

RESPONSE FUNCTION THEORY OF TIME-RESOLVED CARS AND CSRS OF ROTATING MOLECULES IN LIQUIDS UNDER GENERAL POLARIZATION CONDITIONS

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A theoretical treatment of time-resolved CARS and CSRS is given that includes molecular rotation during the time interval between the excitation and probing light pulses. A molecular response function tensor is found that accounts for the vibrational relaxation and the rotational diffusion of the molecules. The ensemble average of this response function with an arbitrary set of polarization conditions for the light pulses yields a sum of three terms. Each term is the product of a polarization factor P_i and a molecular rotational relaxation function M_i . New polarization conditions are proposed that permit to measure each of these three terms separately.

1. Introduction

Time-resolved coherent anti-Stokes Raman scattering (CARS) and coherent Stokes Raman scattering (CSRS) are now widely being used for the study of dephasing of molecular vibrations [1–3]. Most experiments have been performed on molecular crystals [4–13] and liquids [14–20], but gases [21] and supersonic beams [22–24] have also been studied. In the gas phase the rotational motion of the molecules results in a discrete CARS spectrum [25] that can be resolved with high-resolution CARS in frequency domain [26–29], or with Fourier-transform CARS in time domain [24]. In liquids no rotational eigenstates exist and rotation of the molecules can in many cases be described by classical models of rotational diffusion. During rotation the molecules carry the memory of a polarized excitation event within their own coordinate system. Fluorescence or absorption probing of the molecules at some time after the excitation process measures the loss of correlation between the molecular and the laboratory coordinate systems in terms of a loss of polarization with increasing delay time. This applies also to Raman excitation unless the Raman transition tensor involved is rotationally invariant, i.e. isotropic. Hence, when the vibrational relaxation and the rotational diffusion of the molecules occur on the same time scale, both decay mechanisms will contribute to the time-resolved CARS or CSRS signal. A temperature dependence of the decay time can then either indicate a change in the pure-dephasing contribution to vibrational dephasing, or a change in rotational diffusion. The latter could be due to many reasons, e.g., a change in the viscosity of the liquid, a phase transition, or a change in molecular conformation.

CARS or CSRS experiments performed under various polarization conditions will measure various components of the rotational relaxation. Hence a suitably selected set of polarized CARS or CSRS experiments should allow one to separate the molecular rotational dynamics from the vibrational dynamics. In crystals, polarized CARS has been used to measure Raman transitions of various symmetries [30,31]. A special choice of the polarization directions with respect to the crystal axes allowed to observe quantum beats between two factor group components in benzene [31]. For liquids, several polarization arrangements have been discussed with respect to the suppression of non-resonant background signals [32–37]. But no rotational motion of the molecules was considered. In fact, we know of only one paper [20]

in which time-resolved CARS with non-parallel polarization of the excitation pulses was studied. In this paper drastic changes in the CARS decay were observed when polarization conditions were changed. All combinations of parallel and perpendicular polarization directions were studied. The data were interpreted considering an axially symmetric molecule with a single-exponentially decaying rotational autocorrelation function.

It is likely that in the future polarized time-resolved CARS will find more applications in the study of fast molecular rotations. Hence we believe that a general theoretical discussion of the polarization characteristics of time-resolved CARS will be helpful for experimentalists both in the interpretation of their data as well as in the design of new experiments. Our aim in the present paper is to present a general description of time-resolved CARS and CSRS for *all possible polarization conditions without making any assumptions about the details of the molecular rotational dynamics beforehand*. In the following section the problem is formulated and the relevant molecular and laboratory parameters are defined. Response functions are used rather than susceptibilities since we feel that this is the natural approach to time-domain spectroscopy. The use of response functions also permits us to extend the formalism easily to non-equilibrium systems.

Section 3 deals with the ensemble average of tensor operators in molecular systems that rotate between two experimental events. The result is applied to CARS in section 4. The electric field of the signal wave contains three contributions, each being the product of a polarization factor P_i and a molecular rotational relaxation function M_i . It is shown that polarization arrangements with all polarizers either parallel or perpendicular to each other always lead to interferences between these three field contributions. Three new polarizer arrangements are proposed that measure each of the three field contributions and hence each of the three molecular rotational relaxation functions M_i separately.

The particular form of these molecular functions M_i depends on the symmetry of the Raman mode involved as well as on the nature of the rotational motion of the molecule. As examples we discuss non-resonance-enhanced Raman transitions with symmetrical Raman transition polarizabilities and the free rotational diffusion of rigid molecules. A few consequences of these results relevant to steady state CARS or CSRS in frequency domain are also discussed.

A discussion of symmetry properties of rotational correlation functions has been put into an appendix, as well as the transformation of the tensors into the irreducible spherical tensor basis and the back transform of the results to cartesian coordinates. This was done to keep all information directly relevant to the experimentalist close together in sections 3 and 4 without lengthy interruptions of mainly mathematical nature.

2. Formulation of the problem

In a time-resolved CARS or CSRS experiment the sample is exposed to a sequence of three light pulses as schematically shown in fig. 1. The frequencies ω_1 and ω_2 of the first two pulses are chosen so that their difference $|\omega_1 - \omega_2|$ is close to resonance with a Raman transition $|a\rangle \rightarrow |b\rangle$ with transition frequency $\omega_{ba} = (\epsilon_b - \epsilon_a)/\hbar$. The induced material excitation is probed by a third pulse with frequency ω_3 , and the system responds by emitting a signal pulse with frequency $\omega_4 = \omega_3 + \omega_{ba}$ for CARS and $\omega_4 = \omega_3 - \omega_{ba}$ for CSRS. Fig. 2 shows the two time-ordered diagrams that give the largest contribution to the response functions of CARS and CSRS for a molecule in its ground state. In most experiments the light pulses with frequencies ω_1 and ω_3 are obtained from the same laser. In this case $\omega_4 = 2\omega_1 - \omega_2$ for both processes in steady-state experiments or in time-domain experiments on exact resonance, when $|\omega_1 - \omega_2| = \omega_{ba}$. In the following the frequencies ω_1 and ω_3 are distinguished since the time delay and polarization of these two pulses are also different. Through a proper choice of frequencies our results can be applied to all kinds of coherent Raman spectroscopies. For $\omega_1 = \omega_3$ the diagrams I and II describe ordinary CARS and CSRS,

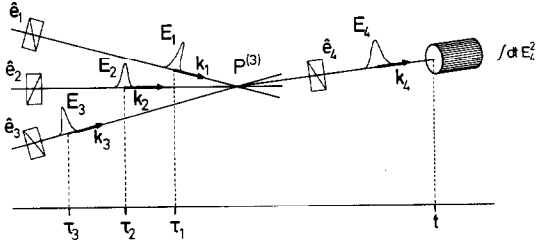


Fig. 1. Schematic view of a generalized time-resolved CARS or CSRS experiment: Three input pulses with envelopes E_n , wave vectors k_n , and polarization e_n ($n = 1, 2, 3$) arrive at times τ_n at the sample to produce the non-linear polarization $P^{(3)}$. The latter radiates a new light field with envelope E_4 and wavevector k_4 which is square-integrated by the detector after passage through the polarizer e_4 .

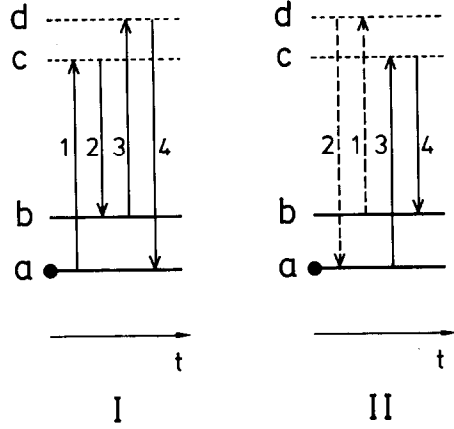


Fig. 2. Diagrammatic representation of the two leading contributions to the molecular response function for a four-wave-mixing process resonant with a ground state Raman transition $a \rightarrow b$. The numbers label the field components involved with time ordering from the left to the right. For $\omega_1 = \omega_3$ diagram I describes CARS and diagram II CSRS with $\omega_4 = 2\omega_1 - \omega_2$. For $\omega_2 = \omega_3$ both diagrams describe Raman resonant transient grating experiments with $\omega_4 = \omega_1$. In particular, diagram I contributes to RIKES whereas diagram II contributes to Raman gain spectroscopy.

respectively. When $\omega_2 = \omega_3$ is chosen, the signal frequency will be $\omega_4 = \omega_1$. This situation is encountered in several grating- or polarization-spectroscopy configurations employing Raman resonances. In particular, diagram I describes RIKES and diagram II Raman gain spectroscopy.

