyper-Raman spectrum. This high similarity in the spectral feature was seen over whole the excitation energy range of the present study. This
fact suggests that the excited state relevant to the resonance enhancement of hyper-Raman scattering is the same as that for resonance Raman scattering.

The mechanism of one-photon resonance Raman scattering of all-trans-retinal has already been discussed in detail\(^\text{17,24}\), and it was concluded that the enhancement arises from the Franck-Condon-type resonance with the “\(^1\text{B}_u\)” state (Albrecht’s \(A\) term \(^\text{25}\)). Therefore, the high similarity between the two-photon resonance hyper-Raman spectra and the one-photon resonance Raman spectra indicates that the resonance hyper-Raman scattering also gains intensity enhancement from the “\(^1\text{B}_u\)” state, not from the “\(^1\text{A}_g\)” state, through the Franck-Condon-type mechanism (Ziegler’s \(A\) term). It seems that the “\(^1\text{A}_g\)” state, which has much larger two-photon transition probability from the \(S_0\) state, does not significantly

![Figure 4-5](image)

**Figure 4-5** (a) Resonance hyper-Raman (RHR) and (b) resonance Raman (RR) spectra of all-trans-retinal in cyclohexane. Excitation wavelength for RHR is 800 nm, whereas that for RR is 400nm. Concentration of all-trans-retinal is \(1 \times 10^{-3}\) mol dm\(^{-3}\). The self-absorption correction of each spectrum has been done. The solvent bands have been subtracted from the RR spectrum.
contribute to the intensity enhancement of the observed two-photon resonance hyper-Raman scattering.

This conclusion confused us first, because the \( ^1\text{Bu}^* \) state has a much smaller two-photon transition probability compared with the \( ^1\text{Ag}^* \) state. However, the hyper-Raman optical process includes not only the two-photon upward transition but also the one-photon downward transition, and therefore, the excited state that exhibits strong two-photon absorption does not necessarily gives rise to strong resonance hyper-Raman enhancement. In fact, a simple discussion about transition probabilities that the \( ^1\text{Bu}^* \) state can induce larger resonance hyper-Raman enhancement than the \( ^1\text{Ag}^* \) state, as described below.

The intensity of hyper-Raman scattering is proportional to the square of molecular hyperpolarizability, and hence, it is proportional to the square of the product of the three electronic transition moments: \( (M_\lambda)^0_y (M_\mu)^0_x (M_\nu)^0_z \). Therefore, the intensity of resonance hyper-Raman scattering \( I_{\text{RHR}} \) can be related to the probabilities of the one-photon and two-photon transitions as follows:

\[
I_{\text{RHR}} \propto \left| \beta_{\lambda \mu \nu} \right|^2 \\
\propto \left| (M_\lambda)^0_y (M_\mu)^0_x (M_\nu)^0_z \right|^2 = \left| (M_\lambda^0)^0_y^0 (M_\mu^0)^0_x^0 (M_\nu^0)^0_z^0 \right|^2 \\
\propto \text{(one – photon oscillator strength)} \times \text{(two – photon absorptivity)}
\]

Birge and co-workers measured one-photon absorption and two-photon excitation spectra of all-trans-retinal in a low-temperature EPA matrix. They evaluated the one-photon oscillator strength of the \( ^1\text{Bu}^* \) state to be about 17 times larger than that of the \( ^1\text{Ag}^* \) state, whereas the two-photon absorptivity of the \( ^1\text{Bu}^* \) state is about seven times smaller than that of the \( ^1\text{Ag}^* \) state\(^{10}\). If we focus only on the transition moment and if we assume that the other factors such as Franck-Condon factors are the same, it can be considered that the resonance hyper-Raman intensity due to the \( ^1\text{Bu}^* \) state is about 2.4 times larger than that due to the \( ^1\text{Ag}^* \) state. This estimation is based on the values obtained in the
low-temperature matrix. Nevertheless, it seems reasonable to consider that the "\(^1B_u^\ast\)" state is the state that predominantly gives rise to the resonance hyper-Raman enhancement also in solution at room temperature.

