stirring the reaction mixture produced no significant rate increase.

Two factors are responsible for making this reaction surfacecontrolled. The first is the much faster rate of diffusion possible with a colloidal catalyst where the effective Nernst layer thickness¹³ is some 10⁴ times smaller than at a rotating disk catalyst. The second reason lies in the low exchange current density of the $S_2O_3^{2-}/S_4O_6^{2-}$ couple.^{25,26} Its anodic current at the mixture potential at the gold surface will therefore be small, and so will

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the catalytic rate if, as seems likely,²⁷ the catalytic mechanism involves electron transfer between ferricyanide and thiosulfate ions through the gold particles.

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FEATURE ARTICLE

Fluorescence and Absorption of Large Anharmonic Molecules. Spectroscopy without **Eigenstates**

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Spectra of polyatomic molecules and molecular clusters provide a unique opportunity for confronting microscopic and macroscopic types of theoretical approaches for the same experimental observables. Traditional spectroscopy of isolated molecules focuses on individual eigenstates (their positions and dipole strengths). Macroscopic line shapes on the other hand contain collective coarse-grained information which is the average of many eigenstates. A reduced correlation-function formulation which allows a microscopic calculation of spectra without having to consider individual eigenstates is then used. Spectra of large polyatomic molecules may be treated with both types of approaches. However, as the molecular size increases, the macroscopic approaches become more applicable and much more efficient. In this article some of the existing methods for the calculation of fluorescence and absorption line shapes in large anharmonic polyatomic molecules are reviewed. Both time-resolved and frequency-resolved spectra are discussed. A macroscopic semiclassical "eigenstate free" procedure is developed and the information content of fluorescence spectra is analyzed.

Introduction

The calculation of molecular optical two-photon processes (fluorescence and Raman spectra and two-photon absorption) in large anharmonic molecules is one of the fundamental problems in molecular dynamics and spectroscopy. Recent experiments, particularly involving ultracold molecules in supersonic beams, are yielding accurate and detailed information (both time resolved and frequency resolved).¹⁻¹³ This creates the need for the development of appropriate theoretical tools that will enable us to extract dynamical information from these spectra.

The calculation of spectral line shapes (and any other response function) in macroscopic systems is usually made by correlation-function methods which are based on a reduced description.¹⁴⁻²⁹ This is the case for pressure broadening in the gas phase, line shapes in liquids and solid matrices, etc. One never attempts to calculate the exact eigenstates of the macroscopic system. The reason is twofold: (1) such a calculation is extremely difficult due to the enormous number of degrees of freedom involved, and (2) the experimental broadened line shapes contain highly averaged information and do not reveal properties of individual eigenstates. The calculation of individual eigenstates of macroscopic systems is therefore neither feasible nor desirable.

The analysis of spectra of isolated molecules on the other hand is traditionally made in terms of properties of individual molecular

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eigenstates (level positions and dipole matrix elements).³⁰ Such an approach is appropriate for small or intermediate size molecules but for large molecules (10 atoms or more) it is impractical. The spectra show intramolecular line broadening in which information on individual eigenstates is highly averaged. This state of affairs is very similar to the behavior of macroscopic systems and it is obvious that methods and techniques developed for the latter may be adopted toward the treatment of intramolecular line broadening of large isolated polyatomic molecules. As a simple demonstration of the usefulness of the macroscopic concepts we recall that in macroscopic systems we usually consider the density of modes per unit volume as a fundamental dynamical quantity whereas in molecules we usually look at the total density of states. It is clear that, for many spectroscopic and dynamical observables, the former quantity is more relevant. When the molecule is large enough, its exact size is not so important as far as the behavior of a single bond is concerned.³¹

In this article we review the various available methods toward the calculation of fluorescence and electronic absorption spectra of polyatomic molecules. In particular we shall develop an easily calculable correlation function procedure which evaluates the spectrum in terms of the correlation function of the electronic potential energy gap. This in turn may be calculated semiclassically. The information content of fluorescence spectra is reviewed and a unified picture valid from the small molecule to the large, statistical limit is presented.

II. Expressions for Fluorescence Spectra

In this section we develop the basic correlation-function expressions for fluorescence line shapes. We show how both frequency-resolved and time-resolved observables may be expressed in terms of the same four-point correlation function of the dipole operator $F(\tau_1, \tau_2, \tau_3)$. This is a general feature of two-photon processes, since the amplitude for these processes is second order

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in the dipole interactions V and the cross section (amplitude square) will be fourth order in $V.^{17,32,33}$

Consider a large polyatomic molecule with a ground electronic state $|a\rangle$ and an electronically excited state $|b\rangle$. Within the Born Oppenheimer (BO) approximation the moelcular Hamiltonian is given by

 $H = |a\rangle H_a \langle a| + |b\rangle H_b \langle b|$

Here

$$H_{\nu} \equiv \sum_{i} \frac{P_{i}^{2}}{2m} + \bar{V}_{\nu}(\mathbf{Q}) \qquad \nu = a, b$$
 (1a)

is the BO Hamiltonian for the vth electronic state, P_i and m_i are the momentum operator and the mass of the *i*th nucleus, and $\bar{V}_{\nu}(\mathbf{Q})$ is the BO potential surface which depends on the nuclear coordinates Q. We further assume that the $|a\rangle$ and $|b\rangle$ states are coupled by the dipole operator to an external classical electromagnetic field with frequency $\omega_{\rm L}$ and to the continuum of spontaneous emission modes ω_s . The total Hamiltonian in the rotating frame is given by

$$H_{\rm T} = H + H_{\rm int}(t) \tag{2}$$

where the radiation-matter interaction $H_{int}(t)$ is

 $H_{\rm int}(t) = \mu_{\rm L}[\phi(t) \exp(i\omega_{\rm L}t) + \phi^*(t) \exp(-i\omega_{\rm L}t)] +$

$$\mu_{\rm s}[a_{\rm s}^{\dagger} \exp(i\omega_{\rm s}t) + a_{\rm s} \exp(-i\omega_{\rm s}t)] \quad (2a)$$

and where

$$\mu_{\rm L} \equiv \bar{\mu}_{\rm L}(|a\rangle\langle b| + |b\rangle\langle a|) \tag{2b}$$

$$\mu_{s} \equiv \bar{\mu}_{s}(|a\rangle\langle b| + |b\rangle\langle a|)$$
(2c)

We further define

$$V \equiv H_{\rm int}(t=0) \tag{3}$$

Here $\mu_{\rm L}$ is the electronic dipole operator which is taken to be independent of the nuclear coordinates. $\phi(t)$ represents the amplitude of the external field with $\phi(t=0) = 1$. For steady-state experiments $\phi(t) = 1$ whereas for pulsed experiments $|\phi(t)|^2$ represents the temporal profile of the pulse intensity. μ_s is the dipole coupling with the μ_s modes and $a_s^{\dagger}(a_s)$ are the usual creation (annihilation) operators. μ_L and μ_s differ by a simple proportionality constant and hereafter we take $\bar{\mu}_s = \bar{\mu}_L = 1$.

