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Intensity enhancement and selective detection of proximate solvent molecules by molecular near-field effect in resonance hyper-Raman scattering

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A new molecular phenomenon associated with resonance hyper-Raman (HR) scattering in solution has been discovered. Resonance HR spectra of *all-trans*- β -carotene and *all-trans*-lycopene in various solvents exhibited several extra bands that were not assignable to the solute but were unequivocally assigned to the solvents. Neat solvents did not show detectable HR signals under the same experimental conditions. Similar experiments with *all-trans*-retinal did not exhibit such enhancement either. *All-trans*- β -carotene and *all-trans*-lycopene have thus been shown to induce enhanced HR scattering of solvent molecules through a novel molecular effect that is not associated with *all-trans*-retinal. We call this new effect the “molecular near-field effect.” In order to explain this newly found effect, an extended vibronic theory of resonance HR scattering is developed where the vibronic interaction including the proximate solvent molecule (intermolecular vibronic coupling) is explicitly introduced in the solute hyperpolarizability tensor. The potential of “molecular near-field HR spectroscopy,” which selectively detects molecules existing in the close vicinity of a HR probe in complex chemical or biological systems, is discussed. © 2008 American Institute of Physics. [DOI: 10.1063/1.2950092]

I. INTRODUCTION

Hyper-Raman (HR) scattering is one of the nonlinear analogs of Raman scattering that provides molecular vibrational spectra. When intense light at the angular frequency ω_0 interacts with a molecule, a new radiation is generated at twice the angular frequency of the incident light along with bands of new radiations at the angular frequencies $2\omega_0 \pm \omega$, where ω corresponds to the angular frequency of a molecular vibration. The new radiation at $2\omega_0$ is called hyper-Rayleigh scattering and those at $2\omega_0 \pm \omega$ are called HR scattering. HR scattering spectra contain rich molecular information that is complementary to the conventional vibrational spectroscopy such as infrared absorption and Raman scattering. According to the selection rules based on molecular symmetry, infrared active vibrational modes are all active in HR scattering. Moreover, infrared and Raman inactive modes (silent modes) of highly symmetrical molecules can be HR active.¹⁻³ Therefore, the observation of HR spectra complements the experimental observation of the vibrational spectra of those molecules. Another useful aspect of HR spectroscopy is its feasibility in observing low frequency modes such as lattice vibrations and librations in crystals. The observation of HR scattering is not interfered by the stray and/or multireflected incident light at the frequency ω_0 because it detects signals at $2\omega_0 \pm \omega$. For isotropic media, hyper-Rayleigh scattering is forbidden, and therefore low frequency HR observation in these media can be performed background-free.^{4,5} Despite

those attractive features, experimental studies of HR scattering have been rather limited because of experimental difficulties.⁶⁻¹¹ Recent developments of HR systems using ultrafast and high-repetition rate laser sources have shortened the measurement time significantly.¹²⁻²⁰ However, it still takes a few hours to obtain high signal to noise HR spectra of organic liquids, whereas corresponding infrared absorption and Raman scattering experiments need only seconds. A new means for enhancing HR intensities is deemed necessary for HR spectroscopy to be a versatile vibrational spectroscopic tool.

When the energy ($\hbar\omega_0$, where \hbar is the Planck constant) or twice the energy ($2\hbar\omega_0$) of incident photon approaches the transition energy between the ground and a particular excited electronic state of a molecule, the HR cross section is greatly enhanced by the resonance effect (resonance HR scattering).²⁰ The resonance enhancement may well increase the HR cross section by several orders of magnitude as in the case of resonance Raman scattering. The mechanism of resonance enhancement in HR scattering is already well understood in terms of a vibronic theory analogous to that of resonance Raman scattering.¹⁰ While only one-photon resonances with single intermediate states are associated with resonance Raman scattering, the process of HR scattering can include resonances with two different intermediate states, the one-photon resonance with the first intermediate state and the two-photon resonance with the second intermediate state. Owing to this two-photon excitation nature of the process, resonance HR spectra can provide information on

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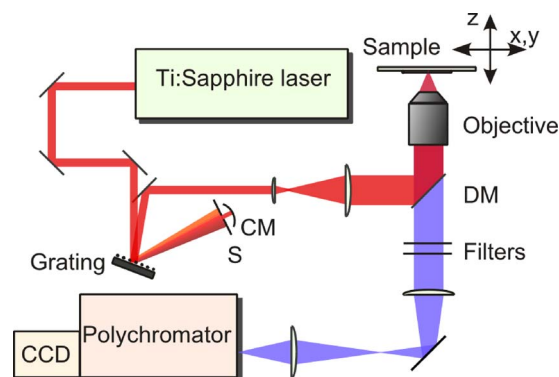


FIG. 1. (Color online) Schematic diagram of experimental setup: S, slit; CM, concave mirror; DM, dichroic mirror.

optically dark states, which are one-photon forbidden but are two-photon allowed and which are not directly accessible by conventional one-photon spectroscopy. Excitation profiles of resonance HR intensities have been discussed in relation to the properties of both one-photon and two-photon allowed excited states of several conjugated molecules.^{14–17}

Recently, we have applied HR scattering to microspectroscopy to develop HR microspectroscopy, which we meant to be a complementary technique to Raman microspectroscopy.¹⁸ It is capable of detecting Raman inactive but infrared active vibrational modes under an optical microscope with a submicrometer spatial resolution. This spatial resolution is an order of magnitude better than that (several microns) of the infrared counterpart. We have been successful in obtaining a high contrast HR image of an infrared active mode of an *all-trans*- β -carotene microcrystal under a two-photon resonance condition. In this sense, “infrared” microspectroscopy with a submicrometer spatial resolution has been achieved. During the course of our HR microspectroscopic studies of *all-trans*- β -carotene, we came across with a new resonance phenomenon of HR scattering which we ascribed to the intermolecular vibronic coupling between the excited electronic states of the solute and the infrared active vibrations of the solvent. We called this new phenomenon the “molecular near-field effect” in resonance HR scattering.¹⁹ In the present paper, we provide a full account of our discovery of the molecular near-field effect including its solvent and solute dependence together with a theoretical formulation of the phenomenon.

