

Partial support of the research reported here by a grant from the Robert A. Welch Foundation is gratefully acknowledged. PJR is an Alfred P. Sloan Foundation Fellow and the recipient of a Dreyfus Teacher-Scholar Award, an NSF Presidential Young Investigator Award, and an NIH Research Career Development Award from the National Cancer Institute, DHHS.

¹R. A. Kuharski and P. J. Rossky, *Chem. Phys. Lett.* **103**, 357 (1984).

²R. A. Kuharski and P. J. Rossky, *J. Chem. Phys.* **82**, 5164 (1985).

³F. H. Stillinger and A. Rahman, *J. Chem. Phys.* **60**, 1545 (1974).

⁴F. H. Stillinger, *Adv. Chem. Phys.* **31**, 1 (1975).

⁵C. W. Kern and M. Karplus in *Water, A Comprehensive Treatise*, edited by F. Franks (Plenum, New York, 1972), Vol. 1.

⁶W. C. Ermler and C. W. Kern, *J. Chem. Phys.* **55**, 4851 (1971).

⁷D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water* (Oxford University, New York, 1969), p. 229.

⁸W. E. Thiessen and A. H. Narten, *J. Chem. Phys.* **77**, 2656 (1982).

Eigenstate-free calculation of Raman line shapes in anharmonic molecules

Shaul Mukamel^(a) and James Sue

Department of Chemistry, University of Rochester, Rochester, New York 14627

(Received 15 October 1984; accepted 10 January 1985)

In this note we make use of the spectral density formalism¹⁻³ to develop an "eigenstate-free" procedure towards the calculation of Raman line shapes in anharmonic molecules and relate them directly to molecular parameters.⁴

Consider a molecule with two electronic states and Born-Oppenheimer nuclear Hamiltonians $H_a = T + V_a$ and $H_b = \omega_{ba} + T + V_b$. T being the kinetic energy of the nuclei, V_a and V_b are the potentials of interaction, and ω_{ba} is the electronic energy difference between their minima. In a Raman experiment we scatter a photon ω_L and observe the emission of an ω_s photon. The cross section for the process is

$$I(\omega_L, \omega_s) = \sum_{gg'} P(g) |\chi_{gg'}(\Delta)|^2 \delta(\omega_{gg'} + \omega_L - \omega_s). \quad (1)$$

Here $\Delta \equiv \omega_L - \omega_{ba}$, $|g\rangle$, and $|g'\rangle$ are the initial and final vibronic eigenstates belonging to the $|a\rangle$ electronic state with energies E_g and $E_{g'}$, $\omega_{gg'} \equiv E_g - E_{g'}$, and $P(g)$ is the equilibrium population of $|g\rangle$. The spectral density method¹⁻³ is based on a time-domain systematic cumulant expansion of the line shape in the energy gap between both electronic states $U \equiv V_b - V_a$. To second order, we calculate the two-time correlation function of the energy gap (the spectral density) i.e.,

$$\begin{aligned} \langle U(0)U(\tau) \rangle &= \text{Tr} [U \exp(iH_a \tau) U \exp(-iH_a \tau) \rho_{\text{eq}}] \\ &= \sum_{j=1}^N \omega_j^2 s_j^2 [(\bar{n}_j + 1) \exp(i\omega_j \tau) + \bar{n}_j \exp(-i\omega_j \tau)], \end{aligned} \quad (2)$$

where ρ_{eq} is the equilibrium density matrix at temperature T , and $\bar{n}_j = [\exp(\hbar\omega_j/kT) - 1]^{-1}$. This correlation function may be evaluated semiclassically without having to calculate any vibronic eigenstates by running a classical trajectory on the ground state anharmonic potential surface.^{1-3,5} ω_j and s_j are obtained from a Fourier decomposition of the spectral density. The Raman spectrum is obtained by substituting the spectral density [Eq. (2)] in Eqs. (71), (85), and (86) of Ref. 1 and performing a triple Fourier transform. It should be noted, however, that Eq. (2) is also the exact spectral density of an *equivalent harmonic molecule* whose number of degrees of freedom (N) is the same as the number of