In a semiclassical description the interaction between the light pulses and the sample molecules is given by the coupling of the molecular dipole operator μ with the electric field vector $E(t)$ of the light. The total electric field $E(t)$ is written as the sum of three pulses E_n :

$$E(\mathbf{r}, t) = \sum_{n=1}^3 [E_n(\mathbf{r}, t) + E_n^*(\mathbf{r}, t)],$$

$$E_n(\mathbf{r}, t) = e_n \mathcal{E}_n(t - \tau_n) \exp[i(\omega_n - \mathbf{k}_n \cdot \mathbf{r})]. \quad (1)$$

Each light pulse is characterized by a carrier frequency ω_n , a wave vector \mathbf{k}_n , a polarization vector e_n , and an envelope \mathcal{E}_n centered at time τ_n .

For an ensemble of non-interacting molecules the response of the sample is local in space and depends only on the electric field strength at that same point in space [38]. Then the third-order polarization responsible for the CARS and CSRS effect is given by the triple time convolution of a molecular response function \mathbf{R} with the field components E_1 , E_2^* , and E_3 :

$$P(\mathbf{r}, t) = \int_{-\infty}^t \int_{-\infty}^t \int_{-\infty}^t dt_1 dt_2 dt_3 [\mathbf{R}(t, t_3, t_2, t_1)]_{av} : E_3(\mathbf{r}, t_3) E_2^*(\mathbf{r}, t_2) E_1(\mathbf{r}, t_1). \quad (2)$$

The spatial dependence of $P(\mathbf{r}, t)$ is the product of the spatial dependences of the three input fields, $\exp[-i(\mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3) \cdot \mathbf{r}]$. This leads to the well-known phase-matching condition [38,39]. For the discussions in this paper it is sufficient to consider only the point $\mathbf{r} = 0$.

The response function \mathbf{R} is sometimes written as a function of the three time intervals $t - t_n$ only, i.e. as $\mathbf{R}(t - t_3, t - t_2, t - t_1)$. This applies, however, only to equilibrium systems in which the response must be invariant against a translation in time. We keep all four time arguments for the following reason: The system under consideration is an ensemble of independently rotating molecules in a liquid. At the beginning of the interaction with the first light pulse, a particular molecule will have a particular orientation with respect to the laboratory frame, and hence the tensor components of the response function of this molecule depend on its initial orientation. Of course, the total response function is the ensemble average of the molecular response function and depends only on the three time-intervals, provided that the initial orientational distribution of molecules is the equilibrium distribution. The use of all four time arguments also permits the treatment of molecules that have been prepared in a non-equilibrium state. An example is time-resolved CARS of molecules in an electronically excited state.

The non-linear polarization $\mathbf{P}(t)$ radiates a new field $\mathbf{E}_4(t)$. In non-birefringent media the vector \mathbf{P} is parallel to \mathbf{E}_4 , i.e. $\mathbf{P} = e_4 P$ [38,39]. When the generated field is detected through an analyzer with polarization direction \mathbf{e}_4 , the measured signal is

$$I(t) = |\mathbf{e}_4^* \cdot \mathbf{E}_4|^2 = GP^2, \quad (3)$$

where the constant G contains dielectric constants and phase-matching factors [38,39].

Thus eq. (2) may be written in the form

$$P(t) = \int \int \int dt_1 dt_2 dt_3 [\mathbf{e}_4^* \cdot \mathbf{R}(t, t_3, t_2, t_1) : \mathbf{e}_3 \mathbf{e}_2^* \mathbf{e}_1]_{av} \\ \times \mathcal{E}_1(t_1 - \tau_1) \mathcal{E}_2^*(t_2 - \tau_2) \mathcal{E}_3(t_3 - \tau_3) \exp[i(\omega_1 t_1 - \omega_2 t_2 + \omega_3 t_3)]. \quad (4)$$

All the polarization dependence is contained in the product of the tensor \mathbf{R} with the four polarization vectors. In cartesian coordinates this product is

$$\mathbf{e}_4^* \mathbf{R} : \mathbf{e}_3 \mathbf{e}_2^* \mathbf{e}_1 = \sum_{ijkl} R_{ijkl} e_{4i}^* e_{3j} e_{2k}^* e_{1l}. \quad (5)$$

In the following we will always assign the field components in ascending order to the cartesian indices of \mathbf{R} from the right to the left, i.e. \mathbf{E}_1 to the last index, \mathbf{E}_2 to the next-to-last index, and so on. The corresponding time arguments of \mathbf{R} are ordered in the same fashion. Please note that this convention does not specify the time ordering of the light pulses. Thus in diagram I the time ordering is $\tau_1 \leq \tau_2$ but in diagram II it is $\tau_1 \geq \tau_2$.

The response functions for the generalized CARS and CSRS effects can be calculated from the diagrams in fig. 2. The method has been briefly discussed in ref. [3], and a detailed discussion will be given elsewhere [40]. Here it is sufficient to state the result:

$$R_{ijkl}^{\text{CARS}} = -i\beta_{ij}^* \alpha_{kl}^{\text{CARS}}(\Omega(t_3)) \exp[-(i\omega_{ab} + \Gamma_{ab})(t_3 - t_2)] \delta(t_2 - t_1) \delta(t - t_3), \quad (6)$$

$$R_{ijkl}^{\text{CSRS}} = i\beta_{ij} \alpha_{kl}^{\text{CSRS}}(\Omega(t_3)) \exp[-(i\omega_{ba} + \Gamma_{ab})(t_3 - t_2)] \delta(t_2 - t_1) \delta(t - t_3). \quad (7)$$

In this expression Γ_{ab} is the phase relaxation time (coherence decay time) for the Raman resonant level pair (ab) .

The polarizabilities α and β are:

$$\alpha_{ij}^{\text{CARS}} = \sum_k \left(\frac{\mu_{ak}^{(j)} \mu_{kb}^{(i)}}{\omega_{ak} + \omega_1 - i\Gamma_{ak}} + \frac{\mu_{ak}^{(i)} \mu_{kb}^{(j)}}{\omega_{ak} - \omega_2 - i\Gamma_{ak}} \right), \quad (8a)$$

$$\beta_{ij}^{\text{CARS}} = \sum_k \left(\frac{\mu_{ak}^{(i)} \mu_{kb}^{(j)}}{\omega_{ak} + \omega_4 + i\Gamma_{ak}} + \frac{\mu_{ak}^{(j)} \mu_{kb}^{(i)}}{\omega_{bk} - \omega_4 - i\Gamma_{bk}} \right), \quad (8b)$$

$$\alpha_{ij}^{\text{CSRS}} = \sum_k \left(\frac{\mu_{ak}^{(i)} \mu_{kb}^{(j)}}{\omega_{ak} + \omega_2 - i\Gamma_{ak}} + \frac{\mu_{ak}^{(j)} \mu_{kb}^{(i)}}{\omega_{ak} - \omega_1 - i\Gamma_{ak}} \right), \quad (8c)$$

$$\beta_{ij}^{\text{CSRS}} = \sum_k \left(\frac{\mu_{ak}^{(j)} \mu_{kb}^{(i)}}{\omega_{bk} + \omega_4 - i\Gamma_{bk}} + \frac{\mu_{ak}^{(i)} \mu_{kb}^{(j)}}{\omega_{ak} - \omega_4 + i\Gamma_{ak}} \right), \quad (8d)$$

where $\mu_{ak}^{(i)} = \langle a | \mu_i | k \rangle$ is the matrix element of the i th cartesian component of the molecular dipole operator between states $|a\rangle$ and $|k\rangle$. The polarizabilities α and β have been calculated considering all possible diagrams in the perturbation series that arise when the lower state $|a\rangle$ of the Raman transition $|a\rangle \rightarrow |b\rangle$ is populated. Fig. 2 shows only the leading diagram when the rotating wave approximation is applied for a molecule in its electronic ground state. Eqs. (8a)–(8d) also describe molecules in excited states. The arguments $\Omega(t_n)$ in eqs. (6) and (7) indicate the orientation of the molecule at time t_n . The components of the tensors α and β in the laboratory are then a function of time when the molecule rotates.