II. EXPERIMENTAL

A. Apparatus

The experimental setup for HR spectroscopy and the sample preparation procedures are similar to those that have been described in a previous paper.¹⁸ In the present study, a slight modification has been made on the HR system as shown in Fig. 1. A mode-locked Ti:sapphire oscillator (Coherent, Vitesse-800, 100 fs pulse duration at 800 nm, 80 MHz repetition rate) is used for the excitation light source without amplification. The output of the oscillator is spectrally filtered by a grating-slit pair in order to achieve sufficient spectral resolution for vibrational spectroscopy (~ 10 cm^{-1}). Filtered laser pulses are tightly focused onto a

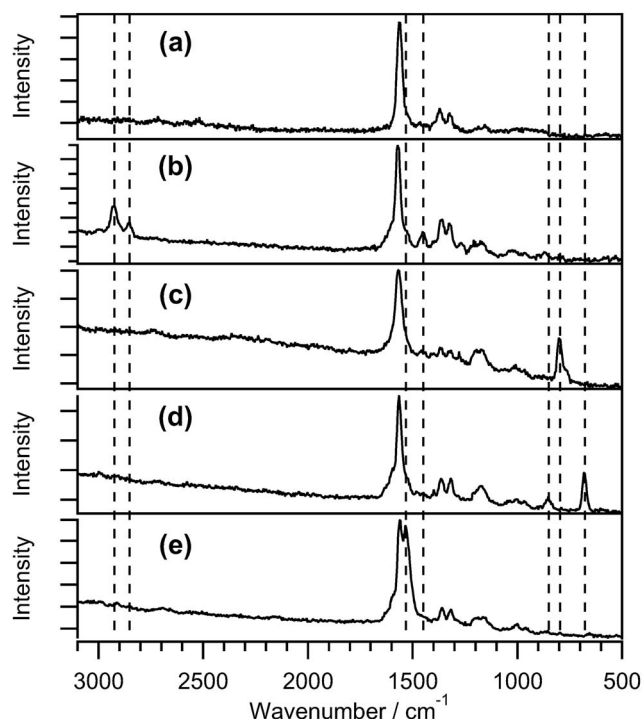


FIG. 2. RHR spectra of *all-trans*- β -carotene in crystalline phase (a) and in solutions [(b)–(e)]. Solvents are cyclohexane (b), carbon tetrachloride (c), benzene (d), and carbon disulfide (e). Vertical dashed lines indicate extra HR bands.

sample with a microscopic objective (40 \times , numerical aperture of 0.9). The HR signal scattered in the backward direction is collected by the same objective. After eliminating the incident light with a couple of glass filters (HOYA, CM-500S), the HR signal is dispersed by a polychromator (Acton, SpectraPro-300i) and detected by a charge coupled device camera (Andor, iDus DU420A-OE). Typical pulse energy of the excitation beam is 100 pJ at the sample point. Each spectrum shown in the following was obtained by averaging several spectra measured with exposure time of 20–30 min. Infrared absorption spectra were recorded on a JASCO FT/IR-670 spectrometer.

B. Sample preparation

All-trans- β -carotene, *all-trans*-lycopene, and *all-trans*-retinal were purchased from WAKO Chemical Corp. and used as received. All solvents (spectroscopic or high liquid performance chromatography grades) were also commercially obtained and used as received. Microcrystalline *all-trans*- β -carotene was obtained by recrystallization from a benzene solution. Sample preparation was made under deep red light in order to avoid photoisomerization. Concentration of carotenoids in each solution was 1–3 mM.

III. RESULTS AND DISCUSSION

A. Enhancements of solvent modes

First we describe the experimental results that show selective enhancements of solvent modes in resonance hyper-Raman (RHR) scattering of *all-trans*- β -carotene. Figure 2 shows RHR spectra of *all-trans*- β -carotene in the crystalline

