# Structural information from two-dimensional fifth-order Raman spectroscopy

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(Received 12 February 1999; accepted 9 April 1999)

Two-dimensional (2D) fifth-order Raman spectroscopy is a coherent spectroscopy that can be used as a structural tool, in a manner analogous to 2D nuclear magnetic resonance (NMR) but with much faster time scale. By including the effect of dipole-induced dipole interactions in the molecular polarizability, it is shown that 2D Raman experiments can be used to extract distances between coupled dipoles, and thus elucidate structural information on a molecular level. The amplitude of cross peaks in the 2D Raman spectrum arising from dipole-induced dipole interactions is related to the distance between the two dipoles (r) and the relative orientation of the dipoles. In an isotropic sample with randomly distributed dipole orientations, such as a liquid, the cross peak amplitude scales as  $r^{-6}$ . In an anisotropic sample such as a solid, where the orientational averaging effects do not nullify the leading order contribution, the amplitude scales as  $r^{-3}$ . These scaling relationships have analogy to the dipole coupling relationships that are observed in solid state and liquid 2D NMR measurements. © 1999 American Institute of Physics. [S0021-9606(99)02425-3]

## I. INTRODUCTION

The expanding interest in the determination of molecular and collective dynamics in condensed phases requires new experimental methods that are sensitive both to structure and its time evolution. When studying complex molecular systems, it is often difficult to extract detailed microscopic information on the sample for several possible reasons; (1) limitations in relating the experimental observable to precise molecular structures, (2) ambiguous observables due to complex ensemble averaging, or (3) insufficient time resolution. One of the most powerful methods for dealing with the first two limitations and extracting detailed structural information is two-dimensional (2D) NMR.<sup>1,2</sup> The power of this coherent correlation spectroscopy is its ability to quantify the strength of interaction between spectral features of well-defined molecular origin. The magnetic shift of a resonance can be used to assign it to a particular functional group of a molecule, and dipolar couplings can be observed between different resonances in a 2D spectrum. The strength of this interaction can be used to determine the distance between dipoles. This becomes the first step in the structure determination of complex molecules in solution.

As a dynamic tool, multidimensional NMR is limited by its time resolution. The inherent time scale associated with 2D NMR measurements is no shorter than milliseconds. On the other hand, most "soft molecular materials," including liquids and solutions,<sup>3,4</sup> glasses,<sup>5</sup> polymers,<sup>6</sup> liquid crystals, and numerous biologically relevant molecules and macromolecules<sup>7–9</sup> show evolution of molecular and collective structure on shorter time scales. With all of these systems it is of interest to be able to gain detailed insight into their structural dynamics on relevant time scales, from fs to ms. The possibility of using the concepts developed in NMR but with significantly increased time resolution requires optical methods. Coherent two-dimensional vibrational<sup>10–15</sup> and electronic spectroscopies<sup>16–20</sup> are alternative approaches that are optical and infrared analogues of the NMR techniques.

One of these methods, 2D Raman spectroscopy, based on a fifth-order nonlinearity, is the subject of much recent theoretical and experimental research.<sup>10-12,21-54</sup> It has become clear that 2D Raman spectroscopy has the potential for structure determination on a picosecond time scale. Although this technique was originally proposed to describe inhomogeneous broadening of Raman active molecular vibrations,<sup>10</sup> it has recently been shown that its 2D nature leads to higher levels of information. Demonstration of the capability of 2D Raman spectroscopy to distinguish the nonlinear dependence of the polarizability and anharmonicity of the vibrational potential<sup>45,46</sup> was a fundamental step for the following theoretical developments,<sup>12,40–42,46–51</sup> and led to studies based on the normal mode analysis, molecular dynamics, and the quantum Fokker-Planck equation.<sup>52-54</sup> The introduction of phase-sensitive heterodyne detection methods34,11 allowed coherent 2D Fourier transform Raman spectroscopy49 to be implemented in a manner analogous to 2D NMR, and demonstrated that vibrational interactions in liquids can be observed. Just as 2D NMR observes the interaction between spins as cross peaks in a 2D spectrum, cross peaks in a 2D Raman spectra arise from the interactions between Raman active vibrational modes. The ability to observe these cross peaks suggests the possibility of using their interaction to extract structural information on a molecular level. The combined advantages of quantifying the strength of vibrational couplings, observing inhomogeneous broadening, and measuring with high time resolution suggest an unusually powerful tool.

In this paper, we address the determination of inter- and intramolecular distances from a 2D Raman spectrum through an understanding of the distance-dependence of vibrational interaction mechanisms. In the previous literature the interactions between vibrations observed in fifth-order Raman spectroscopy have been described in terms of anharmonicity or nonlinear polarizability. The anharmonic mechanism allows mechanical coupling of vibrational modes through cubic expansion terms in the potential. Nonlinear polarizability describes a nonlinear dependence of the molecular polarizability on the nuclear coordinates, due to expansion beyond the traditional linear Placzek terms. In either case, a nonlinearity exists that allows for the interaction of vibrational modes to be observed, and thus is the basis for a broad range of physical processes, including overtone transitions, and interaction-induced effects, and dipole-induced dipole couplings.

In order to probe further into the nature of the nonlinear polarizability in a manner that allows the introduction of a spatial variable in the vibrational interactions, we reformulate the description of the nuclear-coordinate dependence of the molecular polarizability to include dipole-induced dipole effects.<sup>55–61</sup> In the following section, the nonlinear polarizability is expanded in the individual coordinates, while the interactions between coordinates arise from dipole-induced dipole couplings. For the purposes of this work, anharmonic coupling between the coordinates is neglected. In Sec. III, it is shown that cross peaks in the absolute value 2D Raman spectrum arise from dipole-induced-dipole coupling, while diagonal and overtone peaks arise from nonlinear expansion coefficients of the polarizability in the vibrational coordinate. The  $1/r^3$  distance dependence of the dipolar coupling forms the basis for extracting distances between vibrational coordinates (r), forming the basis for extracting structural information. Model 2D Raman spectra with varying distance between interacting coordinates are calculated in Sec. IV. The complex nature of ensemble averaging leads to different scaling relationships for systems with aligned dipoles  $(1/r^3)$ and for isotropically distributed dipoles  $(1/r^6)$ , as shown in Secs. III and V, respectively. These relationships form the basis for extracting structural information from molecules.

### **II. EXTENDED PLACZEK MODEL**

We extend the classical Placzek model,<sup>62</sup> which allows a classical description of the Raman process by postulating a linear dependence of the molecular polarizability on the nuclear coordinate, to include the dipole-induced dipole effect. We have found that the extended Placzek model introduced below can reproduce the leading order results of the quantum Brownian oscillator model, which has been frequently used<sup>43</sup> in the literature. The use of the Feynman diagram for the quantum Brownian oscillator model is a practical necessity at higher orders in order to obtain the correct quantum result through economic calculations. However, we use the extended Placzek model with the Green's function



FIG. 1. The pulse configuration of the 2D Raman spectroscopy. The first femtosecond pulse pair  $(E_1, E'_1)$  excites Raman modes, the second pulse pair  $(E_2, E'_2)$  after the delay time  $T_1$  causes further Raman interactions, and the final probe pulse  $E_f$  after the delay  $T_2$  induces the signal  $E_s$ .

method below, because it is instructive (offering an intuitive classical picture) and it gives the correct result at the lowest order.

The pulse configuration of the 2D Raman experiment is given in Fig. 1, and the electric field is presented below for later calculations,

$$E(t,\mathbf{r}) = E_1(t,\mathbf{r}) + E'_1(t,\mathbf{r}) + E_2(t,\mathbf{r}) + E'_2(t,\mathbf{r}) + E_f(t,\mathbf{r}),$$
(1)

where, for i = 1, 2,

$$E_i(t,\mathbf{r}) = \overline{E}_i(t) \left( e^{-i\omega_i t + i\mathbf{k}_i \cdot \mathbf{r}} + \text{c.c.} \right)/2,$$
(2)

$$E_i'(t,\mathbf{r}) = \overline{E}_i(t) \left( e^{-i\omega_i t + i\mathbf{k}_i' \cdot \mathbf{r}} + \text{c.c.} \right)/2,$$
(3)

$$E_f(t, \mathbf{r}) = \overline{E}_f(t) \left[ e^{-i\omega_f t + i\mathbf{k}_f \cdot \mathbf{r}} + \text{c.c.} \right] / 2.$$
(4)

Here, c.c. stands for the complex conjugate while the amplitudes are given as

$$\bar{E}_1(t) = E_0 \delta_p(t - t_m + T_1 + T_2), \tag{5}$$

$$\bar{E}_{2}(t) = E_{0}\delta_{p}(t - t_{m} + T_{2}), \qquad (6)$$

$$\overline{E}_f(t) = E_0 \delta_p(t - t_m), \tag{7}$$

where  $\delta_p(t)$  is normalized Gaussian function with the width longer than the optical cycle ( $\sim 1/\omega_i$ ) but much shorter than the nuclear dynamics [ $\sim 1/\Omega_s$ , see Eq. (20) below for the precise definition of the characteristic frequency  $\Omega_s$ ]. The time of measurement of the signal is set to  $t_m$ . In the following we assume that the amplitude  $E_0$  is real for simplicity.

For the purposes of describing a possible experiment, we show in Fig. 2 a macromolecule with two nuclear coordi-



FIG. 2. A complex molecule in dilute solution. Each molecule has two functional groups, A and B, both of which has a distinctive Raman active mode. The arrows denote the induced dipoles, which are all in the *z* direction, the direction of the polarization of the applied fields. The dipole pair (A,B) is away from the dipole pairs in the other molecules. For some reason, the structure changes from (i) to (ii), with the change of the distance between *A* and *B*.

nates A and B with corresponding Raman active vibrational transitions. These dipoles can interact with one another through dipole-induced-dipole (DID) effects which decay with the inverse of the A–B distance cubed. As the molecule changes its structure from (i) to (ii), for example during a temperature change, observation of weakened DID couplings would be a direct measure of structural changes to the molecule. For a dilute case, where only A–B interactions need to be considered, the ability to quantify the magnitude of DID interactions would potentially allow direct distances to be extracted.

