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Observation of Resonance Hyper-Raman Scattering of *all-trans*-Retinal[†]

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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 1×10^{-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 a two-photon resonance with the "^1B_u*" state, not with the "^1A_g*" state, through the Franck−Condon (the *A* term) mechanism.

1. Introduction

When intense laser light at frequency ν_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 originates from the nonlinear Raman process that includes two-photon upward and one-photon downward transitions.[1] Hyper-Raman scattering is well-known as one of the oldest nonlinear Raman processes. In the non-resonance case, the intensity of hyper-Raman scattering is estimated to be smaller than that of ordinary Raman scattering by a factor of 10^5−10^6 under a typical excitation condition (~10^{10} W/cm^2).[2,3]

When there exists an electronic state that is resonant with double the excitation energy ($2h\nu_0$), the intensity of 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.[2,3] With use of the adiabatic approximation and the Herzberg−Teller expansion, they expanded the hyperpolarizability into three terms (the *A*, *B*, and *C* terms) according to the order of the vibronic interaction. They studied several fundamental molecules in the gas phase and clarified the resonance mechanism of hyper-Raman scattering. 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 intensity 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. They discussed vibronic interactions in the resonant excited states of these molecules. 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.

all-trans-Retinal is a very important polyene molecule not only in chemistry but also in biology.[7] The excited singlet states of linear polyenes have been intensively studied, and it is now well established that there are two singlet excited states, the one-photon allowed ^1B_u* state and the two-photon allowed ^1A_g* 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 ^1A_g* and ^1B_u* states of linear polyenes. Nevertheless, lowering symmetry causes mixing of the character of ^1B_u* and ^1A_g* states to some extent.[10] The "^1B_u*" state of retinal shows a very strong one-photon absorption but it also exhibits some two-photon absorptivity. On the other hand, the "^1A_g*" state has a clear doubly excited nature and exhibit 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, the "^1B_u*", "^1A_g*", and ^{1}nπ* states, in the low energy region of *all-trans*-retinal. The photochemical properties as well as the dynamics of these three excited states have been subjects of intensive spectroscopic studies.[10,12−14]

In this paper, we report the first resonance hyper-Raman spectra of *all-trans*-retinal in solution. We found that resonance hyper-Raman scattering from this molecule is quite strong, so that it could be measured even from a diluted solution. We

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examined hyper-Raman excitation profiles and discussed the resonance mechanism of the observed hyper-Raman scattering.

2. Experimental Section

Setup. For the measurements of hyper-Raman scattering of *all-trans*-retinal, the following experimental setup was used.[15] A picosecond mode-locked Ti:sapphire laser (Spectra-Physics, Tsunami) pumped by an Ar^+ 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 cw 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 laser pulse are 650−850 μJ, 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 ($f = 50$ mm) onto a thin film-like jet stream (~300 μm) of the sample solution. A typical beam radius at the sample position was about 20 μm, and the energy of the excitation pulse was adjusted in the range of 2−10 μJ 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 color 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-1100PB) 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 nm, ~50 mW, 90 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 the 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.

Samples. *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.

3. Results and Discussion

3.1. Observation of Resonance Hyper-Raman Scattering.

Figure 1 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} band. 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 combination bands in the frequency region from 2500 to 3400 cm^{-1}, as shown in the inset of the figure.