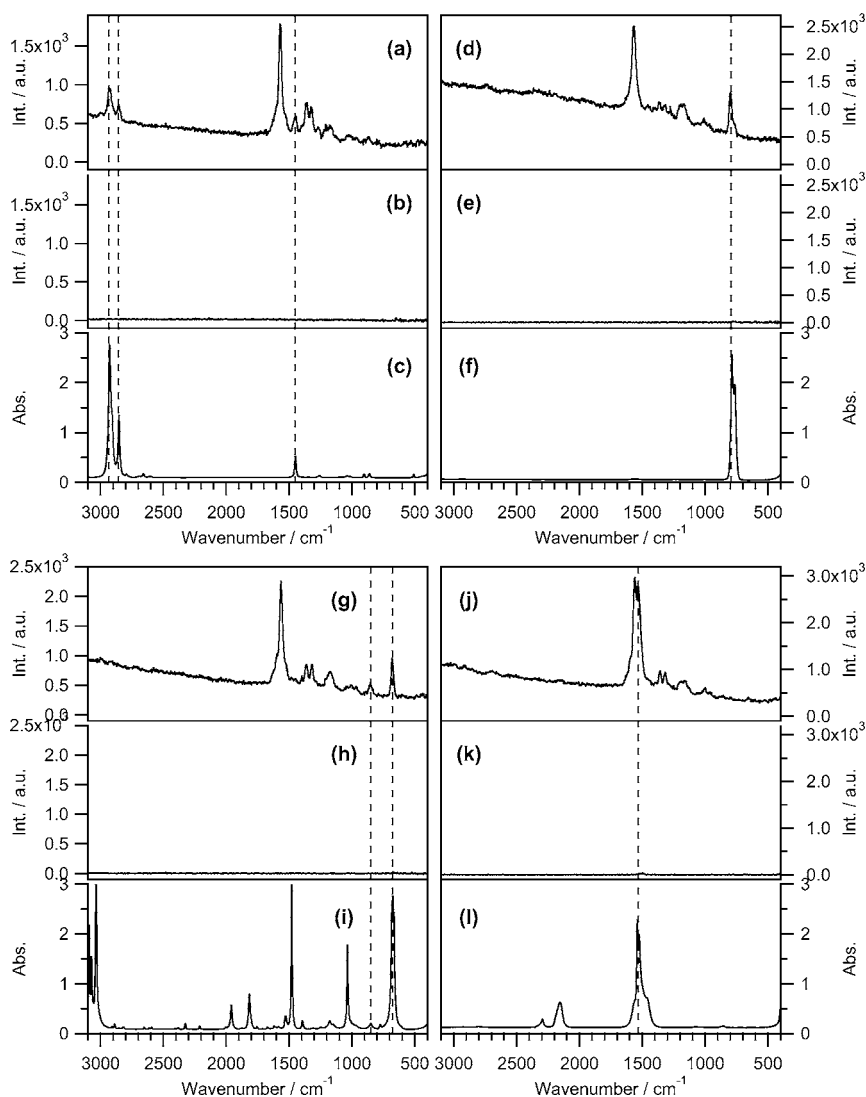


FIG. 3. RHR spectra of *all-trans*- β -carotene in cyclohexane (a), carbon tetrachloride (d), benzene (g) and carbon disulfide (j), HR spectra of neat cyclohexane (b), neat carbon tetrachloride (e), neat benzene (h) and neat carbon disulfide (k), and IR absorption spectra of neat cyclohexane (c), neat carbon tetrachloride (f), neat benzene (i), and neat carbon disulfide (l). Vertical dashed lines indicate extra HR bands.

phase (a) and those in solutions [(b)–(e)] of four different solvents, cyclohexane (b), carbon tetrachloride (c), benzene (d), and carbon disulfide (e). The RHR spectrum of crystalline *all-trans*- β -carotene has already been reported in a previous paper.¹⁸ It shows three prominent bands at 1564, 1370, and 1322 cm^{-1} . These bands are also observed in all the four solution spectra. They are assigned to the infrared active a_u vibrations (under C_i symmetry) of *all-trans*- β -carotene with reference to the IR spectrum and the normal coordinate analysis.²¹ Note that the mutual exclusion principle holds between Raman active and IR/HR active vibrational modes for *all-trans*- β -carotene because of the centrosymmetry of its molecular structure. In addition to these bands, all the spectra measured in solution show one or more solvent dependent extra band(s). The spectrum in cyclohexane shows three additional bands at 1453, 2857, and 2933 cm^{-1} . Similarly, one extra band appears at 794 cm^{-1} in carbon tetrachloride, two bands at 853 cm^{-1} and 679 cm^{-1} in benzene, and one at 1531 cm^{-1} in carbon disulfide.

In Fig. 3, we compare solution RHR spectra in Fig. 2 with HR and infrared absorption spectra of corresponding neat solvents. The peak positions of the three extra HR bands in cyclohexane, 1453, 2857, and 2933 cm^{-1} , agree well with

those of three prominent infrared bands of the neat solvent at 1450, 2853, and 2926 cm^{-1} , respectively. The wavenumbers of the extra bands in carbon tetrachloride (794 cm^{-1}) and carbon disulfide (1531 cm^{-1}) also agree well with those of principal infrared absorption bands (783 and 1530 cm^{-1}) of the respective solvents. Two additional bands observed in benzene (853 and 679 cm^{-1}) also accord with the IR absorption peaks (850 and 675 cm^{-1}) of the neat solvent likewise. Relative intensities of the extra bands in RHR spectra are different from those in IR spectra and some strong IR absorption bands seem to be missing in the RHR spectrum. On the contrary, HR spectra of neat solvents measured under the same experimental conditions [Figs. 3(b), 3(e), 3(h), and 3(k)] do not exhibit any meaningful features, except for a very weak signal in Fig. 3(k). This signal can be assigned to the HR signal from neat carbon disulfide. The intensity of this band in neat carbon disulfide is much lower ($\sim 1/100$) than that of the extra band in the *all-trans*- β -carotene solution spectrum in Fig. 3(j).

In order to confirm that the extra HR bands are due to the solvent, we examined the effect of isotopic substitution of the solvent. Figure 4 shows RHR spectra of *all-trans*- β -carotene in cyclohexane and in cyclohexane- d_{12} .

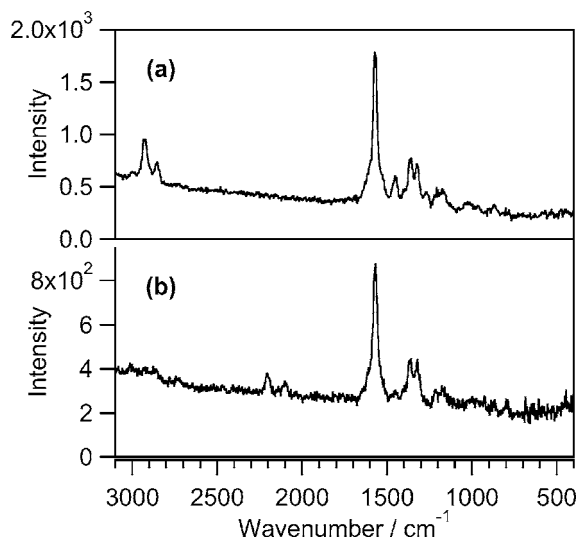


FIG. 4. RHR spectra of *all-trans*- β -carotene in cyclohexane (a) and deuterated cyclohexane (b).

