

RAMAN SPECTROSCOPY AND FOUR WAVE MIXING; A PROBE FOR SOLVATION DYNAMICS

Shaul Mukamel† and Yi Jing Yan
Chemistry Department
University of Rochester
Rochester, New York 14627

†Camille and Henry Dreyfus Teacher Scholar

ABSTRACT

A correlation function theory, based on the reduced density matrix in Liouville-space allows the calculation of molecular linear and nonlinear response functions and solvation dynamics in four wave mixing and Raman spectroscopy. Explicit expression for $\chi^{(3)}$ for a polar solute in a polar solvent, relating the optical lineshapes to the solvent dielectric fluctuations and dielectric function $\epsilon(\omega)$ is derived. Intramolecular vibrations and nonpolar solvents are treated using a Brownian oscillator model and solvent dynamics and vibrational relaxation are related to solvent friction. Applications to spontaneous and coherent Raman excitation profiles and to time dependent fluorescence and hole burning measurements which probe the time development of the Stokes shift are presented.

I. INTRODUCTION

Coherent and spontaneous Raman spectroscopy of solvated polyatomic molecules provides detailed information both static (level positions and dipole matrix elements) and dynamical (intramolecular relaxation, and solvation dynamics).^{1]} The Raman process belongs to a broader class of nonlinear optical spectroscopies known as four wave mixing.^{2-4]} The key quantity which contains all the relevant information for the calculation of any four wave mixing is the third order nonlinear response function $S^{(3)}(\tau_3, \tau_2, \tau_1)$, or the nonlinear susceptibilities $\chi^{(3)}$ which is related to the triple Fourier transform of the response function.^{3-5]} The Raman process is related to two photon resonances of $\chi^{(3)}$. In this article we present several models for solvation dynamics and $\chi^{(3)}$ of polyatomic molecules in polar and nonpolar solvents. These results are then applied to calculate coherent and spontaneous Raman spectra, and time-resolved fluorescence and hole-burning lineshapes. The derivation of these results is based on a new method for the semiclassical evaluation of correlation functions, using a Liouville-space generating function.^{6]}

II. THE NONLINEAR RESPONSE FUNCTION FOR FOUR WAVE MIXING

We consider a solution composed of polyatomic solute molecules dissolved in a polar or nonpolar solvent. The solute is assumed to be present in sufficiently low concentration that interactions between solute molecules are negligible, and we may treat a single solute molecule in its solvent environment. We assume that the solvent molecules do not interact with the radiation field, but do interact with the solute. The density matrix $\rho(t)$ of the solution in the presence of an external electric field $E(r, t)$ obeys the Liouville equation

$$\frac{d\rho}{dt} = -i[H_s, \rho] - i[H_{int}, \rho]. \quad (II-1)$$

In Eq.(II-1) and in the rest of this paper, we set $k = 1$. H is the Hamiltonian for the material system in the absence of the radiation field. H_{int} represents the radiation-matter interaction and is given by

$$H_{int}(t) = -E(r, t) \cdot V, \quad (II-2)$$

V is the dipole operator of the solute. $E(r, t)$ is the external electric field that for a general four wave mixing (4WM) process can be decomposed into three components:

$$E(r, t) = \sum_{j=1}^3 [E_j(t)\exp(ik_j \cdot r - i\omega_j t) + E_j^*(t)\exp(-ik_j \cdot r + i\omega_j t)]. \quad (II-3)$$

In order to calculate the 4WM signal, we start at $t = -\infty$ and assume that the system is in thermal equilibrium with respect to H (without the radiation field)

$$\rho(-\infty) = \exp(-\beta H) / \text{Tr} \exp(-\beta H), \quad (II-4)$$

where $\beta = (k_B T)^{-1}$. The system then evolves in time according to the Liouville equation (Eq.(II-1)) which can be written using Liouville-space notation, 4-6)

$$\frac{d\rho}{dt} = -iL\rho - iL_{int}\rho. \quad (II-5)$$

The action of the Liouville operator on an ordinary (dyadic) operator A is given by

$$LA \equiv [H, A], \quad (II-6a)$$

$$L_{int}A \equiv [H_{int}, A]. \quad (II-6b)$$

We also define the Liouville-space dipole operator \mathcal{V} by

$$\mathcal{V}A \equiv [V, A]. \quad (II-6c)$$

We shall be interested in calculating the polarization $P(r, t)$ at position r at time t . This is given by the expectation value of the dipole operator V :

$$P(r, t) \equiv \langle\langle V | \rho(t) \rangle\rangle, \quad (II-7)$$

where we are using the double bracket notation⁴⁻⁶⁾ to denote an inner product of any two operators, $\langle\langle A|B \rangle\rangle \equiv \text{Tr}(A^\dagger B)$. We shall also define a Liouville-space matrix element by $\langle\langle A|L|B \rangle\rangle \equiv \text{Tr}(A^\dagger LB)$. The polarization $P(r, t)$ can now be expanded in powers of E by solving the Liouville equation perturbatively in L_{int} . We then get

$$P(r, t) = \sum_{n=1}^{\infty} P^{(n)}(r, t) \quad (II-8)$$

The linear polarization $P^{(1)}$ is related to the linear optical properties of the system whereas $P^{(3)}$ is related to four wave mixing and Raman spectroscopy. (In an isotropic medium $P^{(2)} = 0$ so that $P^{(3)}$ is the lowest nonlinear polarization). We then get

$$P^{(3)}(r, t) = \sum_{k_s} \exp(ik_s \cdot r - i\omega_s t) P^{(3)}(k_s, t). \quad (II-9)$$

where $k_s(\omega_s)$ is any combination of k_1, k_2 , and $k_3(\omega_1, \omega_2$, and $\omega_3)$, i.e.,

$$k_s = \pm k_1 \pm k_2 \pm k_3 \quad (\text{II-10a})$$

$$\omega_s = \pm \omega_1 \pm \omega_2 \pm \omega_3. \quad (\text{II-10b})$$

The particular combination in Eq.(II-10) is determined by the specific four wave mixing technique of interest. Hereafter, we shall select a specific choice, namely, $k_s = k_1 - k_2 + k_3$ and $\omega_s = \omega_1 - \omega_2 + \omega_3$. Any other combination may be obtained from our final expression by changing one (or more) k_j and ω_j into $-k_j$ and $-\omega_j$ and $E_j(t)$ into $E_j^*(t)$. Using Eqs.(II-3), (II-5), and (II-7)-(II-9), we then get

$$P^{(3)}(k_s, t) = \sum_{j,k,q=1,2,3} \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1$$

$$S^{(3)}(\nu_3, \nu_2, t_1) \exp[i(\omega_j + \omega_k + \omega_q)\nu_3 + i(\omega_j + \omega_k)\nu_2 + i\omega_j t_1]$$

$$\times E_j(t - t_1 - \nu_2 - \nu_3) E_k(t - \nu_2 - \nu_3) E_q(t - \nu_3). \quad (\text{II-11})$$

$S^{(3)}(\nu_3, \nu_2, t_1)$ is the *nonlinear response function*, which contains all relevant microscopic information for any 4WM process:

$$S^{(3)}(\nu_3, \nu_2, t_1) \equiv i^3 \langle \langle V \hat{\mathcal{G}}(\nu_3) \mathcal{V} \hat{\mathcal{G}}(\nu_2) \mathcal{V} \hat{\mathcal{G}}(t_1) \mathcal{V} | \rho(-\infty) \rangle \rangle. \quad (\text{II-12})$$

The Green function $\hat{\mathcal{G}}(\tau)$ is the formal solution of Eq.(II-5) in the absence of the electromagnetic field:

$$\hat{\mathcal{G}}(\tau) \equiv \exp(-iL\tau). \quad (\text{II-13a})$$

For subsequent manipulations we shall also introduce the Green function in the frequency domain:

$$\hat{\mathcal{G}}(\omega) = -i \int_0^\infty dt \exp(i\omega t) \hat{\mathcal{G}}(\tau) = \frac{1}{\omega - L}. \quad (\text{II-13b})$$