The DID coupling effect is closely related to combination peaks in traditional one-dimensional (1D) spectroscopy; the change in the intensity of combination peaks may reflect structural variations. However, in condensed phase 1D spectroscopy, the interactions between vibrations are difficult to distinguish from more intense fundamental peaks and congested spectra. Two-dimensional data have the advantages of spreading congested information out over two dimensions, and also directly visualizing interactions as cross peaks. An additional advantage to 2D Raman spectroscopy is that even the diagonal peaks in the 2D spectrum arise from weak nonlinearities, so that observing weak DID interactions should not be obscured by strong fundamental peaks. In the following, we describe this ideal property of 2D Raman spectroscopy.

As an example of physical interaction which is sensitive to the structural change of molecules, we employ the conventional dipole-induced dipole interaction as follows.<sup>55–61</sup> The dipole moment associated with the nuclear coordinates *A* and *B* at the time *t*,  $\mathbf{p}_s(t)$  (*s*=*A*,*B*), can be expanded by the electric field at the same time *t*,  $\mathbf{E}(t, \mathbf{r}_s)$ ,

$$\mathbf{p}_{s}(t) = \boldsymbol{\mu}_{s} + \boldsymbol{\alpha}_{s}(t) : \mathbf{E}(t, \mathbf{r}_{s}) + \cdots .$$
(8)

 $\mu_s$  is the permanent dipole moment, and  $\alpha_s(t)$  is the polarizability tensor.<sup>63</sup> For the purposes of this work we do not consider couplings due to permanent dipoles ( $\mu_s = 0$ ).

 $\mathbf{E}(t, \mathbf{r}_A)$  in Eq. (8) is the local electric field at the point of the dipole A and is decomposed as

$$\mathbf{E}(t,\mathbf{r}_A) = \mathbf{E}_{\rm in}(t,\mathbf{r}_A) + \mathbf{E}_{\rm ex}(t,\mathbf{r}_A), \qquad (9)$$

where  $\mathbf{E}_{in}(t,\mathbf{r}_A)$  and  $\mathbf{E}_{ex}(t,\mathbf{r}_A)$  are the local field produced by the dipole *B* at the position of the dipole *A* and the externally applied laser field, respectively. The density of the molecular system is assumed to be low enough to avoid the other molecules contribute to  $\mathbf{E}_{in}(t,\mathbf{r}_A)$ . (In this description we neglect higher-order dipole interactions, self-induced dipoles, and hyperpolarizabilities.) Since the distance between A and B are smaller than the optical wave length, the external field  $\mathbf{E}_{ex}(t,\mathbf{r}_A)$  can be replaced by  $\mathbf{E}_{ex}(t,\mathbf{r}_G)$ , where  $\mathbf{r}_G$  denotes the center of the molecule.

When *A* and *B* are relatively close,  $\mathbf{E}_{in}(t, \mathbf{r}_A)$  can be expressed as (see Discussion for other possibilities)

$$\mathbf{E}_{\rm in}(t, \mathbf{r}_A) = \mathbf{T}(\mathbf{r}_{AB}): \mathbf{p}_B(t), \qquad (10)$$

where the second-rank tensor is given by

$$\mathbf{T}(\mathbf{r})_{\alpha\beta} = \frac{1}{4\pi\epsilon_0} \cdot \frac{3r_{\alpha}r_{\beta} - \delta_{\alpha\beta}}{r^3},\tag{11}$$

where  $\epsilon_0$ , *r*, and  $\hat{r}_{\alpha}$  are the dielectric constant of the vacuum, the magnitude of the vector **r**, and the  $\alpha$  component of the unit vector  $\hat{\mathbf{r}} \equiv \mathbf{r}/r$ , respectively. In the above,  $\mathbf{r}_{AB} = \mathbf{r}_A$  $-\mathbf{r}_B$ , which is regarded as a constant compared with the nuclear dynamics (see below).

The energy of the two induced dipoles in the external field  $\mathrm{is}^{64}$ 

$$V_I(t) = -\frac{1}{2} \mathbf{p}_A(t) \cdot \mathbf{E}_{\text{ex}}(t, \mathbf{r}_A) - \frac{1}{2} \mathbf{p}_B(t) \cdot \mathbf{E}_{\text{ex}}(t, \mathbf{r}_B).$$
(12)

Here, again  $\mathbf{E}_{ex}(t,\mathbf{r}_s)$  can be replaced by  $\mathbf{E}_{ex}(t,\mathbf{r}_G)$ .

To simplify orientational averaging, we assume that  $\alpha_s(t)$  is an isotropic tensor,

$$\boldsymbol{\alpha}_{s}(t) \equiv \boldsymbol{\alpha}_{s}(t) \mathbf{I},\tag{13}$$

where  $\alpha_s(t)$  and **I** are the scalar isotropic polarizability and the unit tensor. Furthermore, we assume that all the polarizations of the fields  $(E_1, E'_1, E_1, E'_2, E_f)$  in Fig. 1 are parallel along the laboratory z axis. The time scale of structural relaxation in most systems will be longer than the delays  $T_1$ and  $T_2$ . This ensures that the induced dipoles are parallel to one another over the course of the experiment.

With these assumptions and from Eqs. (8)–(10), the z component of  $\mathbf{p}_s(t)$  can be expressed as

$$p_A(t) = \alpha_A(t)(E(t) + T_{AB}[\alpha_B(t)\{E(t) + \cdots\}]), \quad (14)$$

$$\equiv \bar{\alpha}_A(t)E(t),\tag{15}$$

where the effective polarizability is given by the DID expansion,

$$\bar{\alpha}_A(t) = \alpha_A + \alpha_A T_{AB} \alpha_B + \alpha_A T_{AB} \alpha_B T_{BA} \alpha_A + \cdots$$
(16)

Here,  $T_{AB}$  is the *zz* element of  $\mathbf{T}_{AB}$  and E(t) is the *z* component of the external field  $\mathbf{E}_{ex}(t, \mathbf{r}_G)$ . Note here that, at any order of the expansion of  $p_A(t)$ , terms show the linear dependence on the external field E(t). Thus, the interaction  $V_I$  becomes quadratic in the external field E(t), which is responsible for the Raman transition,

$$V_I(t) = -\frac{1}{2}E(t)\overline{\alpha}(t)E(t), \qquad (17)$$

where the total effective polarizability is given by

$$\overline{\alpha}(t) = \overline{\alpha}_A(t) + \overline{\alpha}_B(t).$$
(18)

The first few terms can be explicitly written as

$$V_{I}(t) = -\frac{1}{2} [\alpha_{A}(t) + \alpha_{B}(t)]E(t)^{2}$$
  
$$-\alpha_{A}(t)\alpha_{B}(t)T_{AB}E(t)^{2}$$
  
$$-\alpha_{A}(t)\alpha_{B}(t)[\alpha_{A}(t) + \alpha_{B}(t)]T_{AB}^{2}E(t)^{2}$$
  
$$-\cdots.$$
 (19)

For the time being, we limit ourselves to keep up to the first-order terms in  $T_{AB}$ . The second-order contribution is examined in Sec. V.

In our model, the nuclear vibrational coordinate  $Q_s$  associated with  $\alpha_s$  is governed by the following equation of motion,

$$M\frac{d^2Q_s(t)}{dt^2} + M\gamma_s\frac{dQ_s(t)}{dt} + M\Omega_s^2Q_s(t) = F_s(t), \qquad (20)$$

where the force is given by  $F_s(t) = -dV_I(t)/dQ_s(t)$ . If we neglect  $T_{AB}$  in this equation and assume the linear polarizability, it reduces to the equation for the Placzek model. In this paper, we shall not introduce any anharmonicity for simplicity. By using the Green function method, the specific solution of Eq. (20) is given by

$$Q_s(t) = \int_{-\infty}^{\infty} d\tau F_s(t-\tau) D_s(\tau).$$
(21)

Here, the Green function or the propagator  $D_s(\tau)$  is given by<sup>66</sup>

$$D_s(\tau) = \theta(\tau) \frac{1}{M\zeta_s} e^{-\gamma_s t/2} \sin \zeta_s t, \qquad (22)$$

where  $\zeta_s = \sqrt{\Omega_s^2 - \gamma_s^2/4}$  and  $\theta(t)$  is the Heaviside step function.