We shall be interested in a fluorescence process whereby a photon $\omega_{\rm L}$ is being absorbed and a photon $\omega_{\rm s}$ is emitted. The simplest experiment is at steady state ($\phi(t) = 1$) in which the rate of emission of ω_s photons is given by³

$$I(\omega_{\rm L},\omega_{\rm s}) = 2\pi \sum_{\mathbf{g},\mathbf{g}'} P(\mathbf{g}) |\langle \mathbf{g}' | \mathbf{\chi} | \mathbf{g} \rangle|^2 \delta(\omega_{\mathbf{g}\mathbf{g}'} + \omega_{\rm L} - \omega_{\rm s})$$
(4)

Where χ is the amplitude for the two-photon transition, i.e.

$$\langle \mathbf{g}' | \boldsymbol{\chi} | \mathbf{g} \rangle \equiv \langle \mathbf{g}' | \boldsymbol{\chi} (E_{\mathbf{g}} + \omega_{\mathrm{L}}) | \mathbf{g} \rangle = \sum_{j} \frac{\langle \mathbf{g}' | \boldsymbol{V} | \mathbf{j} \rangle \langle \mathbf{j} | \boldsymbol{V} | \mathbf{g} \rangle}{\omega_{\mathbf{g}j} + \omega_{\mathrm{L}} + \frac{i}{2} \gamma_{\mathrm{b}}} \quad (5)$$

Here $|g\rangle$ and $|g'\rangle$ are vibronic eigenstates of H_a whereas $|j\rangle$ are vibronic eigenstates of the electronically excited molecule (H_b) , i.e.

$$H_{a}|g\rangle = E_{g}|g\rangle \tag{6}$$

$$H_{\rm b}|\mathbf{j}\rangle = E_{\rm j}|\mathbf{j}\rangle \tag{7}$$

 $P(\mathbf{g})$ is the equilibrium population of $|\mathbf{g}\rangle$, γ_{b} is the inverse radiative lifetime of the b level, and $\omega_{\alpha\beta} \equiv E_{\alpha} - E_{\beta}$. Had we known the

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molecular vibronic eigenstates (eq 6 and 7), this would be the end of the calculation. The calculation of the molecular eigenstates is, however, a formidable task for large anharmonic molecules (when $\bar{V}_{\nu}(Q)$ is not quadratic in Q). We shall therefore rewrite eq 4 in a correlation-function form which does not involve explicitly the molecular eigenstates. To that end we define the four-point correlation function^{17,32,33}

$$F(\tau_{1},\tau_{2},\tau_{3}) \equiv \langle V_{ab}(0) \ V_{ba}(\tau_{1}) \ V_{ab}(\tau_{2}) \ V_{ba}(\tau_{3}) \rangle \\ \equiv Tr[V_{ab}(0) \ V_{ba}(\tau_{1}) \ V_{ab}(\tau_{2}) \ V_{ba}(\tau_{3}) \ \rho_{eq}] \quad (8)$$

where

$$V(\tau) = \exp(iH\tau) H_{\rm int}(\tau=0) \exp(-iH\tau)$$
(9)

and

$$\rho_{\rm eq} = \exp(-H_{\rm a}/kT)/\operatorname{Tr}\,\exp(-H_{\rm a}/kT) \tag{10}$$

is the equilibrium canonical density matrix of the molecule. Equation 4 may be rearranged by making a simple Fourier transform, in the form 21,22,25,32,33

$$I(\omega_{\rm L},\omega_{\rm s}) = \int_{-\infty}^{\infty} d\tau \int_{0}^{\infty} d\tau_1 \int_{0}^{\infty} d\tau_2 F(\tau_1,\tau+\tau_1,\tau+\tau_1-\tau_2) \times \exp[i\omega_{\rm L}(\tau_2-\tau_1) + i(\omega_{\rm s}-\omega_{\rm L}) \tau - \frac{1}{2}\gamma_{\rm b}(\tau_1+\tau_2)]$$
(11)

The expansion of fluorescence spectra in terms of the four-point correlation function (eq 8) was first introduced by Hizhnyakov and Tehver for impurity spectra in solids,^{21,22} whereby V_a and V_b are linearly displaced harmonic surfaces (see eq 43). In eq 11 the three time arguments of F do not have a fixed order (i.e., τ_1 can be either larger or smaller than $\tau + \tau_1$ and $\tau + \tau_1 - \tau_2$, etc.). By changing variables it is possible to rearrange it in the following form:¹⁷

$$I(\omega_{\rm L},\omega_{\rm s}) = \int_0^\infty d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 \left[\Psi(\tau_1,\tau_2,\tau_3) F(\tau_1,\tau_2,\tau_3) + \Psi(\tau_2,\tau_1,\tau_3) F(\tau_2,\tau_1,\tau_3) + \Psi(\tau_3,\tau_1,\tau_2) F(\tau_3,\tau_1,\tau_2) \right] + \text{c.c.}$$
(12)

where

$$\Psi(\tau_1, \tau_2, \tau_3) = \exp[-i\omega_{\rm L}\tau_3 - i\omega_{\rm s}(\tau_1 - \tau_2) - \frac{1}{2}\gamma_{\rm b}(\tau_1 + \tau_2 - \tau_3)]$$
(13)

In eq 12 $\tau_3 < \tau_2 \le \tau_1$ and each term corresponds to a specific time ordering. This form naturally appears when we do the calculation using the density matrix in Liouville space and is particularly useful for molecular spectra in condensed phases, whereby external broadening mechanisms are significant. A detailed discussion of this point as well as the complete diagrammatics using the density matrix were given elsewhere.^{17,32} The significance of the four-point correlation function may be understood by rewriting it in the form

$$F(\tau_1, \tau_2, \tau_3) = \sum_{\mathbf{g}} P(\mathbf{g}) \langle \mathbf{g} | \exp(iH_b\tau_1) \exp[-iH_a(\tau_1 - \tau_2)] \exp[-iH_b(\tau_2 - \tau_3)] | \mathbf{g} \rangle$$
(14)

with $P(\mathbf{g}) \equiv \langle \mathbf{g} | \rho_{eq} | \mathbf{g} \rangle$. The molecule starts in the initial state $| \mathbf{g} \rangle$. At time τ_3 an ω_L photon is absorbed; the wave function then progresses for a period $\tau_2 - \tau_3$ on the excited \bar{V}_b potential surface, then for a period of $\tau_1 - \tau_2$ on the \bar{V}_a potential surface, and finally for a period $-\tau_1$ on \bar{V}_b . The overlap of the resulting wave function with the initial vibronic state $| \mathbf{g} \rangle$ gives the four-point correlation function. Equation 12 implies that a knowledge of this function for all values of τ_1 , τ_2 , τ_3 allows us to calculate the fluorescence spectrum.

For comparison, the absorption line shape $\bar{I}(\omega_L)$ is given in terms of the two-time dipole correlation function

$$\tilde{I}(\omega_{\rm L}) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau \, \exp(-i\omega_{\rm L}\tau - \frac{1}{2}\gamma_{\rm b}|\tau|) \langle V_{\rm ab}(0) \, V_{\rm ba}(\tau) \rangle \quad (15)$$

with

$$\langle V_{ab}(0) \ V_{ba}(\tau) \rangle \equiv \operatorname{Tr} \left(V_{ab}(0) \ V_{ba}(\tau) \ \rho_{eq} \right) = \sum_{g} P(g) \langle g| \exp(iH_b\tau) \ \exp(-iH_a\tau) |g\rangle$$
 (15a)

Equation 15a implies that the two-time correlation function may be obtained by starting at state $|g\rangle$, propagating the wave function for a time τ on the \vec{V}_a surface, and then propagating for a time $-\tau$ on \vec{V}_b . The overlap of the resulting wavepacket with the state $|g\rangle$ yields the two-time correlation function of the dipole operator.