In a low-temperature EPA glass matrix, it was found that the peak of the "\(^1A_g^\ast\)" ← \(^0S_0\) absorption is located around 428 nm, whereas that of the "\(^1B_u^\ast\)" ← \(^0S_0\) absorption is around 388 nm.\(^{10}\) A recent femtosecond fluorescence study of all-trans-retinal in hexane at room temperature revealed that the intensity maxima of the "\(^1B_u^\ast\)" and "\(^1A_g^\ast\)" fluorescence are located around 430 and 440 nm, respectively\(^{13}\), which implies that the "\(^1B_u^\ast\)" and "\(^1A_g^\ast\)" states are more closely located in solution at room temperature. Therefore, it is natural to expect that the "\(^1A_g^\ast\)" state also contributes to the resonance enhancement of hyper-Raman scattering observed in the present study. However, it seems that the intensity enhancement arising from resonance with the "\(^1A_g^\ast\)" state is negligibly small compared with that attributable to the "\(^1B_u^\ast\)" state. It looks as if the contribution from the "\(^1A_g^\ast\)" state is much smaller than the estimation based on the discussion about the electronic part (the transition moment). One plausible explanation for this discrepancy is the difference in the Franck-Condon factor. If the structural change induced by the "\(^1A_g^\ast\)" ← \(^0S_0\) transition is much smaller than that accompanying with the "\(^1B_u^\ast\)" ← \(^0S_0\) transition, the magnitude of the Franck-Condon overlap giving rise to the vibrational transition can be very small for the hyper-Raman process resonant with the "\(^1A_g^\ast\)" state. In such case, even if the electronic part for the resonance enhancement with the "\(^1A_g^\ast\)" state is sizable, the total contribution to the intensity enhancement from the "\(^1A_g^\ast\)" state can be much smaller than that from the "\(^1B_u^\ast\)" state. Further discussion about the seemingly small contribution from the "\(^1A_g^\ast\)" state may need theoretical study which can afford quantitative information about the structure of the excited "\(^1A_g^\ast\)" and "\(^1B_u^\ast\)" states of all-trans-retinal.

4-4 Conclusion
The first observation of the extremely strong resonance hyper-Raman scattering from all-trans-retinal in a diluted solution is reported. Based on both the analysis of the hyper-Raman excitation profiles and the comparison between the spectral patterns of the resonance hyper-Raman and resonance Raman scattering, the resonant excited state in this hyper-Raman process is the \( ^1B_u^* \) state, rather than the \( ^1A_g^* \) state which is regarded as the strong two-photon transition allowed state. The \( ^1B_u^* \) state predominantly gives rise to the intensity enhancement through the \( A \)-term (Franck-Condon) resonance hyper-Raman mechanism.
References and notes


(2) Ziegler, L. D. J. Raman Spectrosc. 1990, 21, 769.


(9) Hudson, B. S.; Kohler, B. E.; Schulten, K. Excited States 1982, 6, 1.


(11) Although the symmetry of all-trans-retinal belongs to the $C_1$ point group, the terms of $^1A_g^*$ and $^1B_u^*$ are widely used by considering the local symmetry, $C_{2h}$, of the polyene backbone.


(18) In our experiments, the peak power density of the excitation pulse reaches as high as $4 \times 10^{11}$ W cm$^{-2}$ and the duration of the pulse is 2 ps. On the other hand, in the intracavity apparatus of Bonang and Cameron, the peak power density was reported to be $\sim 10^{10}$ W cm$^{-2}$, and the pulse duration was 4 ps. Since the hyper-Raman intensity is proportional to the square of the incident excitation intensity, the intensity of the hyper-Raman scattering...
generated from unit area per pulse in our setup is expected to be 1600 times higher than theirs. However, our repetition rate (1 kHz) is five orders of magnitude lower than theirs (76 MHz), so that the intensity of hyper-Raman scattering generated from unit area per unit time in our setup is estimated to be even ~ 50 times weaker than that in their setup. Although comparison for other experimental conditions (the focus size, the detection sensitivity) cannot be made, this estimation suggests that the high hyper-Raman intensity observed in the present measurement is not merely due to the difference in the excitation laser power.


(22) The hyper-Raman scattering from solvent molecules was not recognized in the present measurement, whereas it was clearly observed in resonance Raman spectra of the same solution excited with double the excitation energy. It manifests that the observed resonance hyper-Raman scattering is not identical with resonance Raman scattering excited by the resonance hyper-Rayleigh scattering (or resonance second harmonic generation).

(23) Since hyper-Rayleigh scattering of methanol could not be measured with pulse energy of 2µJ, we measured it with the pulse energy of 10 µJ. Since hyper-Rayleigh intensity from methanol showed nice quadratic dependence to the laser energy in the range up to 30 µJ, it was safe to estimate the hyper-Rayleigh intensity at the excitation energy used for hyper-Raman measurements.