The time dependence of the polarizability comes from the nuclear coordinate,

$$\alpha_s(t) = \alpha_s^{(0)} + \alpha_s^{(1)} Q_s(t) + \alpha_s^{(2)} Q_s(t)^{2/2} + \cdots$$
 (23)

In the present situation, we assume that there are no couplings between the two modes A and B at the level of the polarizability, i.e., the terms such as  $Q_A(t)Q_B(t)$  can not appear in the expansion of  $\alpha_s(t)$ . Thus, at this level, only DID mechanisms allow the interactions of the polarizability of the modes A and B. This is reasonable since the dipoles A, B are localized, compared with the distance A-B. In this case, the force is evaluated as

$$F_{s}(t) = \frac{1}{2} (\alpha_{s}^{(1)} + \alpha_{s}^{(2)}Q_{s} + \cdots) [1 + 2T_{ss'}(\alpha_{s'}^{(0)} + \alpha_{s'}^{(1)}Q_{s'} + \alpha_{s'}^{(2)}Q_{s'}^{2}/2 + \cdots)]E(t)^{2}, \qquad (24)$$

where (s,s') = (A,B) or (B,A). Decomposing  $Q_s$  as  $Q_s = Q_s^{(2)} + Q_s^{(4)} + \cdots$ , where  $Q_s^{(i)}$  is the *i*th order of  $Q_s$  in terms of the field *E*, we obtain the set of equations [we assume that the homogeneous solution  $Q_s^{(0)}$  is zero],

$$M \frac{d^2 Q_s^{(2)}(t)}{dt^2} + M \gamma_s \frac{d Q_s^{(2)}(t)}{dt} + M \Omega_s^2 Q_s^{(2)}$$
  

$$= \frac{1}{2} \alpha_s^{(1)} (1 + 2 \alpha_{s'}^{(0)} T_{ss'}) E(t)^2,$$
  

$$M \frac{d^2 Q_s^{(4)}(t)}{dt^2} + M \gamma_s \frac{d Q_s^{(4)}(t)}{dt} + M \Omega_s^2 Q_s^{(4)}$$
  

$$= \frac{1}{2} [\alpha_s^{(2)} (1 + 2 \alpha_{s'}^{(0)} T_{ss'}) Q_s^{(2)} + 2 \alpha_{s'}^{(1)} \alpha_{s'}^{(1)} T_{ss'} Q_{s'}^{(2)}] E(t)^2.$$
(25)

Now we can solve these equations by the formula (21). Keeping up to the first order in  $T_{AB}$ , we have

$$Q_s^{(2)}(t) = \frac{1}{2} \alpha_s^{(1)}(1 + 2 \alpha_{s'}^{(0)} T_{ss'}) \int d\tau E(t-\tau)^2 D_s(\tau), \quad (26)$$

$$Q_{s}^{(4)}(t) = \frac{1}{4} \alpha_{s}^{(1)} \alpha_{s}^{(2)} (1 + 4 \alpha_{s'}^{(0)} T_{ss'})$$

$$\times \int d\tau \int d\tau' E(t - \tau)^{2} E(t - \tau - \tau')^{2} D_{s}(\tau) D_{s}(\tau')$$

$$+ \frac{1}{2} \alpha_{s}^{(1)} [\alpha_{s'}^{(1)}]^{2} T_{ss'} \int d\tau \int d\tau' E(t - \tau)^{2}$$

$$\times E(t - \tau - \tau')^{2} D_{s}(\tau) D_{s'}(\tau'). \qquad (27)$$

### **III. CALCULATION OF THE SIGNALS**

The macroscopic polarization, which becomes the source of the signal, is given by

$$P(t,\mathbf{r}) = \sum_{M} [p(t)]_{M} / V_{0} \equiv \langle p(t) \rangle_{V_{0}}, \qquad (28)$$

where  $p(t) = p_A(t) + p_B(t)$ . Here, the summation is taken over all the molecules in the macroscopic volume  $V_0$ . Before calculating the fifth-order signal, we reproduce the wellknown third-order signal, because it presents the prototype of the calculations below. Neglecting  $T_{AB}$ , the third-order of  $p_s$ is given by

$$p_{s}^{(3)} = \alpha_{s}^{(1)} Q_{s}^{(2)} E(t)$$
  
=  $\frac{1}{2} [\alpha_{s}^{(1)}]^{2} \int d\tau E(t) E(t-\tau)^{2} D_{s}(\tau).$  (29)

The propagator  $D_s(\tau)$  contains the factor  $\theta(\tau)$  and it determines the time order of the fields E(t) and  $E(t-\tau)^2$  in the above expression;  $E(t)E(t-\tau)^2$  can be identified with  $E_f(t)E_1(t-\tau)^2$ . [There is no  $E_2(t)$  field in the third-order case.] Neglecting the terms proportional to  $e^{\pm 2i\omega_i t}$ , one obtains

$$E_i(t, \mathbf{r}_s) E_i(t, \mathbf{r}_{s'}) = |\overline{E}_i(t)|^2 [1 + \cos(\Delta \mathbf{k}_i \cdot \mathbf{r}_G)], \qquad (30)$$

where s and s' are A or B. Here, |X| denotes the absolute value of X and  $\Delta \mathbf{k}_i = \mathbf{k}_i - \mathbf{k}'_i$ . It is possible to perform the  $\tau$ integration in Eq. (29) owing to the  $\delta_p(t)$  function, which can be treated as the Dirac delta function for the nuclear dynamics. In this way we find the dipole of a single molecule,  $p^{(3)}(t) = p_A^{(3)}(t) + p_B^{(3)}(t)$ , to be given by

$$p^{(3)}(t) = \frac{1}{2} E_f(t, \mathbf{r}_G) \ E_0^2 \left[ 1 + \cos(\Delta \mathbf{k}_i \cdot \mathbf{r}_G) \right]$$
$$\times \sum_{s=A,B} \left[ \alpha_s^{(1)} \right]^2 D_s(T_1).$$
(31)

At the length scale of the optical wavelength, the molecules are regarded as being distributed continuously. If we assume that all the molecules contribute to the polarization in the same manner [i.e., all molecules have the same  $\alpha_s^{(1)}, \Omega_s, \gamma_s, M_s$ ], the *z* component of the macroscopic polarization  $P(t,\mathbf{r})$  is given, from Eq. (28), by the right-hand side of Eq. (31) multiplied by the number density of the molecules, with  $\mathbf{r}_G$  replaced by  $\mathbf{r}$ . Actually, molecules have different values of  $\alpha_s^{(1)}, \Omega_s, \gamma_s$ , and  $M_s$ , and these parameters in  $P(t,\mathbf{r})$  should be interpreted as averaged values. In this way, we reproduce the well-known expression for the thirdorder signal,

$$E^{(3)}(T_1) \sim E_0^3 \sum_{s} \left[ \alpha_s^{(1)} \right]^2 D_s(T_1).$$
(32)

In the frequency domain, the spectral density is expressed as

 $\operatorname{Im}[E^{(3)}(\omega)]$ 

$$\sim J(\omega) = \sum_{s=A,B} \frac{\left[\alpha_s^{(1)}\right]^2}{M_s} \cdot \frac{\omega \gamma_s}{(\Omega_s^2 - \omega^2)^2 + (\omega \gamma_s)^2}, \qquad (33)$$

where  $E_s^{(3)}(\omega_1) = \int_0^\infty dT_1 e^{i\omega_1 T_1} E_s^{(3)}(T_1, T_2)$ . Here, we have neglected the higher order corrections due to the nonlinearity  $(\alpha_s^{(2)})$ , the DID  $(T_{AB})$ , etc.

To study the fifth-order signal, we calculate the fifthorder of  $p_s(t)$  in terms of the external field E(t). It should be noted here that the fifth-order of  $p_s(t)$  vanishes if  $\alpha_s^{(2)}$  and  $T_{AB}$  are both zero in the harmonic oscillator approximation. The parameters,  $\alpha_s^{(2)}$  and  $T_{AB}$ , which are normally small, produce the leading order contribution and we can observe these weak effects without background. It suggests that, even if there are any fundamental peaks, they are not strong, satisfying the ideal condition mentioned in Sec. II. We shall calculate two contributions separately, one coming from nonlinear dependence on the nuclear coordinate of the polarizability and the other coming from the dipole-induced dipole interaction, which are proportional to  $\alpha_s^{(2)}$  and  $T_{AB}$ , respectively.

To calculate the nonlinear-polarizability contribution  $p_s^{\text{NL}}(t)$ , we neglect  $T_{AB}$  in the fifth-order of  $p_s(t)$  to have

$$p_{s}^{\text{NL}}(t) = (\alpha_{s}^{(1)} \tilde{Q}_{s}^{(4)}(t) + \frac{1}{2} \alpha_{s}^{(2)} [\tilde{Q}_{s}^{(2)}(t)]^{2}) E(t), \qquad (34)$$

where  $\tilde{Q}_s^{(i)}$  is given by Eqs. (26) and (27) with  $T_{AB} = 0$ . To calculate the dipole-induced dipole contribution  $p_s^{\text{DID}}(t)$ , we neglect  $\alpha_s^{(2)}$  to have

$$p_{s}^{\text{DID}}(t) = (\alpha_{s}^{(1)}\hat{Q}_{s}^{(4)}(t) + \alpha_{s}^{(1)}\alpha_{s'}^{(1)}T_{AB}\hat{Q}_{s}^{(2)}(t)\hat{Q}_{s'}^{(2)}(t))E(t),$$
(35)

where  $\hat{Q}_{s}^{(i)}$  is given by Eqs. (26) and (27) with  $\alpha_{s}^{(2)}=0$ .

For the fifth-order impulsive pulse sequence, we find the replacement rule,

$$G_{s}(t)G_{s'}(t) \Rightarrow E_{0}^{4}[1 + \cos(\Delta \mathbf{k}_{1} \cdot \mathbf{r}_{G})][1 + \cos(\Delta \mathbf{k}_{2} \cdot \mathbf{r}_{G})]$$

$$\times [D_{s}(T_{2})D_{s'}(T_{1} + T_{2})]$$

$$+ D_{s'}(T_{2})D_{s}(T_{1} + T_{2})], \qquad (36)$$

where

$$G_s(t) = \int d\tau E(t-\tau)^2 D_s(\tau).$$
(37)

This is understood by noting the relation

$$G_{s}(t)G_{s'}(t) = \int d\tau \int d\tau' \,\theta(\tau')E(t-\tau)^{2}E(t-\tau-\tau')^{2} \\ \times [D_{s}(\tau)D_{s'}(\tau+\tau') + D_{s'}(\tau)D_{s}(\tau+\tau')],$$
(38)

and by following a similar line to the one explained in the third-order case.