We shall turn now to a more detailed experimental observable, i.e., when we have both time *and* frequency resolution. Let us consider a final state $|g'\rangle$ with photon ω_s . The amplitude of this state given that the molecule was in the state $|g\rangle$ at $t \rightarrow -\infty$ may be calculated from second-order perturbation theory, resulting in

$$C_{g'g}(t) = \int_{-\infty}^{t} d\tau_1 \int_{-\infty}^{\tau_1} d\tau_2 \phi(\tau_2) \exp[-i\omega_{\rm L}\tau_2 + i\omega_{\rm s}\tau_1 - \frac{1}{2}\gamma_{\rm b}(\tau_1 - \tau_2)] \langle g' | V_{\rm ab}(\tau_1) V_{\rm ba}(\tau_2) | g \rangle$$
(16)

The emission rate of ω_s photons at time t will be therefore

$$\hat{I}(\omega_{\rm L},\omega_{\rm s},t) = \frac{\rm d}{{\rm d}t} \sum_{\rm gg'} P(\rm g) |C_{\rm g'g}(t)|^2$$
(17)

Note that the steady-state expression (eq 11) may be obtained from this equation by switching the field adiabatically, i.e., by taking

and then $\tilde{I}(\omega_L, \omega_s, t>0)$ will be equal to $I(\omega_L, \omega_s)$. Again by using the Liouville space formulation (or changing integration variables in eq 17) we may bring it to the form³²

$$\hat{I}(\omega_{\rm L},\omega_{\rm s},t) = \int_{-\infty}^{t} d\tau_1 \int_{-\infty}^{\tau_1} d\tau_2 \int_{-\infty}^{\tau_2} d\tau_3 F(t-\tau_3,\tau_1-\tau_3,\tau_2-\tau_3) \Psi(t-\tau_3,\tau_1-\tau_3,\tau_2-\tau_3) \phi(\tau_2) \phi(\tau_3) + F(\tau_1-\tau_3,t-\tau_3,\tau_2-\tau_3) \Psi(\tau_1-\tau_3,t-\tau_3,\tau_2-\tau_3) \phi(\tau_2) \phi(\tau_3) + F(\tau_2-\tau_3,t-\tau_3,\tau_1-\tau_3) \Psi(\tau_2-\tau_3,t-\tau_3,\tau_1-\tau_3) \phi(\tau_1) \phi(\tau_3)$$
(19)

It should be noted that $\hat{I}(\omega_{\rm L}, \omega_{\rm s}, t)$ is not an experimental observable since it implies infinite temporal and frequency resolution which is impossible in principle. However, the result of any realistic measurement performed on the system $\hat{I}_{\rm expt}$ may be obtained from \hat{I} by properly convoluting it with a function $\theta(\omega, \tau)$ characteristic of the detection device

$$\hat{I}_{expt}(\omega_{L},\omega_{s},t) = \int \int \hat{I}(\omega_{L},\omega_{s}+\omega,t+\tau) \ \theta(\omega,\tau) \ d\omega \ d\tau \quad (20)$$

In concluding this section we note that we have shown how any observable in fluorescence is actually probing the four-point correlation function $F(\tau_1,\tau_2,\tau_3)$ (eq 8) whereas the absorption is probing the corresponding two-time correlation function $\langle V_{ab}(0)V_{ba}(\tau)\rangle$ (eq 15a). In the next two sections we shall consider methods for the evaluation of F.

III. The Doorway State Picture

The doorway state formalism provides a simple visualization of fluorescence spectra. It was developed for radiationless transitions in intermediate size molecules.³⁴ Let us assume that we know the vibrational eigenstates $|g\rangle$, $|g'\rangle$ of the ground electronic state. The doorway state corresponding to $|g\rangle$ is defined as

$$|s\rangle \equiv \mu |g\rangle = \sum_{j} |j\rangle \langle j|\mu|g\rangle \qquad (21a)$$

similarly

$$|\mathbf{s}'\rangle \equiv \mu |\mathbf{g}'\rangle \equiv \sum_{j} |j\rangle \langle j|\mu |\mathbf{g}'\rangle$$
 (21b)

Each doorway state is a wave packet of excited molecular states. Upon the substitution of eq 21 in eq 8 we get

$$F(\tau_{1},\tau_{2},\tau_{3}) = \langle V_{ab}(0) \ V_{ba}(\tau_{1}) \ V_{ab}(\tau_{2}) \ V_{ba}(\tau_{3}) \rangle = \sum_{gg'} P(g) \langle s(\tau_{1}) \ s'(0) \rangle \langle s'(0) | s(\tau_{2} - \tau_{3}) \rangle \ \exp[-iE_{g}\tau_{3} - iE_{g'}(\tau_{1} - \tau_{2})]$$
(22)

Here

$$\langle \mathbf{s}'(0)|\mathbf{s}(\tau)\rangle \equiv \langle \mathbf{s}'|\exp(-iH_{\mathbf{b}}\tau)|\mathbf{s}\rangle$$
(23)

is the projection of the $|s\rangle$ doorway state propagated with the $H_{\rm b}$ Hamiltonian, on $|s'\rangle$. When eq 22 is substituted into eq 11 we obtain the steady-state fluorescence rate

$$I(\omega_{\rm L},\omega_{\rm s}) = 2\pi \sum_{gg'} P(g) |C_{g'g}|^2 \, \delta(\omega_{gg'} + \omega_{\rm L} - \omega_{\rm s}) \qquad (24)$$

where

$$C_{g'g} = \int_0^\infty d\tau \, \langle \mathbf{s}(\tau) | \mathbf{s}'(0) \rangle \, \exp[-i(E_g + \omega_L)\tau - \frac{1}{2}\gamma_b\tau] \qquad (24a)$$

Similarly, the absorption line shape (eq 15) assumes the form $\tilde{I}(\omega_1) =$

$$\frac{1}{2\pi}\sum_{g} P(g) \int_{-\infty}^{\infty} d\tau \exp[-i(E_{g} + \omega_{L})\tau - \frac{1}{2\gamma_{b}\tau}] \langle s(\tau)s(0) \rangle \quad (25)$$

The time-dependent photon emission rate is given by eq 17 where

$$C_{g'g}(t) = \int_{-\infty}^{t} d\tau_1 \int_{-\infty}^{\tau_1} d\tau_2 \phi(\tau_2) \langle s'(0) | s(\tau_1 - \tau_2) \rangle \times \exp[-i(E_g + \omega_L)\tau_2 + i(E_{g'} + \omega_s)\tau_1 - \frac{1}{2}\gamma_b(\tau_1 - \tau_2)]$$
(26)

The doorway state picture provides a transparent interpretation of two-photon processes. If we wish to calculate a process in which the molecule initially at state $|g\rangle$ absorbs an ω_L photon and emits an ω_s photon into state $|g'\rangle$ we do the following: We create the doorway state $|s\rangle$ of $|g\rangle$ (eq 21a), let it evolve in time on the excited-state potential surface, and find the projection of $|s'\rangle$ on $|s(t)\rangle$ ($|s'\rangle$ being the doorway state corresponding to $|g'\rangle$), i.e., eq 21b. From this projection we can calculate both the frequency-resolved and the time-resolved spectra via eq 24 and 26. The absorption spectrum may be calculated from eq 25. This is a very simple way to treat and interpret spectra of intermediate size molecules, quantum beat spectroscopy, etc.³⁴ The doorway state formalism was subsequently used to develop a semiclassical wavepacket method toward the calculation of $\langle s(t)|s'(0) \rangle$.³⁵ This method is based on the approximation (which is exact for harmonic molecules) that the wave function remains a Gaussian wavepacket at all times. Extension of these results beyond the Gaussian approximation were made recently.³⁶

The problem with the doorway state method is that its application requires the knowledge of the exact vibronic eigenstates of the ground electronic state $|g\rangle$ and $|g'\rangle$. This, in general, is very difficult to obtain for large anharmonic molecules. This procedure is therefore not truly an "eigenvalue free" spectroscopy, and it accomplishes only half of the mission: It relieves us only from solving for the excited vibronic states [j). Good progress has been made in calculating spectra of small molecules with this approach.35,36

IV. A Complete Semiclassical Calculation of Intramolecular Line Shapes. Spectroscopy without Eigenstates

In the previous section we considered the doorway state formalism which enables us to interpret fluorescence spectra in terms of correlation functions of doorway states $\langle s'(0)|s(\tau)\rangle$ on the excited potential surface. The latter may be evaluated from the effective Hamiltonian or semiclassical dynamics on the excitedstate potential surface.^{34,35} In either case this approach requires the knowledge of the true molecular eigenstates on the ground potential surface ($|g\rangle$ and $|g'\rangle$). We shall now present a complete semiclassical correlation-function method which enables us to calculate the spectra without calculating any molecular eigenstates even on the ground potential surface. For the sake of calculating spectra of supercooled molecules this is a necessity since the calculation of the eigenstates of the ground electronic state $(|g\rangle)$ and particularly $|g'\rangle$) is no less difficult than the calculation of the vibronic eigenstates of the electronically excited state $(|j\rangle)$.