Chapter 5

Concluding remarks
In this thesis, the studies on the following three photochemical systems in the condensed phase were described. The molecular structure and the nature of the electronic states of the short-lived species were clarified by time-resolved Raman and infrared spectroscopy and hyper-Raman spectroscopy.

In Chapter 2, time-resolved infrared and resonance Raman studies of the excited-state benzil were described. The structural change of the excited-state benzil was investigated. Nanosecond time-resolved infrared spectra of T1 benzil as well as picosecond time-resolved resonance Raman spectra of S1 benzil were measured. The assignment of the T1 infrared bands was carried out based on the frequency shifts on isotopic substitutions. The spectral pattern of the resonance Raman spectrum of the energy relaxed S1 state was quite similar to that of the T1 state. For the C=O stretch bands in the carbonyl group, which is regarded as one of the key bands to characterize the molecular structure of excited-state benzil, the anti-symmetric frequency was downshifted from 1676 to 1312 cm\(^{-1}\) and the symmetric frequency was downshifted from 1685 to 1426 cm\(^{-1}\) on going from the S0 state to the T1 state. For the central C–C stretch band, the other key band, the frequency was upshifted from 1050 to 1140 cm\(^{-1}\) on going from the S0 state to the S1 state, and further to 1160 cm\(^{-1}\) in the T1 state. In the S0 state, several bands simultaneously were observed in both the infrared and Raman spectra because benzil does not have an inversion center. On the contrary, the mutual exclusion rule between the infrared and Raman bands was held in the T1-state spectra. The decrease of C=O bond order and the increase of the central C–C bond order as well as the observation of the mutual exclusion rule in the T1-state spectra provided the conclusion that T1 benzil is the trans-planar structure. It was considered that the structure of the relaxed S1 state is also trans-planar because of the similarity of Raman spectra of both the S1 and T1 states.

In Chapter 3, picosecond and femtosecond time-resolved resonance Raman studies of the hydrated electron were described. The local structure, nature of the electronic states,
and relaxation dynamics of the hydrated electron were discussed from a viewpoint of the vibrational spectroscopy. In Section 3-2, picosecond time-resolved resonance Raman spectra of the hydrated electron were reported. Under the resonance condition with the electronic transition of the hydrated electron, it was found for the first time that the vibrational Raman bands due to the water molecule which directly interacts with the electron in the first solvation shell are strongly enhanced. The enhancement factors were as high as $\sim 10^5$ for the bend band, and $\sim 10^3$ for the stretch. The extremely high resonance Raman enhancement arises from the strong interaction between the electronic state of the electron and the vibrational state of the solvating water molecule. Based on the vibronic theory of resonance Raman scattering, it was concluded that the observed resonance Raman enhancement is induced from the $A$-term polarizability (the Franck-Condon mechanism) by regarding the local solvation structure around the electron as a "quasi-molecule". The measurements of the probe wavelength dependence of the bend- and stretch-band intensity and the polarized resonance Raman spectra of the bend band of the hydrated electron afforded us the novel information on the nature of the electronic states. Excitation profiles suggested that resonance Raman intensity of the hydrated electron is enhanced under the resonance condition with the $s \rightarrow p$ transition, but not significantly with the $s \rightarrow$ conduction band transition. A non-zero depolarization ratio indicated that the three sublevels of the $p$ state are nondegenerated. The bending and stretching frequencies of the water molecule solvating the electron were downshifted by $\sim 30$ cm$^{-1}$ and $\sim 150$ cm$^{-1}$ from those of bulk water, respectively, which implied that the OH bond of the solvating water molecule is toward the electron because of the strong interaction between the electron and water molecules.

In Section 3-3, the application of femtosecond time-resolved resonance Raman spectroscopy to the study of the relaxation dynamics of the hydrated electron was described. It was shown that femtosecond time-resolved Raman spectroscopy is suitable method to observe the ultrafast relaxation dynamics of the electron in water. Femtosecond time-resolved resonance Raman spectra of the hydrated electron were measured with the
800-nm probing, which is resonant with both the equilibrated and nonequilibrated hydrated electron. The Raman and luminescence signals of the hydrated electron exhibited the same temporal behavior in the whole temporal region, indicating that these signals originate from the same electronic transition. The rise-up time of the Raman bands was reproduced neither by the equilibrated-electron population nor by the transient absorption at the probe wavelength. This experimental result provided us the conclusion that the electronic state of the nonequilibrated hydrated electron is the ground state, and that the effective resonance condition changes with time. It indicated that the transient absorption signal monitored at 800 nm is not solely due to the $s \rightarrow p$ transition giving rise to the resonance Raman signal but partly due to the $s \rightarrow$ conduction band transition. This dynamic energy-level shift was confirmed by the observation of the slower rise-up time of the Raman signal probed at 600 nm. The resonance anti-Stokes Raman scattering from the nonequilibrated electron was not observed. This suggested that the electron ejected into water does not have sufficient energy to excite the water molecule to the vibrational hot state giving rise to the anti-Stokes Raman bands due to the libration as well as the bend mode.

