

Nonlinear Response Function for Four-Wave Mixing: Application to Coherent Raman Lineshapes in Polyatomics and to the Optical Anderson Transition

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In this article, we summarize recent theoretical developments for calculating nonlinear susceptibilities and four-wave mixing (4WM) signals from complex molecular systems[1-5]. In particular, we make two applications to CARS lineshapes of polyatomic molecules in condensed phases and to the usage of transient grating techniques to probe the optical Anderson transition in molecular crystals.

1. Nonlinear Susceptibilities and CARS Lineshapes of Polyatomic Molecules in Condensed Phases

We consider a polyatomic harmonic molecule with two electronic states, $|g\rangle$ and $|e\rangle$ and with N vibrational modes. Its Hamiltonian is given by

$$H = |g\rangle H_g \langle g| + |e\rangle [H_e + \omega_{eg}(t)] \langle e|, \tag{1a}$$

$$H_g = \frac{1}{2} \sum_{j=1}^N \omega_j^2 (p_j^2 + q_j^2 - 1), \tag{1b}$$

$$H_e = \frac{1}{2} \sum_{j=1}^N \omega_j^2 (p_j^2 + q_j^2 - 1) - (1/2)^N. \tag{1c}$$

p_j^i, q_j^i , and ω_j^i are the dimensionless momentum, coordinate, and frequency of mode j in the ground state and p_j^i, q_j^i , and ω_j^i are the corresponding excited state quantities. We further have:

$$q_j^i = (\omega_j^i/\omega_j^g)^{1/2} q_j^g + D_j. \tag{2}$$

D_j is the dimensionless displacement between the equilibrium configuration of the two electronic states. $\omega_{eg}(t) = \bar{\omega}_{eg} + \delta\omega_{eg}(t)$, $\bar{\omega}_{eg}$ is the fundamental (0-0) transition frequency, and $\delta\omega_{eg}(t)$ is a stochastic modulation of the electronic energy gap by interactions with a thermal bath. $\delta\omega_{eg}(t)$ is assumed to be a Gaussian Markov process, with $\langle \delta\omega_{eg}(t) \rangle = 0$ and

$$\langle \delta\omega_{eg}(t_1) \delta\omega_{eg}(t_2) \rangle = \Delta^2 \exp[-\lambda |t_1 - t_2|]. \tag{3}$$

The angular brackets in (3) denote an average over the stochastic process. Δ is the root-mean-squared amplitude, and λ^{-1} is the correlation time of the bath fluctuations. The choice of the stochastic Hamiltonian (Eq.(1)) is based on the assumption that the bath couples mainly to the electronic degrees of freedom, so that the ground state and the excited state manifolds are being stochastically modulated with respect to each other, but no modulation occurs for frequencies of levels belonging to the same electronic manifold. We have developed a general theory for any 4WM process in large polyatomic molecules characterized by the Hamiltonian (1) in condensed phases (e.g., solution, solid matrices, and glasses). The key quantity in the present formulation is the nonlinear response function $R(t_1, t_2, t_1')$, which contains all the microscopic information relevant for any type of 4WM. $R(t_1, t_2, t_1')$ is expressed in terms of a four-point correlation function of the dipole operator, which can be evaluated efficiently for this model in a closed form using Green function techniques. This eliminates the necessity of performing the multiple summations over vibronic states, which make such calculations tedious and impractical for large polyatomic molecules. The computational effort involved in the present Fourier transform method does not increase substantially as the molecular size increases. The nonlinear

susceptibility $\chi^{(3)}$ is obtained by an appropriate Fourier transform of the response function R . This result is extremely helpful and allows a convenient calculation of the response functions, both in the time domain and in the frequency domain. As an illustration, we have calculated CARS lineshapes and compared them with ordinary spontaneous Raman lineshapes. The former are given by the absolute square of $\chi^{(3)}$, whereas the latter are related to the imaginary part of $\chi^{(3)}$. In Fig. 1 we show the result of a seven mode ($N=7$) calculation for the S_0-S_1 transition in

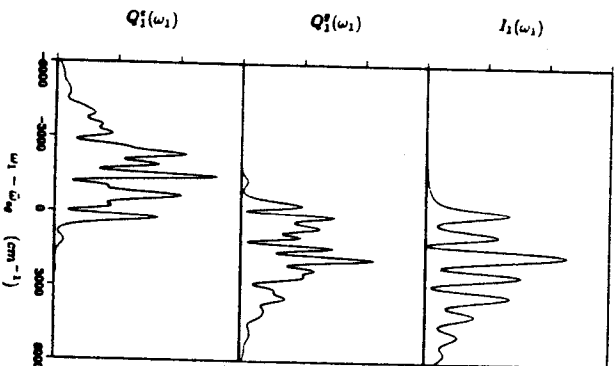


Fig. 1

The spontaneous Raman profile

$I_1(\omega_1)$, the ground-state CARS $Q_1^g(\omega_1)$ and the excited state CARS $Q_1^e(\omega_1)$ for the fundamental (0-1) transition of the 1260 cm^{-1} mode of azulene in CS_2 at 300°K. The broadening parameters are $\Delta=180 \text{ cm}^{-1}$ and $\lambda=18 \text{ cm}^{-1}$ [3].