In a similar way, the expression,

$$G_{ss'}(t) \equiv \int d\tau E(t-\tau)^2 D_s(\tau)$$
$$\times \int d\tau' E(t-\tau-\tau')^2 D_{s'}(\tau'), \qquad (39)$$

can be replaced as

$$G_{ss'}(t) \Rightarrow E_0^4 [1 + \cos(\Delta \mathbf{k}_1 \cdot \mathbf{r}_G)] [1 + \cos(\Delta \mathbf{k}_2 \cdot \mathbf{r}_G)] \\ \times D_s(T_2) D_{s'}(T_1).$$
(40)

After these replacements, we obtain the following expression for the NL and DID contributions from a single molecule,

$$p^{\rm NL}(t) = \frac{1}{4} E_f(t, \mathbf{r}_G) E_0^4 [1 + \cos(\Delta \mathbf{k}_1 \cdot \mathbf{r}_G)] [1 + \cos(\Delta \mathbf{k}_2 \cdot \mathbf{r}_G)] \\ \times [\alpha_A^{(1)}]^2 \alpha_A^{(2)} D_A(T_2) [D_A(T_1) + D_A(T_1 + T_2)] \\ + (A \leftrightarrow B),$$
(41)

$$p^{\text{DID}}(t) = \frac{1}{2} E_f(t, \mathbf{r}_G) E_0^4 [1 + \cos(\Delta \mathbf{k}_1 \cdot \mathbf{r}_G)] [1 + \cos(\Delta \mathbf{k}_2 + \mathbf{r}_G)] [\alpha_A^{(1)} \alpha_B^{(1)}]^2 T_{AB} D_A(T_2) [D_B(T_1) + D_B(T_1 + T_2)] + (A \leftrightarrow B), \qquad (42)$$

where  $p^{X}(t) \equiv p_{A}^{X}(t) + p_{B}^{X}(t)$  (X=NL,DID). Here, the notation ( $A \leftrightarrow B$ ) implies the term obtained by interchanging A and B in the previous term. The nonlinear contribution  $p^{\text{NL}}(t)$  reproduces the expression previously obtained in Ref. 10. Both contributions can be more economically obtained by using Feynman rule.<sup>68</sup> Although these expressions have been derived by classical calculation in this paper for the heuristic purpose, we checked, by use of the Feynman rule, that they agree with the leading contributions of quantum calculation.

From Eq. (28), the z component of the macroscopic polarization  $P(t,\mathbf{r})$  is given by the sum of Eqs. (41) and (42) multiplied by the number density. Here,  $\mathbf{r}_G$  should be replaced by  $\mathbf{r}$ , if we assume that all the molecules contribute to the polarization in the same manner [i.e., all molecules have the same  $\mathbf{r}_{AB}$ ,  $\alpha_s^{(i)}$ ,  $\Omega_s$ ,  $\gamma_s$ ,  $M_s$ ]. Actually, as in the thirdorder case, the parameters  $\mathbf{r}_{AB}$ ,  $\alpha_s^{(i)}$ ,  $\Omega_s$ ,  $\gamma_s$ , and  $M_s$  in  $P(t,\mathbf{r})$  should be interpreted as averaged values. Note here that we can regard  $\mathbf{r}_{AB}$  as time-independent constant compared with the dynamics of  $Q_A$  and  $Q_B$ , when the structural dynamics are slower than the nuclear dynamics. Thus,  $P(t,\mathbf{r})$  is given by the sum of Eqs. (41) and (42), where  $T_{AB}$ defined by

$$T_{AB} = \frac{1}{4\pi\epsilon_0} \left\langle \frac{3\cos^2\theta_{AB} - 1}{r_{AB}^3} \right\rangle_{V_0},\tag{43}$$

where  $\theta_{AB}$  and  $r_{AB}$  are the angle which the vector  $\mathbf{r}_{AB}$  makes against the *z* direction (the direction of the polarization of the applied fields) and the magnitude of the vector  $\mathbf{r}_{AB}$ , respectively. If  $\theta_{AB}$  and  $r_{AB}$  are independently distributed,  $T_{AB}$  is given by

$$T_{AB} = \frac{c}{4\pi\epsilon_0} \cdot \frac{1}{\langle r_{AB} \rangle_{V_0}^3},\tag{44}$$

where  $c \equiv \langle 3 \cos^2 \theta_{AB} - 1 \rangle_{V_0}$ . For an isotropic distribution of  $\theta_{AB}$ , *c* becomes zero.<sup>69</sup> For aligned systems such as a liquid

rystal where  $\theta_{AB}$ 's of all the molecules take the same value  $\theta_0$ , *c* depends directly on the value  $\theta_0$ . It reaches the maximum when  $\theta_0=0$ . In this section and the next section we assume that *c* is nonzero and thus the results are applicable for the system with a certain anisotropy (in the sense that this average is nonzero). The isotropic case that considers randomly distributed dipole orientations is treated in Sec. V.

Aside from the above interpretations of the DID factor  $T_{AB}$ , the signal field amplitude is uniquely given by

$$E^{(5)}(T_1, T_2) = E^{\rm NL} + E^{\rm DID}, \tag{45}$$

where

$$E^{\rm NL} \sim \frac{1}{4} E_0^5 [\alpha_A^{(1)}]^2 \alpha_A^{(2)} D_A(T_2) [D_A(T_1) + D_A(T_1 + T_2)] + (A \leftrightarrow B),$$
(46)

$$E^{\text{DID}} \sim \frac{1}{2} E_0^5 [\alpha_A^{(1)} \alpha_B^{(1)}]^2 T_{AB} D_A(T_2) [D_B(T_1) + D_B(T_1 + T_2)] + (A \leftrightarrow B).$$
(47)

The 2D Fourier transformation of the observable is defined as

$$S(\omega_1, \omega_2) \sim \int_0^\infty dT_1 \int_0^\infty dT_2 e^{i\omega_1 T_1} e^{i\omega_2 T_2} E^{(5)}(T_1, T_2).$$
(48)

The complete analytical expression of the 2D Raman signal amplitude,  $S(\omega_1, \omega_2)$ , is given in Eq. (A9) in Appendix. It is worth while noting that the expression (A9) is given by a linear combination of the function  $F_n^{(ss')}$ , which takes the following form in the underdamped limit ( $\gamma_s \rightarrow 0$ ),

$$F_{n}^{ss'} \rightarrow -\frac{\omega_{1}\omega_{2} + \Omega_{1n}^{(ss')}\Omega_{2n}^{(ss')}}{[\omega_{1}^{2} - (\Omega_{1n}^{(ss')})^{2}][\omega_{2}^{2} - (\Omega_{2n}^{(ss')})^{2}]},$$
(49)

where

$$\begin{pmatrix} \Omega_{11}^{(ss')} & \Omega_{21}^{(ss')} \\ \Omega_{12}^{(ss')} & \Omega_{22}^{(ss')} \\ \Omega_{13}^{(ss')} & \Omega_{23}^{(ss')} \\ \Omega_{14}^{(ss')} & \Omega_{24}^{(ss')} \end{pmatrix} \rightarrow \begin{pmatrix} \Omega_{s'} & \Omega_{s} \\ -\Omega_{s'} & \Omega_{s} \\ \Omega_{s'} & \Omega_{s} + \Omega_{s'} \\ -\Omega_{s'} & \Omega_{s} - \Omega_{s'} \end{pmatrix}.$$
(50)

From the complete analytical expression, we see that the nonlinear contribution  $E^{\text{NL}}$  gives rise to the following peaks. We note here that the essential points of the following statements can be easily understood from the limit expression (49):

(1) Eight diagonal peaks at  $(\omega_1, \omega_2) = (\pm \Omega_A, \pm \Omega_A)$  and  $(\omega_1, \omega_2) = (\pm \Omega_B, \pm \Omega_B)$ . The approximate analytical expression of the signal around the first four peaks (of the A mode) is given by

$$\left|S(\omega_{1},\omega_{2})\right| = \frac{(\alpha_{A}^{(1)})^{2}\alpha_{A}^{(2)}}{8M_{A}^{2}} \left|\frac{F_{1}^{(AA)} - F_{2}^{(AA)}}{\zeta_{A}^{2}}\right|,$$
(51)

where  $F_n^{(ss')}$  is given in Eqs. (A7) and (A4). These are obtained by picking up the terms with resonant denominator [in  $F_n^{(ss')}$ ] at the four peak positions (in the zero damping limit). In the first and third quadrants, the numerator of  $F_2^{(AA)}$  in Eq. (A7) *almost* cancels out to take the value,  $\Gamma^{(AA)}\Gamma_2^{(AA)}$  [in the limit expression (49) it becomes zero], while that of  $F_1^{(AA)}$  is enhanced, and in the second and fourth quadrants vice versa. This fact implies that the four peaks have the same intensity. In addition, from the above approximate expression, we see that the width along both the  $\omega_1$  and  $\omega_2$  axes is given by  $\gamma_A/2$ . This implies that these diagonal peaks are symmetric with respect to the two axes.

The same description applies to the four other peaks of the B mode, with the widths given by  $\gamma_B/2$ .

(2) Eight overtone peaks at (ω<sub>1</sub>, ω<sub>2</sub>) = (±Ω<sub>A</sub>, ±2Ω<sub>A</sub>) and (ω<sub>1</sub>, ω<sub>2</sub>) = (±Ω<sub>B</sub>, ±2Ω<sub>B</sub>). The approximate analytical expression of the signal around the first four peaks (of the A mode) is given by

$$|S(\omega_1,\omega_2)| = \frac{(\alpha_A^{(1)})^2 \alpha_A^{(2)}}{8M_A^2} \left| \frac{F_3^{(AA)}}{\zeta_A^2} \right|.$$
 (52)

However, we see that by the cancellation mechanism as mentioned in the above the peaks in the second and fourth quadrants are weaker than in the first and third quadrants. The width along the  $\omega_1$  and  $\omega_2$  axes are given by  $\gamma_A/2$  and  $\gamma_A$ , respectively. This implies that the peak shape is elongated in the direction of the second axis.