The complete semiclassical expansion is derived as follows:^{17,32,33} We first rearrange eq 8 in the form

$$F(\tau_1, \tau_2, \tau_3) = \left\langle \exp_{-\left[i \int_0^{\tau_1} d\tau \ U(\tau)\right]} \exp_{+\left[-i \int_0^{\tau_2} d\tau \ U(\tau)\right]} \times \exp_{-\left[i \int_0^{\tau_3} d\tau \ U(\tau)\right]} \right\rangle$$
(27)

where

$$U \equiv \bar{V}_{\rm b} - \bar{V}_{\rm a} \tag{27a}$$

$$U(\tau) \equiv \exp(iH_a)U \exp(-iH_a)$$
 (27b)

and exp_{\pm} are the positive (negative) time-ordered exponentials

$$\exp_{+}\left[-i\int_{0}^{\tau_{2}} d\tau \ U(\tau)\right] \equiv 1 - i\int_{0}^{\tau_{2}} d\tau \ U(\tau) + (-i)^{2}\int_{0}^{\tau_{2}} d\tau \ \int_{0}^{\tau} d\tau' \ U(\tau) \ U(\tau') + \dots (27c)$$

$$\exp\left[i\int_{0}^{\tau_{1}} d\tau \ U(\tau)\right] \equiv 1 + i\int_{0}^{\tau_{1}} d\tau \ U(\tau) + (i)^{2}\int_{0}^{\tau_{1}} d\tau \ \int_{0}^{\tau} d\tau' \ U(\tau') \ U(\tau) + \dots \ (27d)$$

 $U(\tau)$ is the electronic energy gap which evolves in time on the ground-state potential surface (H_a) . It is a key quantity responsible for the absorption and fluorescence line profiles. When U = 0, i.e., $\bar{V}_a = \bar{V}_b$, the \bar{V}_a and \bar{V}_b surfaces are parallel and the absorption and emission spectra will consist of a single line (no vibrational progressions). It is the functional dependence of U on nuclear coordinates and its time evolution which determine the fluorescence spectrum. Equation 27 may now be used to generate a simple and easily calculable expression for the four-point correlation functions $F(\tau_1, \tau_2, \tau_3)$. This is done by expanding it to second order in U and then making the cumulant expansion (second-order cumulant expansion). The electronic transition frequency ω_{ba} can always be modified to include $\langle U \rangle$, so that without loss of generality we choose $\langle U \rangle = 0$. We then get

$$F(\tau_1, \tau_2, \tau_3) = \exp[i\omega_{ba}(\tau_1 - \tau_2 + \tau_3)] \exp[-g(\tau_1) - g(\tau_3) - g(\tau_2 - \tau_1) - g(\tau_3 - \tau_2) + g(\tau_2) + g(\tau_3 - \tau_1)]$$
(28)

where $g(\tau)$ may be expressed in terms of the spectral density $J(\tau)$ $J(\tau) \equiv \langle U(0) \ U(\tau) \rangle = \operatorname{Tr}[U \exp(iH_a \tau)U \exp(-iH_a \tau)\rho_{eq}] \quad (29)$

i.e.

$$g(t) = \int_0^t d\tau \ (t-\tau)J(\tau) = \int_{-\infty}^\infty d\omega \ \frac{J(\omega)}{\omega^2} [\exp(i\omega t) - i\omega\tau - 1]$$
(30)

 $J(\omega)$ being the Fourier transform of $J(\tau)$, i.e.

$$J(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} J(\tau) \exp(-i\omega\tau) \,\mathrm{d}\tau \tag{31}$$

The microscopic information that enters the spectrum, within this approximation, is contained in the spectral density $J(\omega)$ which is related to the two-point correlation function of the energy gap $\langle U(0) U(\tau) \rangle$. We should point out that proceeding along the same lines it is easy to derive a corresponding expression for the two-time correlation function appearing in the absorption line shape $\bar{I}(\omega_{\rm L})$ (eq 15)), i.e.

$$\langle V_{ab}(0) | V_{ba}(\tau) \rangle = \exp[i\omega_{ba}\tau - g(\tau)]$$
 (32)

The calculation of the fluorescence spectrum thus involves two steps: the first is to calculate the spectral density (eq 29) and the second is to perform the triple Fourier transform (eq 11 or eq 19) and get the spectrum. We shall consider now both steps in detail.

The spectral density may be easily evaluated in the classical limit by using standard semiclassical procedures.^{33,37-40} We

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Figure 1. The spectral density $J(\omega)$ for a two-level absorber in a rigid (solidlike) cluster. The cluster size (N) is indicated in each panel.⁴⁰

calculate a sufficiently long classical trajectory on the ground potential surface and get $U(\tau) \equiv U(\mathbf{Q}(\tau)), \mathbf{Q}(\tau)$ being the nuclear coordinates at time τ . We then decompose $U(\tau)$ in a Fourier series

$$U(\tau) = \sum_{j} U_{j} \exp(i\omega_{j}\tau)$$
(33)

Assuming that we can replace the average over initial points in phase space by considering a single long enough trajectory, we get

$$J(\tau) = \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{\infty} \exp(i\omega\tau) |\int_{0}^{T} d\tau_{1} U(\tau_{1}) \exp(i\omega\tau_{1})|^{2} d\omega \quad (34)$$

so that

$$V_{\rm c}(\tau) = \sum_{j} |U_j|^2 [\exp(i\omega_j \tau) + \exp(-i\omega_j \tau)]$$
(35)

and

$$g_{c}(\tau) \equiv \int_{0}^{\tau} d\tau_{1} (\tau - \tau_{1}) J(\tau) = -\sum_{j} \left| \frac{U_{j}}{\omega_{j}} \right|^{2} \{ [\exp(i\omega_{j}\tau) - i\omega_{j}\tau - 1] + [\exp(-i\omega_{j}\tau) + i\omega_{j}\tau - 1] \}$$
(36)

where the subscript c stands for classical. Note that using eq 35 we have

$$J(-\omega) = J(\omega) \tag{37a}$$



Figure 2. The absorption lines shape \tilde{I} for a two-level absorber in a rigid cluster.⁴⁰ The calculations were made with eq 15 and $J(\omega)$ of Figure 1. $\Delta = \omega_{\rm L} - \omega_{\rm ba}.$

whereas the quantum spectral density should obey the fluctuation dissipation theorem, i.e.^{18,19,33}

$$J(-\omega) = \exp(-\hbar\omega/kT) J(\omega)$$
(37b)

We can generate an improved approximation for $J(\omega)$ by defining the quantity

$$\kappa(\omega) = \frac{1}{1 + \exp(-\hbar\omega/kT)}$$
(38)

and introducing a semiclassical approximation for $J(\omega)$ which satisfies the fluctuation dissipation theorem, i.e.^{33,37,40}

$$J_{\rm sc}(\omega) = 2\kappa(\omega) J_{\rm c}(\omega)$$
(39)

we then get

$$g_{sc}(\tau) = -\sum_{j} 2 \left| \frac{U_j}{\omega_j} \right|^2 \{ \kappa_j [\exp(i\omega_j \tau) - i\omega_j \tau - 1] + (1 - \kappa_j) [\exp(-i\omega_j \tau) + i\omega_j \tau - 1] \}$$
(40)

where $\kappa_j \equiv \kappa(\omega_j)$. In the high-temperature (classical) limit $\kappa_j \rightarrow \infty$ 1/2 and $g_{sc}(\tau)$ reduces to $g_c(\tau)$. At zero temperature $\kappa_j \rightarrow 1$ and we simply neglect the negative frequency part in eq 40.

