

**FLUORESCENCE LINESHAPES OF POLYATOMIC MOLECULES -
SPECTROSCOPY WITHOUT EIGENSTATES**

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Abstract

Traditional spectroscopy of isolated molecules focuses on individual molecular eigenstates (their positions and dipole strengths). Macroscopic lineshapes 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 using both types of approaches. However, as the molecular size increases, the macroscopic approaches become more applicable and much more efficient. In this article we develop a Green function correlation function approach which provides a reduced description of molecular lineshapes. Effects of intramolecular vibrational redistribution (IVR) and intramolecular dephasing are readily accounted for. Application is made to the dispersed fluorescence of ultracold Anthracene in a supersonic beam.

I. INTRODUCTION

The calculation of molecular Fluorescence and Raman spectra in large anharmonic molecules is one of the fundamental problems in molecular dynamics and spectroscopy. Recent

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experiments, particularly involving ultracold molecules in supersonic beams are yielding accurate and detailed information (both time-resolved and frequency-resolved) [1-5]. This creates the need for the development of appropriate theoretical tools which could be used to extract dynamical information from these spectra.

The calculation of spectral lineshapes (and any other response function) in macroscopic systems is usually made using correlation function methods which are based on a reduced description [6-8]. This is the case for pressure broadening in the gas phase, lineshapes in liquids and solid matrices, etc. One never attempts to calculate the exact eigenstates of the macroscopic system. The reason is two-fold: first, such a calculation is extremely difficult due to the enormous number of degrees of freedom involved, and second, the experimental broadened lineshapes 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 eigenstates (level positions and dipole matrix elements) [9]. 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 towards the treatment of intramolecular line broadening of large isolated polyatomic molecules [10-12]. 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. This is an intramolecular "thermodynamic limit".

In this article we develop a stochastic model which is most suitable for the calculation of emission lineshapes of large isolated polyatomic molecules as well as molecular clusters and molecules in condensed phases [10,13]. The photon emission process is illustrated in Fig. 1.

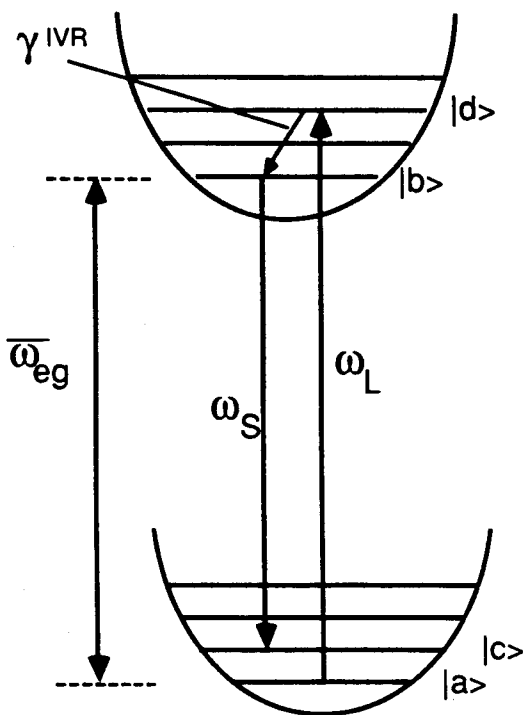


Fig. 1 The level scheme for molecular fluorescence. The incident light with frequency ω_L excites the doorway state $|d\rangle$. The emitted ω_S photon can originate either from the doorway state or from a lower lying state $|b\rangle$ which is accessible via intramolecular vibrational redistribution (IVR).

A molecule initially in the vibronic state $|a\rangle$ and energy ϵ_a absorbs a photon ω_L and emits a photon ω_S , and ends up in the vibronic state $|c\rangle$ with energy ϵ_c . $|b\rangle$ and $|d\rangle$ denote a manifold of vibronic states belonging to an excited electronic state $|e\rangle$, whereas $|a\rangle$ and $|c\rangle$ are vibronic states belonging to the ground electronic state $|g\rangle$. For isolated molecules (e.g. in supersonic beams or in the gas phase at low pressure), the steady state rate of emission of ω_S photons is given by the Kramers-Heisenberg expression:

$$I_0(\omega_L, \omega_S) = 2\pi \sum_{a,c} P(a) \left| \sum_b \frac{\mu_{cb}\mu_{ba}}{\omega_L - \omega_{ba} + i\gamma_b/2} \right|^2 \delta(\omega_L - \omega_S - \omega_{ca}) \quad (1)$$