When all light frequencies are far off from any electronic resonance, the Γ -parameters in the denominators in eq. (8) can be neglected, leading to $\alpha^{\text{CARS}} = (\alpha^{\text{CSRS}})^t$ and $\beta^{\text{CARS}} = (\beta^{\text{CSRS}})^t$. When the levels $|a\rangle$ and $|b\rangle$ are both non-degenerate, the dipole matrix-elements are real, and with the neglect of the Γ -parameters the polarizabilities are real, too.

The response functions in eqs. (6) and (7) have the following meaning: The first two light pulses E_1 and E_2 generate a Raman coherence in the molecule through the polarizability α . Since no electronic resonance is involved, both pulses must arrive at the same time, $t_1 = t_2$. During the time interval between t_2 and t_3 , the Raman coherence will decay with $\exp[-\Gamma_{ab}(t_3 - t_2)]$. At time t_3 , the molecule has the new orientation $\Omega(t_3)$. The light pulse E_3 probes the molecule through the polarizability β in this new orientation, and the signal pulse is generated instantaneously ($t = t_3$) since no electronic resonance is involved in the probing process.

To this Raman resonant response a non-resonant response of the system is added which originates from the non-resonant third-order susceptibility χ^{NR} . The corresponding non-resonant response function is:

$$R_{ijkl}^{\text{NR}}(t, t_3, t_2, t_1) = \chi_{ijkl}^{\text{NR}} \delta(t - t_3) \delta(t_3 - t_2) \delta(t_2 - t_1). \quad (9)$$

This response will only contribute to the signal when all three light pulses overlap in the sample.

With the response function of eq. (6), the polarization for the CARS process takes the following form:

$$P(t) = -i[e_4^* \cdot \beta^*(\Omega(t)) \cdot e_3] \mathcal{E}_3(t - t_3) \exp(-\Gamma_{ab}t) \exp[i(\omega_3 + \omega_{ba})t] \\ \times \int_{-\infty}^t dt' [e_2^* \cdot \alpha(\Omega(t')) \cdot e_1] \mathcal{E}_1(t' - t_1) \mathcal{E}_2^*(t' - t_2) \exp[i(\omega_{ab} + \omega_1 - \omega_2 - i\Gamma_{ab})t']. \quad (10)$$

To obtain meaningful results in a time-domain experiment, the pulse-envelopes must be short compared to the decay time of the Raman coherence and the rotational relaxation time. Thus t' in $\alpha(\Omega(t'))$ and $\exp(\Gamma_{ab}t')$ can be replaced by τ_2 , and similarly t by τ_3 in $\beta^*(\Omega(t))$ and in $\exp(-\Gamma_{ab}t)$. On resonance we have also $\omega_{ab} + \omega_1 - \omega_2 = 0$. Hence eq. (10) can be written as

$$P(t) = -iS \exp[-\Gamma_{ab}(\tau_3 - \tau_2)] \mathcal{E}_3(t - \tau_3) \exp(i\omega_4 t) \langle \mathcal{E}_1 \mathcal{E}_2^* \rangle, \quad (11)$$

with

$$S = \{ [e_4^* \cdot \beta^*(\Omega(\tau_3)) \cdot e_3] [e_2^* \cdot \alpha(\Omega(\tau_2)) \cdot e_1] \}_{\text{av}}, \\ \langle \mathcal{E}_1 \mathcal{E}_2^* \rangle = \int dt' \mathcal{E}_1(t' - \tau_1) \mathcal{E}_2^*(t' - \tau_2). \quad (12)$$

The contribution of the non-resonant susceptibility is

$$P^{\text{NR}}(t) = S^{\text{NR}} \mathcal{E}_3(t - \tau_3) \mathcal{E}_2^*(t - \tau_2) \mathcal{E}_1(t - \tau_1) \exp(i\omega_4 t),$$

$$S^{\text{NR}} = \chi^{\text{NR}} : e_4^* e_3 e_2^* e_1. \quad (13)$$

The integrated intensity at the detector is finally

$$I_4 = G \int dt |P(t) + P^{\text{NR}}(t)|^2 = G \exp[-2\Gamma_{ab}(\tau_3 - \tau_2)] |S|^2 \langle \mathcal{E}_3 \mathcal{E}_3^* \rangle |\langle \mathcal{E}_1 \mathcal{E}_2^* \rangle|^2$$

$$+ G \exp[-\Gamma_{ab}(\tau_3 - \tau_2)] 2 \text{Im}(SS^{\text{NR}*} \langle \mathcal{E}_1 \mathcal{E}_2^* \rangle \langle \mathcal{E}_1 \mathcal{E}_2^* \mathcal{E}_3 \mathcal{E}_3^* \rangle) + G |S^{\text{NR}}|^2 \langle \mathcal{E}_1 \mathcal{E}_1^* \mathcal{E}_2 \mathcal{E}_2^* \mathcal{E}_3 \mathcal{E}_3^* \rangle, \quad (14)$$

where $\langle \dots \rangle$ indicates a total time integral as in eq. (12). For time intervals $\tau_3 - \tau_2$ larger than the pulse duration the non-resonant term S^{NR} will not contribute, and the decay of the signal as a function of the delay $\tau_3 - \tau_2$ contains two components: It decays exponentially with twice the decay constant Γ_{ab} of the Raman coherence. And it decays through rotational relaxation of the molecules contained in the term S defined in eq. (12).

3. The orientational average

The expression that we wish to average is of the form

$$S = [(\mathbf{X} \cdot \mathbf{A})(\mathbf{Y} \cdot \mathbf{B})]_{\text{av}}, \quad (15)$$

where \mathbf{X} and \mathbf{Y} are molecular tensors and \mathbf{A} and \mathbf{B} are laboratory tensors. By $(\mathbf{X} \cdot \mathbf{A})$ we denote a scalar product (or projection) of two tensors of the same rank which in cartesian coordinates is given by

$$\mathbf{X} \cdot \mathbf{A} = \sum_{ijk \dots} X_{ijk} \dots A_{ijk} \dots. \quad (16)$$

The components of both tensors must be expressed in the same reference frame, which we take to be the laboratory frame. In this frame the laboratory tensors (\mathbf{A} , \mathbf{B}) have fixed components given by a particular choice of experimental conditions. In our case this corresponds to a particular choice of directions for the polarization vectors e_1 , e_2 , e_3 , and e_4 .

The molecular tensors (\mathbf{X} , \mathbf{Y}) are attached to a molecular frame in which they have fixed components. Their components in the laboratory frame depend on the orientation of the molecule. In cartesian coordinates,

$$X_{ijk} \dots = \sum_{i'j'k' \dots} X_{i'j'k' \dots} R_{ii'} R_{jj'} R_{kk'} \dots, \quad (17)$$

where the unprimed indices refer to the laboratory frame (L-frame), the primed indices to the molecular frame (X-frame), and the $R_{ii'}$ are the direction cosines.