We have calculated the electronic spectrum of a two-level molecule (the "absorber") embedded in a cluster⁴¹⁻⁴⁴ consisting

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Figure 3. The spectral density $J(\omega)$ for a two-level absorber in a nonrigid (droplike) cluster. The cluster size (N) is indicated in each panel.⁴⁰

of perturbers which do not interact directly with the radiation field, as a function of cluster size. The model applies, e.g., to the supersonic beam spectra of van der Waals clusters of polyatomic molecules with rare gas perturbers.⁴⁰ Both rigid (solidlike) and nonrigid (dropletlike) models for the clusters were considered. The rigid model consists of a one-dimensional "solid" whereby the perturbers form a harmonic chain and the absorber is located at the center. We further assume that the force constant between the absorber and its two neighbors changes upon excitation. In Figure 1 we show the spectral density $J(\omega)$ for rigid clusters with various sizes (2, 4, 8, 20, 40, and an infinite numbers of perturbers), and in Figure 2 we show the corresponding line shape functions obtained by substituting $J(\omega)$ in eq 15, 30, and 32. $J(\omega)$ was calculated both exactly by using eq 29 and semiclassically (eq 39) and the results are practically the same. The nonrigid model for clusters consists of one absorber + several perturbers in a finite volume, with no interaction among the perturbers but a repulsive exponential interaction between the absorber and the perturbers. In Figure 3 we display $J(\omega)$ for the nonrigid (dropletlike) clusters with 2, 4, 8, 20, and an infinite number of perturbers. We also show the semiclassical calculation (which for this model does not depend on cluster size). In Figure 4 we show the corresponding line shapes $\tilde{I}(\omega_{\rm L})$ obtained by substituting $J(\omega)$ of Figure 3 in eq 15, 30, and 32.

A close examination of Figures 1-4 results in the following observations. For small clusters both $J(\omega)$ and $\tilde{I}(\omega_L)$ consist of a series of isolated discrete lines. In these cases, the information content of the spectra is simply the line positions and their strength (dipole matrix elements). This is the traditional way of analyzing molecular spectra. As the cluster size increases, however, there is a gradual loss of information and the spectrum probes global properties (envelopes consisting of many transitions) rather than individual lines. Our calculations enable us to monitor how this



Figure 4. The absorption line shape \tilde{I} for a two-level absorber in a nonrigid cluster with N perturbers.⁴⁰ The calculations were made with eq 15 together with $J(\omega)$ of Figure 3. $\Delta = \omega_L - \omega_{ba}$.

loss of information takes place. First, the molecular eigenstates are grouped together to form $J(\omega)$, and for large clusters $J(\omega)$ becomes practically continuous. The traditional spectroscopic information is then coarse grained and lost under the envelope of $J(\omega)$. Moreover, the spectrum $\tilde{I}(\omega_L)$ is not always sensitive to the details of $J(\omega)$. An extreme example is the Markovian limit in which the observed line width of $\tilde{I}(\omega_L)$ is much narrower than the spectral width of $J(\omega)$. (See, e.g., the infinite cluster in Figures 3 and 4 where the line width of $\tilde{I}(\omega_L)$ is ~0.4 cm⁻¹ whereas the spectral width of $J(\omega)$ is ~200 cm⁻¹.) In this case, we have (on the time scale relevant for the line broadening)

$$J(\tau) \equiv \hat{\Gamma} \,\,\delta(\tau) \tag{41a}$$

where

$$\hat{\Gamma} = \pi J(\omega = 0) \tag{41b}$$

and

so that

$$g(\tau) = \hat{\Gamma} \tau \qquad (41c)$$

$$\tilde{I}(\omega_{\rm L}) = \frac{1}{\pi} \frac{\Gamma}{(\omega_{\rm L} - \omega_{\rm ba})^2 + \Gamma^2}$$
(42)

where

$$\Gamma \equiv \frac{1}{2}\gamma_{\rm b} + \hat{\Gamma} \tag{42a}$$

In the Markovian limit which is common in macroscopic line broadening $\tilde{I}(\omega_L)$ carries therefore very little information and assumes a simple Lorentzian form. It is clear from our calculations that the spectral density method is particularly useful for large clusters (and large molecules) where many eigenstates contribute to the spectrum and the loss of information is substantial. In these



Figure 5. The energy gap $U(\tau)$ for methylbenzene at zero temperature calculated by a classical trajectory.37



Figure 6. The absorption spectrum of methylbenzene calculated by using $U(\tau)$ of Figure 5: (A) semiclassical calculation (eq 40 together with eq 15); (B) classical calculation (eq 36 together with eq 15); (C) an alternative classical calculation. For details see ref 37. $\Delta \equiv \omega_L - \omega_{ba}$. The three spectra were normalized to have the same intensity of the fundamental 0-0 band.37

cases calculating individual eigenstates becomes impractical and unnecessary.

In Figure 5 we display $U(\tau)$ as calculated classically for methylbenzene using realistic potential surfaces for \bar{V}_{a} and \bar{V}_{b} . In Figure 6 we show the corresponding absorption line shape \tilde{I} .³⁷ Calculation A uses the fluctuation dissipation theorem (eq 40 with $\kappa_j = 1$), and calculation B uses the classical $J(\omega)$ (eq 40 with $\kappa_j = 1/2$). Figure 6C results from an alternative classical approximation³⁷ obtained by writing $\mu(\tau) = \exp[i\int_0^{\tau} d\tau_1 U(\tau_1)]$ where $U(\tau)$ is shown in Figure 5. The classical correlation function of μ is then calculated resulting in the line shape. This calculation is nonperturbative in $U(\tau)$ but it cannot be easily modified to incorporate the fluctuation dissipation theorem. We note that line shapes B and C are symmetric $[I(-\Delta) = I(\Delta)]$, as they should be in the high-temperature limit and only in line shape A $I(-\Delta)$ = 0 as the zero temperature spectrum should be. Moreover, line shapes B and C contain hot combination bands (e.g., the 200-cm⁻¹ feature) which should not exist at zero temperature. These are totally suppressed in line shape A. It is clear that the spectral density method A is most adequate for the calculation of nonlinear



Figure 7. The sixth overtone line shape of 2,3,5,6-tetradeuteriobenzene calculated via the spectral density method55 (eq 15 together with eq 40), T = 300 K. The spacing between divisions on the frequency axis is 20 cm^{-1} . (A) is calculated by using a model calculation for U. (B), (C), (D), and (E) correspond to $U(\tau)$ reduced by factors of 2, 3, 5, and 8, respectively, with respect to (A). The figure illustrates the strong non-linear dependence of the line and shape on the magnitude of the energy gap $U(\tau)$. This model corresponds to a pure dephasing contribution to the line width.



Figure 8. Temperature dependence of the overtone line shape A of Figure . The spacing between divisions on the frequency axis is 20 cm⁻¹.

spectra of large ultracold polyatomic molecules.

It is possible to use the spectral density toward the calculation of overtone line shapes as well.⁴⁵⁻⁵⁴ In this case we choose $|a\rangle$

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and $|b\rangle$ to be two "local mode" states and Q are the rest of the nuclear coordinates. Equation 15 then accounts for a pure dephasing (T_2) contribution to the overtone line shape. The lineshape A in Figure 7 is the sixth CH overtone of 2,3,5,6-tetradeuteriobenzene calculated by modeling the CH stretch as a Morse oscillator whose parameters (dissociation energy and characteristic length) depend parametrically on the nuclear configuration in the vicinity of the CH bond.^{31,55} Calculations B, C, D, and E are obtained by assuming a smaller coupling and dividing U of Figure 7A by 2, 3, 5, and 8, respectively. This illustrates the highly nonlinear dependence of the line shape on $U(\tau)$. In Figure 8 we show how line shape A of Figure 7, calculated at 300 K, is affected by reducing the temperature. A strong temperature dependence is obtained and the broadening disappears as $T \rightarrow 0$.