The summation in Eq.(II-11) is over all $3! = 6$ permutations of $\omega_j, \omega_k, \omega_q$ with $\omega_1, -\omega_2, \omega_3$ and E_j, E_k, E_q with E_1, E_2^*, E_3 . In an ideal time resolved 4WM process the incoming fields are infinitely short. The signal is then proportional to $|S^{(3)}(\nu_3, \nu_2, t_1)|^2$, t_1 and ν_2 being the time intervals between the pulses and the detection is made at time ν_3 after the third pulse. The other extreme limit of 4WM is a stationary frequency-domain experiment in which the field amplitudes $E_1(\tau), E_2(\tau)$, and $E_3(\tau)$ are time independent. In this case we have^{3]}

$$P^{(3)}(k_s, t) = \chi^{(3)}(-\omega_s; \omega_1, \omega_2, \omega_3) E_1 E_2 E_3, \quad (\text{II-14})$$

where the nonlinear susceptibility $\chi^{(3)}$ is given by

$$\chi^{(3)}(-\omega_s; \omega_1, \omega_2, \omega_3) = i^3 \sum_{j,k,q=1,2,3} \hat{S}^{(3)}(\omega_j + \omega_k + \omega_q, \omega_j + \omega_k, \omega_j), \quad (\text{II-15a})$$

with

$$\hat{S}^{(3)}(\omega_j + \omega_k + \omega_q, \omega_j + \omega_k, \omega_j) \equiv (-i)^3 \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1$$

$$\exp[i(\omega_j + \omega_k + \omega_q)\nu_3 + i(\omega_j + \omega_k)\nu_2 + i\omega_j t_1] S^{(3)}(\nu_3, \nu_2, t_1)$$

$$= i^3 \langle \langle V \hat{\mathcal{G}}(\omega_j + \omega_k + \omega_q) \mathcal{V} \hat{\mathcal{G}}(\omega_j + \omega_k) \mathcal{V} \hat{\mathcal{G}}(\omega_j) \mathcal{V} | \rho(-\infty) \rangle \rangle. \quad (\text{II-15b})$$

The 4WM signal is in this case proportional to $|x^{(3)}|^2$. Similarly we define the linear response function

$$P^{(1)}(k_j, t) = \int_0^\infty dt_1 S^{(1)}(t_1) \exp(i\omega_j t) E_j(t - t_1) \quad (\text{II-16})$$

where

$$S^{(1)}(t_1) = i \langle \langle V | g^{(1)}(t_1) \mathcal{V} | p \rangle \langle -\infty \rangle \rangle. \quad (\text{II-17})$$

In an ordinary absorption experiment the field $E_j(t)$ is time independent. In this case

$$P^{(1)}(k_j, t) = \chi^{(1)}(-\omega_j; \omega_j) E_j \quad (\text{II-18})$$

where the linear susceptibility is

$$\chi^{(1)}(-\omega_j; \omega_j) = i \hat{S}^{(1)}(\omega_j) \quad (\text{II-19a})$$

and

$$\begin{aligned} \hat{S}^{(1)}(\omega_j) &= -i \int_0^\infty dt_1 \exp(i\omega_j t_1) S^{(1)}(t_1) \\ &= i \langle \langle V | g^{(1)}(\omega_j) \mathcal{V} | p \rangle \langle -\infty \rangle \rangle. \end{aligned} \quad (\text{II-19b})$$

The n th order response function $S^{(n)}$ contains the Liouville space dipole operator \mathcal{V}^n times. Since each \mathcal{V} represents a commutator, which can act either from the left or from the right, $S^{(n)}$ will contain 2^n terms once these commutators are evaluated. In this paper, we shall focus on the linear response function $S^{(1)}$ and the lowest order nonlinear response function in an isotropic medium $S^{(3)}$. When the commutators in Eq.(II-12) and (II-17) are evaluated it can be shown that only half of the 2^n terms need

to be evaluated, since the contribution of the other half are simply the complex conjugate of the former. We then have:

$$S^{(1)}(t_1) = i [J(t_1) - J^*(t_1)] \quad (\text{II-20a})$$

$$S^{(3)}(t_3, t_2, t_1) = i^3 [R(t_3, t_2, t_1) - R^*(t_3, t_2, t_1)]. \quad (\text{II-20b})$$

The form of Eqs.(II-20) guarantees that $S^{(1)}$ and $S^{(3)}$ are real functions. In fact it can be shown in general that all $S^{(n)}$ are real since they relate two real quantities, the electric field $E_j(r, t)$ and the polarization $P(r, t)$.

III. APPLICATION TO A POLAR SOLUTE IN A POLAR SOLVENT

We consider two electronic states of the solute: the ground state $|g\rangle$ and the excited state $|e\rangle$. The model Hamiltonian for the molecular system is given by^{7]}

$$H = |g\rangle \langle H_g + h_g | \langle g| + |e\rangle \langle H_e + h_e + H_0 e_g | \langle e|, \quad (\text{III-1a})$$

$$V = \sum_{a,b} \mu_{ab} |a\rangle \langle b| + \mu_{ba} |b\rangle \langle a|, \quad (\text{III-1b})$$

where

$$h_j = h_0 + W_j. \quad (\text{III-1c})$$

In Eqs.(III-1), h_0 is the Hamiltonian governing the nuclear degrees of freedom of the solvent in the absence of the solute. The Hamiltonian representing the nuclear degrees of freedom of the solute is H_g when the solute is in the state $|g\rangle$ and H_e when it is in the state $|e\rangle$. V is the transition dipole operator of the solute. We assume that the time scale of the response of the solvent electrons to a change in the solute electronic charge density is short compared to the inverse of the linewidth of a vibronic transition in the solute. Under these circumstances, the electronic solvation will simply shift the

electronic energy gap ω_{eg} . W_j is the interaction between the solute and nuclear degrees of freedom of the solvent when the solute occupies the electronic state $|j\rangle$ ($j=g,e$),

$$W_j \equiv - \int dr \xi(r) \cdot E_0^{(j)}(r). \quad (\text{III-2})$$

The polarization operator for the nuclear (orientational) degrees of freedom of the solvent is denoted $\xi(r)$. $E_0^{(j)}(r)$ is the electric field that would arise from the solute molecule in electronic state $|j\rangle$ in the absence of the solvent. The Hamiltonians H_g and H_e will be specified by their vibronic eigenstates as shown in Figure 1.

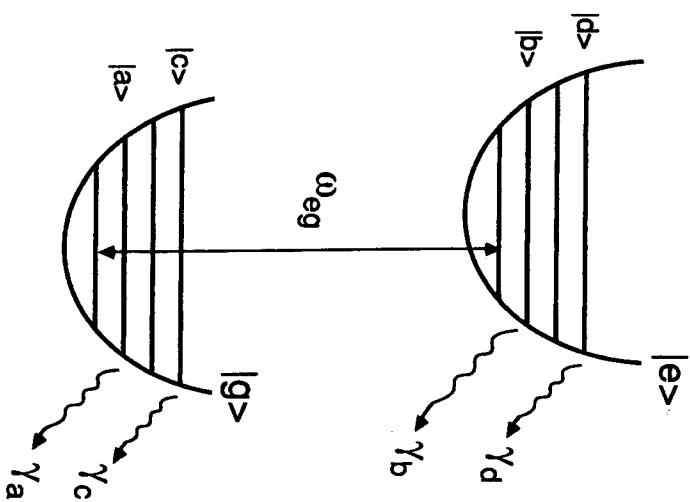


FIGURE 1: The two electronic level schemes used in the calculation of the response functions and four wave mixing $|a\rangle$, $|c\rangle$... denote vibronic states belonging to the ground state manifold and $|b\rangle$, $|d\rangle$... denote vibronic states belonging to the electronically excited manifold. The electronic dipole operator couples vibronic states belonging to different electronic levels.

Throughout this article the vibronic eigenstates of H_g will be denoted $|a\rangle$, $|c\rangle$

$$H_g |v\rangle = (E_v - i\gamma_v) |v\rangle; \quad v=a,c,\dots \quad (\text{III-3a})$$

whereas the vibronic levels of H_e will be denoted $|b\rangle$, $|d\rangle$

$$(\omega_{eg} + H_e) |v\rangle = (E_v - i\gamma_v) |v\rangle; \quad v=b,d,\dots \quad (\text{III-3b})$$

Here E_v and γ_v are the energy and the inverse lifetime, respectively, of state $|v\rangle$.