It is much more convenient to express the tensors in the spherical tensor notation [41,42] in which each tensor component is characterized by two indices, l and m . These tensor components transform under rotation like the corresponding spherical harmonics. In this basis the scalar product $\mathbf{X} \cdot \mathbf{A}$ is given by (Edmonds [42], eq. 5.2.4):

$$\mathbf{X} \cdot \mathbf{A} = \sum_l \sum_{m=-l}^l X_m^l (-1)^m A_{-m}^l = \sum_l (\mathbf{XA})_l. \quad (18)$$

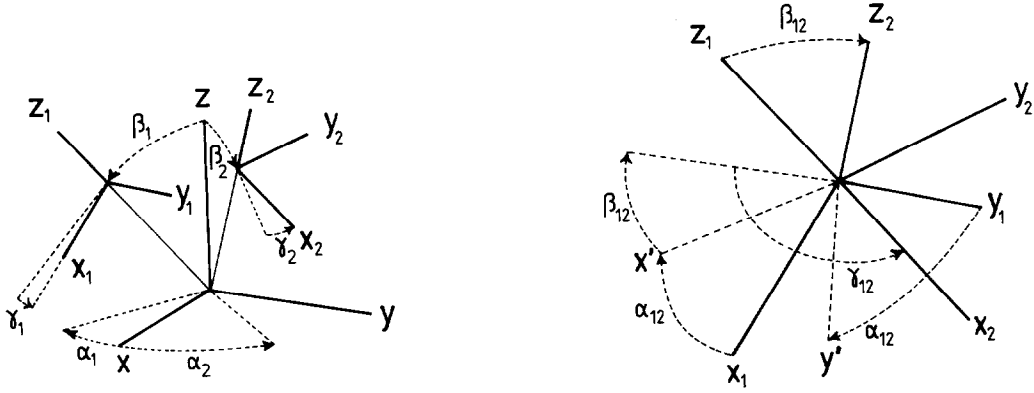


Fig. 3. Left part: Two orientations of the molecular coordinate frame $x_1y_1z_1$ and $x_2y_2z_2$ with respect to the laboratory frame xyz characterized through Euler angles $\Omega_1 = (\alpha_1, \beta_1, \gamma_1)$ and $\Omega_2 = (\alpha_2, \beta_2, \gamma_2)$. Right part: The rotation $\Omega_{12} = (\alpha_{12}, \beta_{12}, \gamma_{12})$ that relates the two orientations of the molecule within the molecular frame, i.e. $\Omega_2 = \Omega_1 + \Omega_{12}$. In the example shown, $\Omega_1 = (-25^\circ, 40^\circ, 10^\circ)$, $\Omega_2 = (50^\circ, 30^\circ, 20^\circ)$, and $\Omega_{12} = (-56.5^\circ, -41.7^\circ, 131.1^\circ)$.

The orientation of the molecule is characterized by the set of Euler angles $\Omega_{LX} = (\alpha_{LX}, \beta_{LX}, \gamma_{LX})$ that rotate the L-frame into the X-frame, as shown in fig. 3.

The components $X_m^l(\Omega)$ of the tensor \mathbf{X} of this molecule in the L-frame are then expressed in terms of the components $X_k^l(0)$ of this tensor in the X-frame as

$$X_m^l(\Omega_{LX}) = \sum_{k=-l}^l X_k^l(0) D_{km}^{(l)}(\Omega_{LX}). \quad (19)$$

The matrix elements of the Wigner rotation matrices are

$$D_{km}^{(l)}(\alpha\beta\gamma) = e^{ik\gamma} d_{km}^{(l)}(\beta) e^{im\alpha}. \quad (20)$$

(For a discussion of rotation operators and phase-conventions see refs. [41,43].)

With the help of eqs. (18) and (19), the average in eq. (15) can be written as

$$S = \sum_{lkm} \sum_{l'k'm'} A_m^l (-1)^{-m} X_{-k}^l B_{-m'}^{l'} (-1)^{m'} Y_{k'}^{l'} \left\langle D_{km}^{(l)*}(\Omega_{LX}) D_{k'm'}^{(l')}(\Omega_{LY}) \right\rangle. \quad (21)$$

In this expression the components of \mathbf{A} and \mathbf{B} refer to the laboratory frame, whereas the components of \mathbf{X} and \mathbf{Y} refer to the X-frame and the Y-frame, respectively. The rotational correlation functions are defined [44] as

$$\langle f(\Omega') g(\Omega) \rangle = \int \int d\Omega' d\Omega f(\Omega') g(\Omega) p(\Omega't | \Omega 0) p_0(\Omega), \quad (22)$$

where $p_0(\Omega)$ is the initial probability distribution function for the molecular orientations. $p(\Omega't | \Omega 0)$ is the probability of finding a molecule with orientation Ω' at time t when it had orientation Ω at time $t = 0$. In isotropic media the correlation function in eq. (21) is independent of m and vanishes for $m \neq m'$ or $l \neq l'$ (see appendix A). Thus eq. (21) reduces to

$$S = \sum_l \frac{1}{2l+1} P_l M_l, \quad (23)$$

where

$$M_l = [\mathbf{XY}]_l = \sum_{kk'} Y_{k'}^l (-1)^k X_{-k}^l (2l+1) \langle D_{k0}^{(l)*}(\Omega_{LX}) D_{k'0}^{(l)}(\Omega_{LY}) \rangle, \quad P_l = (\mathbf{AB})_l. \quad (24)$$

P_l is the product of the two laboratory tensors \mathbf{A}^l and \mathbf{B}^l as defined in eq. (18). Thus the averaging separates the molecular tensors from the laboratory tensors: The P_l depend only on the experimental setup, i.e. on the setting of the polarizers, and are hence called polarization factors in the following discussions. The scalar quantities M_l depend only on the molecular tensor components and the molecular rotational dynamics. These rotational relaxation functions are discussed in section 4.2. In the special case that the molecules do not rotate, $[\mathbf{XY}]_l$ reduces to $(\mathbf{XY})_l$ (see eq. (A.13)) and the orientational average of eq. (23) becomes symmetric in the molecular and laboratory tensors:

$$S = \sum_l (\mathbf{AB})_l \frac{1}{2l+1} (\mathbf{XY})_l. \quad (25)$$

4. Discussion

To apply the results of the previous section to the CARS problem we have to identify the tensors \mathbf{A} , \mathbf{B} , \mathbf{X} , and \mathbf{Y} as:

$$\mathbf{A} = \mathbf{e}_4^* \otimes \mathbf{e}_3, \quad \mathbf{B} = \mathbf{e}_1 \otimes \mathbf{e}_2^*, \quad \mathbf{X} = \beta^* \text{CARS}, \quad \mathbf{Y} = \alpha \text{CARS}. \quad (26)$$

For CSRS the same \mathbf{A} and \mathbf{B} apply, but $\mathbf{X} = \beta^* \text{CSRS}$ and $\mathbf{Y} = \alpha^* \text{CSRS}$. In the following we use the short-hand notation β^* and α .

The tensors \mathbf{A} , \mathbf{B} , \mathbf{X} , and \mathbf{Y} are all of rank 2, leading to three polarization parameters $P_l = ((\mathbf{e}_4^* \otimes \mathbf{e}_3)(\mathbf{e}_2^* \otimes \mathbf{e}_1))_l$ and three molecular relaxation functions $M_l = [\beta^* \alpha]_l$ with $l = 0, 1, 2$:

$$S = \sum_{l=0}^2 (2l+1)^{-1} P_l [\beta^* \alpha]_l. \quad (27)$$

The non-resonant term S^{NR} can also be written as a sum with the same polarization factors P_l (see appendix B):

$$S^{\text{NR}} = \sum_{l=0}^2 (2l+1)^{-1} P_l \chi_l^{\text{NR}}. \quad (28)$$

Consequently, with three linearly independent combinations of polarization vectors, a maximum of three molecular relaxation functions $[\beta^* \alpha]_l$ can be measured.