We are now in a position to consider the second stage of the calculation, i.e., performing the triple integration (eq 11 or 19). One possibility is to perform the integrations numerically, which is feasible but quite tedious. There exists, however, an alternative procedure which allows us to obtain $I(\omega_L, \omega_s)$ much more conveniently. Let us consider the following model system of a molecule with two linearly displaced harmonic surfaces:

$$H_{a} = \sum_{j=1}^{N} \hbar \omega_{j} (P_{j}^{2} + Q_{j}^{2})$$
(43a)

and

$$H_{\rm b} = H_{\rm a} + \sum_{j=1}^{N} \hbar \,\omega_j \Delta_j Q_j \tag{43b}$$

where

$$\Delta_j = \frac{2^{1/2} |U_j|}{\hbar \,\omega_j (\bar{n}_j + \frac{1}{2})^{1/2}} \tag{44}$$

and

$$\bar{n}_j = [\exp(\hbar\omega_j/kT) - 1]^{-1}$$
(45)

Note that P_j and Q_j are the dimensionless momentum and coordinate of the *j*th oscillator. U_j and ω_j are the Fourier components and frequencies of $U(\tau)$ of our original anharmonic molecule (see eq 33).

Equation 43 represents an effective harmonic molecule whose number of modes (N) is equal to the number of Fourier components of $U(\tau)$. For this model system, the second-order cumulant expansion is exact and $F(\tau_1, \tau_2, \tau_3)$ is given rigorously by eq 28.^{21,22,33,56} In other words, the approximate spectrum of the original anharmonic system (eq 1) is equal to the exact spectrum of our effective harmonic system (eq 43). The latter can be easily evaluated from eq 4 and 5 since the eigenvalues and eigenstates of the harmonic system are known. We have thus converted the calculation of the spectrum to that of an effective harmonic system whose number of degrees of freedom (N) is equal to the number of Fourier components of U! The fluorescence spectrum is then given by

$$I(\omega_{\rm L},\omega_{\rm s}) = \sum_{\rm n,m} P({\bf n}) |\langle {\bf m} | \chi(E_{\rm n} + \omega_{\rm L}) | {\bf n} \rangle |^2 \, \delta(\omega_{\rm L} - \omega_{\rm s} + E_{\rm n} - E_{\rm m})$$
(46)

where

$$\langle \mathbf{m} | \chi(E_{n} + \omega_{L}) | \mathbf{n} \rangle = \sum_{\mathbf{k}} \frac{\langle \mathbf{m} | \mathbf{k} \rangle \langle \mathbf{k} | \mathbf{n} \rangle}{E_{n} + \omega_{L} - E_{k} + i\gamma_{b}/2}$$
 (46a)

Here $|\mathbf{n}\rangle$ and $|\mathbf{m}\rangle$ are eigenstates of H_a (eq 43a) whereas $|\mathbf{k}\rangle$ are

eigenstates of H_b (eq 43b). (m|k) and (k|n) are factorized as products of Franck-Condon factors of the various modes

$$\langle \mathbf{k} | \mathbf{n} \rangle = \prod_{j=1}^{N} \langle k_j | n_j \rangle$$
 (46b)

$$\langle \mathbf{m} | \mathbf{k} \rangle = \prod_{j=1}^{N} \langle m_j | k_j \rangle$$
 (46c)

and $\langle k_j | n_j \rangle$ and $\langle m_j | k_j \rangle$ are the usual Franck-Condon factors of displaced harmonic oscillators.⁵⁶ The energies E_n are given by

$$E_{\mathbf{n}} = \sum_{j=1}^{N} \omega_j n_j \tag{46d}$$

and similarly for $E_{\rm m}$ and $E_{\rm k}$. The summation over intermediate states $|{\bf k}\rangle$ in eq 46a may become quite tedious for systems with a large number of degrees of freedom (N) or for large detunings (Raman spectra) where the number of terms is very large. The summation can be carried out, however, explicitly in the time domain by using the cumulant expansion.^{17,33} For a single mode (N = 1) we have

$$\langle m|\chi(E)|n\rangle = -i \int_0^\infty d\tau \exp(iE\tau) \langle m|\chi(\tau)|n\rangle$$
 (47a)

When the molecule is initially in the ground state (n = 0), we have

$$\langle m|\chi(\tau)|0\rangle = \frac{1}{(m!)^{1/2}} [f(\tau)]^m \exp\left[\frac{\Delta}{2^{1/2}} f(\tau)\right]$$
 (47b)

where

$$f(\tau) = \frac{\Delta}{2^{1/2}} [\exp(-i\omega\tau) - 1]$$
 (47c)

For the more general case, we get

$$\langle m|\chi(\tau)|n\rangle = \exp\left[-i\frac{\omega\tau}{2}(m+n) + \frac{\Delta}{2^{1/2}}f(\tau)\right] \times \\ (m!n!)^{1/2} \left(-i(2)^{1/2}\Delta\sin\frac{\omega\tau}{2}\right)^{m-n} \sum_{k=0}^{n} \frac{(-1)^{k} \left(2^{1/2}\Delta\sin\frac{\omega\tau}{2}\right)^{2k}}{k!(m-n+k)!(n-k)!}$$
(47d)

where we have taken $m \ge n$. (For n > m we may use the symmetry $\langle m | \chi(-\tau) n \rangle = \langle n | \chi(\tau) | m \rangle^*$). For N > 1 we simply write

$$\langle \mathbf{m} | \chi(\tau) | \mathbf{n} \rangle = \prod_{j=1}^{N} \langle m_j | \chi_j(\tau) | n_j \rangle$$
 (47e)

where $\langle m_j | \chi_j(\tau) | n_j \rangle \langle m | \chi(-\tau) | n \rangle$ given by eq 47d with n, m, ω , and Δ replaced by n_j, m_j, ω_j , and Δ_j , respectively. Our semiclassical procedure thus consists of running a classical trajectory for the actual anharmonic molecule to find the Fourier components of U, which define the effective harmonic system $(N, \Delta_j, \text{ and } \omega_j)$. The fluorescence spectrum is then calculated with eq 46 or 47. A different method for evaluating eq 46 is the transform method^{21,22,24,25} which is based on expanding $I(\omega_L, \omega_S)$ in successive orders of phonon numbers (single-phonon transitions, two-phonon transitions, etc.). The method was developed for the displaced harmonic model (eq 43), and the present work shows that it can be used for anharmonic systems as well, via the effective harmonic system.