(3) Four zero-frequency or axial peaks at  $(\omega_1, \omega_2) = (\pm \Omega_A, 0)$  and  $(\omega_1, \omega_2) = (\pm \Omega_B, 0)$ . The approximate analytical expression of the signal around the first four peaks (of the A mode) is given by

$$|S(\omega_1, \omega_2)| = \frac{(\alpha_A^{(1)})^2 \alpha_A^{(2)}}{8M_A^2} \left| \frac{F_4^{(AA)}}{\zeta_A^2} \right|.$$
 (53)

The width along the  $\omega_1$  and  $\omega_2$  axes are given by  $\gamma_A/2$  and  $\gamma_A$ , respectively, making the peak shape elongated in the direction of the second axis.

In the similar way, we see that  $E^{\text{DID}}$  gives rise to the following cross peaks:

(1) Eight cross peaks at  $(\omega_1, \omega_2) = (\pm \Omega_A, \pm \Omega_B)$  and  $(\omega_1, \omega_2) = (\pm \Omega_B, \pm \Omega_A)$ . The approximate analytical expression of the signal around the first four peaks is given by

$$|S(\omega_1,\omega_2)| = T_{AB} \frac{(\alpha_A^{(1)} \alpha_B^{(1)})^2}{4M_A M_B} \left| \frac{F_1^{(BA)} - F_2^{(BA)}}{\zeta_A \zeta_B} \right|.$$
 (54)

In the first and third quadrants the numerator in  $F_2^{(BA)}$ almost cancels out as in the above, while that of  $F_1^{(BA)}$  is enhanced, and in the second and fourth quadrants vice 'versa. This fact implies that the four peaks have the same intensity. In addition, we see that the width along the  $\omega_1$  and  $\omega_2$  axes are given by  $\gamma_A/2$  and  $\gamma_B/2$ , respectively.

The parallel discussion applies to the last four peaks at  $(\omega_1, \omega_2) = (\pm \Omega_B, \pm \Omega_A)$ . In this case, the width along the  $\omega_1$  and  $\omega_2$  axes are given by  $\gamma_B/2$  and  $\gamma_A/2$ , respectively.

(2) Eight cross peaks at  $(\omega_1, \omega_2) = (\pm \Omega_A, \pm (\Omega_A + \Omega_B))$ and  $(\omega_1, \omega_2) = (\pm \Omega_B, \pm (\Omega_A + \Omega_B))$ . The approximate analytical expression of the signal around the first four peaks is given by

$$|S(\omega_1,\omega_2)| = T_{AB} \frac{(\alpha_A^{(1)} \alpha_B^{(1)})^2}{4M_A M_B} \left| \frac{F_3^{(BA)}}{\zeta_A \zeta_B} \right|.$$
(55)

Due to the cancellation the peaks in the second and fourth quadrants is weaker than in the first and third. The width along the  $\omega_1$  and  $\omega_2$  axes are given by  $\gamma_A/2$  and  $(\gamma_A + \gamma_B)/2$ , respectively. This implies that the peak shape is elongated in the direction of the second axis.

For the last four cross peaks,  $(\omega_1, \omega_2) = (\pm \Omega_B, \pm (\Omega_A + \Omega_B))$ , the width along the  $\omega_1$  and  $\omega_2$  axes are given by  $\gamma_B/2$  and  $(\gamma_A + \gamma_B)/2$ , respectively.

(3) Eight cross peaks at (ω<sub>1</sub>, ω<sub>2</sub>)=(±Ω<sub>A</sub>, ±(Ω<sub>A</sub>-Ω<sub>B</sub>)) and (ω<sub>1</sub>, ω<sub>2</sub>)=(±Ω<sub>B</sub>, ±(Ω<sub>A</sub>-Ω<sub>B</sub>)). The approximate analytical expression of the signal around the first four peaks is given by

$$|S(\omega_1,\omega_2)| = T_{AB} \frac{(\alpha_A^{(1)} \alpha_B^{(1)})^2}{4M_A M_B} \left| \frac{F_4^{(BA)}}{\zeta_A \zeta_B} \right|.$$
(56)

When  $\omega_B > \omega_A$ , the peaks in the second and the fourth quadrants are stronger than in the first and the fourth. The width along the  $\omega_1$  and  $\omega_2$  axes are given by  $\gamma_A/2$  and  $(\gamma_A + \gamma_B)/2$ , respectively, implying that the peak shape is elongated in the direction of the second axis.

As for the last four peaks,  $(\omega_1, \omega_2) = (\pm \Omega_B, \pm (\Omega_A - \Omega_B))$ , the peaks in the first and the third quadrants are stronger than in the second and fourth (when  $\omega_B > \omega_A$ ), the width along the  $\omega_1$  and  $\omega_2$  axes are given by  $\gamma_B/2$  and  $(\gamma_A + \gamma_B)/2$ , respectively.

It should be noted here that all the above discussion becomes rigorous only when damping constants are small enough for all peaks to be well separated. In the case where damping constants are not small enough, interference between the peaks should be observed.

From the above discussion, it is clear that the amplitude of cross peaks scale as  $1/r_{AB}^3$ , while the other peaks originating from the nonlinearity in the polarizability are independent of  $r_{AB}$ . To be precise, let us concentrate on the cross peak at  $(\omega_1, \omega_2) = (\Omega_A, \Omega_B)$ . In the weak damping limit  $(\gamma_s \rightarrow 0)$ , the peak intensity is given by

$$S(\Omega_A, \Omega_B) \to \frac{T_{AB}(\alpha_A^{(1)}\alpha_B^{(1)})^2}{2M_A \gamma_A \Omega_A M_B \gamma_B \Omega_B}.$$
(57)

For example, let us assume that we measure the 2D Raman signals at two different temperatures  $(T_L \text{ and } T_H)$  and get different peak intensities  $[I_{AB,L}^{(5)}]$  and  $I_{AB,H}^{(5)}]$  at  $(\omega_1, \omega_2) = (\Omega_A, \Omega_B)$ . Then, the ratio of the change of distance is given by

$$r_{AB,L}/r_{AB,H} \sim (I_{AB,H}^{(5)}/I_{AB,L}^{(5)})^{1/3}.$$
(58)

(This relation is good for weak damping case.) Since only the relative (not the absolute) value of peak intensities are available from usual measurements, we should, in practice, renormalize  $I_{AB,L}^{(5)}$  and  $I_{AB,H}^{(5)}$  by other peak intensities which do not depend on the temperature when using Eq. (58); for example, we can use the diagonal peak in-



FIG. 3. The third-order signal in the frequency domain, Eq. (33), from two modes at the frequencies,  $\Omega_A = 400$  and  $\Omega_B = 600$ , with the damping constant  $\gamma_A = \gamma_B = 20$  in the unit [cm<sup>-1</sup>]. (See the details in the text.)

tensities at  $(\omega_1, \omega_2) = (\Omega_A, \Omega_A)$ , for the normalization, which are denoted  $I_{A,s}^{(5)}$  (s=L,H). It should be noted that  $\tilde{I}_{AB,s}^{(5)} \equiv I_{AB,s}^{(5)}/I_{A,s}^{(5)}$  (s=L or H) can be determined ambiguously from the experiment in which only the relative amplitudes are available. Although  $\tilde{I}_{AB,s}^{(5)}$  itself depends on parameters not available from the experiment [such as  $\alpha_A^{(2)}$ ], we still have the relation,

$$r_{AB,L}/r_{AB,H} \sim (\tilde{I}_{AB,H}^{(5)}/\tilde{I}_{AB,L}^{(5)})^{1/3}.$$
 (59)

Here, the parameters not readily available are assumed to depend on the temperature only weakly. In this way, we can determine the ratio Eq. (58) within the experimentally available quantities.

The determination of the absolute value of  $r_{AB}$  may be difficult in practice. Mathematically, the peak intensity of the third order signal is given by

$$J(\Omega_s) = \frac{(\alpha_s^{(1)})^2}{M_s \gamma_s \Omega_s},\tag{60}$$

and thus the absolute value may be given by

$$r_{AB} = \left(\frac{J(\Omega_A)J(\Omega_B)}{\pi\epsilon_0 I_{AB}^{(5)}}\right)^{1/3}.$$
(61)

However, in practice, the absolute value of peak intensities are not usually available from measurements.

### **IV. NUMERICAL RESULTS**

As an example, we assume the nuclear coordinates A and B have the characteristic frequencies,  $\Omega_A = 400$  and  $\Omega_B = 600$ , the damping constants,  $\gamma_A = 20$  and  $\gamma_B = 20$ , respectively, in the unit of  $[\text{cm}^{-1}]$ . The third-order signal  $E_s^{(3)}$ in this case is given in Fig. 3. The ratio of the strength of the two oscillations  $(\alpha_A^{(1)}/\alpha_B^{(1)})^2$  is set to make the two peak intensities the same (see the Appendix for the detail). In practice, we can determine all these parameters from a thirdorder experiment or molecular dynamics simulation. The signal is of course independent of the distance  $\mathbf{r}_{AB}$ .

In Figs. 4(i) and 4(ii), we showed the absolute value of the fifth-order spectrum  $|S(\omega_1, \omega_2)|$  using the same parameters as in Fig. 3. In these plots, we see the cross peaks or combination peaks in addition to the diagonal and overtone peaks, as discussed in the previous section. The diagonal and overtone peaks originate from the nonlinear polarizability  $\alpha_s^{(2)}$ , while the cross peaks from the dipole-induced dipole interaction  $T_{AB}$ . General features of the peaks discussed in



FIG. 4. The fifth-order signal in the frequency domain [absolute value of Eq. (A9)] dependent on the distance of the two functional groups A and B by using the same parameters in Fig. 3. The average distance  $\langle r_{AB} \rangle_{V_0}$  in (ii) is four times as large as that in (i), while the orientation is fixed ( $\theta_{AB}=0$ ). The cross or combination peaks are seen in addition to the diagonal and overtone peaks. The relative intensity of the cross peaks diminish as the distance becomes larger.

the previous section based on the analytical expression are almost perfectly reflected in the plots. One may see slight disagreements, which should be due to interference between the peaks as mentioned before.