The extra bands at 2857 and 2933 cm^{-1} in cyclohexane shift down to 2101 and 2203 cm^{-1} in the deuterated solvent. These peak shifts are exactly what are expected from the deuteration shifts of cyclohexane.

Agreement of peak positions of all the extra bands with those of the solvent IR-active modes indicates that those bands originate from solvents. On the other hand, HR measurements on neat solvents show that solvent molecules themselves do not possess sufficient HR cross sections to generate detectable HR signals. Therefore we conclude that the HR scattering of solvent molecules is enhanced by the solute, *all-trans*- β -carotene, through unknown mechanism associated with the RHR scattering process.

One may think of a possibility that the observed solvent bands are Raman scattering from bulk solvents excited by hyper-Rayleigh scattering. This possibility can be ruled out for the following two reasons. First, the frequencies of the observed bands are in good accord with the infrared active modes of solvents and not with the Raman active ones. Second, the observed intensity of hyper-Rayleigh scattering is too weak to be a Raman excitation source for relatively strong signals in Figs. 2–5.

B. Solute dependence of the enhancement effect

We have found that the HR intensity enhancement described above shows marked dependence on the symmetry of the solute molecule. Figure 5 shows RHR spectra of *all-trans*- β -carotene (a), *all-trans*-lycopene (b), and *all-trans*-retinal (c) in cyclohexane. Note that *all-trans*- β -carotene and *all-trans*-lycopene are centrosymmetric molecules while *all-trans*-retinal is not. The RHR spectrum of *all-trans*-retinal in cyclohexane has already been reported previously¹⁴ and the observed spectrum in this work shows good agreement with the previous one. RHR spectrum of *all-trans*-lycopene has not been reported before to the best of our knowledge. The RHR spectrum of *all-trans*-lycopene shows characteristic band features at 1453, 2860, and 2927 cm^{-1} , where the enhanced bands of the solvent cyclo-

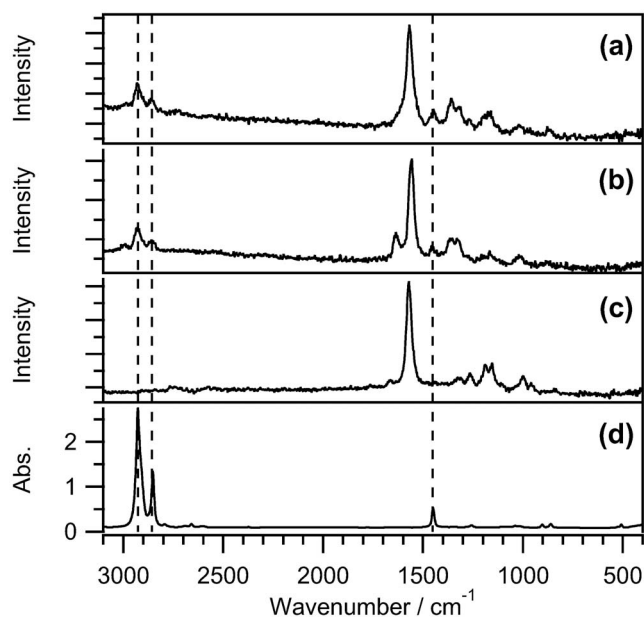


FIG. 5. HR spectra of *all-trans*- β -carotene (a), *all-trans*-lycopene (b), and *all-trans*-retinal (c) in cyclohexane solution, and infrared absorption spectrum of neat cyclohexane (d).

hexane are observed in the *all-trans*- β -carotene solution. In fact, the peak positions and relative intensities of these bands are in excellent accord with those for *all-trans*- β -carotene. This fact implies that *all-trans*-lycopene also exhibits the enhancement effect of RHR scattering of the solvent modes. On the other hand, the RHR spectrum of *all-trans*-retinal does not show such enhancement for any bands of cyclohexane.

C. Enhancement mechanism of HR scattering in solution spectra

The theory of HR scattering has been examined by a number of workers.^{1–3,10,20,22,23} The selection rules of HR scattering can be discussed by introducing vibronic interaction into the hyperpolarizability tensor components, although a diversity of mathematical treatments is used by different authors. In the present paper, we extend the theory to include the vibronic interaction with the proximate solvent molecule, so as to explain the newly found resonance effect.

For a HR transition from the initial state $|i\rangle$ to the final states $|f\rangle$, an element of the first hyperpolarizability tensor $\beta_{\lambda\mu\nu}$ of a molecule may be written in the following form:^{11,20,23}

$$\begin{aligned}
 (\beta_{\lambda\mu\nu})_{if} \equiv & \sum_n \sum_m \left[\frac{\langle f | R_\lambda | n \rangle \langle n | R_\mu | m \rangle \langle m | R_\nu | i \rangle}{(\varepsilon_m - \varepsilon_i - \hbar\omega_0)(\varepsilon_n - \varepsilon_i - 2\hbar\omega_0)} \right. \\
 & + \frac{\langle f | R_\nu | n \rangle \langle n | R_\lambda | m \rangle \langle m | R_\mu | i \rangle}{(\varepsilon_m - \varepsilon_i - \hbar\omega_0)(\varepsilon_n - \varepsilon_f + \hbar\omega_0)} \\
 & \left. + \frac{\langle f | R_\mu | n \rangle \langle n | R_\nu | m \rangle \langle m | R_\lambda | i \rangle}{(\varepsilon_n - \varepsilon_f + \hbar\omega_0)(\varepsilon_m - \varepsilon_f + 2\hbar\omega_0)} \right]. \quad (1)
 \end{aligned}$$