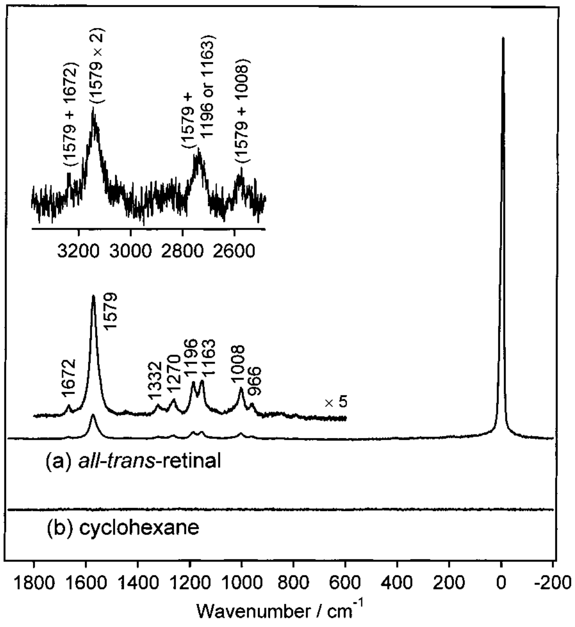

Figure 1. (a) Resonance hyper-Raman spectra of *all-trans*-retinal in cyclohexane. Excitation wavelength is 800 nm. Laser energy is 10 μJ. A spectrum in the overtone region is also shown in the inset. Concentrations of *all-trans*-retinal are 1×10^{-3} and 3×10^{-3} mol dm^{-3} for measuring the frequency 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.

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 1×10^{-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 from *all-trans*-retinal is quite strong. In fact, we first observed hyper-Raman scattering of *all-trans*-retinal unexpectedly, when we performed picosecond time-resolved spontaneous Raman measurements using 800 nm probe pulses. The hyper-Raman scattering was detected as the second-order light in the spectrometer, and its intensity was comparable to the spontaneous Raman signal that was detected as the first-order light. Quantitative comparison of the hyper-Raman intensity measured by a different apparatus is not easy because the intensity of the nonlinear hyper-Raman signal depends strongly on the excitation condition. However, our estimation indicated that the high hyper-Raman intensity observed in the present measurement is not merely due to the difference in the excitation laser intensity.[18]

The molecular hyperpolarizability (β) of *all-trans*-retinal has been evaluated by the measurement of hyper-Rayleigh scattering,[19,20] and it was reported to be 730×10^{-30} esu in methanol at 1064 nm. This value is much higher than the hyperpolarizability of *p*-nitroaniline (34.5×10^{-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 we measured hyper-Raman scattering under the resonance condition. Nevertheless, the very large hyperpolarizability value in the literature suggests that the hyper-Raman scattering of *all-trans*-retinal is exceptionally strong not only because of the two-photon resonance enhancement but also owing to the intrinsically high optical nonlinearity of this molecule.

It may be worth mentioning the hyper-Rayleigh scattering observed in the present measurement. The observed hyper-Rayleigh scattering is also attributed solely to *all-trans*-retinal because no hyper-Rayleigh scattering was recognized from neat cyclohexane. Theoretically, hyper-Rayleigh scattering is not observed from isotropic systems, because the second-order susceptibility ($\chi^{(2)}$) is zero when the system has the inversion symmetry. The fact that we observed hyper-Rayleigh scattering 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.[20] Actually, when we measured hyper-Raman scattering of *all-trans*-retinal in methanol, we 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.[22]

3.2. Excitation Profiles of Resonance Hyper-Raman Scattering. In nonpolar solvents, it is known that the three low-lying excited singlet states of *all-trans*-retinal are located in the order of "^1B_u*" > "^1A_g*" > $^1n\pi^*$ in energy.[7,13,14] Among the three, the $^1n\pi^*$ state is not important for resonance hyper-Raman enhancement, because it has very small one-photon and two-photon 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. The excitation energy dependence of hyper-Raman scattering (the excitation profile) affords information about the relevant resonant electronic state as well as the mechanism of resonance enhancement. Therefore, we examined the excitation profiles of the resonance hyper-Raman scattering of *all-trans*-retinal.

To compare quantitatively the hyper-Raman spectra taken with different excitation wavelengths, we first checked the laser power dependence of the hyper-Raman intensity of *all-trans*-retinal. The observed hyper-Raman intensity showed a good quadratic dependence on the incident pulse energy for 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 cannot show good square dependence any more. Thus, we set the laser pulse energy at ~2 μJ to avoid this saturation effect when we measured the excitation profiles of hyper-Raman scattering.