The important difference between Figs. 4(i) and 4(ii) is a change in the average distance of  $\langle r_{AB} \rangle_{V_0}$  by a factor of 4. Since only  $T_{AB}$  depends on the average distance  $\langle r_{AB} \rangle_{V_0}$ , the intensities of the cross peaks in the figure decrease as the distance becomes larger. Thus, the intensity of the cross peaks are the measure of the distance of the nuclear coordinates A and B. It should be noted here that the cross peak intensities scale as  $1/r_{AB}^3$ , thereby giving direct structural information [see Eq. (58)].

We mention the parameters used in Fig. 4. As a demonstration, we considered the case where distance and orientation of dipoles are independent variables [Eq. (44)], and assume that all induced dipoles are aligned (c=2). The analytical expression in general case is given in Eq. (A9), and the isotropic case (c=0) is treated in Sec. V.] In addition to the parameters used to calculate the 1D spectrum in Fig. 3, the ratios of the parameters  $\alpha_s^{(2)}$  and  $r_{AB}$  are required to calculate the fifth-order signal. To demonstrate the salient features of our analytical results, we set  $\bar{\alpha}_{\rm A}^{(2)}/(\bar{\alpha}_{\rm A}^{(1)})^2$  $=\overline{\alpha}_{\rm B}^{(2)}/(\overline{\alpha}_{\rm B}^{(1)})^2 (\equiv a)$ , and  $r_{\rm AB}^{(ii)}/r_{\rm AB}^{(i)} = 4$  in Fig. 4. The parameter  $\bar{\alpha}_s^{(i)}$  is the dimensionless counterpart of  $\alpha_s^{(i)}$ , as defined in the Appendix, and  $r_{AB}^{(i)}$  and  $r_{AB}^{(ii)}$  are the values of  $r_{AB}$  in Figs. 4(i) and 4(ii), respectively. For example, when we set a = 1/500,  $r_{AB} = 7.5$  and 30 (Å) in Figs. 4(i) and 4(ii), respectively, and, when a = 1/0.5,  $r_{AB} = 0.75$  and 3 (Å), respectively. See the details for Appendix. These parameter settings are important only for a visual presentation; important quantitative structural information can be obtained with no regard to  $\alpha_s^{(i)}$  as mentioned around Eq. (59).

For these numerical calculations, we have assumed an ordered system, such as a crystal, in which the dipoles are aligned end to end ( $\theta_{AB}=0,c=2$ ), while the magnitude of the distance between A and B is distributed with some average value. As the distribution of  $\theta_{AB}$  randomizes, the cross peak intensities decrease due to the variation of  $\theta_{AB}$  about zero for a fixed  $r_{AB}$ . More generally, the distance  $r_{AB}$  also changes when  $\theta_{AB}$  deviates from the purely anisotropic dis-

tribution, for which cases Eq. (44) is not valid. In addition, if  $\theta_{AB}$  is distributed around a *finite* average value, the deviation can even increase the cross peak intensities. The isotropic system where these difficulties do not exist is treated in the next section.

# V. CROSS PEAK INTENSITY IN THE ISOTROPIC SYSTEM

In the isotropic system, the first-order contribution in  $T_{AB}$  is averaged to zero and the cross peaks are produced by the second-order contribution. Within the linear polarizability approximation, the second-order contribution is given by

$$p_{A}^{(5)} + p_{B}^{(5)}$$

$$= \frac{1}{2} E_{f}(t, \mathbf{r}_{G}) E_{0}^{4} [1 + \cos(\Delta \mathbf{k}_{1} \cdot \mathbf{r}_{G})] [1 + \cos(\Delta \mathbf{k}_{2} \cdot \mathbf{r}_{G})]$$

$$\times T_{AB}^{2} \{(\alpha_{A}^{(0)})^{4} \alpha_{B}^{(0)} D_{A}(T_{2}) [D_{A}(T_{1}) + D_{A}(T_{1} + T_{2})]$$

$$+ 3(\alpha_{B}^{(0)} + \alpha_{B}^{(0)}) (\alpha_{A}^{(1)} \alpha_{B}^{(1)})^{2} D_{A}(T_{2})$$

$$\times [D_{B}(T_{1}) + D_{B}(T_{1} + T_{2})] \} + (A \leftrightarrow B). \qquad (62)$$

Note here that the Fourier transformed expression of Eq. (62) is completely given through Eqs. (A5) and (A6).

Equation (62) can be obtained through the calculations similar to the ones in the previous sections. These second-order terms (in  $T_{AB}$ ) appears through two mechanisms; one through the first-order perturbation of the third term in the right-hand side of Eq. (19) and the other through the second-order perturbation of the second term in Eq. (19). We have checked that a quantum calculation by using the Feynman rule (see Ref. 68) also gives Eq. (62).

From the above expression, we can show that the cross peak intensities, if any, scale as  $T_{AB}^2$ . In Sec. III, we have shown that the factors  $D_s(T_2)[D_{s'}(T_1)+D_{s'}(T_1+T_2)]$  (s = A, s' = B) lead to the cross peaks, whereas  $D_s(T_2) \times [D_s(T_1)+D_s(T_1+T_2)]$  lead to diagonal, overtone, and axial peaks. Since the right-hand side of Eq. (62) is proportional to  $T_{AB}^2$  and contains terms proportional to  $D_s(T_2) \times [D_{s'}(T_1)+D_{s'}(T_1+T_2)]$  (s=A,s'=B), we see that the cross peaks scale as  $T_{AB}^2$  in the present case.

In the isotropic system, the orientational average of  $T_{AB}^2$  is nonzero while that of  $T_{AB}$  is zero. Thus, in the isotropically distributed system, the cross peak intensities scale as  $1/r_{AB}^6$  and the relation to extract the structural information (58) is replaced by

$$r_{\rm AB,L}/r_{\rm AB,H} \sim (I_{\rm AB,H}^{(5)}/I_{\rm AB,L}^{(5)})^{1/6}.$$
 (63)

It is emphasized here that the right-hand side can be completely obtained by the quantities available from the usual relative amplitude measurements as mentioned around Eq. (59).

### **VI. DISCUSSION**

In this section, we explain the optical processes contributing to the formation of cross peaks and the role of the five optical pulses in the processes. We also compare our results with 2D NMR and mention a possible deviation from our scaling law.

In the present model, quantum states of a molecule can be characterized by the matrix  $|n_A, n_B\rangle\langle n_B, n_A|$ , where  $n_s$  is the quantum number for the vibration of the s mode at the frequency  $\Omega_s$ . For simplicity, we assume that the molecule is initially in the state  $|0,0\rangle\langle 0,0|$ . By using this notation, one of the possible processes which contributes to the formation of the cross peaks for the *anisotropic system* [see Eq. (45)] can be described as follows. The first pair of pulses nonresonantly excites the A mode through a one-quantum Raman transition; the molecule is in the coherence state  $|1,0\rangle\langle 0,0|$ during the first time period  $T_1$ . The second pair excites the B mode and de-excites the A mode through the DID coupling (two simultaneous one-quantum transitions); the molecule is in the coherent state  $|0,1\rangle\langle 0,0|$  during the second time period  $T_2$ . The final probe pulse then brings back the molecule to the state  $|0,0\rangle\langle 0,0|$ .

Basically, the molecule experiences the interaction with the light field three times; a one-quantum transition of the A mode, a one-quantum transition of the B mode, and the two simultaneous one-quantum transition of A and B modes through the DID coupling. These three interactions correspond respectively to the terms  $\alpha_A(t)E(t)^2$ ,  $\alpha_B(t)E(t)^2$ , and  $\alpha_{\rm A}(t)\alpha_{\rm B}(t)T_{\rm AB}E(t)^2$ , appearing in Eq. (19). Among the six possible orders of these three interactions, four cases [where the last interaction is not due to  $\alpha_A(t)\alpha_B(t)T_{AB}E(t)^2$ ] contribute to the formation of the cross peaks, since the final interaction cannot be the DID coupling. The cross peak intensities are proportional to  $(\alpha_A^{(1)}\alpha_B^{(1)})^2$ ; each mode experiences a one-quantum excitation followed by a one-quantum de-excitation. [Note that  $\alpha_s^{(i)}$  is associated with  $(Q_s)^i$ , which can cause transitions with *i*-quanta.] Thus, 16 sequences contribute to the cross peaks. In all the 16 cases, at least one of the two modes is in the coherence state during  $T_1$  and  $T_2$ ; both time periods probe the dynamics of coherence states.