Here, ε_m , ε_n , ε_i , and ε_f represent the energies of the intermediate states $|m\rangle$, $|n\rangle$ and those of the initial $|i\rangle$ and final $|f\rangle$ states, respectively. λ , μ , and ν refer to the polarization di-

rections of the incident and scattered radiation fields in the molecular fixed frame with ω_0 denoting the angular frequency of the incident light. As already stated above, the process of HR scattering includes two possible resonances, the one-photon resonance with the first intermediate state $|m\rangle$ and the two-photon resonance with the second $|n\rangle$. As already pointed out by Long and Stanton,²⁰ the first term in Eq. (1) is responsible for the two-photon resonance effect when twice the energy ($2\hbar\omega_0$) of the incident photon approaches the transition energy between the second intermediate state $|n\rangle$ and the initial state $|i\rangle$ (with a condition $\varepsilon_n > \varepsilon_i$). In addition, both the first and the second terms are responsible for the one-photon resonance when the energy ($\hbar\omega_0$) of the incident photon approaches the transition energy between the first intermediate states $|m\rangle$ and $|i\rangle$ (with a condition $\varepsilon_m > \varepsilon_i$). The last term becomes important only when the initial state is an excited electronic state and intermediate states exist lower in energy than $|i\rangle$.

In the present experiment, we use a laser line at 800 nm for excitation. Twice the energy of the incident photon falls within the strong absorption band ($1B_u$) of carotenoids. It can be safely considered that the observed HR spectra gain intensity enhancement through a two-photon resonance. It is not clear whether or not there is an additional one-photon resonance, i.e., double resonance. Nevertheless, the contribution from the first term will always exceed that from the second term under a two-photon resonant condition because the first two terms share exactly the same energy denominator for the one-photon resonance. Therefore we retain only the first term in Eq. (1) and disregard any contributions from the second and the third terms for the following discussion. Equation (1) under a two-photon resonant condition is expressed as follows:

$$(\beta_{\lambda\mu\nu})_{if} = \sum_m \frac{\langle f|R_\lambda|n\rangle\langle n|R_\mu|m\rangle\langle m|R_\nu|i\rangle}{(\varepsilon_m - \varepsilon_i - \hbar\omega_0)(\varepsilon_n - \varepsilon_i - 2\hbar\omega_0 - i\Gamma_{ni})}. \quad (2)$$

The damping constant Γ_{ni} is introduced to avoid the divergence of Eq. (2) under the two-photon resonant condition. Adiabatic approximations are introduced to the initial, intermediate, and final states,

$$|i\rangle = |g\rangle |i\rangle, |f\rangle = |g\rangle |f\rangle, |m\rangle = |m\rangle |u\rangle \quad (3)$$

and

$$|n\rangle = |n\rangle |v\rangle,$$

where only the HR transition between the vibrational sub-states $|i\rangle$ and $|f\rangle$ of the ground electronic state $|g\rangle$ is considered. $| \]$ and $| \)$ denote ket vectors in the electronic and vibrational spaces, respectively. The molecular Hamiltonian is divided into three parts H_{el} , H_{vib} , and H_{ev} , corresponding to the electronic, vibrational, and vibronic interaction energies, respectively,

$$H = H_{el} + H_{vib} + H_{ev}.$$

In the following, we regard H_{ev} as a perturbation to $H_{el} + H_{vib}$ and expand the adiabatic electronic states into Taylor's series in the nuclear coordinate of the molecule. In this expansion, the zeroth-order electronic kets $|g^0\rangle$, $|m^0\rangle$, and

$|n^0\rangle$ are the eigenkets of H_{el} with energies ε_g^0 , ε_m^0 , and ε_n^0 , respectively. For the two intermediate states $|n\rangle$ and $|m\rangle$, the expansions are given as

$$|n\rangle = |n^0\rangle + \sum_a \sum_{e \neq n} |e^0\rangle \frac{h_{en}^a}{(\varepsilon_n^0 - \varepsilon_e^0)} Q_a^{\text{solute}} + \sum_\alpha \sum_{e \neq n} |e^0\rangle \frac{h_{en}^\alpha}{(\varepsilon_n^0 - \varepsilon_e^0)} Q_\alpha^{\text{solvent}} + \dots, \quad (4)$$

$$|m\rangle = |m^0\rangle + \sum_a \sum_{e \neq m} |e^0\rangle \frac{h_{em}^a}{(\varepsilon_m^0 - \varepsilon_e^0)} Q_a^{\text{solute}} + \sum_\alpha \sum_{e \neq m} |e^0\rangle \frac{h_{em}^\alpha}{(\varepsilon_m^0 - \varepsilon_e^0)} Q_\alpha^{\text{solvent}} + \dots, \quad (5)$$

where

$$h_{en}^a = [e^0 | \left(\frac{\partial H_{ev}}{\partial Q_a^{\text{solute}}} \right) | n^0]$$

and

$$h_{en}^\alpha = [e^0 | \left(\frac{\partial H_{ev}}{\partial Q_\alpha^{\text{solvent}}} \right) | n^0],$$

and ε_e^0 denotes the energy of the zeroth-order adiabatic electronic state $|e^0\rangle$ that is vibronically coupled with $|n^0\rangle$ or $|m^0\rangle$. We assume here that some excited electronic states are sensitive enough to be affected not only by the solute nuclear motions but also by those of proximate solvent molecule(s). Thus the Herzberg–Teller expansions of $|n\rangle$ and $|m\rangle$ contain not only the nuclear coordinate of the solute (Q_a^{solute}) but also that of the proximate solvent molecule(s) ($Q_\alpha^{\text{solvent}}$).