Here ϵ_i is the energy of state $|i\rangle$ and γ_i is its inverse lifetime, $\omega_{ij} = \epsilon_i - \epsilon_j$, $P(a)$ is the equilibrium population of $|a\rangle$, and μ_{ij} is the dipole matrix element between states $|i\rangle$ and $|j\rangle$. The absorption line shape is given by

$$\sigma_0(\omega_L) = \sum_{a,b} P(a) |\mu_{ba}|^2 \frac{\gamma_b/2}{(\omega_L - \omega_{ba})^2 + (\gamma_b/2)^2} \quad (2)$$

Eqs. (1) and (2) involve multiple summations over molecular eigenstates. These summations can be easily carried out for small molecules with a few relevant levels. However for large polyatomic molecules they become intractable. This is the motivation for developing a reduced approximate description which may eliminate the necessity to perform these summations. The stochastic model presented here [13-17] provides a convenient means to achieve that goal. It is based on partitioning the degrees of freedom into "system" modes which are directly coupled to the radiation field and "bath" modes which are treated in an approximate way. The model was first developed for polyatomic molecules in a solvent [13]. In that case the "system" modes are all the molecular degrees of freedom and the bath consists of the solvent molecules. However, under certain conditions the model applies also to large isolated molecules whereby we adopt a reduced description in which we consider explicitly only a few relevant vibrational modes which are directly coupled to the optical transition, and all the rest are treated as a bath [18,19].

II. The Stochastic Langevin Model

In this section we present our general stochastic model for the emission line shapes of polyatomic molecules. We consider a molecule with two electronic states, the ground state $|g\rangle$ and an excited state $|e\rangle$. The molecular Hamiltonian is partitioned as follows.

$$H = |g\rangle H_g \langle g| + |e\rangle [H_e + \omega_{eg}(t) - (1/2)\gamma] \langle e| \quad (3)$$

Here γ is the inverse lifetime of the electronic excited state and ω_{eg} is the electronic energy gap (0-0 transition) between the two states. For an isolated small molecule, H_g and H_e contain all the vibrational degrees of freedom and ω_{eg} is independent on time. We, however, adopt a different partitioning. H_g and H_e will contain only the optically active modes. All the rest are treated as a thermal bath which exerts a random force on the optically active degrees of freedom. The main assumption of the present model is that this effect can be described by assuming that ω_{eg} becomes a stochastic function of time, i.e.,

$$\omega_{eg}(t) = \bar{\omega}_{eg} + \delta\omega_{eg}(t), \quad (4a)$$

where $\bar{\omega}_{eg}$ is the mean electronic energy gap. $\delta\omega_{eg}(t)$ is taken to be a Gaussian Markovian process with zero mean

$$\langle \delta\omega_{eg}(t) \rangle = 0, \quad (4b)$$

and its correlation function is

$$\langle \delta\omega_{eg}(t) \delta\omega_{eg}(0) \rangle = \Delta^2 \exp(-\Lambda t) \quad (4c)$$

Here $\langle \dots \rangle$ denotes averaging over the stochastic variables. Δ is the amplitude of the stochastic fluctuations, and Λ is their time scale (correlation time). The states $|a\rangle$, $|c\rangle$, etc. (Fig. 1) are the vibronic eigenstates of H_g

$$H_g |i\rangle = \epsilon_i |i\rangle, \quad i = a, c, \dots \quad (5a)$$

whereas the states $|b\rangle$, $|d\rangle$ are the vibronic eigenstates of H_e , i.e.,

$$(\bar{\omega}_{eg} + H_e) |i\rangle = \epsilon_i |i\rangle, \quad i = b, d, \dots \quad (5b)$$

The choice (Eqs.(4)) of $\delta\omega_{eg}(t)$ 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. This is often a realistic assumption. The Gaussian nature of $\delta\omega_{eg}(t)$ can often be justified using the central limit theorem. The absorber is coupled to the applied radiation field by the electronic dipole operator which couples vibronic states belonging to different electronic states, i.e.

$$V = \sum_{\substack{a,b, \\ c,d}} [\mu_{ab} |a\rangle\langle b| + \mu_{ad} |a\rangle\langle d| + \mu_{cb} |c\rangle\langle b| + \mu_{cd} |c\rangle\langle d| + \text{h.c.}] \quad (6)$$

where the summation runs over the entire manifolds of ground and electronically excited states.