For the isotropic case where the signal is given through Eq. (62), six sets of three interaction combinations represented by [see Eq. (19)]

$$\alpha_{A}(t) \alpha_{B}(t) T_{AB}E(t)^{2}, \alpha_{A}(t) \alpha_{B}(t) T_{AB}E(t)^{2}, \alpha_{A}(t)E(t)^{2} \alpha_{A}(t) \alpha_{B}(t) T_{AB}E(t)^{2}, \alpha_{A}(t) \alpha_{B}(t) T_{AB}E(t)^{2}, \alpha_{B}(t)E(t)^{2} \alpha_{B}(t)E(t)^{2}, (\alpha_{A}(t))^{2} \alpha_{B}(t) T_{AB}^{2}E(t)^{2}, \alpha_{A}(t)E(t)^{2} (\alpha_{A}(t))^{2} \alpha_{B}(t) T_{AB}^{2}E(t)^{2}, \alpha_{B}(t)E(t)^{2}, \alpha_{B}(t)E(t)^{2} (\alpha_{B}(t))^{2} \alpha_{A}(t) T_{AB}^{2}E(t)^{2}, \alpha_{A}(t)E(t)^{2}, \alpha_{B}(t)E(t)^{2} (\alpha_{B}(t))^{2} \alpha_{A}(t) T_{AB}^{2}E(t)^{2}, \alpha_{A}(t)E(t)^{2}, \alpha_{A}(t)E(t)^{2}$$
 (64)

all contribute to the cross peaks. Since the DID coupling cannot be the last interaction, only one order of the three interactions is possible for each of the first two sets, while four orders are possible for each of the other four sets. From Eq. (62), we see that the cross peak intensities are proportional to  $(\alpha_A^{(1)}\alpha_B^{(1)})^2\alpha_A^{(0)}$  or  $(\alpha_A^{(1)}\alpha_B^{(1)})^2\alpha_B^{(0)}$ . This implies that each mode experiences a one-quantum excitation and a one-quantum de-excitation. Although the excitation is followed by the de-excitation in the process where the interaction  $\alpha_A(t)\alpha_B(t)T_{AB}E(t)^2$  acts twice [i.e., the first two sets in Eq. (64)], the excitation and the de-excitation of a single mode can also occur simultaneously (zero-quantum transition) in the process with interaction  $(\alpha_A(t))^2 \alpha_A(t) T_{AB}^2 E(t)^2$ or  $(\alpha_B(t))^2 \alpha_A(t) T_{AB}^2 E(t)^2$  [i.e., the last four sets in Eq. (64)]. Unlike the anisotropic cases, the time-periods  $T_1$  and  $T_2$  do not necessarily describe the dynamics of the coherence state. At least one of the time periods do describe the coherence dynamics, while the other time period probes the dynamics of the ground population state in some processes.

The scaling relationships observed for the ordered sample and the isotropically distributed sample are similar to those observed for 2D NMR. In liquid state NMR, the amplitude of cross peaks arising from dipolar coupling scales as  $1/r^6$ , whereas  $1/r^3$  terms contribute to solid state NMR. It should be pointed out that significant differences still exist between the orientational averages in these experiments. Orientational dynamics have not been considered here, but rather only the distribution within an ensemble. Orientational relaxation processes exist on faster time scales than the experiment in both solid state and liquid state NMR, while orientational relaxation is either on equal or longer time scales than the 2D Raman experiment. These effects will be significant contributions to analysis 2D Raman spectra of real systems, and will need further consideration.

We mention about a possible deviation from the scaling law of the cross peak intensities. The DID coupling  $T_{AB}$ comes from the electric field produced by a dipole. In general, the field consists of the three terms proportional to  $1/r_{AB}$ ,  $1/r_{AB}^2$ , and  $1/r_{AB}^3$  (see Chap. 9.2 of Ref. 65). If the two nuclear coordinates A and B are close, then the  $1/r_{AB}^3$ term dominates and the expression (11) is justified; this is the type of DID interaction which has been frequently employed. If we can observe a weak DID coupling effect when  $r_{AB}$  is large, we may extract structural information at larger scale; however, in such a case,  $T_{AB}$  may no longer scale as  $1/r_{AB}^3$ . In addition, strong anharmonicity can contribute to cross peaks and can be a source of deviation from our scaling law. In the practical use of our theory, these points should be kept in mind.

## **VII. CONCLUSION**

We reproduced the third-order signal in the impulsive measurement in a heuristic way within the Placzek model by using the Green function method or by using the propagator. In the similar way, we obtained the fifth-order signal taking into account the dipole-induced dipole coupling between the two specific dipoles A and B of a complex molecule. Although we used an extended Placzek model for the derivation, the results analytically agree with the ones from the quantum Brownian oscillator model with the dipole-induced dipole interaction at this order of calculation.

In the present model, the fifth-order signal is shown to be formed from the two reasons; nonlinear polarizability (NL) and dipole-induced dipole (DID) coupling. NL spawns the fundamental and overtone peaks while DID the cross or combination peaks. Since the fundamental peaks come from the small nonlinear effect, they can be comparable to weak cross peaks.

While the nonlinear polarizability expansion coefficients are independent of distance, the DID interaction tensor  $T_{AB}$ varies with the inverse cube of the distance vector  $r_{AB}$  between the dipoles A and B. We can thereby visualize structural change in the system as the change of cross peak intensities relative to diagonal peaks. The cross peak intensity drops as the average dipole separation increases.

The scaling of the cross peak amplitude as a function of distance depends on the effects of dipole orientational averaging that is appropriate for the system. In a system with randomly distributed dipole orientations, such as a liquid, the cross peak amplitude scales as  $1/r^6$ , while a  $1/r^3$  dependence is observed in an anisotropic, aligned system. These scaling relationships have analogy to the dipole coupling scaling relationships observed in liquid and solid state NMR, respectively.

These scaling relationships form the basis for quantitatively extracting structural information from 2D Raman experiments. Clearly the variation of cross peak amplitude as a function of variation in external variables allows structural change to be followed, but the goal of using 2D Raman experiments to extract absolute distances is still a challenge. The ratio of change in distances can be determined from the change in intensity of a cross peak [see Eqs. (58) and (63)] and the intensity change can be completely determined from knowledge available from the experiment [see Eq. (59)]. However, the determination of absolute distance will require parameters not readily available, such as the polarizability expansion coefficients  $\alpha_s^{(i)}$  [see Eq. (61)]. Determination of these expansion coefficients and distinguishing signal contributions from anharmonic coupling are challenges that need to be addressed in the future.

#### ACKNOWLEDGMENTS

The present work was supported by a Grant-in-Aid for Encouragement of Young Scientists from the Japanese Ministry of Education, Science, Sports, and Culture. A.T. acknowledges support from the National Science Foundation (CHE-9900342).

# APPENDIX: ANALYTICAL AND DIMENSIONLESS EXPRESSIONS

In this Appendix, we present analytical expressions used in the numerical simulations. We also introduce dimensionless parameters, which are used to specify the parameters in the text. By rewriting products of trigonometric functions by trigonometric functions with combined arguments [i.e., by using relations such as,  $\sin x \sin y = -\{\cos(x+y) - \cos(x-y)\}/2\}$ , one finds

$$D_{s}(T_{2})D_{s'}(T_{1}) = -\theta(T_{2})\theta(T_{1})\frac{f_{1}^{(ss')} - f_{2}^{(ss')}}{2M_{s}M_{s'}\zeta_{s}\zeta_{s'}},$$
 (A1)

$$D_{s}(T_{2})D_{s'}(T_{1}+T_{2}) = -\theta(T_{2})\theta(T_{1}+T_{2})\frac{f_{3}^{(ss')}-f_{4}^{(ss')}}{2M_{s}M_{s'}\zeta_{s}\zeta_{s'}},$$
(A2)

where

$$f_n^{(ss')} = e^{-\Gamma^{(ss')}T_1 - \Gamma_n^{(ss')}T_2} \cos(\Omega_{1n}^{(ss')}T_1 + \Omega_{2n}^{(ss')}T_2).$$
(A3)

Here, the damping constants and the (complex) frequencies are given by

$$\Gamma^{(ss')} = \gamma_{s'}/2, \begin{pmatrix} \Gamma_{1}^{(ss')} & \Omega_{11}^{(ss')} & \Omega_{21}^{(ss')} \\ \Gamma_{2}^{(ss')} & \Omega_{12}^{(ss')} & \Omega_{22}^{(ss')} \\ \Gamma_{3}^{(ss')} & \Omega_{13}^{(ss')} & \Omega_{23}^{(ss')} \\ \Gamma_{4}^{(ss')} & \Omega_{14}^{(ss')} & \Omega_{24}^{(ss')} \end{pmatrix}$$
$$= \begin{pmatrix} \gamma_{s}/2 & \zeta_{s'} & \zeta_{s} \\ \gamma_{s}/2 & -\zeta_{s'} & \zeta_{s} \\ (\gamma_{s} + \gamma_{s'})/2 & \zeta_{s'} & \zeta_{s} + \zeta_{s'} \\ (\gamma_{s} + \gamma_{s'})/2 & -\zeta_{s'} & \zeta_{s} - \zeta_{s'} \end{pmatrix}.$$
(A4)

The two-dimensional Fourier transform is then given by

$$\mathcal{F}[D_{s}(T_{2})D_{s'}(T_{1})] = -\frac{F_{1}^{(ss')} - F_{2}^{(ss')}}{2M_{s}M_{s'}\zeta_{s}\zeta_{s'}},\tag{A5}$$

$$\mathcal{F}[D_{s}(T_{2})D_{s'}(T_{1}+T_{2})] = -\frac{F_{3}^{(ss')} - F_{4}^{(ss')}}{2M_{s}M_{s'}\zeta_{s}\zeta_{s'}},\qquad(A6)$$

where

$$F_{n}^{(ss')} = -\frac{(\omega_{1} + i\Gamma^{(ss')})(\omega_{2} + i\Gamma_{n}^{(ss')}) + \Omega_{1n}^{(ss')}\Omega_{2n}^{(ss')}}{[(\omega_{1} + i\Gamma^{(ss')})^{2} - (\Omega_{1n}^{(ss')})^{2}][(\omega_{2} + i\Gamma_{n}^{(ss')})^{2} - (\Omega_{2n}^{(ss')})^{2}]}.$$
(A7)