Resonance hyper-Raman spectra were measured with eight different excitation wavelengths in the range from 770 to 840 nm. The obtained raw spectra were normalized and corrected in the following way. First, we normalized the hyper-Raman intensity measured at different excitation wavelengths, by taking account of the 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. We measured hyper-Rayleigh scattering of methanol under the same experimental condition at each excitation wavelength and used its intensity as the external intensity standard for the normalization procedure.[23] Second, we corrected the self-absorption effect. Since the wavelength region of the hyper-Raman scattering is overlapped with the one-photon absorption band due to the "^1B_u*" ← S_0 transition, the generated hyper-Raman scattering is reabsorbed by the solution, and the spectral feature is severely distorted. To correct this spectral distortion, we used a correction curve that was produced as follows. We measured resonance Raman spectra of the sample and the neat solvent using the second harmonic of the excitation pulse and evaluated the magnitude of the self-absorption effect by comparing the intensity of the solvent band in these two spectra. We used three solvent Raman bands in each Raman spectrum so that, in total, we had 24 experimental data points in the wavelength region from 397 to 447 nm. We fitted a model function to these experimental data points and obtained a correction curve that can be used for the correction of all the observed hyper-Raman spectra.

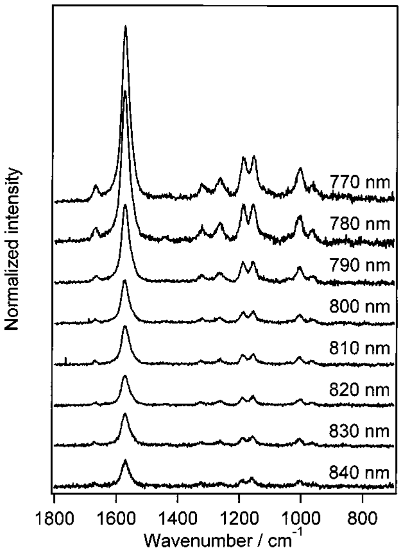

Figure 2. Resonance hyper-Raman spectra of *all-trans*-retinal in cyclohexane excited from 770 to 840 nm. Excitation wavelength of each spectrum is indicated in the figure. Concentration of *all-trans*-retinal is 1×10^{-3} mol dm^{-3}. Laser energy is 2 μJ. The intensity normalization and the self-absorption correction of each spectrum have been done.

The hyper-Raman spectra obtained after the intensity normalization and the reabsorption correction are shown in Figure 2. 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 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 and 1157 cm^{-1}) are plotted in Figure 3. The one-photon absorption spectra, which exhibits 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 increase of the hyper-Raman intensity assured 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 when double the excitation energy approaches the intensity maximum of the one-photon absorption.

To consider the resonance mechanism of hyper-Raman scattering, 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, resonance

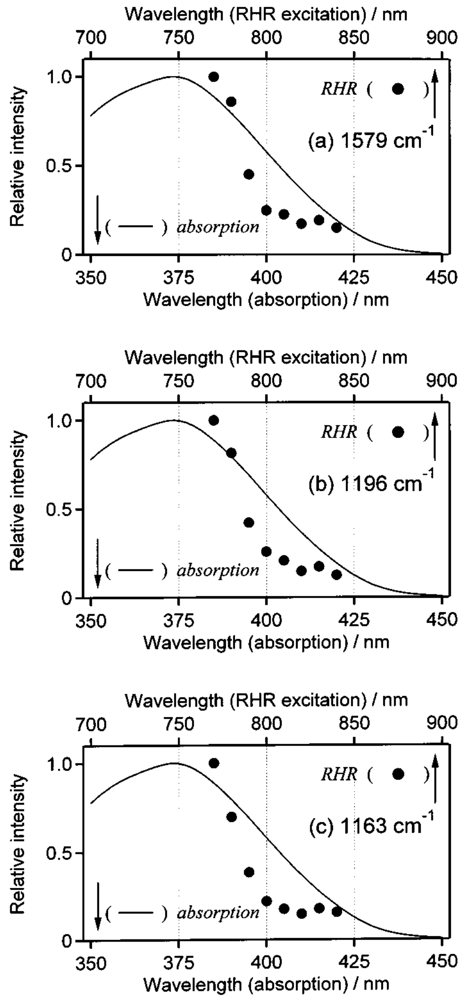

Figure 3. The hyper-Raman excitation profiles of (a) 1579 cm^{-1} (the C═C stretch), (b) 1196 cm^{-1} (the C−C stretch), and (c) 1163 cm^{-1} (the C−C stretch). Black circles and solid lines indicate the intensity of resonance hyper-Raman (RHR) bands and one-photon absorption spectrum, respectively. The excitation profiles of each hyper-Raman band have been normalized by the hyper-Raman intensity measured at 770 nm.