4.1. The polarization factors

The explicit form of the polarization factors P_l in terms of the four polarization vectors is (see appendix B):

$$P_0 = \frac{1}{3} (\mathbf{e}_1 \cdot \mathbf{e}_2^*) (\mathbf{e}_3 \cdot \mathbf{e}_4^*), \quad (29a)$$

$$P_1 = \frac{1}{2} (\mathbf{e}_1 \times \mathbf{e}_2^*) \cdot (\mathbf{e}_3 \times \mathbf{e}_4^*), \quad (29b)$$

$$P_2 = \frac{1}{2} (\mathbf{e}_1 \cdot \mathbf{e}_4^*) (\mathbf{e}_2^* \cdot \mathbf{e}_3) + \frac{1}{2} (\mathbf{e}_1 \cdot \mathbf{e}_3) (\mathbf{e}_2^* \cdot \mathbf{e}_4^*) - \frac{1}{3} (\mathbf{e}_1 \cdot \mathbf{e}_2^*) (\mathbf{e}_3 \cdot \mathbf{e}_4^*). \quad (29c)$$

Table 1

Values of the polarization parameters P_0 , P_1 , and P_2 for several combinations of polarizers e_1 , e_2 , e_3 , and e_4 . For discussion see text

	e_1	e_2	e_3	e_4	P_0	P_1	P_2	
1	↑	↑	↑	↑	1/3	0	2/3	
2	↑	→	↑	→	0	1/2	1/2	
3	↑	↑	→	→	1/3	0	-1/3	
4	↑	↑	↗ φ	↗ φ	1/3	0	$\cos^2\varphi - 1/3$	$\varphi_{\text{opt}} = 54.7^\circ$
5	↑	→	↗ φ	↗ φ	0	0	$\sin(2\varphi)/2$	$\varphi_{\text{opt}} = 45^\circ$
6	↑	→	↗ φ	↘ φ	0	1/2	$\cos(2\varphi)/2$	$\varphi_{\text{opt}} = 45^\circ$

The following symmetry properties of the P_i can be verified:

(i) All P_i are invariant against an exchange of the pair of excitation polarizers (e_1 , e_2^*) against the pair of probing polarizers (e_3 , e_4^*).

(ii) An exchange of the two probing polarizers, $e_3 \leftrightarrow e_4^*$, leaves P_0 and P_2 unchanged but reverses the sign of P_1 .

(iii) An exchange of the two excitation polarizers also leaves P_0 and P_2 unchanged but reverses the sign of P_1 .

Table 1 gives values for the P_i for various combinations of polarizations. All polarizers are assumed to produce linearly polarized light with all polarization directions lying in the same plane. This corresponds to the situation of copropagating or nearly copropagating beams most frequently used. Eqs. (29a)–(29c) are, of course, applicable for elliptically polarized light as well as for any angles between the four beams. Such situations might appear in large-angle scattering geometries [46] or in transient grating experiments employing Raman resonances. Cases 1, 2, and 3 are the setups commonly used: In case 1 all polarizations are parallel. In case 2, e_1 and e_3 are parallel, and e_2 and e_4 are both perpendicular to e_1 . This is easily achieved in CARS experiments where the fields \mathcal{E}_1 and \mathcal{E}_3 are derived from the same laser. In case 3 the two excitation polarizations are parallel and both probing polarizations are perpendicular to the excitation–polarization direction. In all three cases two of the P_i are non-vanishing, and thus two molecular rotational relaxation functions contribute to the signal. Since the signal is the absolute square of the sum of these contributions, interference terms arise that lead to further complication in the analysis of the data. Hence one would prefer setups of the polarizers that single out a particular molecular rotational relaxation function M_i through letting all P_i but one vanish. This is accomplished by the polarizer settings shown in cases 4, 5, and 6. In case 4 the pair of excitation polarizers are parallel, as well as the pair of probing polarizers. The polarization axes of both groups form an angle φ . Then $P_1 = 0$ since $e_1 \parallel e_2$. Furthermore, $P_2 = \cos^2\varphi - 1/3$ will vanish for $\varphi = 54.7^\circ$, the well-known magic angle of polarized fluorescence spectroscopy. An experiment with $\varphi = 54.7^\circ$ will thus single out the rotational relaxation function M_0 . As will be shown in the following, M_0 is the isotropic part of the molecular response and hence not time dependent. An experiment with polarizer settings according to case 4 and $\varphi = 54.7^\circ$ measures the pure vibrational relaxation of the molecule. This should be very useful in temperature-dependent experiments since it allows us to separate the temperature dependence of the vibrational relaxation (pure dephasing) from the viscosity and temperature dependence of the rotational diffusion.

Case 5 is similar to case 4 in that both probing polarizations are inclined with respect to e_1 by an angle φ . However, e_2 is now perpendicular to e_1 with the result that $P_0 = 0$. Since e_3 and e_4 are parallel, P_1 also

vanishes. $P_2 = \sin(2\varphi)/2$ will not vanish unless $\varphi = 0$ or $\varphi = 90^\circ$. The maximum signal is expected for $\varphi = 45^\circ$. Such an experiment will hence measure the rotational relaxation function M_2 . It has been argued previously that no CARS signal can be obtained from an isotropic sample when $\mathbf{e}_1 \perp \mathbf{e}_2$ and $\mathbf{e}_3 \parallel \mathbf{e}_4$ [20]. However, in this case it was implicitly assumed that $\varphi = 0$, i.e. $\mathbf{e}_1 \parallel \mathbf{e}_3 \parallel \mathbf{e}_4 \perp \mathbf{e}_2$.

Case 6 shows an arrangement which permits the measurement of the rotational relaxation function M_1 . It is similar to case 2 in that $\mathbf{e}_1 \perp \mathbf{e}_2$ and $\mathbf{e}_3 \perp \mathbf{e}_4$. However, \mathbf{e}_1 and \mathbf{e}_3 are not parallel but form an angle φ . Thus $P_2 = \cos(2\varphi)/2$ can be made to vanish for $\varphi = 45^\circ$.

4.2. The rotational relaxation functions

We now turn to the discussion of the rotational relaxation functions M_l :

$$M_l = \sum_{kk'} (-1)^k (2l+1) \alpha_k^l \beta_k^l \langle D_{k0}^{(l)*}(\Omega_{L\beta}) D_{k'0}^{(l)}(\Omega_{L\alpha}) \rangle. \quad (30)$$

They depend on the transition polarizabilities α and β of the Raman mode involved in the CARS or CSRS process. A particular choice of symmetry for this Raman mode will select particular tensor components and hence particular indices k and k' for the rotational correlation functions $\langle D_{k0}^{(l)*} D_{k'0}^{(l)} \rangle$. These rotational correlation functions depend on the characteristics of the molecular motion. In the context of fluorescence depolarization several models have been considered, including restricted motion (e.g. within a cone) or jumps between discrete positions [44] ^{*}. Here we will only discuss few examples: With respect to the model for molecular motion we discuss the model of a freely rotating rigid molecule. With respect to the polarizabilities we discuss the case that all light fields involved are far off any electronic resonance. The isotropic relaxation function M_0 can directly be calculated without assumptions and is discussed separately.

4.2.1. The isotropic relaxation function M_0

The term M_0 can be calculated directly since $D_{00}^{(0)} = 1$:

$$M_0 = \alpha_0^0 \beta_0^0 = \frac{1}{3} \text{Tr}(\alpha) \text{Tr}(\beta). \quad (31)$$

M_0 is time independent and unaffected by the rotational motion of the molecule. An experiment with the polarizers set as in case 4, table 1, will measure only M_0 and hence the pure vibrational dephasing of the corresponding Raman transition. Completely depolarized Raman transitions have $\text{Tr}(\alpha) = 0$ and will not appear for this polarizer arrangement. This fact can be used in frequency-domain CARS and CSRS experiments to simplify the spectra: In the polarization case 4 of table 1 all transitions with traceless Raman polarizabilities are eliminated from the spectra, e.g., all b_g modes for a molecule with an A_g electronic ground state. The tensor patterns for two-photon transition polarizabilities have been tabulated for all molecular point groups [47]. The same tensor patterns apply to Raman polarizabilities, and the vibrational symmetries with traceless tensors are easily identified.