We shall expand the response functions (Eq.(II-20)) in the electronic basis set $|g\rangle$ and $|e\rangle$. In a two electronic state system $J(t_1)$ contains one term and $R(t_3, t_2, t_1)$ contains four terms representing the system nuclear degrees of freedom. In our model we neglect the effect of the molecular internal degrees of freedom on $E_0^{(j)}$ so that the solvent interacts only with the electronic (but not nuclear) degrees of freedom of the molecule. In this case, we can factorize every nuclear term into a product of a solute (S) and a solvent, bath, (B) contributions. We then have:

$$J(t_1) = J^{(S)}(t_1) J^{(B)}(t_1) \quad (\text{III-4a})$$

$$R(t_3, t_2, t_1) = \sum_{\alpha=1}^4 R_{\alpha}^{(S)}(t_3, t_2, t_1) \quad (\text{III-4b})$$

with

$$R_{\alpha}^{(S)}(t_3, t_2, t_1) = R_{\alpha}^{(S)}(t_3, t_2, t_1) R_{\alpha}^{(B)}(t_3, t_2, t_1). \quad (\text{III-4c})$$

The system contributions may be obtained from Eq.(III-1) by neglecting the bath Hamiltonians H_j and keeping only H_g and H_e . They may be expressed in terms of the vibronic levels:

$$J^{(S)}(t_1) = \sum_{a,b} P(a) \mu_{ab} \mu_{ba} I_{ba}(t_1)$$

$$R_1^{(S)}(t_3, t_2, t_1) = \sum_{a,b,c,d} P(a) \mu_{ab} \mu_{bc} \mu_{cd} \mu_{da} I_{dc}(t_3) I_{db}(t_2) I_{da}(t_1)$$

$$R_2^{(S)}(t_3, t_2, t_1) = \sum_{a,b,c,d} P(a) \mu_{ab} \mu_{bc} \mu_{cd} \mu_{da} I_{dc}(t_3) I_{db}(t_2) I_{ab}(t_1)$$

$$R_3^{(S)}(t_3, t_2, t_1) = \sum_{a,b,c,d} P(a) \mu_{ab} \mu_{bc} \mu_{cd} \mu_{da} I_{dc}(t_3) I_{ac}(t_2) I_{ab}(t_1)$$

$$R_4^{(S)}(t_3, t_2, t_1) = \sum_{a,b,c,d} P(a) \mu_{ab} \mu_{bc} \mu_{cd} \mu_{da} I_{ba}(t_3) I_{ca}(t_2) I_{da}(t_1). \quad (\text{III-5})$$

Here

$$P(a) = \exp(-\beta \epsilon_a) / \sum_a \exp(-\beta \epsilon_a) \quad (\text{III-6})$$

$$I_{\nu\nu'}(t) = \exp(-i\omega_{\nu\nu'} t - \Gamma_{\nu\nu'} |t|)$$

$$\omega_{\nu\nu'} = \epsilon_{\nu'} - \epsilon_{\nu}$$

$$\Gamma_{\nu\nu'} = (\gamma_{\nu} + \gamma_{\nu'})/2 \quad \nu, \nu' = a, b, c, d \quad (\text{III-7})$$

γ_{ν}^{-1} is the lifetime of level $|\nu\rangle$ which is introduced phenomenologically. Note that $I_{\nu\nu'}$ satisfy the relations $I_{\nu\nu'}(t) = I_{\nu'\nu}^*(t) = I_{\nu'\nu}(-t)$. The solvent contributions to the response functions come from the Hamiltonians H_j and assume the form

$$J^{(B)}(t_1) = \langle G_{eg}(t_1) \rho_g \rangle$$

$$R_1^{(B)}(t_3, t_2, t_1) = \langle G_{eg}(t_3) G_{cc}(t_2) G_{eg}(t_1) \rho_g \rangle$$

$$R_2^{(B)}(t_3, t_2, t_1) = \langle G_{eg}(t_3) G_{cc}(t_2) G_{ge}(t_1) \rho_g \rangle$$

$$R_3^{(B)}(t_3, t_2, t_1) = \langle G_{eg}(t_3) G_{gg}(t_2) G_{ge}(t_1) \rho_g \rangle$$

$$R_4^{(B)}(t_3, t_2, t_1) = \langle G_{eg}(t_3) G_{gg}(t_2) G_{eg}(t_1) \rho_g \rangle \quad (\text{III-8})$$

Here $G_{mn}(t)$ represents the bath Liouville-space Green function, defined by its action on an arbitrary operator A :

$$G_{mn}(t) A \equiv \exp(-ih_n t) A \exp(ih_m t) \quad (\text{III-9})$$

and

$$\rho_g = \exp(-\beta h_g) / \text{Tr} \exp(-\beta h_g), \quad (\text{III-10})$$

denotes the equilibrium bath density matrix when the solute is in the $|g\rangle$ state. The four Liouville-space pathways corresponding to R_{α} are displayed in Figure 2.

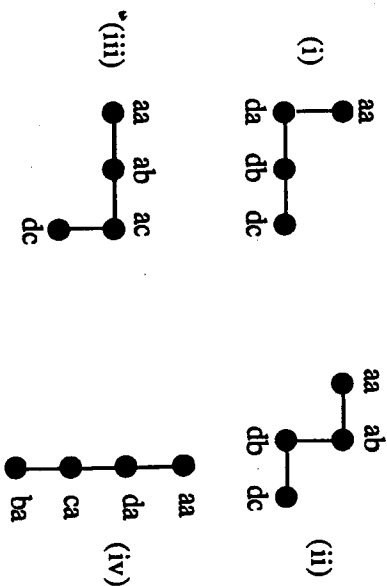


FIGURE 2: The four Liouville-space pathways that contribute to the nonlinear response function (Eqs. (II-20b) and (II-4b)). R_1 , R_2 , R_3 , and R_4 (Eqs. (III-5) and (III-8)) correspond, respectively, to pathways (i), (ii), (iii), and (iv).

We have evaluated the solvent contributions using a Liouville-space generating function. When the solvent-solute interaction is treated perturbatively, we can relate it to the dielectric function $\epsilon(\omega)$ of the solvent. We then get^{6]}

$$J^{(B)}(t) = \exp[-g(t)]$$

$$R_1^{(B)}(t_3, t_2, t_1) = \exp[-g^*(t_3) - g(t_1) - f_+(t_3, t_2, t_1)]$$

$$R_2^{(B)}(t_3, t_2, t_1) = \exp[-g^*(t_3) - g^*(t_1) + f_+(t_3, t_2, t_1)]$$

$$R_3^{(B)}(t_3, t_2, t_1) = \exp[-g(t_3) - g^*(t_1) + f_-(t_3, t_2, t_1)]$$

$$R_4^{(B)}(t_3, t_2, t_1) = \exp[-g(t_3) - g(t_1) - f_-(t_3, t_2, t_1)],$$

(III-11)

where

$$f_-(t_3, t_2, t_1) = g(t_2) - g(t_2+t_3) - g(t_1+t_2) + g(t_1+t_2+t_3)$$

$$f_+(t_3, t_2, t_1) = g^*(t_2) - g^*(t_2+t_3) - g(t_1+t_2) + g(t_1+t_2+t_3).$$

(III-12)

Here $g(t)$ is the line broadening function

$$g(t) = i\lambda \int_0^t dt_1 \int_0^{t_1} dt_2 M(t_2),$$

(III-13)

To lowest order in the solvent solute interaction, λ , Δ , and $M(t)$ may be expressed in terms of correlation functions of the solvation coordinate, $U \cong h_e - h_g = W_e - W_g$, which may further be related to the solvent dielectric function $\epsilon(\omega)$. We then have^{6,7]}

$$\lambda = \langle U \rho_g \rangle = \frac{1}{8\pi} \int dr [E_0^{(e)}(r) - E_0^{(g)}(r)]^2 [1/\epsilon_\infty - 1/\epsilon_0]$$

(III-14a)

$$\Delta^2 = \langle U^2 \rho_g \rangle = 2\lambda kT$$

(III-14b)

and

$$M(t) = \frac{\langle \exp(ih_g t) U \exp(-ih_g t) U \rho_g \rangle = \langle U \rho_g \rangle^2}{\langle U^2 \rho_g \rangle = \langle U \rho_g \rangle^2}$$

$$= \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{d\omega \exp(i\omega t)}{\omega} \frac{1/\epsilon(\omega) - 1/\epsilon_0}{1/\epsilon_\infty - 1/\epsilon_0}$$