In Chapter 4, resonance hyper-Raman study of all-trans-retinal was described. It was discovered that the intensity of resonance hyper-Raman scattering of all-trans-retinal was so strong that it can be observed from a diluted solution at room temperature. It was considered that the resonance enhancement of the hyper-Raman scattering of all-trans-retinal is derived from the $A$-term hyperpolarizability (the Franck-Condon type) in the framework of the vibronic theory. From the excitation profiles, it was found that the intensity of all the hyper-Raman bands monotonically increased with shortening the excitation wavelength, $\lambda_{ex}$, in the range of 770 – 840 nm ($\lambda_{ex}/2$, 385 – 420 nm). The spectral pattern of the resonance hyper-Raman spectrum probed at $\lambda_{ex}$ was almost identical with that of the resonance Raman spectrum excited at $\lambda_{ex}/2$ over whole the excitation energy range. This suggested that the excited state relevant to the resonance enhancement of hyper-Raman scattering is the same as that of ordinary Raman scattering. Therefore, it was concluded that the resonance
hyper-Raman scattering of \textit{all-trans}-retinal gains intensity enhancement from the \textit{\textsuperscript{1}B_{u}*} state, not from the \textit{\textsuperscript{1}A_{g}*} state, because the resonance enhancement of ordinary Raman scattering originates from the \textit{A-term} resonance with the \textit{\textsuperscript{1}B_{u}*} state.

This thesis anew demonstrated the usefulness of the time-resolved vibrational spectroscopy and hyper-Raman spectroscopy for the study of the photochemistry not only of the basic molecule but also of the “non-”molecule in the condensed phase. Time-resolved vibrational spectroscopy will continue to play an important role to clarify the molecular structure of short-lived species in cooperation with other time-resolved spectroscopy, such as X-ray crystallography or NMR spectroscopy. Nonlinear Raman spectroscopy will be applied to further various scientific fields because it affords unique information on the nature of molecules.
List of publications

*Paper*

1) Transient resonance Raman and *ab initio* MO calculation studies of the structures and vibrational assignments of the $T_1$ state and the anion radical of coumarin and its isotopically substituted analogues
   
   Yuki Uesugi, Misao Mizuno, Atsuhiko Shimojima, and Hiroaki Takahashi
   

2) Picosecond-nanosecond time-resolved resonance Raman study of the structure and dynamics of the excited states of 5-dibenzosuberene derivatives
   
   Makoto Sakai, Misao Mizuno, and Hiroaki Takahashi
   

3) Picosecond time-resolved absorption spectroscopy of luciferin
   
   Elena Yu. Cherednikova, Andrey Yu. Chikishev, Ol’ga V. Kosobokova, Misao Mizuno, Makoto Sakai, and Hiroaki Takahashi
   

4) Novel resonance Raman enhancement of local structure around solvated electrons in water
   
   Misao Mizuno and Tahei Tahara
   

5) Observation of resonance hyper-Raman scattering from *all-trans* retinal
   
   Misao Mizuno, Hiro-o Hamaguchi, and Tahei Tahara
6) Picosecond time-resolved resonance Raman study of the solvated electron in water
   Misao Mizuno and Tahei Tahara

7) Time-resolved infrared and resonance Raman studies of benzil. Vibrational analysis and
   structures of the excited states”
   Misao Mizuno, Koichi Iwata, and Hiroaki Takahashi

8) Time-resolved absorption and time-resolved Raman spectroscopies of the
   photochemistry of carbazole and N-ethylcarbazole
   Reiko Hiyoshi, Hidefumi Hiura, Yaeko Sakamoto, Misao Mizuno, Makoto Sakai,
   and Hiroaki Takahashi

9) Temporal fluorescence rejection in Raman spectroscopy using femtosecond
   up-conversion with single- and multi-channel detection
   Debabrata Mandal, Misao Mizuno, and Tahei Tahara
   *J. Mol. Struct.* in press.
Proceedings

1) Femtosecond dynamics of the Solvated Electron in Water Studied by Time-Resolved Raman Spectroscopy

Misao Mizuno, Shoichi Yamaguchi, and Tahei Tahara

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