Our solution for the absorption and the emission lineshapes is given using the following auxiliary functions [18]:

$$J_s(\tau) = [1 - \exp(-\Lambda\tau)]^s \exp[-g(\tau)] \quad s = 0, 1, \dots \quad (7)$$

where

$$g(\tau) = \kappa^{-2} [\exp(-\Lambda\tau) - 1 + \Lambda\tau] \quad (7a)$$

with

$$\kappa = \Lambda/\Delta \quad (7b)$$

In addition we introduce the operators:

$$T(t) = V \exp(-iH_e t) V \quad (8a)$$

$$\bar{T}(t) = V \exp(-iH_g t) V \quad (8b)$$

and

$$\tilde{T}(t) = V \rho_g \exp(-iH_g t) V . \quad (8c)$$

Here ρ_g is the equilibrium cononical density matrix of the $|g\rangle$ state, i.e.

$$\rho_g = \exp(-\beta H_g) / \text{Tr} \exp(-\beta H_g) , \quad (9)$$

with $\beta = (kT)^{-1}$. We further define

$$K^{(s)}(\omega) = -i \frac{\kappa^{-s}}{\sqrt{s!}} \int_0^\infty d\tau \exp[i\omega\tau - \gamma\tau/2] J_s(\tau) T(\tau), \quad (10a)$$

$$\bar{K}^{(s)}(\omega) = -i \frac{\kappa^{-s}}{\sqrt{s!}} \int_0^\infty d\tau \exp[i\omega\tau - \gamma\tau/2] J_s(\tau) \tilde{T}(\tau) \quad (10b)$$

and

$$\tilde{K}^{(s)}(\omega) = -i \frac{\kappa^{-s}}{\sqrt{s!}} \int_0^\infty d\tau \exp[i\omega\tau - \gamma\tau/2] J_s(\tau) \tilde{T}(\tau) . \quad (10c)$$

Using these quantities we can write the emission spectrum as[18]:

$$\begin{aligned} I(\omega_L, \omega_S) = & -2 \text{Im} \{ \\ & \sum_{a,c} P(a) \sum_{s=0}^{\infty} \frac{1}{\omega_S - \omega_L + \omega_{ca} + i s \Lambda} K_{ca}^{(s)}(\epsilon_c + \omega_S) K_{ca}^{(s)*}(\epsilon_a + \omega_L) \\ & + \sum_{b,d} \sum_{s=0}^{\infty} \frac{1}{\omega_{bd} + i(s\Lambda + \gamma)} \bar{K}_{db}^{(s)}(\epsilon_b - \omega_L) \\ & [\bar{K}_{db}^{(s)*}(\epsilon_d - \omega_S) - (-1)^s \bar{K}_{bd}^{(s)}(\epsilon_b - \omega_S)] \} \quad (11) \end{aligned}$$

The absorption line shape is given by

$$\sigma(\omega_L) = -2 \text{Im} \sum_a P(a) K_{aa}^{(0)}(\epsilon_a + \omega_L) \quad (12)$$

III. The fast and the slow modulation limits; The distinction between Raman and fluorescence components

We are now in a position to analyze our general expression for the emission. First, it will be useful to explore the partitioning of $I(\omega_L, \omega_S)$ (Eq.(11)) into a Raman and a fluorescence component denoted $I_R(\omega_L, \omega_S)$ and $I_F(\omega_L, \omega_S)$ respectively. Such a distinction can be made, when the emission spectrum consists of relatively narrow 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 emission which does not vary considerably as we tune ω_L . When this situation holds, we denote the former lines as Raman and the latter broad emission as fluorescence.