(III-15)

Here ϵ_0 is the static ($\omega=0$), and ϵ_∞ is the high-frequency (optical) value of $\epsilon(\omega)$. $E_0^{(g)}(r)$ and $E_0^{(e)}(r)$ denote the electric field at position r , created by the solute in the $|g\rangle$ and in the $|e\rangle$ states, respectively, in the absence of the solvent. If we model the molecular electric field by a permanent dipole in a spherical cavity, we obtain the following expression for λ :^{7]}

$$\lambda = r^{-3} \mu_e - \mu_g^2 (1/\epsilon_\infty - 1/\epsilon_0).$$

(III-16)

Here μ_g and μ_e are the permanent dipole moments of the solute in its ground and excited electronic states, respectively. r is the effective solute radius. Eqs.(II-20), (III-4)-(III-5), and (III-11)-(III-16) provide closed expressions for the response functions and relate them to the solvent dielectric function. The solvent dynamics are contained in $M(t)$, which is the normalized correlation function of the solvation coordinate. λ and Δ are static parameters which reflect the interaction strength of the solvent and solute. The second equality in Eq.(III-14b) is a high temperature approximation.

IV. THE RESPONSE FUNCTIONS AND $\chi^{(3)}$ FOR A POLAR SOLUTE IN A DEBYE SOLVENT

The Debye model is the simplest model for dielectric relaxation in which the solvent is characterized by a single relaxation time, the Debye relaxation time τ_D , and $\epsilon(\omega)$ is given by^{8]}

$$\epsilon(\omega) = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty) (1 + i\omega\tau_D)^{-1}. \quad (\text{IV-1})$$

In this case, $M(t)$ (Eq.(III-15)) is exponential:

$$M(t) = \exp(-t/\tau_L) \quad (\text{IV-2})$$

with the characteristic timescale equal to the longitudinal relaxation time

$$\tau_L \equiv \tau_D \epsilon_\infty / \epsilon_0. \quad (\text{IV-3})$$

The line broadening function (Eq.(III-13)) then becomes

$$g(t) = i\lambda\tau_L [1 - \exp(-t/\tau_L)] + (\Delta\tau_L)^2 [t/\tau_L - 1 + \exp(-t/\tau_L)] \quad (\text{IV-4})$$

and Eqs.(III-12) reduce to

$$f_-(t_3, t_2, t_1) = z \exp(-t_2/\tau_L) [1 - \exp(-t_1/\tau_L)] [1 - \exp(-t_3/\tau_L)]$$

$$f_+(t_3, t_2, t_1) = z \exp(-t_2/\tau_L) [z^*/z - \exp(-t_1/\tau_L)] [1 - \exp(-t_3/\tau_L)] \quad (\text{IV-5})$$

with

$$z = (\Delta\tau_L)^2 - i\lambda\tau_L. \quad (\text{IV-6})$$

We further define the auxiliary functions

$$J_n(t) \equiv \exp[-g(t)] [1 - \exp(-t/\tau_L)]^n,$$

$$\tilde{J}_n(t) \equiv \exp[-g(t)] [z^*/z - \exp(-t/\tau_L)]^n. \quad (\text{IV-7})$$

With this notation, Eqs.(III-11) assume the form:

$$J^{(B)}(t) = \exp[-g(t)] \equiv J_0(t)$$

$$R_1^{(B)}(t_3, t_2, t_1) = \sum_{n=0}^{\infty} \frac{(-1)^n z^n}{n!} \exp(-nt_2/\tau_L) \tilde{J}_n(t_1) J_n^*(t_3)$$

$$R_2^{(B)}(t_3, t_2, t_1) = \sum_{n=0}^{\infty} \frac{z^n}{n!} \exp(-nt_2/\tau_L) \tilde{J}_n^*(t_1) J_n^*(t_3)$$

$$R_3^{(B)}(t_3, t_2, t_1) = \sum_{n=0}^{\infty} \frac{z^n}{n!} \exp(-nt_2/\tau_L) J_n^*(t_1) J_n(t_3)$$

$$R_4^{(B)}(t_3, t_2, t_1) = \sum_{n=0}^{\infty} \frac{(-1)^n z^n}{n!} \exp(-nt_2/\tau_L) J_n(t_1) J_n(t_3). \quad (\text{IV-8})$$

When Eqs.(IV-8) and (III-5) are substituted in Eqs.(III-4) and (II-20), we obtain final closed expressions for the linear and the nonlinear response functions in the time domain. We can further perform the time integrations and get closed expressions in the frequency domain. For subsequent manipulations we shall introduce the following definitions

$$\hat{J}(\omega_1) = -i \int_0^{\infty} dt_1 \exp(i\omega_1 t_1) J(t_1)$$

$$\hat{R}_\alpha(\omega_1 - \omega_2 + \omega_3, \omega_1 - \omega_2, \omega_1) = (-i)^3 \int_0^{\infty} dt_3 \int_0^{\infty} dt_2 \int_0^{\infty} dt_1$$

$$\exp[i(\omega_1 - \omega_2 + \omega_3)t_3 + i(\omega_1 - \omega_2)t_2 + i\omega_1 t_1] R_\alpha(t_3, t_2, t_1), \quad \alpha=1, \dots, 4. \quad (\text{IV-9})$$

Using Eqs.(II-20), (III-4b), and (IV-9), we can express $\chi^{(1)}$ (Eq.(II-19)) and $\chi^{(3)}$ (Eq.(II-15)) in the forms:

$$\begin{aligned} \chi^{(1)}(-\omega_1, \omega_1) &= -[\hat{J}(\omega_1) + \hat{J}^*(-\omega_1)] \\ \chi^{(3)}(-\omega_3, \omega_1, \omega_2, \omega_3) &= - \sum_{j,k,q} \sum_{\alpha=1}^4 [\hat{R}_\alpha(\omega_j + \omega_k + \omega_q, \omega_j + \omega_k, \omega_j) \\ &\quad + \hat{R}_\alpha^*(-\omega_j - \omega_k - \omega_q, -\omega_j - \omega_k, -\omega_j)] \end{aligned} \quad (\text{IV-10})$$

The first summation in Eq. (IV-10) runs over all $3! = 6$ permutations of the three fields, and generally $\chi^{(3)}$ (Eq. (IV-10)) contains $6 \times 8 = 48$ terms. For a polyatomic molecule (Eqs. (III-5)) in a Debye solvent (Eqs. (IV-8)), we finally have

$$\begin{aligned} \hat{J}(\omega_1) &= \sum_{a,b} P(a) \mu_a \mu_b \mu_a J_0(\omega_1 - \omega_{ba} + i\Gamma_{ba}) \\ \hat{R}_1(\omega_1 - \omega_2 + \omega_3, \omega_1 - \omega_2, \omega_1) &= - \sum_{n=0}^{\infty} \sum_{a,b,c,d} P(a) \mu_a \mu_b \mu_c \mu_d \mu_a \\ &\quad \times \frac{(-1)^n z^n}{n!} \frac{J_n^*(\omega_{dc} - \omega_1 + \omega_2 - \omega_3 + i\Gamma_{dc}) \bar{J}_n(\omega_1 - \omega_{da} + i\Gamma_{da})}{\omega_1 - \omega_2 - \omega_{db} + i(\Gamma_{db} + n/\tau_d)} \\ \hat{R}_2(\omega_1 - \omega_2 + \omega_3, \omega_1 - \omega_2, \omega_1) &= \sum_{n=0}^{\infty} \sum_{a,b,c,d} P(a) \mu_a \mu_b \mu_c \mu_d \mu_a \\ &\quad \times \frac{z^n}{n!} \frac{J_n^*(\omega_{dc} - \omega_1 + \omega_2 - \omega_3 + i\Gamma_{dc}) \bar{J}_n(\omega_{db} - \omega_1 + i\Gamma_{db})}{\omega_1 - \omega_2 - \omega_{db} + i(\Gamma_{db} + n/\tau_d)} \end{aligned}$$