One problem with this semiclassical approach lies in its "all or nothing" character, i.e., once we get $F(\tau_1, \tau_2, \tau_3)$ we have the entire spectrum $I(\omega_L, \omega_s)$, the full dispersed emission for any value of the excitation frequency ω_L . It would be both helpful and convenient to be able to solve for "one ω_L at a time" (i.e., fix ω_L and get the entire dispersed fluorescence for that particular ω_L). This will greatly reduce the computational effort since we are often interested only in a few values of ω_L . Formally, this can be done in a straightforward way by introducing the polarizability operator of the $|a\rangle$ electronic state, i.e.

$$\alpha(\omega_{\rm L}) \equiv \langle \mathbf{a} | \chi(E_{\rm g} + \omega_{\rm L}) | \mathbf{a} \rangle = \sum_{\rm gg'} | g' \rangle \langle g' | \chi | g \rangle \langle g | \quad (48a)$$

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here
$$\chi$$
 was defined in eq 5. Defining further

$$\alpha(\omega_{\rm L},\tau) \equiv \exp(iH_{\rm a}\tau) \ \alpha(\omega_{\rm L}) \ \exp(-iH_{\rm a}\tau) \tag{48b}$$

We can write eq 4 in the form⁵⁷

$$I(\omega_{\rm L},\omega_{\rm s}) = \int_{-\infty}^{\infty} \mathrm{d}\tau \, \langle \alpha^{\dagger}(\omega_{\rm L}) \, \alpha(\omega_{\rm L},\tau) \rangle \, \exp[i(\omega_{\rm s}-\omega_{\rm L})\tau] \qquad (49)$$

Equation 49 formally accomplishes our goal: $\alpha(\omega_{\rm L},\tau)$ and the correlation function $\langle \alpha^{\dagger}(\omega_{\rm L}) \alpha(\omega_{\rm L},\tau) \rangle$ depend only on the excitation frequency $\omega_{\rm L}$. The emission frequency $\omega_{\rm s}$ enters solely in the Fourier transform $\exp[i(\omega_s - \omega_L)\tau]$. We can therefore evaluate, in principle, the correlation function of α for a fixed value of $\omega_{\rm L}$ and then solve for the entire ω_s dependence of the dispersed fluorescence. The problem with this procedure is that the polarizability operator α is a complicated quantity since it involves the inverse of the Hamiltonian (see eq 4) and requires the knowledge of the entire vibronic spectrum of H_{a} .

There is one limiting case in which α may be evaluated in a simple way. This occurs in the case of Raman spectroscopy in which the excitation frequency is tuned very far off resonance from any molecular transition (i.e., the detuning $\omega_{\rm L} - \omega_{\rm ba}$ is very large compared with all other energy parameters in the problem). In this case, $\omega_{\rm L}$ is the dominant factor in the denominator of eq 5 and we may write

$$\alpha(\omega) \simeq \frac{V^2}{\omega_{\rm L} - \omega_{\rm ba}} \tag{50}$$

The polarizability correlation function (eq 49) may then be evaluated by the same method developed for the spectral density (i.e., eq 34 with U replaced by α). It is also possible to improve approximation (50) by a peturbative expansion of eq 5 in $H_a/(\omega_L)$ $-\omega_{\rm ba}$).²⁴ The calculation of a Raman spectrum is therefore equivalent in complexity to that of an ordinary infrared spectrum³⁹ where $\omega_{\rm L} - \omega_{\rm s}$ plays the role of the frequency. A Raman spectrum is not so sensitive to the structure and dynamics of the electronically excited state and probes mainly properties of the ground electronic state. This form (eq 49) may be further applied to fluroescence spectra (i.e., when ω_L is resonant with a molecular transition) by developing efficient computational methods toward calculating the polarizability.

Another problem which may be easily addressed within our formalism is the effects of incoherence in the radiation field on the fluroescence spectra. Up to this point, we have assumed that the field $\omega_{\rm I}$ is fully coherent. Partial or complete incoherence in the radiation field may be straightforwardly incorporated in these results by assuming that the field pulse envelope function $\phi(\tau)$ has some stochastic character and performing the necessary average over the stochastic ensemble. This average will be denoted by (...).

Let us consider a simple stochastic model for $\phi(\tau)$, i.e., assuming that the frequency ω_L undergoes a stochastic modulation so that in eq 2a we set^{32,58}

$$\phi(t) = \phi_0(t) \exp\left[-i \int_0^t d\tau \,\,\delta\omega(\tau)\right] \tag{51}$$

This is the conventional phase diffusion model for laser radiation. Here $\phi_0(t)$ is the external pulse envelope ($\phi_0 = 1$ for a steady-state experiment), and $\delta\omega(t)$ denotes a stochastic Gaussian modulation of the phase of the field with $\langle \delta \omega \rangle = 0$. We then get

$$\langle \phi(\tau) \ \phi(\tau') \rangle = \phi_0(\tau) \ \phi_0(\tau') \ S(\tau - \tau') \tag{52}$$

where

$$S(\tau - \tau') \equiv \exp\left[-\int_0^{|\tau - \tau'|} d\tau_1 \int_0^{\tau_1} d\tau_2 \left\langle \delta\omega(0) \ \delta\omega(\tau_2) \right\rangle\right] (53)$$

We shall further define

$$S(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau \, \exp(i\omega\tau) \, S(\tau)$$
 (53a)



Figure 9. The quantum beat pattern⁵⁸ of a ten level system excited by a pulse with duration T = 15. Shown is the time-resolved photon emission rate $(\langle \hat{I}(\omega_L, \omega_s, t) \rangle$ (eq 54b) integrated over ω_s). The incoherence of the field was introduced by a Lorentzian profile for $S(\omega)$ with fwhm (Γ) indicated in each panel. The quantum beats are averaged as Γ increases but are not lost completely. For $\Gamma \ge 10$ they remain unchanged.

Equation 19 will then be modified by replacing the $\phi(\tau) \ \phi(\tau')$ factors on the right-hand side by $\langle \phi(\tau) \phi(\tau') \rangle$ (eq 52). As for the steady-state observables (eq 11 or 12), they will be modified by multiplying $F(\tau_1, \tau_2, \tau_3)$ by $\bar{S}(\tau_3)$. When this is done we can rewrite these equations in the form^{32,58}

$$\langle I(\omega_{\rm L},\omega_{\rm s})\rangle = \int d\omega \ I_0(\omega_{\rm L}+\omega,\omega_{\rm s}) \ S(\omega)$$
 (54a)

and

$$\langle \hat{I}(\omega_{\rm L},\omega_{\rm s},t)\rangle = \int d\omega \ \hat{I}_0(\omega_{\rm L}+\omega,\omega_{\rm s},t) \ S(\omega)$$
 (54b)

where I_0 and \hat{I}_0 are the previous results for a coherent field ($\delta\omega$ = 0) and $\langle I \rangle$ and $\langle \hat{I} \rangle$ represent these quantities averaged over the stochastic field. The entire effect of field fluctuations is therefore simply to convolute the line shapes with $S(\omega)$.

In Figures 9 and 10 we consider a typical quantum beat pattern^{59,60} in an experiment where we have only time and no frequency resolution of the scattered light, i.e., we observe $\langle \hat{I}(\omega_{\rm L},\omega_{\rm s},t) \rangle$ integrated over ω_s . We have studied the effects of laser field incoherence by performing the convolution (eq 54). $S(\omega)$ was taken to be a Lorentzian whose fwhm (Γ) is indicated in each panel.⁵⁸ As Γ increases, the quantum beat pattern broadens and undergoes averaging. This averaging, however, attains a limiting value and for $\Gamma \ge 10$ the beat pattern remains the same. It is also clear from eq 54 that the shorter the light pulse, the less

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Figure 10. The effect of the pulse duration (T) on the quantum beat spectrum (eq 54b); (A) coherent excitation, T = 1; (B) effect of field incoherence on (A) (eq 54b) with $\Gamma = 10$, T = 1; (C) coherent excitation, T = 5; (D) effect of field incoherence on (C) (eq 54b) with $\Gamma = 10$, T = 5; (B) and (D) should be compared with the $\Gamma = 10$ panel of Figure 9 for which all other parameters are the same except T = 15. It is clear that, as the excitation pulse becomes shorter, the effect of incoherence decreases.

effective will be the averaging due to the incoherence. The reason is that, for short pulses, the doorway state does not have sufficient time to evolve during the pulse and the molecular state following the pulse is simply the doorway state $|s\rangle$ regardless of any incoherence. This effect is demonstrated in Figure 10 which uses the same parameters of Figure 9 but with shorter pulses (T = 5 and T = 1 compared with T = 15 in Figure 9). $\Gamma = 10$ was taken in all cases. It is clear that the averaging in panel D (T = 5) is much more significant than that of panel B (T = 1) of Figure 10.