4.2.2. Non-resonance-enhanced CARS

When all laser frequencies employed in the CARS or CSRS experiment are far off any electronic resonance, the polarizabilities are all real, symmetric, and equal:

$$\alpha^{\text{CARS}} = \beta^{\text{CARS}} = \alpha^{\text{CSRS}} = \beta^{\text{CSRS}} = : \alpha. \quad (32)$$

^{*} The author of ref. [44] uses an alternative convention for rotation operators according to ref. [45]. Our $D_{mn}^{(l)}(\alpha, \beta, \gamma)$ is $D_{mn}^{(l)}(-\gamma, -\beta, -\alpha)$ in his notation.

Then the molecular α -frame and β -frame are identical and eq. (A.12) can be applied with the result

$$M_l = \sum_{kk'} (-1)^k \alpha_k^l \alpha_{-k}^l \langle D_{kk'}^{(l)*}(\tilde{\Omega}) \rangle, \quad (33)$$

where $\tilde{\Omega} = (\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma})$ is the Euler angle of the rotation of the molecular α -frame during the time interval between the pair of excitation light pulses and the probing light pulse.

Since the transition polarizability tensor α is symmetric the antisymmetric contribution α^1 vanishes and hence also M_1 . Thus the polarizer setup of case 6 in table 1 will suppress all non-resonance-enhanced CARS transitions. In a frequency-domain experiment this effect could be used to suppress strong solvent lines in the resonance CARS spectra of dilute samples. (In fact, in frequency-domain CARS experiments this polarization scheme is known as the ASTERISK-configuration [32]. It has been introduced for the elimination of non-resonant background signals, since $\chi_1^{\text{NR}} = 3(\chi_{1221}^{\text{NR}} - \chi_{1212}^{\text{NR}})$ vanishes when Kleinman symmetry [48,49] applies.)

The explicit form of M_2 depends on the symmetry of the α -tensor. When one cartesian component, say α_{zz} , is dominant, the only contribution is

$$M_2 = \frac{2}{3} \alpha_{zz}^2 \langle D_{00}^{(2)}(\tilde{\Omega}) \rangle = \frac{2}{3} \alpha_{zz}^2 \langle P_2(\cos \tilde{\beta}) \rangle, \quad (34)$$

where $P_2(x)$ is the second Legendre polynomial. For b_g vibrations two cartesian components will be non-vanishing, e.g. $\alpha_{xz} = \alpha_{zx}$. In the irreducible tensor representation the non-vanishing terms are $\alpha_1^2 = -\alpha_{-1}^2 = -\alpha_{xz}$, leading to:

$$M_2 = 2\alpha_{xz}^2 \text{Re} \left[\langle D_{11}^{(2)}(\tilde{\Omega}) \rangle + \langle D_{1-1}^{(2)}(\tilde{\Omega}) \rangle \right]. \quad (35)$$

In the general case the polarizability tensor α has three independent components α_{xx} , α_{yy} , α_{zz} when the molecular frame is taken to be the main axis frame of α . Then

$$\alpha_0^2 = -(\alpha_{xx} + \alpha_{yy} - 2\alpha_{zz})/6^{1/2}, \quad \alpha_2^2 = \alpha_{-2}^2 = (\alpha_{xx} - \alpha_{yy})/2, \quad (36)$$

and

$$M_2 = (\alpha_0^2)^2 \langle D_{00}^{(2)}(\tilde{\Omega}) \rangle + 2(\alpha_0^2 \alpha_2^2) \text{Re} \langle D_{20}^{(2)}(\tilde{\Omega}) + D_{02}^{(2)}(\tilde{\Omega}) \rangle + 2(\alpha_2^2)^2 \text{Re} \langle D_{22}^{(2)}(\tilde{\Omega}) + D_{2-2}^{(2)}(\tilde{\Omega}) \rangle. \quad (37)$$

For totally symmetric vibrations in molecules having a threefold or higher axis, $\alpha_{xx} = \alpha_{yy}$ [47] and only the first term remains.

4.2.3. Free rotational diffusion

The theory of the rotational brownian motion of a rigid molecule has been treated by Favro in detail [50]. The probability $p(\Omega, t)$ that the molecule will rotate by the Euler angle Ω within a time interval t is found as the solution of the differential equation

$$\dot{p}(\Omega, t) = - \sum_{jk} \hat{M}_j D_{jk} \hat{M}_k p(\Omega, t). \quad (38)$$

In this expression D_{jk} is a diffusion tensor, and \hat{M}_j is the component of the angular momentum operator along the molecular axis j . The solution to eq. (38) can be written in the form

$$p(\Omega, t) = \sum_q \varphi_q^*(0) \varphi_q(\Omega) \exp(-E_q t), \quad (39)$$

where the φ_q are the complete set of eigenfunctions of the operator $\sum_{jk} \hat{M}_j D_{jk} \hat{M}_k$, and the E_q are the corresponding eigenvalues. The problem is equivalent to the rigid rotator problem and is conveniently solved in the molecular coordinate system in which D_{jk} is diagonal. For a symmetric rotator ($D_1 = D_2 \neq D_3$) the eigenfunctions are the Wigner matrices, and the result is

$$p(\Omega, t) = \sum_{lm} \left(\frac{2l+1}{8\pi^2} \right) D_{mm}^{(l)}(\Omega) \exp\left\{-[l(l+1)D_1 + m^2(D_3 - D_1)]t\right\}. \quad (40)$$

Hence

$$\langle D_{mn}^{(l)}(\Omega) \rangle = \delta_{mn} \exp\left[-[l(l+1)D_1 + m^2(D_3 - D_1)]t\right]. \quad (41)$$

The rotational relaxation function M_2 can contain three exponential decays with $m = 0, 1, 2$. Through the choice of a mode with suitable symmetry a particular component can be selected. As we have seen above, a totally symmetric mode in a molecule with a threefold or higher axis will only contribute a term with $m = 0$. In the situation discussed in eq. (35) only the term with $m = 1$ arises, provided that the molecule is rotationally symmetric around the z -axis.

When the molecule is not rotationally symmetric, the eigenfunctions φ_q are linear combinations of the $D_{mn}^{(l)}$ for different m and n . $2l+1$ different eigenvalues arise [51–53], and in the most general case the rotational relaxation function M_2 is a superposition of five exponentials.

5. Summary

The theory of time-resolved four-wave mixing employing Raman resonances of molecules in liquids has been developed for arbitrary polarization of the three ingoing light pulses and the generated light pulse. The ensemble average of the molecular response is of the form $P_0 M_0 + P_1 M_1 + P_2 M_2$. The polarization factors P_i are scalar quantities depending only on the relative orientation of the four polarization vectors. Particular polarizer arrangements are proposed for which always two of the three P_i vanish thus permitting an independent measurement of the molecular relaxation function M_i associated with the third polarization factor.

The molecular relaxation functions M_i contain rotational correlation functions and tensor components of the transition polarizability tensor α of the Raman transition involved in the CARS or CSRS process: The trace of α contributes to M_0 , the antisymmetric part to M_1 , and the symmetric traceless part to M_2 . M_0 is independent of the rotational motion of the molecule, and an experiment with the corresponding polarizer setup ($P_1 = P_2 = 0$, $P_0 \neq 0$) measures solely the vibrational dephasing of the Raman resonance of interest.

The three polarizer setups mentioned above have also applications in steady-state frequency-domain experiments. When P_0 is the only non-vanishing polarization factor (case 4 of table 1), Raman resonances with traceless transition polarizabilities will not appear in the CARS spectrum. E.g., all b_g vibrations of centrosymmetric molecules will be suppressed. The polarizer arrangement with P_1 as the only non-vanishing polarization factor will suppress all Raman modes with symmetric transition polarizability α (case 6 of table 1). This effect can be used to suppress strong solvent lines in resonance-enhanced CARS spectra. Finally, the linewidths of the CARS-resonances will be different for various polarizer arrangements: with $P_0 \neq 0$, $P_1 = P_2 = 0$ (case 4 of table 1) the linewidth 2Γ will be twice the inverse of the phase-relaxation time T_2 . For other polarizer arrangements the lineshape of the resonance will be the Fourier transform of the corresponding M_i convoluted with a lorentzian of width $2\Gamma = 2/T_2$. When the rotational correlation function is dominated by a single-exponential decay with rotational decay time T_R , the resulting lineshape will again be lorentzian with a width of $2\Gamma = 2/T_2 + 2/T_R$.