Fourier components of the spectral density.⁶ The frequencies of the equivalent harmonic system are ω_j , and its excited state potential V_b is linearly displaced with respect of V_a , i.e.,

$$U = \sum_{j=1}^N s_j \omega_j Q_j,$$

where Q_j are the dimensionless coordinates. This equivalence allows us to carry out the necessary triple Fourier transform and recast the spectrum in the form of Eq. (1). For a single Fourier component ($N = 1$) with frequency ω and choosing $|g\rangle = |0\rangle$ (the ground vibronic state) and $|g'\rangle = |n\rangle$, and assuming a phenomenological lifetime $(2\gamma)^{-1}$ of the $|b\rangle$ state, we then get Eq. (1) with $\omega_{g'g} = \omega_{n0} = n\omega$, and where

$$\chi_{n0}(\Delta) = -i \int_0^\infty d\tau \exp(i\Delta\tau - \gamma\tau) \chi_{n0}(\tau), \quad (3)$$

$$\chi_{n0}(\tau) = \frac{1}{\sqrt{n!}} [f(\tau)]^n \exp\left[-\frac{s}{\sqrt{2}} f(\tau)\right],$$

and

$$f(\tau) = \frac{s}{\sqrt{2}} [\exp(-i\omega\tau) - 1].$$

Equation (3) was derived by using the Magnus expansion. Closed expressions may be obtained also for the general amplitude⁶ $\chi_{nm}(\tau)$ where $m \neq 0$. $\chi_{n0}(\tau)$ were derived also by Tannor and Heller.^{7(a)} For a multidimensional system with N Fourier components we have

$$\chi(\tau) = \prod_{j=1}^N \chi^{(j)}(\tau)$$

where $\chi^{(j)}$ is given by Eq. (3) with $\omega = \omega_j$, $s = s_j$, $n = n_j$, and $m = m_j$. Also

$$\omega_{g'g} = \sum_{j=1}^N (n_j - m_j) \omega_j.$$

HST^{7(b)} have derived recently an alternative expression for the Raman amplitudes $\chi_{10}(\tau)$, and $\chi_{20}(\tau)$, using short-time

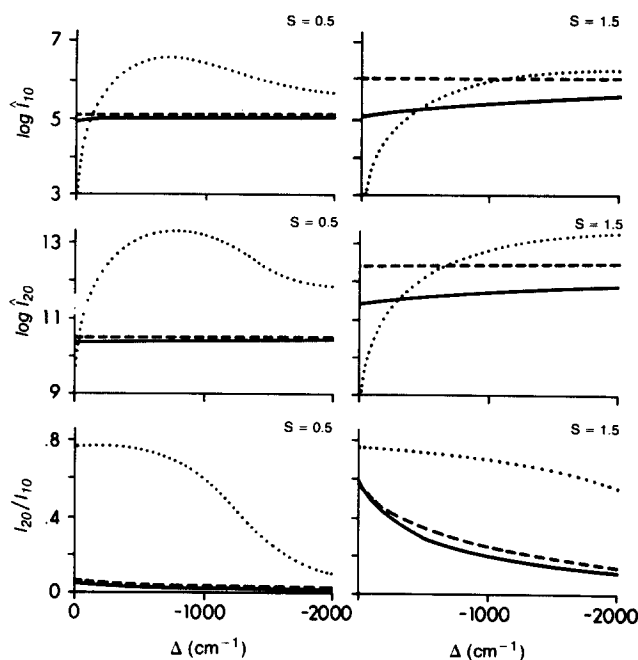


FIG. 1. The Raman intensities for a single displaced harmonic oscillator $\omega = 1000 \text{ cm}^{-1}$, $\gamma = 10 \text{ cm}^{-1}$, and $I_{10} \equiv |\chi_{10}|^2$, $I_{20} \equiv |\chi_{20}|^2$. Shown are the Raman fundamental $\hat{I}_{10} \equiv I_{10} |\Delta + i\gamma| |\Delta - \omega + i\gamma|^2$, and the first overtone $\hat{I}_{20} \equiv I_{20} |\Delta + i\gamma| |\Delta - \omega + i\gamma| |\Delta - 2\omega + i\gamma|^2$ (on a logarithmic scale, base 10), and the ratio I_{20}/I_{10} . Solid line—the spectral density (exact) result [Eq. (3)], dotted line—the Gaussian wave packet short-time approximation (Ref. 7) [Eq. (4)], dashed line—the perturbative calculation [Eq. (5)].