If we neglect the terms higher than the second order to the normal coordinates as well as cross terms when substituting Eqs. (3)–(5) into Eq. (2) and rearrange terms in orders of normal coordinate dependence, we obtain

$$(\beta_{\lambda\mu\nu})_{if} = A + B_1 + B'_1 + B_2 + B'_2,$$

$$A = \sum_{mu,v} F(\omega_0) (M_\lambda)_{gn} (M_\mu)_{nm} (M_\nu)_{mg} (f|v)(v|u)(u|i),$$

$$B_1 = \sum_{mu,v} \sum_a \sum_{e \neq n} F(\omega_0) \times \left\{ (M_\lambda)_{ge} h_{en}^a (M_\mu)_{nm} (M_\nu)_{mg} \frac{(f|Q_a^{\text{solute}}|v)(v|u)(u|i)}{\varepsilon_n^0 - \varepsilon_e^0} + (M_\lambda)_{gn} h_{ne}^a (M_\mu)_{em} (M_\nu)_{mg} \frac{(f|v)(v|Q_a^{\text{solute}}|u)(u|i)}{\varepsilon_e^0 - \varepsilon_n^0} \right\},$$

$$B'_1 = \sum_{mu,v} \sum_\alpha \sum_{e \neq n} F(\omega_0) \times \left\{ (M_\lambda)_{ge} h_{en}^\alpha (M_\mu)_{nm} (M_\nu)_{mg} \frac{(f|Q_\alpha^{\text{solvent}}|v)(v|u)(u|i)}{\varepsilon_n^0 - \varepsilon_e^0} + (M_\lambda)_{gn} h_{ne}^\alpha (M_\mu)_{em} (M_\nu)_{mg} \frac{(f|v)(v|Q_\alpha^{\text{solvent}}|u)(u|i)}{\varepsilon_e^0 - \varepsilon_n^0} \right\},$$

$$\begin{aligned}
 B_2 &= \sum_{mu,v} \sum_a \sum_{e \neq m} F(\omega_0) \\
 &\times \left\{ (M_{\lambda})_{gn} (M_{\mu})_{ne} h_{em}^a (M_{\nu})_{mg} \frac{(f|v)(v|Q_a^{\text{solute}}|u)(u|i)}{\epsilon_m^0 - \epsilon_e^0} \right. \\
 &\left. + (M_{\lambda})_{gn} (M_{\mu})_{nm} h_{me}^a (M_{\nu})_{eg} \frac{(f|v)(v|u)(u|Q_a^{\text{solute}}|i)}{\epsilon_e^0 - \epsilon_m^0} \right\}, \\
 B'_2 &= \sum_{mu,v} \sum_{\alpha} \sum_{e \neq m} F(\omega_0) \\
 &\times \left\{ (M_{\lambda})_{gn} (M_{\mu})_{ne} h_{em}^{\alpha} (M_{\nu})_{mg} \frac{(f|v)(v|Q_{\alpha}^{\text{solvent}}|u)(u|i)}{\epsilon_m^0 - \epsilon_e^0} \right. \\
 &\left. + (M_{\lambda})_{gn} (M_{\mu})_{nm} h_{me}^{\alpha} (M_{\nu})_{eg} \frac{(f|v)(v|u)(u|Q_{\alpha}^{\text{solvent}}|i)}{\epsilon_e^0 - \epsilon_m^0} \right\},
 \end{aligned} \tag{6}$$

where

$$F(\omega_0) = \{(\epsilon_{mu} - \epsilon_{gi} - \hbar\omega_0)(\epsilon_{nv} - \epsilon_{gi} - 2\hbar\omega_0 - i\Gamma_{nv,gi})\}^{-1},$$

$$(M_{\lambda})_{nm} = [n^0 | R_{\lambda} | m^0].$$

The A-term (the zeroth-order term) gives the HR transition under the Condon approximation. The B-terms (B_1 , B'_1 , B_2 , and B'_2) contain first order Herzberg–Teller coupling in the intermediate states and they correspond to Albrecht's B-term in linear resonance Raman scattering.²⁴ Subscripts 1 and 2 denote the vibronic coupling in the electronic state n and m , respectively, and the prime symbol (') denotes the vibronic transition induced by the solvent normal coordinates. The B_1 - and B'_1 -terms represent the HR transitions where optically "allowed" two-photon absorption and optically "allowed" one-photon emission are coupled through vibronic interaction. The B_2 - and B'_2 -terms represent the transitions where optically "forbidden" but vibronically "allowed" two-photon absorption is coupled to optically "allowed" one-photon emission. A Herzberg–Teller expansion of the ground state $|g\rangle$ gives rise to C-terms (C and C') analogous to Albrecht's C-term.²⁴ The explicit expressions for these terms are not given here because they become important only when the low-lying intermediate state exists and this is not the case for our present experiments. The second order terms (corresponding to Chung and Ziegler's¹⁰ C-term) are not considered either.

For noncentrosymmetric molecules, in which an excited electronic state can be both one and two photon allowed, the A-term plays a major role in RHR. *All-trans-retinal* is an example of this type of molecules. It is experimentally confirmed by the measurement of excitation profiles that RHR activity of *all-trans-retinal* is resonantly enhanced through the A-term.¹⁴

On the other hand, the contribution from the A-term vanishes for centrosymmetric molecules with inversion symmetry such as *all-trans-β-carotene* and *all-trans-lycopene* because no resonant electronic state can be simultaneously two-photon and one-photon allowed by symmetry. Instead, the B-terms become dominant in the RHR process, where two-photon and one-photon allowed states are coupled

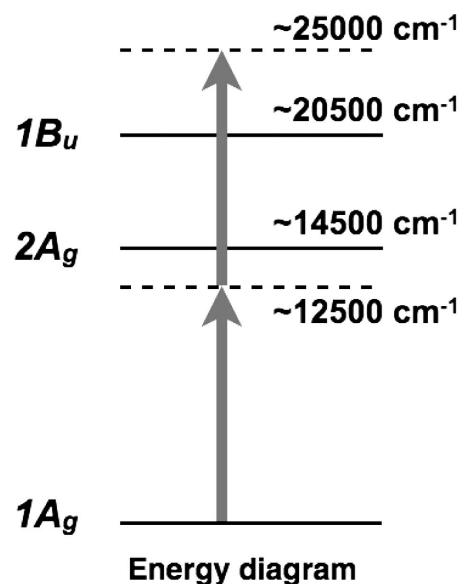


FIG. 6. A schematic energy diagram of *all-trans-lycopene*. Length of a vertical arrow corresponds to photon energy of excitation light.