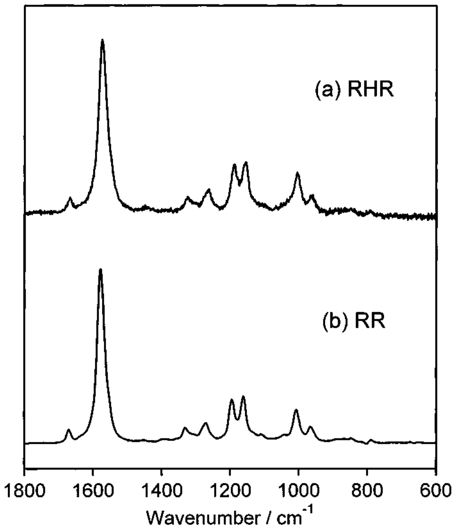

Figure 4. (a) Resonance hyper-Raman (RHR) and (b) resonance Raman (RR) spectra of *all-trans*-retinal in cyclohexane. Excitation wavelength for RHR is 800 nm, whereas that for RR is 400 nm. Concentration of *all-trans*-retinal is 1 × 10^{-3} mol dm^{-3}. The self-absorption correction of each spectrum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

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 to that 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.

3.3. Resonance Mechanism of Hyper-Raman Scattering of *all-trans*-Retinal. In the vibronic theory for resonance hyper-Raman scattering,[2,3] the hyperpolarizability $\beta_{\lambda\mu\nu}$ is expanded to give the following terms:

$$A = \sum_{sr,v} \frac{(M_\lambda)_{\mathrm{ge}}{}^0 (M_\mu)_{\mathrm{es}}{}^0 (M_\nu)_{\mathrm{sg}}{}^0 \langle f|v\rangle\langle v|r\rangle\langle r|o\rangle}{(\nu_{\mathrm{go,sr}} - \nu_0)(\nu_{\mathrm{go,ev}} - 2\nu_0 - i\Gamma_{\mathrm{go,ev}}/2)} \tag{1A}$$

$$\begin{aligned} B = \sum_a \sum_{sr,v} |[& (M_\lambda^a)'_{\mathrm{ge}} (M_\mu)_{\mathrm{es}}{}^0 (M_\nu)_{\mathrm{sg}}{}^0 \langle f|Q_a|v\rangle\langle v|r\rangle\langle r|o\rangle + \\ & (M_\lambda)_{\mathrm{ge}}{}^0 (M_\mu^a)'_{\mathrm{es}} (M_\nu)_{\mathrm{sg}}{}^0 \langle f|v\rangle\langle v|Q_a|r\rangle\langle r|o\rangle + \\ & (M_\lambda)_{\mathrm{ge}}{}^0 (M_\mu)_{\mathrm{es}}{}^0 (M_\nu^a)'_{\mathrm{sg}} \langle f|v\rangle\langle v|r\rangle\langle r|Q_a|o\rangle] \times \\ & \frac{1}{(\nu_{\mathrm{go,sr}} - \nu_0)(\nu_{\mathrm{go,ev}} - 2\nu_0 - i\Gamma_{\mathrm{go,ev}}/2)} \end{aligned} \tag{1B}$$

Here, the electronic state *e* is the two-photon resonant state. The higher order terms (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. In the above formulas, the *A* term arises from the two-photon allowed upward and one-photon allowed downward transitions. No vibronic transition moment is required for this Franck−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 from 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).