$$\begin{aligned} \hat{R}_3(\omega_1 - \omega_2 + \omega_3, \omega_1 - \omega_2, \omega_1) &= - \sum_{n=0}^{\infty} \sum_{a,b,c,d} P(a) \mu_a \mu_b \mu_c \mu_d \mu_a \\ &\quad \times \frac{z^n}{n!} \frac{J_n(\omega_1 - \omega_2 + \omega_3 - \omega_{dc} + i\Gamma_{dc}) J_n^*(\omega_{db} - \omega_1 + i\Gamma_{db})}{\omega_1 - \omega_2 - \omega_{dc} + i(\Gamma_{dc} + n/\tau_c)} \end{aligned}$$

$$\begin{aligned} \hat{R}_4(\omega_1 - \omega_2 + \omega_3, \omega_1 - \omega_2, \omega_1) &= \sum_{n=0}^{\infty} \sum_{a,b,c,d} P(a) \mu_a \mu_b \mu_c \mu_d \mu_a \\ &\quad \times \frac{(-1)^n z^n}{n!} \frac{J_n(\omega_1 - \omega_2 + \omega_3 - \omega_{ba} + i\Gamma_{ba}) \bar{J}_n(\omega_1 - \omega_{da} + i\Gamma_{da})}{\omega_1 - \omega_2 - \omega_{ca} + i(\Gamma_{ca} + n/\tau_c)}. \end{aligned} \quad (\text{IV-11})$$

Here

$$\begin{aligned} J_n(\omega) &\equiv -i \int_0^{\infty} dt \exp(i\omega t) J_n(t) \\ \bar{J}_n(\omega) &\equiv -i \int_0^{\infty} dt \exp(i\omega t) \bar{J}_n(t) \end{aligned} \quad (\text{IV-12})$$

are the auxiliary lineshape functions for the Debye model with $J_n(t)$ and $\bar{J}_n(t)$ defined in Eq. (IV-7). A recursive relation in $J_n(\omega)$ or $\bar{J}_n(\omega)$ can be derived and an analytic form for $J_0(\omega) = \tilde{J}_0(\omega)$ can be found in terms of a continued fraction.^{9,10} Furthermore $J_n(\omega)$ or $\bar{J}_n(\omega)$ can also be expressed in terms of the confluent hypergeometric function.⁹ These expressions are particularly suitable for numerical computations. The effect of solvent dielectric fluctuations on the linear and the nonlinear response functions, and on the optical susceptibilities $\chi^{(1)}$ and $\chi^{(3)}$ can be analyzed using the present theory. The solvent enters into our expressions through the three parameters:

λ , Δ , and τ_L . To gain further insight on these expressions let us consider the absorption lineshape which is equal to the imaginary part of $\chi^{(1)}(\omega; \omega)$. Similarly, the steady state fluorescence spectrum is given by the imaginary part of $\chi^{(1)}(\omega; -\omega)$. $\chi^{(1)}$ is given by Eq.(IV-10) together with (IV-11), (IV-12), and (IV-7), and $g(t)$ is given by Eq.(IV-4). The nature of these lineshapes is determined^{4,9]} by the dimensionless parameter $k \equiv (\Delta\tau_L)^{-1}$. For $k \ll 1$ we can evaluate $g(t)$ for short times resulting in $g(t) \sim i\lambda t + \frac{1}{2}\Delta^2 t^2$. In this case the lineshape function I_0 is inhomogeneously broadened and assumes a Gaussian form. λ is a solvent induced spectral shift (the Stokes shift). The absorption lineshape maximum will be at the frequency $\omega_{eg} + \lambda$, the fluorescence maximum will be at $\omega_{eg} - \lambda$ and their difference (the Stokes shift) is 2λ .^{7]} Δ is the solvent induced line broadening. In the other extreme $k \gg 1$, we have $\Delta \gg \tau_L$ and $g(t) \sim \Gamma_L$ with $\Gamma_L \approx \Delta^2 \tau_L$. The lineshape is then homogeneously broadened with a Lorentzian form with a linewidth Γ_L . A stochastic model commonly used in lineshape analysis^{10]} is obtained from the present results if we set $\lambda = 0$. In the stochastic model the solute is not allowed to affect the solvent and consequently the model shows no Stokes shift. The Stokes shift for polar molecules in polar solvents is usually very large (hundreds of wavenumbers).^{11]} The common expression of $\chi^{(3)}$ based on the Bloch equations^{2,3]} is obtained from the present model in the limit $k \gg 1$. In this limit $\Gamma_L \approx \Delta^2 \tau_L$ is the electronic dephasing rate. Since τ_L is very short in this case we can take only the $n=0$ terms in Eq.(IV-11), which yield Bloembergen's expression^{3]} for $\chi^{(3)}$. Recent advances in ultrafast laser techniques make it possible to conduct time and frequency resolved nonlinear optical measurements with a femtosecond time resolution.^{12,13]} We have applied the present theory to calculate time resolved fluorescence and hole burning lineshapes of polar solutes in polar solvents.^{7]} The results are displayed in Figures 3 and 4. In both cases we note a significant narrowing of the spectra at short times where the excitation is selective and the emission is "Raman like". At longer times we observe a time dependent Stokes shift and broadening due to the solvent dielectric relaxation processes.

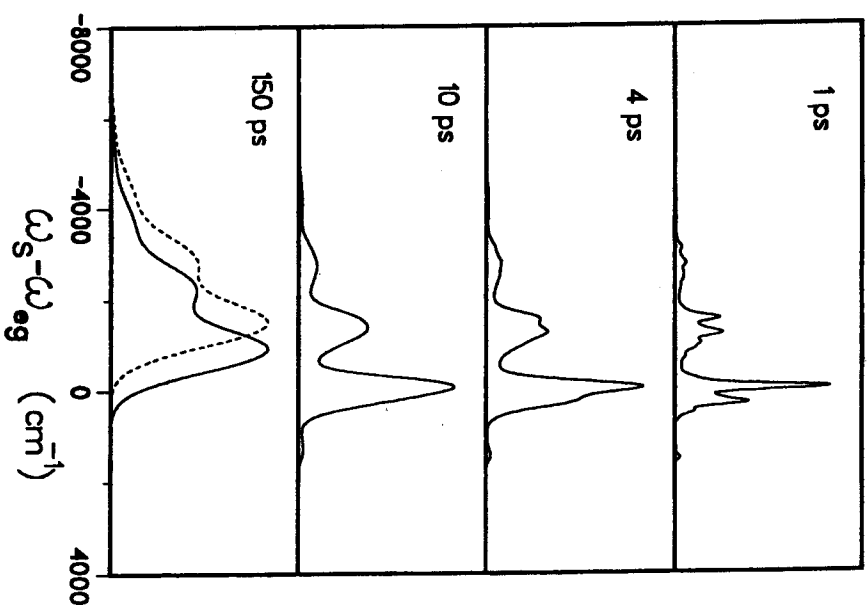


FIGURE 3: Time-resolved fluorescence spectra of a polycationic solute in ethanol at 247 K following a 1 ps excitation pulse.^{7]} The model solute has the 29 Raman active vibrational modes of the retinal chromophore in bacteriorhodospin,^{14]} and undergoes rapid vibrational relaxation. The excess vibrational energy is $\omega_r - \omega_{eg} - \lambda = 1528 \text{ cm}^{-1}$, $\tau_L = 150 \text{ fs}$. The permanent dipole moment changes by 10 D upon electronic excitations, and the effective radius of the model solute is $r = 3\text{ \AA}$ corresponding to $\Delta = 502 \text{ cm}^{-1}$.