Appendix A

This appendix discusses a few properties of the rotational correlation function

$$K_{mnm'n'}^{ll'} = \left\langle D_{mn}^{(l)*}(\Omega_{\text{LX}}) D_{m'n'}^{(l')}(\Omega_{\text{LY}}) \right\rangle. \quad (\text{A.1})$$

For an isotropic system this correlation function must be independent of the choice of the laboratory reference frame. Thus in an other laboratory $\tilde{\text{L}}$ -frame the orientation of the molecule is given by

$$\Omega_{\tilde{\text{LX}}} = \Omega_{\tilde{\text{LL}}} + \Omega_{\text{LX}}, \quad \Omega_{\tilde{\text{LY}}}^0 = \Omega_{\tilde{\text{LL}}} + \Omega_{\text{LY}}^0. \quad (\text{A.2})$$

The plus sign in eq. (A.2) indicates that the rotations are performed successively in the order from the left to the right. The Euler angle $\Omega_{\tilde{\text{LL}}}$ rotates the $\tilde{\text{L}}$ -frame into the L-frame and is independent of time. The Wigner rotation matrices in the new frame are (eq. (4.6.5a) in ref. [42]):

$$D_{mn}^{(l)}(\Omega_{\tilde{\text{LX}}}) = \sum_k D_{mk}^{(l)}(\Omega_{\text{LX}}) D_{kn}^{(l)}(\Omega_{\tilde{\text{LL}}}). \quad (\text{A.3})$$

Thus the rotational correlation function in the $\tilde{\text{L}}$ -frame is

$$\begin{aligned} \tilde{K}_{mnm'n'}^{ll'} &= \sum_{kk'} \left\langle D_{mk}^{(l)*}(\Omega_{\text{LX}}) D_{m'k'}^{(l')}(\Omega_{\text{LY}}^0) \right\rangle D_{kn}^{(l)*}(\Omega_{\tilde{\text{LL}}}) D_{k'n'}^{(l')}(\Omega_{\tilde{\text{LL}}}) \\ &= \sum_{kk'} K_{mkm'k'}^{ll'} D_{kn}^{(l)*}(\Omega_{\tilde{\text{LL}}}) D_{k'n'}^{(l')}(\Omega_{\tilde{\text{LL}}}). \end{aligned} \quad (\text{A.4})$$

Integrating both sides with $d\Omega_{\tilde{\text{LL}}}/8\pi^2$ yields due to the orthogonality of the Wigner matrices

$$K_{mnm'n'}^{ll'} = \sum_{kk'} K_{mkm'k'}^{ll'} (2l+1)^{-1} \delta_{ll'} \delta_{nn'} \delta_{kk'}. \quad (\text{A.5})$$

This yields the conditions $l = l'$ and $n = n'$. For the non-vanishing terms we find the further condition

$$K_{mnm'n}^{ll} = \sum_k K_{mkm'k}^{ll} (2l+1)^{-1}. \quad (\text{A.6})$$

The rhs of eq. (A.6) does not depend on n . Therefore, the $2l+1$ rotational correlation functions for all values of k must be equal and it is sufficient to evaluate the term for $k = 0$. Thus we have the final result for an isotropic system

$$\left\langle D_{mn}^{(l)*}(\Omega_{\text{LX}}) D_{m'n'}^{(l')}(\Omega_{\text{LY}}^0) \right\rangle = \delta_{ll'} \delta_{nn'} \left\langle D_{m0}^{(l)*}(\Omega_{\text{LX}}) D_{m'0}^{(l)}(\Omega_{\text{LY}}^0) \right\rangle. \quad (\text{A.7})$$

So far we have not made any restriction on the molecular reference frames. Especially did we not assume that the orientation of the X-frame with respect to the Y-frame is constant in time. For example, the X-frame and the Y-frame could refer to different regions of a macromolecule that can move with respect to each others within certain limits.

If we make the restriction that the X-frame and the Y-frame are fixed with respect to each others for all times we can write

$$\Omega_{\text{LX}}(t) = \Omega_{\text{LY}}(0) + \Omega_{\text{YY}}(t) + \Omega_{\text{YX}}^0. \quad (\text{A.8})$$

where $\Omega_{YY}(t)$ gives the rotation of the Y-frame from its orientation at time $t = 0$ to its orientation at some later time t . With the help of the addition theorem [eq. (A.3)] we obtain

$$\begin{aligned} K_{mnm'n'}^{ll'} &= \int \int d\Omega_{LX} d\Omega_{LY}^0 D_{mn}^{(l)*}(\Omega_{LX}) D_{m'n'}^{(l')*}(\Omega_{LY}^0) p(\Omega_{LX}t | \Omega_{LY}^0 0) p_0(\Omega_{LY}^0) \\ &= \sum_{kk'} \int d\Omega_{LY}^0 (8\pi^2)^{-1} D_{kn}^{(l)*}(\Omega_{LY}^0) D_{m'n'}^{(l')*}(\Omega_{LY}^0) \\ &\quad \times \int d\Omega_{YY} D_{kk'}^{(l)*}(\Omega_{YY}) p(\Omega_{YY}t | 00) D_{mk}^{(l)*}(\Omega_{YX}^0). \end{aligned} \quad (A.9)$$

Here we have used the isotropic properties of the system, $p_0(\Omega) = 1/8\pi^2$, and

$$p(\Omega_{LX}t | \Omega_{LY}^0 0) = p(\Omega_{YY}t | 00). \quad (A.10)$$

Thus the integration in eq. (A.9) leads to

$$K_{mnm'n'}^{ll'} = \frac{\delta_{nn'}\delta_{ll'}}{2l+1} \sum_k D_{mk}^{(l)*}(\Omega_{YX}^0) \langle D_{km}^{(l)*}(\Omega_{YY}) \rangle. \quad (A.11)$$

A special case exists when the X-frame and the Y-frame are identical at all times. Then $\Omega_{YX}^0 = 0$ and $D_{mk}^{(l)}(0) = \delta_{mk}$ leading to

$$K_{mnm'n'}^{ll'} = (2l+1)^{-1} \delta_{nn'} \delta_{ll'} \langle D_{mm}^{(l)*}(\Omega_{YY}) \rangle. \quad (A.12)$$

When the molecules do not rotate at all, the probability distribution $p(\tilde{\Omega}t | 00)$ reduces to $\delta(\tilde{\Omega})$, and eq. (A.12) becomes:

$$K_{mnm'n'}^{ll'} = (2l+1)^{-1} \delta_{ll'} \delta_{mm'} \delta_{nn'}. \quad (A.13)$$

It is sometimes convenient to measure the rotational motion of a molecule with respect to another molecule-fixed P-frame. This P-frame can be chosen to reflect certain symmetry properties of the molecule, whereas the X-frame and the Y-frame define the components of the corresponding molecular tensor. A rotation Ω_{PP} of the P-frame

$$\Omega_{LP}(t) = \Omega_{LP}^0 + \Omega_{PP}(t), \quad (A.14)$$

is related to the rotation $\Omega_{YY}(t)$ of the Y-frame for the same movement of the molecule by:

$$\Omega_{YY}(t) = \Omega_{YP} + \Omega_{PP}(t) + \Omega_{PY}, \quad (A.15)$$

where Ω_{PY} and its inverse Ω_{YP} are independent of time. This allows us to express the rotational correlation functions with $\Omega_{YY}(t)$ as an argument in terms of those with $\Omega_{PP}(t)$ as an argument. When the molecules are rotationally symmetric around the z-axis of the P-frame, we obtain

$$\langle D_{mn}^{(l)}(\Omega_{PP}) \rangle = \delta_{mn} \langle D_{mm}^{(l)}(\Omega_{PP}) \rangle, \quad (A.16)$$

from the condition that the rotational correlation function must be invariant to the choice of a different P'-frame with $\Omega_{PP'} = (0, 0, \gamma)$.