through vibronic coupling. As already pointed out by Chung and Ziegler,¹⁰ RHR scattering due to the B-terms is generally much weaker (typically two orders of magnitude) than that from the A-term, unless the strength of vibronic coupling is unusually strong. We here note that the resonance HR intensities of both *β-carotene* and *lycopene* are comparable with that of *retinal*. If we assume that the resonance conditions are similar for those three polyenes, the high HR intensities of *all-trans-β-carotene* and *all-trans-lycopene* imply that the vibronic coupling is exceptionally strong for these molecules. Such strong vibronic coupling is probably because of the small energy gap between the excited electronic states, so that the denominator $\epsilon_n^0 - \epsilon_e^0$ is small. Figure 6 shows the energy diagram of *all-trans-lycopene*.^{25–27} The energy gaps corresponding to the one- and two-photon excitations from the ground state are also indicated. Detailed electronic structures above the $1B_u$ (S_2) state have not been elucidated, although some theoretical calculation for shorter polyenes pre-

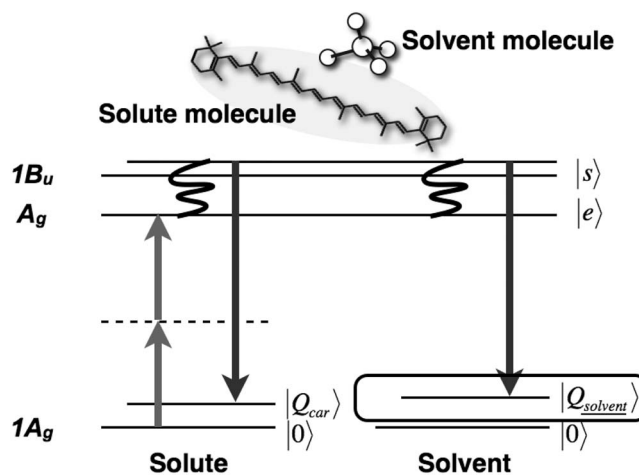


FIG. 7. A schematic diagram of RHR process via intra- and intermolecular vibronic coupling.

dicts existence of $3A_g$ state near the $1B_u$ (S_2) state,²⁸ being a possible candidate for the coupled state. It is also known that the position of the $1B_u$ state is highly sensitive to the solvent environment.²⁹ Under these circumstances, the vibrations of solvent molecules located very close to β -carotene and lycopene may well couple the closely lying A_g and $1B_u$ (S_2) states. Then, the B' -term gives rise to solvent HR bands through the “intermolecular” vibronic coupling, $h^\alpha Q_\alpha^{\text{solvent}}$, which could be extraordinarily strong for β -carotene and lycopene. Schematic diagrams of the B_1 - and B'_1 -term active RHR processes are shown in Fig. 7. Note that the B -terms may also play roles for noncentrosymmetric molecules and become a source for the solvent mode enhancement in resonance HR scattering. However, the observation of the en-

hancement effect becomes possible only when the magnitudes of the B' -terms are unusually large, as large as that of the A -term, on account of the very small energy gap as in the cases of *all-trans*- β -carotene and *all-trans*-lycopene. This is not likely to be the case with *all-trans*-retinal.

As illustrated in Fig. 6, the energy gap between the ground state and the $2A_g$ state is in fact close to the energy of the incident photon. Let us consider the possibility of double resonance under the present experimental setup. Here, double resonance means that $\hbar\omega_0$ and $2\hbar\omega_0$ approach the energy gaps between the ground state and the excited electronic states $2A_g$ (S_1) and $1B_u$ (S_2) simultaneously. Equation (2) under such a condition may be expressed in the following form by the use of adiabatic approximation [Eq. (3)]:

$$(\beta_{\lambda\mu\nu})_{if} = \sum_{u,v} \frac{(f|[g|R_\lambda|n]|v)(v|[n|R_\mu|m]|u)(u|[m|R_\nu|g]|i)}{(\epsilon_{mu} - \epsilon_{gi} - \hbar\omega_0 - i\Gamma_{mu,gi})(\epsilon_{nv} - \epsilon_{gi} - 2\hbar\omega_0 - i\Gamma_{nv,gi})}, \quad (7)$$

where g , m , and n are $1A_g$ (S_0), $2A_g$ (S_1), and $1B_u$ (S_2) states, respectively. The Herzberg–Teller expansion of the adiabatic electronic kets m and n will lead to a series of terms similar to the ones discussed before. If we let $(M)_{mg} = [m^0|R|g^0] = 0$, then the only remaining terms will be

$$(\beta_{\lambda\mu\nu})_{if} = B_2 + B'_2,$$

$$B_2 = \sum_{u,v} \sum_a \sum_{e \neq m} F(\omega_0) \times (M_\lambda)_{gn} (M_\mu)_{nm} h_{me}^\alpha (M_\nu)_{eg} \frac{(f|v)(v|u)(u|Q_\alpha^{\text{solute}}|i)}{\epsilon_e^0 - \epsilon_m^0},$$

$$B'_2 = \sum_{u,v} \sum_\alpha \sum_{e \neq m} F(\omega_0) \times (M_\lambda)_{gn} (M_\mu)_{nm} h_{me}^\alpha (M_\nu)_{eg} \frac{(f|v)(v|u)(u|Q_\alpha^{\text{solvent}}|i)}{\epsilon_e^0 - \epsilon_m^0},$$

where

$$F(\omega_0) = \{(\epsilon_{mu} - \epsilon_{gi} - \hbar\omega_0 - i\Gamma_{mu,gi}) \times (\epsilon_{nv} - \epsilon_{gi} - 2\hbar\omega_0 - i\Gamma_{nv,gi})\}^{-1}.$$

The presence of the nonvanishing terms in $(\beta_{\lambda\mu\nu})_{if}$ indicates the possibility of double resonance enhancement through the B_2 - and B'_2 -terms. Though the magnitude of the contribution from this double resonance to the observed signal is not clear at present, we note the possibility that it may facilitate further resonance enhancement of HR intensities by introducing two wavelength tunable excitation lasers. It may also lead to the finding of other HR probe molecules that make the molecular near-field effect feasible.