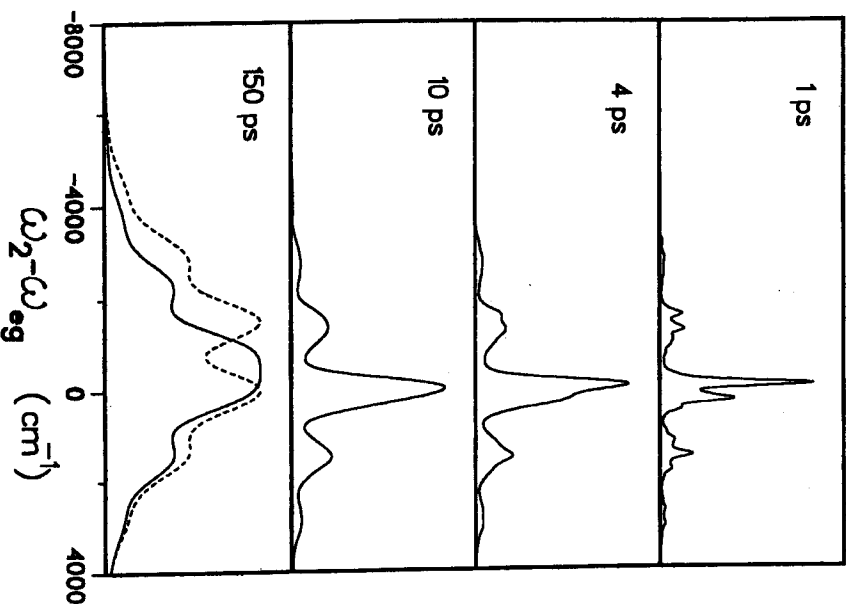


FIGURE 4: Hole-burning lineshapes of a polyatomic solute in ethanol at 247 K following a 1 ps pump pulse.⁷¹ The model solute has the 29 Raman active vibrational modes of the retinal chromophore in bacteriorhodospin, and undergoes rapid vibrational relaxation. The pump frequency $\omega_1 = \omega_{eg} + \lambda + 1528\text{cm}^{-1}$. All other parameters are identical to those of Figure 3.

V. APPLICATION TO SPONTANEOUS AND COHERENT RAMAN SPECTRA

As can be seen from Eq.(IV-10) and (IV-11), each term in $\chi^{(3)}$ contains a product of factors in which a single field frequency ω_j or a combination of two $\omega_j \pm \omega_k$ or three $\omega_j \pm \omega_k \pm \omega_m$ field frequencies is resonant with a molecular transition $\omega_{\nu\nu'}$. These factors represent single photon, two photon, and three photon resonances respectively. In the Raman process we are looking at two photon resonances whereby a difference in two field frequencies is resonant with a molecular vibrational transition, $\omega_1 - \omega_2 = \omega_{\nu\nu'}$. In a spontaneous Raman process the system is subject to a single incident field with frequency ω_L and the spontaneous emission is monitored as a function of its frequency ω_S . In general the emission will consist of relatively sharp Raman lines centered around $\omega_L - \omega_S = \omega_{ca}$ where $|c\rangle$ and $|a\rangle$ are two ground state vibronic levels, and a much broader fluorescence emission which does not vary considerably as we tune ω_L . The Raman resonances are contained in \hat{R}_3 and \hat{R}_4 in Eq.(IV-11), and the Raman spectrum is given by^{4,9]}

$$SR(\omega_L, \omega_S) \sim 2 \text{Im} \hat{R}_3(\omega_S, \omega_S - \omega_L, -\omega_L). \quad (\text{V-1})$$

It should be noted that \hat{R}_3 (Eq.(IV-11)) contains a succession of resonances with widths of n/τ_L , $n=0, 1, 2, \dots$. Since usually in solution τ_L is extremely fast (typically sub femtosecond), only the $n=0$ term in Eq.(IV-11) will represent a narrow Raman resonance. The terms with $n=1, 2, \dots$ will naturally belong in the background (fluorescence) emission. We thus have:

$$SR(\omega_L, \omega_S) = -2 \text{Im} \sum_{a,b,c,d} P(a) \text{Habi} \text{Hcb} \text{Hcd} \text{Idc} \\ \times \frac{J_0(\omega_S - \omega_{dc} + i\Gamma_{dc}) J_0^*(\omega_L - \omega_{ba} + i\Gamma_{ba})}{\omega_S - \omega_L - \omega_{ac} + i\Gamma_{ac}}. \quad (\text{V-2})$$

When $\Gamma_{ac} \rightarrow 0$, we have

$$(\omega_S - \omega_L - \omega_{ac} + i\Gamma_{ac})^{-1} = PP(\omega_S - \omega_L - \omega_{ac})^{-1} - i\pi\delta(\omega_S - \omega_L - \omega_{ac}). \quad (\text{V-3})$$

Substituting Eq.(V-3) in Eq.(V-2) we finally obtain

$$S_R(\omega_L, \omega_S) = 2\pi \sum_{a,c} P(a) \left| \sum_b \mu_{ab} \mu_{ba} J_0(\omega_L - \omega_{ba} + i\Gamma_{ba}) \right|^2 \times \delta(\omega_S - \omega_L - \omega_{ac}) \quad (V-4)$$

A coherent Raman process is a four wave mixing process involving the interaction of molecules with two laser fields with wavevectors k_1 and k_2 and frequencies ω_1 and ω_2 , and detecting the coherently generated signal with

$$\begin{aligned} k_S &= 2k_1 - k_2 \\ \omega_S &= 2\omega_1 - \omega_2. \end{aligned} \quad (V-5)$$

This is a special case of 4WM with $k_3 = k_1$. The narrow Raman resonances are observed whenever the frequencies of both fields differ by a ground state vibrational transition $\omega_1 - \omega_2 = \omega_{ca}$ or an excited state vibrational transition $\omega_1 - \omega_2 = \omega_{cb}$. Coherent Raman experiments may be time resolved or steady state frequency resolved.¹⁵⁻¹⁹ The technique is widely used in the gas phase¹⁵ and in condensed phases, solvations^{17,19} and molecular crystals.^{16,18} Coherent Raman spectroscopy is characterized by a much better signal to noise compared with the spontaneous Raman, due to the directionality (phase matching) of the signal. The terminology of coherent anti-Stokes Raman spectroscopy (CARS) and coherent Stokes Raman spectroscopy (CSRS) refer to $\omega_1 > \omega_2$ and $\omega_1 < \omega_2$, respectively. In CARS, the signal frequency ω_S (Eq.(V-5)) is greater than either of the two incident frequencies, whereas in CSRS, ω_S is smaller than either of the incident frequencies. In the following we shall consider CARS. Within the rotating wave approximation, only four terms in Eq.(IV-10) survive. The CARS signal is then given by

$$SCARS(\omega_1, \omega_2) = \left| \chi_{CARS}^{(3)}(-\omega_2; \omega_1, -\omega_2, \omega_1) \right|^2 \quad (V-6)$$

where

$$\begin{aligned} \chi_{CARS}^{(3)}(-\omega_S; \omega_1, -\omega_2, \omega_1) &= -[\hat{R}_1(2\omega_1 - \omega_2, \omega_1 - \omega_2, \omega_1) + \hat{R}_2(2\omega_1 - \omega_2, \omega_1 - \omega_2, -\omega_2) \\ &+ \hat{R}_3(2\omega_1 - \omega_2, \omega_1 - \omega_2, -\omega_2) + \hat{R}_4(2\omega_1 - \omega_2, \omega_1 - \omega_2, \omega_1)] \end{aligned} \quad (V-7)$$

Substituting Eqs.(IV-11) in (V-7), we obtain

$$\begin{aligned} \chi_{CARS}^{(3)}(-\omega_S; \omega_1, -\omega_2, \omega_1) &= \sum_{n=0}^{\infty} \sum_{a,b,c,d} P(a) \mu_{ab} \mu_{bc} \mu_{cd} \mu_{da} \frac{1}{n!} \frac{J_n(\omega_{bc} - 2\omega_1 + \omega_2 + i\Gamma_{dc})}{\omega_1 - \omega_2 - \omega_{cb} + i(\Gamma_{ab} + n/\tau_c)} \\ &\times [(-1)^n z^n \bar{J}_n(\omega_1 - \omega_{ca} + i\Gamma_{da}) - z^{*n} \bar{J}_n(\omega_2 - \omega_{ba} + i\Gamma_{ba})] \\ &\times [z^{*n} P(c) \bar{J}_n(\omega_2 - \omega_{dc} + i\Gamma_{dc}) - (-1)^n z^n P(a) J_n(\omega_1 - \omega_{ca} + i\Gamma_{da})] \end{aligned} \quad (V-8)$$