Appendix B

In this article we make extensive use of the irreducible spherical tensor basis for the representation of molecular and laboratory tensors. However, the “natural” coordinate system of the experiment is cartesian. Therefore, we will give here the transformation between both systems for tensors of rank 1 and 2. These allow us to calculate the rotational invariants directly from the cartesian 3×3 matrices.

For a vector \mathbf{a} the relations between its cartesian coordinates (a_x, a_y, a_z) and its spherical coordinates (a_1^1, a_0^1, a_{-1}^1) are:

$$a_0^1 = a_z, \quad a_1^1 = -(a_x + i a_y)/\sqrt{2}, \quad a_{-1}^1 = (a_x - i a_y)/\sqrt{2}. \quad (\text{B.1})$$

Tensors of higher rank can be transformed to the spherical coordinate basis applying the transformation (B.1) to all cartesian indices. From these reducible representations the irreducible tensors are calculated with the help of the vector coupling techniques for angular momenta.

For tensors of rank 2 three irreducible tensors are found with $l = 0, 1, 2$. The cartesian and the irreducible representation are related by the unitary transformation:

$$\begin{pmatrix} A_0^0 \\ A_0^1 \\ A_0^2 \\ A_2^2 \\ A_{-2}^2 \end{pmatrix} = \begin{pmatrix} -1/\sqrt{3} & -1/\sqrt{3} & -1/\sqrt{3} & 0 & 0 \\ 0 & 0 & 0 & i\sqrt{2} & -i/\sqrt{2} \\ -1/\sqrt{6} & -1/\sqrt{6} & \sqrt{2/3} & 0 & 0 \\ 1/2 & -1/2 & 0 & i/2 & i/2 \\ 1/2 & -1/2 & 0 & -i/2 & -i/2 \end{pmatrix} \begin{pmatrix} A_{xx} \\ A_{yy} \\ A_{zz} \\ A_{xy} \\ A_{yx} \end{pmatrix},$$

$$\begin{pmatrix} A_1^1 \\ A_{-1}^1 \\ A_1^2 \\ A_{-1}^2 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} -i & i & 1 & -1 \\ i & -i & 1 & -1 \\ -i & -i & -1 & -1 \\ -i & -i & -1 & 1 \end{pmatrix} \begin{pmatrix} A_{yz} \\ A_{zy} \\ A_{zx} \\ A_{xz} \end{pmatrix}. \quad (\text{B.2})$$

With these coefficients it is a straightforward task to calculate the rotational invariants $(\mathbf{AB})_l$ for two tensors of rank 2. The result is

$$(\mathbf{AB})_0 = \frac{1}{3} \sum_{ij} A_{ii} B_{jj} = \frac{1}{3} \text{Tr}(\mathbf{A}) \text{Tr}(\mathbf{B}), \quad (\text{B.3a})$$

$$(\mathbf{AB})_1 = \sum_{ij} A_{ij}^a B_{ji}^a = \text{Tr}(\mathbf{A}^a \mathbf{B}^a), \quad (\text{B.3b})$$

$$(\mathbf{AB})_2 = \sum_{ij} A_{ij}^s B_{ji}^s = \text{Tr}(\mathbf{A}^s \mathbf{B}^s), \quad (\text{B.3c})$$

where the components of the asymmetric matrix \mathbf{A}^a and the symmetric traceless matrix \mathbf{A}^s are

$$A_{ij}^a = \frac{1}{2}(A_{ij} - A_{ji}), \quad A_{ij}^s = \frac{1}{2}(A_{ij} + A_{ji}) - \frac{1}{3} \text{Tr}(\mathbf{A}) \delta_{ij}. \quad (\text{B.4})$$

A special case is given when \mathbf{A} and \mathbf{B} are each the tensorial product of two vectors, $\mathbf{A} = \mathbf{a} \otimes \mathbf{b}$ and $\mathbf{B} = \mathbf{c} \otimes \mathbf{d}$. Then their cartesian components are:

$$A_{ij} = a_i b_j; \quad B_{ij} = c_i d_j, \quad (\text{B.5})$$

and the invariants are found to be:

$$(\mathbf{AB})_0 = \frac{1}{3}(\mathbf{a} \cdot \mathbf{b})(\mathbf{c} \cdot \mathbf{d}), \quad (\text{B.6a})$$

$$(\mathbf{AB})_1 = \frac{1}{2}(\mathbf{a} \times \mathbf{b}) \cdot (\mathbf{d} \times \mathbf{c}), \quad (\text{B.6b})$$

$$(\mathbf{AB})_2 = \frac{1}{2}(\mathbf{a} \cdot \mathbf{c})(\mathbf{b} \cdot \mathbf{d}) + \frac{1}{2}(\mathbf{a} \cdot \mathbf{d})(\mathbf{c} \cdot \mathbf{b}) - \frac{1}{3}(\mathbf{a} \cdot \mathbf{b})(\mathbf{c} \cdot \mathbf{d}). \quad (\text{B.6c})$$

To calculate the contribution of the non-resonant susceptibility to the response function the product of two fourth-rank tensors must be calculated:

$$S^{\text{NR}} = \chi^{\text{NR}} \cdot \mathbf{Q} = \sum_{ijkl} \chi_{ijkl}^{\text{NR}} (e_{4i}^* e_{3j} e_{2k}^* e_{1l}) = \sum_{lqm} (\chi^{\text{NR}})_m^{lq} (-1)^m Q_m^{lq}. \quad (\text{B.7})$$

The decomposition of a fourth-rank cartesian tensor into irreducible representations yields three tensors with $l=0$, six with $l=1$, six with $l=2$, three with $l=3$, and one with $l=4$. The index q in eq. (B.7) labels the different tensors with the same l . In isotropic media only the tensors with $l=0$ do not vanish

$$S^{\text{NR}} = \sum_{q=0}^2 (\chi^{\text{NR}})_0^{0q} Q_0^{0q}. \quad (\text{B.8})$$

The explicit form of the Q_0^{0q} with $q=0, 1, 2$ depends on the angular momentum coupling scheme adopted. When Q is the tensorial product of two second-rank tensors \mathbf{A} and \mathbf{B} , whose reduction into three tensors with $j=0, 1, 2$ is unique, one obtains (see eq. (5.25) in ref. [41])

$$Q_0^{0j} = \{\mathbf{A}^j \otimes \mathbf{B}^j\}_0^0 = \frac{(-1)^j}{(2j+1)^{1/2}} \sum_m A_m^j (-1)^m B_{-m}^j = \left[(-1)^j / (2j+1)^{1/2} \right] (\mathbf{AB})_j, \quad (\text{B.9})$$

where the $(\mathbf{AB})_j$ are those discussed above.

The corresponding $(\chi^{\text{NR}})_0^{0j}$ are found by expressing the Q_0^{0j} in terms of the cartesian components of \mathbf{A} and \mathbf{B} and replacing all products $A_{ij} B_{kl}$ by the corresponding χ_{ijkl}^{NR} . The result is

$$(\chi^{\text{NR}})_0^{0j} = \left[(-1)^j / (2j+1)^{1/2} \right] \chi_j^{\text{NR}}, \quad (\text{B.10})$$

with

$$\chi_0^{\text{NR}} = \chi_{1111}^{\text{NR}} + 2\chi_{1122}^{\text{NR}}, \quad \chi_1^{\text{NR}} = 3(\chi_{1221} - \chi_{1212}), \quad \chi_2^{\text{NR}} = 5(\chi_{1212} + \chi_{1221}). \quad (\text{B.11})$$

Hence the non-resonant contribution can be written as

$$S^{\text{NR}} = \chi^{\text{NR}} \cdot \mathbf{Q} = \sum_{j=0}^2 (2j+1)^{-1} P_j \chi_j^{\text{NR}}, \quad (\text{B.12})$$

where the $P_j = (\mathbf{AB})_j$ are those given in eq. (29).

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