The possibility of intermolecular vibronic coupling has already been discussed for molecular complexes in solution, which have well-defined structures with specific electronic

interactions.³⁰ It is worthwhile to note that the intermolecular vibronic coupling that we discuss here does not require the formation of molecular complex between the solute and solvent molecules. We observe the HR intensity enhancements equally for the four nonpolar solvents. It is unlikely that all of them form specific molecular complexes (or clusters) with *all-trans*- β -carotene and *all-trans*-lycopene. Instead, it is more appropriate to attribute the feasibility of the intermolecular vibronic coupling to the solute characteristics as discussed in the following. The process of RHR scattering involves an electronic excitation that produces a strong oscillating near field at the angular frequency $2\omega_0$ in the vicinity of the molecule. This near field is modulated with the vibration of the proximate solvent molecule(s) and become radiative to emit HR radiation at $2\omega_0 \pm \omega$. This process is expressed by the B' -terms with the concept of intermolecular vibronic coupling. The near-field produced by the electronic excitation acts as a sensitive probe for the surrounding environment of the solute molecule. We thus propose a new term the “molecular near field” to express this local probing field, which is generated by the photoexcited molecule as an antenna. The “near field” produced by the photoexcited molecule bears analogy with the locally confined electromagnetic field generated by a photoexcited surface plasmon in a metal particle. This analogy may be useful for understanding how the locally confined electromagnetic field couples the molecular vibration to give rise to surface-enhanced Raman scattering.

D. The selection rules for the enhanced bands

It has so far been shown that only the infrared active solvent bands are subject to the near-field enhancement. In addition, a further selection rule has been observed for the HR spectrum of *all-trans*- β -carotene in benzene. Among the many infrared active modes of benzene, no enhancement ef-

fect is found for the in-plane vibrational modes such as ν_{20} , ν_{19} , and ν_{18} at 3090, 1482, and 1037 cm^{-1} , respectively, while it is clearly observed for the out-of-plane modes, i.e., ν_{10} at 850 cm^{-1} and ν_{11} at 676 cm^{-1} [Figs. 3(g) and 3(i)]. This observation indicates a strong relationship between the HR enhancement efficiency and the orientation of the solvent molecules relative to the solute. According to the theoretical considerations given above, the selection rule for the HR enhancement is basically determined by the intermolecular vibronic coupling constant, h^α . The magnitude of h^α can depend on several factors such as solvent vibrational modes, symmetry and amplitude, and the relative configuration of the solute and solvent molecules. Further investigation is needed to fully account for the selection rules of the molecular near-field enhancement effect.

E. Enhancement factor

Finally, we estimate the magnitude of the molecular near-field enhancement effect. In our scheme, a solvent molecule can gain its HR intensity by virtue of electronic resonance of *all-trans*- β -carotene. Electronic resonance enhancement factor depends mostly on the denominator of Eq. (1), which can increase by three to four orders of magnitude on going from an off-resonance condition to a rigorous resonance condition. Intensity of HR scattering is proportional to the square of the hyperpolarizability tensor element; thus the enhancement factor of HR intensities by the molecular near-field effect can be estimated to be six to eight orders of magnitude. It is difficult to experimentally determine the enhancement factor because most of the solvents did not show any HR band under our experimental conditions. However, a rough estimate can be carried out using a weak HR signal from neat carbon disulfide [Fig. 3(k)]. The intensity of the CS_2 band observed in *all-trans*- β -carotene solution is roughly 10^2 times stronger than that observed in the neat solvent. The number of solvent molecules responsible for the observed signal may differ by four orders of magnitude between the neat solvent and solution samples because the solvent/solute molecular ratio in 1 m mol dm^{-3} solution is 10^4 . The overall enhancement factor is thus estimated to be as large as six orders of magnitude, if we assume that only a single solvent molecule is involved in the intermolecular vibronic coupling. This estimated enhancement factor is consistent with the magnitude calculated from the electronic resonance consideration.

IV. FUTURE PERSPECTIVES

A combination of the molecular near-field effect with HR spectroscopy may open up a new vibrational spectroscopy, “molecular near-field HR spectroscopy,” which selectively detects molecules existing in the vicinity of a HR probe in complex chemical or biological systems. Furthermore, it may be possible to utilize the molecular near-field effect in other spectroscopies since the scheme of the “intermolecular vibronic coupling” presented in this paper is not restricted only to the RHR process. In fact, intensity enhancement of solvent vibrations has been reported by Jas *et al.*³¹ in the excited-state resonance Raman spectra of anthra-

cene in cyclohexane and other solvents. They observed increased intensities of the *C–H* stretch modes of solvents after excitation of the solute and suggested a possible contribution of vibronic interaction between the solute and solvent molecules. Their results may be related to the molecular near-field effect, although some uncertainties remain with regard to the differentiation of the enhanced signals from the bulk solvent signals. When combined with the molecular near-field effect, HR scattering is superior to other spectroscopies. The near-field HR signals can be detected background-free because of the extreme weak intrinsic signals from the bulk solvent molecules. On the other hand, the bulk signals overlap and mask the near-field signals in resonance Raman or other spectroscopies, making the detection of the near-field signals much more difficult. If those background signals are removed appropriately by any means, we may be able to observe signals from the molecular near-field effect also in many other spectroscopies. Further investigation and deeper understanding of the molecular near-field effect will lead us to a new frontier of space-resolved molecular spectroscopy in the single nanometer scale.

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