propagation of a Gaussian wave packet on the excited potential surface. Their result for a single displaced harmonic oscillator is given by (in our notation):

$$\chi_{10}(\tau) = \frac{is\omega\tau}{\sqrt{2}} \exp(i\phi\tau - s^2\omega^2\tau^2/4); \quad \chi_{20}(\tau) = \frac{s\omega\tau}{2} \chi_{10}(\tau), \quad (4)$$

where

$$\phi \equiv \omega/2(1/2 - s^2).$$

Alternatively, if we expand χ_{gg} in powers of U , we get to lowest order perturbation theory.^{8,9}

$$\chi_{10}(\Delta) = \frac{s\omega}{\sqrt{2}(\Delta + i\gamma)(\Delta - \omega + i\gamma)}; \quad \chi_{20}(\Delta) = \frac{s^2\omega^2}{\sqrt{2}(\Delta + i\gamma)(\Delta - \omega + i\gamma)(\Delta - 2\omega + i\gamma)}. \quad (5)$$

In Fig. 1 we display the Raman intensities ($I_{n0} \equiv |\chi_{n0}|^2$, $n = 1, 2$) for a single displaced harmonic system ($N = 1$).

It is clear that for typical values of s_j , which commonly appear in molecular spectra ($|s_j| < 1.5$), the HST theory [Eq. (4)] does not improve upon the simple perturbative expression [Eq. (5)] and may differ by several orders of magnitude from the exact result of the spectral density [Eq. (3)].

In conclusion, we note the following:

(i) The spectral density formalism is truly eigenstate free. The ground state frequencies ω_{gg} , and the amplitudes

χ_{gg} in this procedure are obtained not from *a priori* knowledge of vibronic eigenstates, but from the Fourier components of the spectral density $\langle U(0)U(\tau) \rangle$ which, in turn, may be generated by running a classical trajectory on the electronic ground state. The Gaussian wave packet⁷ approach, which focuses on the time evolution of the doorway state,¹⁰ requires, on the other hand, the calculation of the exact vibronic eigenstates of the ground electronic state and therefore is not an eigenstate-free theory.

(ii) For molecules which are in contact with a thermal bath it is straightforward to incorporate external line broadening mechanisms, including pure dephasing (T_2) processes into the spectral density approach.² This is crucial for spectra in solution and matrices, for chromophores on proteins, etc. The Gaussian wave packet approach does not allow such a *reduced description* since it uses amplitudes and wave functions rather than the density matrix. Only diagonal lifetime (T_1) relaxation can be put phenomenologically into the theory.¹¹

(iii) Our mapping of an anharmonic molecule into an equivalent harmonic molecule with more degrees of freedom may allow us to use other powerful transform methods which were specifically constructed for harmonic molecules.^{4,12}

Acknowledgment is made to the National Science Foundation and to the donors of the Petroleum Research Fund, administered by the American Chemical Society for their support of this work.

^{a1} Camille and Henry Dreyfus Teacher-Scholar.

¹ Mukamel, J. Chem. Phys. **77**, 173 (1982).

² S. Mukamel, Phys. Rep. **93**, 1 (1982).

³ R. Islampour and S. Mukamel, J. Chem. Phys. **80**, 5487 (1984); Chem. Phys. Lett. **107**, 239 (1984); **108**, 161 (1984).

⁴ J. Tang and A. C. Albrecht, in *Raman Spectroscopy*, edited by H. A. Szymanski (Plenum, New York, 1970), Vol. 2, p. 33; P. M. Champion and A. C. Albrecht, Annu. Rev. Phys. Chem. **33**, 353 (1982).

⁵ A. Warshel, P. S. Stern, and S. Mukamel, J. Chem. Phys. **78**, 7498 (1983).

⁶ S. Mukamel, J. Phys. Chem. **89**, 1077 (1985).

⁷ (a) D. J. Tannor and E. J. Heller, J. Chem. Phys. **77**, 202 (1982); (b) E. J. Heller, R. L. Sundberg, W. D. Tannor, J. Phys. Chem. **86**, 1822 (1982).

⁸ A. Warshel and P. Dauber, J. Chem. Phys. **66**, 5477 (1977).

⁹ A. Blazej and W. L. Peticolas, Proc. Natl. Acad. Sci. U.S.A. **74**, 2639 (1977).

¹⁰ S. Mukamel and J. Jortner, in *Excited States*, edited by E. C. Lim (Academic, New York, 1977), Vol. 3, p. 57.

¹¹ A. B. Myres, R. A. Harris, and R. A. Mathies, J. Chem. Phys. **79**, 603 (1983).

¹² V. Hizhnyanov and I. Tehver, Phys. Status Solidi **21**, 755 (1967); J. B. Page and D. L. Tonks, J. Chem. Phys. **75**, 5694 (1981).