In summary, eq 54 interpolates all the way from the coherent driving whereby $S(\omega) = \delta(\omega)$ and $\langle I(\omega_L,t) \rangle$ reduces to $I_0(\omega_L,t)$, to the complete incoherent excitation $(S(\omega) \sim \text{constant})$. It is clear that the quantum beat pattern is averaged as the degree of incoherence increases, and this averaging depends crucially on the duration of the excitation pulse. We have also shown that the quantum beats do not necessarily disappear in the extreme incoherent limit.

V. Discussion

The information content of spectra of small molecules is usually viewed as *static* in nature and is traditionally treated in the *frequency domain* (level positions, dipole strengths). For spectra of large macroscopic systems a *dynamical* (correlation function) viewpoint is more appropriate and they are usually treated in the *time domain*. Large polyatomic molecules and molecular clusters which are "intermediate" in size provide us with a unique opportunity to approach the problem from both ends and to bridge the gap between the macroscopic and the microscopic approaches. This "freedom of choice" of approach and level of description allows us to adopt different terminologies and concepts in describing the same phenomena. In this section we shall briefly summarize the various methods (some of which were described here in detail) for the theoretical description of molecular fluorescence spectra. (i) A Complete Description. In a complete description, we solve for the exact molecular vibronic eigenstates. The result of any spectroscopic measurement (absorption, fluorescence, etc.) may then be interpreted in terms of the level positions and the transition dipole matrix elements. Equations 4 and 5 give the fluorescence spectra using these quantities. In this picture, there is no dynamics involved in the spectrum and this is a completely static viewpoint. Such an approach is feasible only for small enough systems and is impractical for large anharmonic molecules.

(ii) Effective Hamiltonian Techniques. Reduction over States. This is similar to method i and we still consider eigenstates as the quantities of interest. However, in many situations we have a natural zero order basis set in which there are some "relevant" states which participate directly in the radiative processes and one or many manifolds (quasicontinua) of states which enter indirectly into the radiative processes. Examples for the latter types of states are triplet manifolds in electronically excited states, the quasicontinuum in intramolecular vibrational redistribution and multiphoton processes,⁶¹ etc. The effective Hamiltonian allows us to project these continua and include their effects by adding complex parts to the Hamiltonian. This results in a reduced level of description where the reduction is over the "irrelevant states". The usuage of the effective Hamiltonian, when the level scheme is appropriate, allows us to treat systems with large numbers of states relatively easily. The price is that the effective Hamiltonian is non-Hermitian and some care needs to be made in handling its eigenstates. Detailed expressions for fluorescence spectra using the effective Hamiltonian are available.³⁴

(*iii*) Doorway State Techniques. Using this approach, described in section III, we consider explicitly the vibronic eigenstates of the ground electronic state but treat the excited state approximately (effective Hamiltonian, semiclassical propagator, etc). This method brings us halfway into "eigenstate free" spectroscopy since only the ground vibronic states need to be calculated.³⁴⁻³⁶

(iv) Semiclassical Approach. Pure Dephasing. Our semiclassical approach of section IV focuses on the fluctuations in the electronic energy gap $U(\tau)$ as the source for the structure in molecular line shapes. Here we consider explicitly only the two-level electronic system; all the nuclear degrees of freedom are a bath. The line broadening in absorption and fluorescence is then viewed as a *pure dephasing process*. No vibronic eigenstates need to be calculated.

(v) Master Equation Approach. Reduction over Degrees of Freedom. Usually, in a large molecule, we have many selection rules and only few nuclear degrees of freedom are optically active. The rest serve as a bath which induces intramolecular relaxations. It is suggestive therefore to derive relaxation equations for the active "system" modes and to incorporate the effects of the bath via relaxation terms (T_1 and T_2 relaxation processes). This approach is fundamentally different from the previous ones since it involves reduction over degrees of freedom. It is very similar to what is done in matrix spectroscopy or collisional line broadening. Such an approach was developed for infrared multiphoton processes⁶¹ and for the dispersed fluorescence in supersonic beams.⁴ In the limit of fast intramolecular relaxation, the spectrum factorizes into a product of an absorption line shape times an emission shape from a fully relaxed molecule in the electronically excited state. The calculation of the spectrum greatly simplifies in this case since it is a simple product of two single-photon processes. Recent evidence for the applicability of the master equation approach to intramolecular line shapes was found in tetrazine and tetrazine-argon complexes.62

(vi) Random Matrix Approach. Statistical Spectroscopy. Random matrix methods have been suggested by Wigner in the context of nuclear spectroscopy and nuclear reaction theory.^{63,64}

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The idea is to try to characterize the spectra in terms of ensembles of Hamiltonians with simple statistical properties of their matrix elements. The statistical properties of the resulting eigenvalues and eigenvectors are then analyzed and compared with the experiment. This approach had remarkable success in nuclear physics. The statistical properties of interest are connected with properties of "n level distribution functions" such as distributions of level spacings, fluctuations in spectra, etc. Several attempts were made recently to apply these ideas to molecular absorption spectra.⁶⁵⁻⁶⁹ An interesting open question is whether, by making some simple assumptions regarding the distribution of molecular frequencies, anharmonicities, etc., it will be possible to predict and characterize fluorescence spectra in a statistical way.

The present summary shows that intramolecular relaxation and dephasing, as reflected in fluorescence line shapes, are subjective

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101, 215. (69) Mukamel, S.; Pandey, A.; Sue, J. Chem. Phys. Lett. 1984, 105, 134. quantities which depend on our level of theoretical description. In methods i and ii the spectrum is static and carries no dynamical information. Method iv interprets the spectra as pure dephasing. In method v the key quantities are T_1 and T_2 , relaxation processes, and in method vi the information is purely statistical. All these approaches are useful and there is no contradiction among the various interpretations. The right approach should be adopted depending on the level of information contained in the experiment which depends on molecular size, degree of excitation, experimental resolution, etc. There is no point in interpreting a simple Lorentzian line in terms of millions of unresolved eigenstates. A question that is often raised is whether a particular intramolecular line shape arises from dephasing (T_2) or relaxation of population (T_1) processes. The present analysis shows that this question has no significance unless we specify our level of description.⁷⁰ The same line shape can be interpreted in a variety of ways and the convenience and the information content should dictate which approach to choose.

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ARTICLES

Vibrational Overtone Spectra of Methyl-Substituted Silanes

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Absorption spectra between 12 800 and 18 200 cm⁻¹ have been recorded for gaseous CH₃SiH₃, (CH₃)₂SiH₂, (CH₃)₃SiH, and (CH₃)₄Si by using intracavity photoacoustic detection with CW dye lasers at 1-cm⁻¹ resolution. Transitions corresponding to the $\Delta v_{CH} = 5, 6, 7$ overtones of the C-H stretch and $\Delta v_{SiH} = 8$ and 9 overtones of the Si-H stretch can be assigned. These can be described appropriately in a local-mode representation with spectroscopic constants consisting of an effective harmonic frequency and a diagonal anharmonic constant. The spectra consist of additional features, many of which can be assigned as combinations with the local-mode oscillator. Comparison of the C-H and Si-H stretching overtones are made with those observed in CH_4 and SiH_4 .

Introduction

High-energy molecular vibrational states have received considerable recent attention, partly because of their potential role in photochemical reactions that possibly could be driven in a mode-specific direction.¹⁻⁴ Vibrational excitation in the visible spectral region can be detected in liquids with thermal lensing techniques¹ and in gases with photoacoustic methods.⁵ Previous photoacoustic studies of the Si-H stretch in our laboratory have revealed several interesting results.⁶⁻⁸ First, the Si-H stretch is

very well described as a local-mode oscillator in SiH₄, SiD₃H, SiHCl₃, and SiH₂Cl₂. The transition energies show a remarkable

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