For molecules in solution, Γ_{ac} and Γ_{bd} are usually much smaller than a characteristic broadening, $1/\tau_c$, which is typically a few hundred cm^{-1} . For finding the sharp component of $\chi_{CARS}^{(3)}$, we need only consider $n=0$ terms in Eqs.(V-8), and neglect $n>0$ terms which contributes to the broad background. Further, a Lorentzian

with a width of Γ_{ac} or Γ_{bd} may therefore be approximated by a delta function. We then write

$$\begin{aligned} & \left| \frac{1}{\omega_1 - \omega_2 - \alpha_{ca} + i\Gamma_{ca}} \right|^2 \equiv \frac{\pi \delta(\omega_1 - \omega_2 - \alpha_{ca})}{\Gamma_{ca}}, \\ & \left| \frac{1}{\omega_1 - \omega_2 - \alpha_{db} + i\Gamma_{db}} \right|^2 \equiv \frac{\pi \delta(\omega_1 - \omega_2 - \alpha_{db})}{\Gamma_{db}}, \end{aligned} \quad (V-9)$$

Making use of Eqs. (V-6)-(V-9), and ignoring background terms, we finally obtain for the coherent Raman lineshapes^{4,19)}

$$S_{\text{CARS}}(\omega_1, \omega_2) = \sum_{ac} Q_{ca}^2(\omega_1) \delta(\omega_1 - \omega_2 - \alpha_{ca}) + \sum_{bd} Q_{db}^2(\omega_1) \delta(\omega_1 - \omega_2 - \alpha_{db}) \quad (V-10)$$

and similarly, for the spontaneous Raman lineshape (Eq. (V-4)) is

$$S_{\text{R}}(\omega_L, \omega_S) = \sum_{ac} Q_{ca}(\omega_L) \delta(\omega_L - \omega_S - \alpha_{ca}) \quad (V-11)$$

where

$$Q_{ca}^2(\omega_1) = \frac{\pi}{\Gamma_{ca}} \left| P(a) \sum_b \mu_{ab} \mu_{bc} J_0(\omega_1 - \alpha_{bc} + i\Gamma_{bc}) \right|^2 \\ \times \left| \sum_d \mu_{cd} \mu_{da} J_0(\omega_1 - \alpha_{da} + i\Gamma_{da}) - \exp(-\alpha_{ca}/kT) J_0^*(\omega_1 - \alpha_{ca} + i\Gamma_{ca}) \right|^2 \quad (V-12)$$

$$Q_{db}^2(\omega_1) = \frac{\pi}{\Gamma_{db}} \left| \sum_c \mu_{cb} \mu_{cd} J_0(\alpha_{bc} - \omega_1 + i\Gamma_{bc}) \right|^2 \\ \times \left| \sum_a P(a) \mu_{ab} \mu_{da} J_0(\omega_1 - \alpha_{da} + i\Gamma_{da}) - J_0^*(\omega_1 - \alpha_{da} + i\Gamma_{da}) \right|^2 \quad (V-13)$$

$$Q_{ca}(\omega_L) = 2\pi P(a) \left| \sum_b \mu_{cb} \mu_{ba} J_0(\omega_L - \alpha_{ba} + i\Gamma_{ba}) \right|^2 \quad (V-14)$$

$Q_{ca}^2(\omega_1)$ is the coherent Raman excitation profile corresponding to a ground-state resonance $\omega_1 - \omega_2 = \alpha_{ca}$ and $Q_{db}^2(\omega_1)$ is the coherent Raman excitation profile for an excited-state resonance $\omega_1 - \omega_2 = \alpha_{db}$. $Q_{ca}(\omega_L)$ is the spontaneous Raman excitation profile. These profiles are easily measured by probing the intensity of a particular Raman line ($\omega_1 - \omega_2$ or $\omega_L - \omega_S$ fixed) as a function of ω_1 or ω_L . It should be noted that the excited-state resonances Q_{db}^2 are induced by the interaction with the solvent. In the absence of a thermal bath, an interference causes these resonances to vanish. These terms have been therefore denoted PIER4 (pressure induced extra resonances)¹⁵⁾ or DICE (dephasing induced coherent emission).¹⁶⁾ In time resolved CARS, this interference does not take place and excited state resonances may be observed even at very low temperatures.^{4,18)} In Figure 5, we display the absorption spectrum and the

Raman excitation profiles of β -carotene calculated using a stochastic model for the solvent (Eq. (IV-4) with $\lambda=0$). The calculated profiles are compared with the experimental spectra taken in isopentane at 118K. In Figure 6, we compare spontaneous Raman and CARS excitation profiles for the same system.

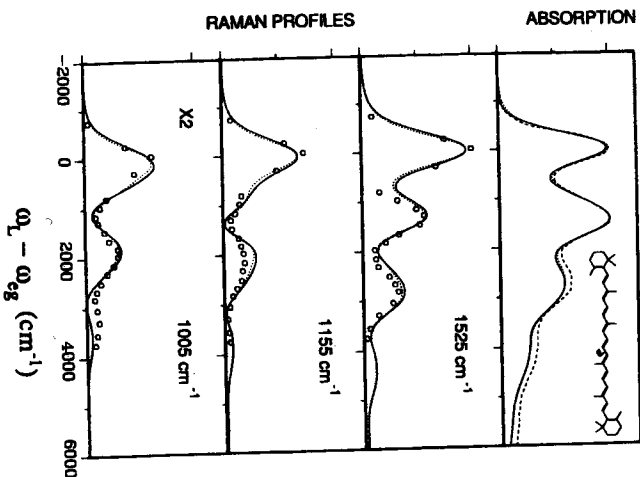


FIGURE 5: Absorption (imaginary part of $\chi^{(1)}$) (Eq. (IV-10)) (upper panel) and resonance Raman excitation profiles $\Omega_{ca}(\omega_L)$ (Eq. (V-14)) of the indicated transitions (three lower panels) of β -carotene. 19] The dashed curve in the upper panel and the circles in the three lower panels are the experimental data of Reference (20) taken in isopentane at 118K. The solid and the dotted lines are theoretical curves computed using a three-active-mode harmonic model for β -carotene. Solid lines: $\tau_L = 50$ fs, $\Delta = 362\text{cm}^{-1}$, and no inhomogeneous broadening; dotted lines: $\tau_L = 16$ fs, $\Delta = 413\text{cm}^{-1}$, and an additional inhomogeneous width of 75cm^{-1} .

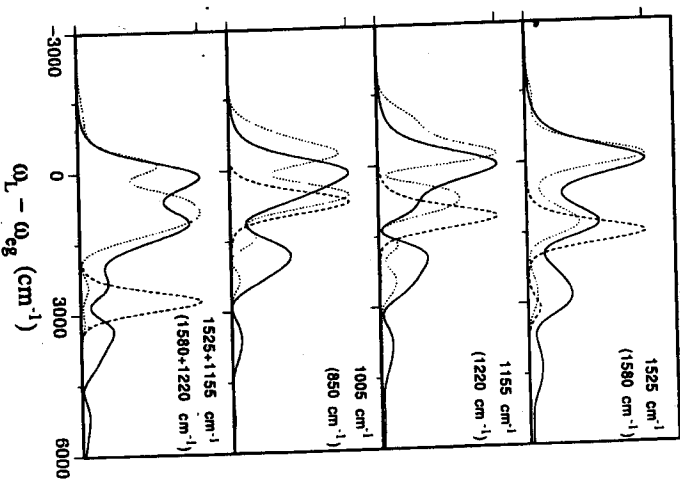


FIGURE 6: Calculated spontaneous Raman (solid lines), ground-state CARS (dotted lines) and excited-state CARS (dashed lines) Raman excitation profiles of β -carotene. 19] The ground-state Raman frequencies and the excited-state Raman frequencies (in parentheses) are given. All curves were normalized to the same maximum peak value. Line broadening parameters of the model solvent are $\tau_L = 16$ fs, $\Delta = 413\text{cm}^{-1}$ and an inhomogeneous width of 75cm^{-1} was included.