azulene[3]. Shown are Raman fundamentals for one of the modes with $\omega''=1260 \text{ cm}^{-1}$, $\omega'=1193 \text{ cm}^{-1}$, and $D=0.77$. The top panel shows the spontaneous Raman excitation profile $I_1(\omega_1)$ (intensity of the Raman line $\omega_1, \omega_2=1260 \text{ cm}^{-1}$ vs. ω_1). ω_1 and ω_2 being the excitation and the emitted frequency, respectively. In CARS, we can see both the ground-state profile $\omega_1, \omega_2=1260 \text{ cm}^{-1}$ and the excited-state profile $\omega_1, \omega_2=1193 \text{ cm}^{-1}$. These are denoted $Q_1^g(\omega_1)$ and $Q_1^e(\omega_1)$ respectively and are shown in the middle and in the bottom panels of Fig. 1. The broadening parameters in Fig. 1 are $\Delta=180 \text{ cm}^{-1}$ and $\Lambda=18 \text{ cm}^{-1}$.

11. The Optical Anderson Transition as Probed by 4WM

A novel theory of quantum mechanical transport in disordered systems has been developed[4]. The theory is based on the Effective Dephasing Approximation (EDA), in which the ensemble-averaged Liouville space propagator is mapped into the propagator of an ordered lattice with an effective frequency-dependent dephasing rate. This generalized dephasing rate is determined self-consistently. This approach is applicable to strongly disordered systems and yields results that interpolate between the limits of coherent and incoherent excitation transport and that predict the optical analog of a metal-insulator phase transition (Anderson localization). Our results agree with the predictions of the scaling theory of the Anderson transition. We have applied the EDA to the calculation of the transient grating signal from a crystal with an inhomogeneously broadened absorption spectrum (static, site energy disorder). The transient grating experiment is shown to be a sensitive probe of the optical Anderson transition. We consider the light-binding Hamiltonian,

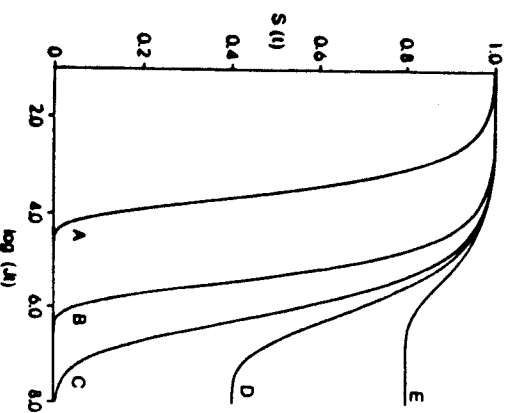


Fig. 2
The transient grating signal for a simple cubic lattice with varying degrees of site energy disorder (inhomogeneous line broadening). Curves A through E were calculated respectively for $\chi=0, 3.900, 3.957, 3.970$, and 3.980 . The optical Anderson transition occurs at $\chi^*=3.957$. For $\chi < \chi^*$, the excitations can sample the entire system, and the signal decays exponentially to zero. For $\chi > \chi^*$, the excitations are localized, and the signal decays to a finite value at long times. The excited state lifetime is not included[4].

$$H = \sum_{i,j} E_{ij} |i\rangle\langle j| + \sum_{i,j} J_{ij} (|i\rangle\langle j| + |j\rangle\langle i|). \quad (4)$$

$|j\rangle$ denotes a state in which the excitation resides on site j , J_{ij} is the transfer matrix element between molecules located at sites i and j , and E_j is the excited-state energy of the molecule at site j . We consider the case in which J_{ij} has the value J , if sites i and j are nearest neighbors on the lattice, and is zero otherwise. The site energies E_i are randomly distributed according to a given distribution $P(E)$, whose second moment is denoted Δ^2 , i.e.

$$\Delta^2 = \int_{-\infty}^{\infty} dE E^2 P(E). \quad (5)$$

The site energy disorder of the lattice enters into the EDA expression for the TG signal through $\chi \approx \Delta^2/J^2$. We predict the Anderson transition to occur at $\chi^*=3.957$. The calculated transient grating signal for various values of χ both above and below the transition is displayed in Fig. 2.

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