In the above, we have used the notation  $\mathcal{F}[X(T_1,T_2)] = \int dT_1 \int dT_2 e^{i\omega_1 T_1 + i\omega_2 T_2} X(T_1,T_2)$ . Thus, the 2D Fourier transformation of  $p^{\text{NL}}(t) + p^{\text{DID}}(t)$  is given by

$$\mathcal{F}[p^{\mathrm{NL}}(t) + p^{\mathrm{DID}}(t)] = E_0^4 E_f(t, \mathbf{r}_G) [1 + \cos(\Delta \mathbf{k}_1 \cdot \mathbf{r}_G)] \\ \times [1 + \cos(\Delta \mathbf{k}_2 \cdot \mathbf{r}_G)] S(\omega_1, \omega_2).$$
(A8)

Here, the 2D Raman signal  $S(T_1, T_2)$  is given by

$$S(\omega_1, \omega_2) = S^{\rm NL} + S^{\rm DID}, \tag{A9}$$

where

$$S^{\rm NL} = -\frac{(\alpha_{\rm A}^{(1)})^2 \, \alpha_{\rm A}^{(2)}}{8(M_{\rm A} \, \zeta_{\rm A})^2} (F_1^{(\rm AA)} - F_2^{(\rm AA)} + F_3^{(\rm AA)} - F_4^{(\rm AA)}) + (\rm A \leftrightarrow B), \tag{A10}$$

$$S^{\text{DID}} = -T_{\text{AB}} \frac{(\alpha_{\text{A}}^{(1)} \alpha_{\text{B}}^{(1)})^2}{4M_{\text{A}} M_{\text{B}} \zeta_{\text{A}} \zeta_{\text{B}}} (2(F_1^{(\text{AB})} - F_2^{(\text{AB})}) + F_3^{(\text{AB})} - F_4^{(\text{AB})}) + (\text{A} \leftrightarrow \text{B}),$$
(A11)

where  $T_{AB}$  should be interpreted as an averaged quantity [see Eq. (43)]. We have plotted the absolute value of  $S^{NL} + S^{DID}$  in Fig. 4.

To specify the parameters used in the numerical calculations, we introduce dimensionless expansion coefficients  $\bar{\alpha}_{s}^{(i)}$  by

$$\alpha_s^{(1)} = \overline{\alpha}_s^{(1)} \cdot \alpha_0 \sqrt{M_s \,\Omega_0 / \hbar},\tag{A12}$$

$$\alpha_s^{(2)} = \bar{\alpha}_s^{(2)} \cdot \alpha_0 M_s \,\Omega_0 / \hbar, \tag{A13}$$

where  $\alpha_0$  and  $\Omega_0$  are arbitrary units for polarizability and frequency. Here, we take  $\alpha_0 = 4\pi\epsilon_0 r_0^3$  with  $r_0 = 1$ [Å] and  $\Omega_0/(2\pi c) = 1$ [cm<sup>-1</sup>].

The prefactors in Eqs. (A10) and (A11) are reduced to

$$\frac{(\alpha_s^{(1)})^2 \,\alpha_s^{(2)}}{2(M_s \,\zeta_s)^2} = \frac{\alpha_0^3}{\hbar^2} \cdot \frac{(\bar{\alpha}_s^{(1)})^2 \,\bar{\alpha}_s^{(2)}}{2\bar{\zeta}_s^2},\tag{A14}$$

$$T_{\rm AB} \ \frac{(\alpha_{\rm A}^{(1)}\alpha_{\rm B}^{(1)})^2}{M_{\rm A}M_{\rm B}\zeta_{\rm A}\zeta_{\rm B}} = \frac{\alpha_0^3}{\hbar^2} \cdot \frac{(\bar{\alpha}_{\rm A}^{(1)}\bar{\alpha}_{\rm B}^{(1)})^2}{\bar{\zeta}_{\rm A}\bar{\zeta}_{\rm B}} \cdot \bar{T}_{\rm AB}, \qquad (A15)$$

where  $\overline{\zeta}_s = \zeta_s / \Omega_0$  and  $\overline{T}_{AB} = T_{AB} \alpha_0$ . Under Eq. (44),  $\overline{T}_{AB} = c/\overline{r}_{AB}^3$ , where  $\overline{r}_{AB} = \langle r_{AB} \rangle_{V_0} / r_0$ . The prefactor of the third-order signal in Eq. (33) is reduced to

$$\frac{[\alpha_s^{(1)}]^2}{M_s} = \frac{\alpha_0^2}{\hbar^2} \cdot [\bar{\alpha}_s^{(1)}]^2 \,\Omega_0, \qquad (A16)$$

and, thus, the ratio of  $\bar{\alpha}_{A}^{(1)}$  to  $\bar{\alpha}_{B}^{(1)}$  is determined by comparison of experimental data with simulations, together with  $\Omega_s$  and  $\gamma_s$ . To make the two peak intensities in the third-order spectrum, we have set  $J(\Omega_A) = J(\Omega_B)$ , which reduces to  $(\bar{\alpha}_A^{(1)})^2/(\gamma_A \Omega_A) = (\bar{\alpha}_B^{(1)})^2/(\gamma_B \Omega_B)$ . Since  $\gamma_A = \gamma_B$ , this is equivalent to set  $\eta_B/\eta_A = 2.25$ , where  $\eta_i = (\bar{\alpha}_i^{(1)})^2 \Omega_i$  in Figs. 3 and 4.

In addition to the parameters appearing in the third-order signal, there are three more parameters,  $\bar{\alpha}_s^{(2)}$  (s=A,B) and  $\overline{r}_{AB}$ , which should be fitted to the experimental data, in the fifth-order case. However, these three parameters are not independent. This is understood as follows. The essential parameters for the fifth-order signal are the prefactors in Eqs. (A14) and (A15), and independent parameters are the two parameters; one is Eq. (A14) for s = A divided by Eq. (A15) and the other is Eq. (A14) for s = B divided by Eq. (A15),  $\bar{\alpha}_{\rm A}^{(2)}\Omega_{\rm B}\bar{r}_{\rm AB}^3/[(\bar{\alpha}_{\rm B}^{(1)})^2\Omega_{\rm A}]$  and  $\bar{\alpha}_{\rm B}^{(2)}\Omega_{\rm A}\bar{r}_{\rm AB}^3/[(\bar{\alpha}_{\rm B}^{(1)})^2\Omega_{\rm A}]$ is, that  $\times [(\bar{\alpha}_{A}^{(1)})^{2}\Omega_{B}]$  if we assume  $\Omega_{s} >> \gamma_{s}$ . In the present case where  $J(\Omega_A) = J(\Omega_B)$ , these reduce to  $\bar{\alpha}_A^{(2)} \bar{r}_{AB}^3 / (\bar{\alpha}_A^{(1)})^2$  and  $\bar{\alpha}_{\rm B}^{(2)}\bar{r}_{\rm AB}^3/(\bar{\alpha}_{\rm B}^{(1)})^2$ , respectively. In Figs. 4(i) and 4(ii), we set  $a\bar{r}_{AB}^3 = 2$  and 54, respectively, where  $a \equiv \bar{\alpha}_A^{(2)} / (\bar{\alpha}_A^{(1)})^2$  $=\bar{\alpha}_{\rm B}^{(2)}/(\bar{\alpha}_{\rm B}^{(1)})^2$ . This implies that  $r_{\rm AB}=7.5$  and 30 (Å) in Figs. 4(i) and 4(ii), respectively, when a = 1/500, and  $r_{AB}$ = 0.75 and 3 (Å), respectively, when a = 1/0.5.

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- <sup>63</sup> With this definition of  $\alpha_s(t)$ , the polarizability of the A mode  $\alpha_A(t)$  should depend on the B mode in general, since  $\mu_s(t)$ ,  $\alpha_s(t)$ , etc. are merely expansion coefficients of the dipole  $\mathbf{p}_s(t)$  (interacting with other dipoles) in terms of the electric field at the time t; this is not the polarizability for an isolated mode although this point might not been emphasized in the literature. This understanding allows us to expand the polarizability in terms of the nuclear coordinates of A which is affected by the B mode as we discuss below. It should be noted that  $\alpha_s(t)$  depends on the electric field at the time *before* t in general as we see below.

- <sup>64</sup> For the energy of induced dipoles in an external field, the factor  $\frac{1}{2}$  is required, (Refs. 65,55,56) although the energy of a rigid dipole in an external field is given without this factor. One way of understanding this is as follows. Imagine that the external field is produced by one single *external* charge *e* and the whole system consists of this charge and *induced* dipoles  $\mathbf{p}_A$  and  $\mathbf{p}_B$ . Then the total electric-field energy of the system is given by  $U = e \phi/2$ , where  $\phi$  is the potential at the position of the true charge because the induced dipoles have any true charges. Since  $\phi$  is produced by the two dipoles, it is given by  $\phi = \mathbf{p}_A \cdot \mathbf{r}_A / r_A^3 + \mathbf{p}_B \cdot \mathbf{r}_B / r_B^3$ where  $\mathbf{r}_A$  and  $r_A$  are the distance vector between the charge and the dipole *A* and its magnitude. Thus, the energy can be written as  $U = -\mathbf{p}_A \cdot \mathbf{E}_{ex}(\mathbf{r}_A)/2 - \mathbf{p}_B \cdot \mathbf{E}_{ex}(\mathbf{r}_B)/2$ , where  $\mathbf{E}_{ex}(\mathbf{r})$  is the field produced by the external charge, or  $\mathbf{E}_{ex}(\mathbf{r}) = -e\mathbf{r}/r^3$ . Note here that the minus sign comes from the definition of the direction of the vector  $\mathbf{r}_A$  and  $\mathbf{r}_B$ . This argument is easily extended to the case of the time dependent external field.
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- <sup>69</sup>In the purely isotropic case,  $\theta_{AB}$  is randomly distributed;  $c = \int_{0}^{\pi} d\theta \sin \theta (3 \cos^2 \theta 1)/\pi = 0.$