When there are no excited singlet states that can be one-photon resonant in the two-photon upward transition process, we can sum over vibrational level *r* of the intermediate state *s* in formula (1A). Then, the *A* term of the hyperpolarizability can be written as

$$A = \sum_{s,v} \frac{(M_\lambda)_{\mathrm{ge}}{}^0 (M_\mu)_{\mathrm{es}}{}^0 (M_\nu)_{\mathrm{sg}}{}^0 \langle f|v\rangle\langle v|o\rangle}{(\nu_{\mathrm{go,s}} - \nu_0)(\nu_{\mathrm{go,ev}} - 2\nu_0 - i\Gamma_{\mathrm{go,ev}}/2)} \tag{2}$$

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. The mechanism of one-photon resonance Raman scattering of *all-trans*-retinal has already been discussed in detail,[17,24] and it was concluded that the enhancement arises from the Franck−Condon-type resonance with "^1B_u*" state (Albrecht's *A* term[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 "^1B_u*" state, not from "^1A_g*" state, through the Franck−Condon-type mechanism (Ziegler's *A* term). It seems that the "^1A_g*" state, which has much larger two-photon transition probability from the S_0 state, does not significantly contribute to the intensity enhancement of the observed two-photon resonance hyper-Raman scattering.

We were first puzzled by this conclusion, because the "^1B_u*" state has a much smaller two-photon transition probability compared with the "^1A_g*" 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 the transition probabilities suggests that the "^1B_u*" state can induce larger resonance hyper-Raman enhancement than the "^1A_g*" 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 ($(M_\lambda)_{ge}^0(M_\mu)_{es}^0(M_\nu)_{sg}^0$). Therefore, the intensity of resonance hyper-Raman scattering I_{RHR} can be related to the probabilities of the one-photon and two-photon transitions as follows:

$$\begin{aligned} I_{RHR} &\propto |\beta_{\lambda\mu\nu}|^2 \\ &\propto |(M_\lambda)_{ge}^0(M_\mu)_{es}^0(M_\nu)_{sg}^0|^2 = |(M_\lambda)_{ge}^0|^2|(M_\mu)_{es}^0(M_\nu)_{sg}^0|^2 \\ &\propto \text{(one−photon oscillator strength)} \\ &\qquad\qquad \text{(two−photon absorptivity)} \qquad (3) \end{aligned}$$

Birge and co-workers measured one-photon absorption and two-photon excitation spectra of *all-trans*-retinal in a low-temperature EPA matrix.[10] They evaluated the one-photon oscillator strength of the "^1B_u*" state to be about 17 times larger than that of the "^1A_g*" state, whereas the two-photon absorptivity of the "^1B_u*" state is about seven times smaller than that of the "^1A_g*" 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, we can consider that the resonance hyper-Raman intensity due to the "^1B_u*" state is about 2.4 times larger than that due to the "^1A_g*" state. This estimation is based on the values obtained in the low-temperature matrix. Nevertheless, it seems reasonable to consider that the "^1B_u*" 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*" ← S_0 absorption is located around 428 nm, whereas that of the "^1B_u*" ← S_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*" and "^1A_g*" fluorescence are located around 430 and 440 nm, respectively,[13] which implies that the "^1B_u*" and "^1A_g*" states are more closely located in solution at room temperature. Therefore, it is natural to expect that the "^1A_g*" 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" state is negligibly small compared with that attributable to the "^1B_u*" state. It looks as if the contribution from the "^1A_g" 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*" ← S_0 transition is much smaller than that accompanying with the "^1B_u*" ← S_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*" state. In such a case, even if the electronic part for the resonance enhancement with the "^1A_g*" state is sizable, the total contribution to the intensity enhancement from the "^1A_g*" state can be much smaller than that from the "^1B_u*" state. Further discussion about the seemingly small contribution from the "^1A_g*" state may need theoretical study which can afford quantitative information about the structure of the excited "^1A_g*" and "^1B_u*" states of *all-trans*-retinal.

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(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.

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(18) In our experiments, the peak power density of the excitation pulse reaches as high as 4×10^{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 5 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.

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

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