VI. RESPONSE FUNCTIONS RESULTING FROM COUPLING TO A HARMONIC COORDINATE

In this section, we calculate the response functions for an exactly solvable model which can represent intramolecular harmonic vibrations as well as coupling to a general (polar or nonpolar) solvent. 6] The model assumes a single harmonic coordinate, coupled to the electronic system and to a bath. The Hamiltonians H_g and H_e for the nuclear motions of the system are given by

$$H_g = \frac{1}{2} M\omega (p^2 + q^2)$$

$$H_e = \frac{1}{2} M\omega [p^2 + (q+D)^2].$$

(VI-1)

Here p and q are the dimensionless momentum and coordinate, and D is a dimensionless displacement of the equilibrium position between the two states. We further assume that the oscillator is subject to a stochastic Langevin force. Our starting point will thus be the Langevin equation:

$$\dot{q}(t) = \omega p(t)$$

$$\dot{p}(t) = -\omega q(t) - \gamma p(t) + f(t).$$

(VI-2)

Here γ is a Markovian friction constant, and $f(t)$ is a Gaussian-Markovian stochastic random force representing the effects of the solvent on our coordinate q . They satisfy the fluctuation-dissipation relation:

$$\langle f(t) f(0) \rangle = (\bar{n} + \frac{1}{2}) 2\gamma \delta(t).$$

(VI-3)

Here

$$\bar{n} = [\exp(\hbar\omega/k_B T) - 1]^{-1}$$

(VI-4)

is the thermally averaged occupation number of the oscillator. Eq. (VI-2) holds in the ground state $|g\rangle$. A similar equation with $q(t) \rightarrow q(t) + D$ holds in the excited state $|e\rangle$. For this model, the response functions $J(t)$ and $R_e(t)$, (t_2, t_1) have the same forms as Eqs. (III-11)-(III-12), and the lineshape function $g(t)$ is given by Eq. (III-13) with

$$\lambda = \omega D^2 / 2$$

$$\Delta^2 = \omega^2 D^2 (\bar{n} + 1/2)$$

(VI-5)

and

$$M(t) = \frac{1}{2} [\alpha_e \exp(-i\alpha_e \Omega t) + \alpha_g \exp(i\alpha_g \Omega t)],$$

(VI-6)

Here

$$\Omega = \sqrt{\omega^2 - (\gamma/2)^2},$$

(VI-7)

and

$$\alpha_e = 1 \pm i\gamma/(2\Omega).$$

(VI-8)

At high temperature $k_B T \gg \hbar\omega$, we have $\Delta^2 = 2\lambda k_B T$, in agreement with Eq. (III-14b).

This model represents a molecule with a single optically active vibrational mode, which undergoes vibrational relaxation. The response functions for polyatomic harmonic molecules, with several optically active modes can be factorized as products of contributions from individual modes.⁹⁾ The present result can thus be used for calculating spectra of polyatomic molecules as well. In addition, q may represent a collective coordinate of the solvent (the solvation coordinate) or some local low frequency solvent modes. In that case, the present model may represent the solvent contribution to electronic dephasing.

We shall consider now two limiting cases of this model. In the absence of friction ($\gamma=0$), Eq. (VI-6) reduces to

$$M(t) = \cos \omega t$$

(VI-9)

and the line broadening function (Eq. (III-13)) assumes

$$g(t) = -\frac{1}{2} D^2 \{ (\bar{n}+1) [\exp(-i\omega t) - 1] + \bar{n} [\exp(i\omega t) - 1] \}.$$

(VI-10)

Eqs. (III-11)-(III-12) together with Eq. (VI-10) constitute the well-known lineshape functions for the isolated linearly displaced oscillator. When $\gamma \gg \omega$, the oscillator is overdamped, and we get

$$M(\zeta) = \exp(-\zeta/\tau_0)$$

with

$$\tau_0 = \gamma/\omega^2.$$

(VI-11)

(VI-12)

This is the same as the Debye model (Eq. (IV-2)) with τ_0 replacing τ_L .

In concluding this article we note that we have presented a general model for the linear and the nonlinear optical properties of a polyatomic solute in a polar or nonpolar medium. The response functions are expressed in terms of molecular and solvent properties. Coherent and spontaneous Raman lineshapes as well as other time and frequency resolved nonlinear optical measurements²¹ may be conveniently analyzed using the present theory.

ACKNOWLEDGEMENTS

The support of the National Science Foundation, the Office of Naval Research, the U. S. Army Research Office, and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

REFERENCES

1. See Papers in Proceedings of the 10th International Conference on Raman Spectroscopy, W. L. Peticolas and B. Hudson, editors, U. of Oregon, Eugene (1986).
2. Bloembergen, N., *Nonlinear Optics*, Benjamin, New York (1965); Shen, Y. R., *The Principles of Nonlinear Optics*, Wiley, New York (1984).
3. Bloembergen, N., Lore, H., and Lynch, R. T., *Indian J. Pure Appl. Phys.* **16**, 151 (1978).
4. Mukamel, S., *Adv. Chem. Phys.* **70**, 165 (1988); Mukamel S. and Loring, R. F., *J. Opt. Soc. Am. B* **3**, 595 (1986).
5. Mukamel, S., *J. Chem. Phys.* **71**, 2884 (1979); *Phys. Reports* **93**, 1 (1982); *Phys. Rev. A* **28**, 3480 (1983).
6. Yan, Y. J., Sparragione, M., and Mukamel, S., *J. Phys. Chem.* **92**, 4842 (1988); Yan, Y. J. and Mukamel, S., *J. Chem. Phys.* **88**, 5735 (1988).
7. Loring, R. F., Yan, Y. J., and Mukamel, S., *Chem. Phys. Lett.* **135**, 23 (1987); *J. Phys. Chem.* **91**, 1302 (1987); *J. Chem. Phys.* **87**, 5840 (1987).
8. Botcher, C. J. F., *Theory of Electric Polarization*, Elsevier, Amsterdam, Vols. I, II (1973).
9. Mukamel, S., *J. Chem. Phys.* **82**, 5398 (1985); Sue, J., Yan, Y. J., and Mukamel, S., *J. Chem. Phys.* **85**, 462 (1986); Yan, Y. J. and Mukamel, S., *J. Chem. Phys.* **86**, 6085 (1987).
10. Bloembergen, N., Purcell, E. M., and Pound, R. V., *Phys. Rev.* **73**, 679 (1948); Anderson, P. W. and Weiss, P. R., *Rev. Mod. Phys.* **25**, 269 (1953); Kubo, R., in *Fluctuations, Relaxation and Resonance in Magnetic Systems* (D. ter Haar, ed.) Oliver and Boyd, Edinburgh (1962).
11. Mazurenko, Yu T. and Bakshiev, N. G., *Opt. Spec.* **28**, 490 (1970).
12. Castner, E. W., Maroncelli, M. and Fleming, G. R., *J. Chem. Phys.* **86**, 1090 (1987); Maroncelli, M. and Fleming, G. R., *ibid.* **86**, 6221 (1987).
13. Brito Cruz, C. H., Fork, R. L., Knox, W., and Shank, C. V., *Chem. Phys. Lett.* **132**, 341 (1986); Mathies, R. A., Brito Cruz, C. H., Pollard, W. T., and Shank, C. V., *Science* **240**, 777 (1988).
14. Myers, A. B., Harris, R. A., and Mathies, R. A., *J. Chem. Phys.* **79**, 603 (1983).
15. Rothberg, L. J. and Bloembergen, N., *Phys. Rev. A* **30**, 820 (1984).
16. Andrews, J. R. and Hoeschtrasser, R. M., *Chem. Phys. Lett.* **82**, 381 (1981).
17. Laubereau, A. and Kaiser, W., *Rev. Mod. Phys.* **50**, 607 (1978); Zinth, W., Pollard, H. J., Laubereau, A., and Kaiser, W., *Appl. Phys. B* **26**, 77 (1981).
18. Hesp, B. H. and Wiersma, D. A., *Chem. Phys. Lett.* **75**, 423 (1980); Weitekamp, D. P., Duppen, K., and Wiersma, D. A., *Phys. Rev. A* **27**, 3089 (1983).
19. Sue, J. and Mukamel, S., *J. Chem. Phys.* **88**, 651 (1988); *J. Opt. Soc. Am. B* **5**, 1462 (1988).
20. Ho, Z. Z., Moore, T. A., Lin, S. H., and Hanson, R. C., *J. Chem. Phys.* **74**, 873 (1981).
21. Fleming, G. R., *Chemical Applications of Ultrafast Spectroscopy*, Oxford, London (1986).