The only term in Eq.(11) which can contribute to a Raman type of emission is

$$\frac{1}{\omega_S - \omega_L + \omega_{ca} + is\Lambda} = \frac{\omega_S - \omega_L + \omega_{ca}}{(\omega_S - \omega_L + \omega_{ca})^2 + (s\Lambda)^2} - \frac{is\Lambda}{(\omega_S - \omega_L + \omega_{ca})^2 + (s\Lambda)^2} \quad (13)$$

Typically $\Lambda \gg (\gamma_a + \gamma_c)$. Therefore the imaginary part of Eq.(13) with $s=0$ will result in narrow resonances at $\omega_L - \omega_S = \omega_{ca}$ whereas the terms with $s>0$ will be much broader.

We thus conclude that the $K_{ca}^{(0)}$ term is responsible for

the Raman components whereas all the other terms in Eq.(11) contribute to the fluorescence. A more detailed analysis of this point was made elsewhere[13]. We thus have:

$$I(\omega_L, \omega_S) = I_R(\omega_L, \omega_S) + I_F(\omega_L, \omega_S) \quad , \quad (14a)$$

where the Raman component is

$$I_R(\omega_L, \omega_S) = 2\pi \sum_{a,c} P(a) |K_{ca}^{(0)}(\epsilon_a + \omega_L)|^2 \delta(\omega_S - \omega_L + \omega_{ca}) \quad (14b)$$

We shall now consider some limiting cases. The fast modulation (homogeneous) limit is obtained when the correlation time of the bath fluctuations is very fast compared with their magnitude, i.e., $\kappa \gg 1$. In this case, the $\exp(-\Lambda\tau)$ in the r.h.s. of Eq.(7a) vanishes very rapidly and may be ignored. We then get $g(\tau) = \hat{\Gamma}\tau$, where $\hat{\Gamma} = \Delta^2/\Lambda$. In the limit Eqs.(10) assume the form

$$K^{(0)}(\omega) = \sum_b \frac{V|b\rangle\langle b|V}{\omega - \epsilon_b + i\Gamma} \quad , \quad (15a)$$

$$\bar{K}^{(0)}(\omega) = \sum_c \frac{V|c\rangle\langle c|V}{\omega - \epsilon_c + i\Gamma} \quad (15b)$$

and

$$\bar{K}^{(0)}(\omega) = \sum_a P(a) \frac{V|a\rangle\langle a|V}{\omega - \epsilon_a + i\Gamma}, \quad (15c)$$

where $\Gamma = \gamma/2 + \hat{\Gamma}$. In this case, only the $s=0$ terms contribute to Eq.(11) and the absorption line shape becomes a sum of Lorentzian terms corresponding to homogeneous dephasing.

$$\begin{aligned} I(\omega_L, \omega_S) &= \sum_{\substack{a,c \\ b,d}} \mu_{ab} \mu_{bc} \mu_{cd} \mu_{da} P(a) \\ &\times \frac{1}{\omega_{ba} - \omega_L + i\Gamma} \frac{1}{\omega_{da} - \omega_L - i\Gamma} \\ &\times \{2\pi\delta(\omega_{ac} + \omega_L - \omega_S) - \frac{2\hat{\Gamma}}{\omega_{bd} + i\gamma}\} \\ &\times \left[\frac{1}{\omega_{bc} - \omega_S + i\Gamma} + \frac{1}{\omega_{cd} + \omega_S + i\Gamma} \right] \end{aligned} \quad (16)$$

Note that in the absence of broadening ($\hat{\Gamma}=0$) Eq.(16) reduces to the Kramers-Heisenberg form (Eq.(1)). The slow modulation (static, inhomogeneous) limit is obtained when $\kappa \ll 1$. In this case, we can make a Taylor expansion of Eq.(7a) (short-time approximation) resulting in $g(\tau) = \Delta^2 \tau^2 / 2$. We then have

$$\sigma(\omega_L) = \int d\omega \sigma_0(\omega_L + \omega) S(\omega) \quad (17a)$$

$$I(\omega_L, \omega_S) = \int d\omega I_0(\omega_L + \omega, \omega_S + \omega) S(\omega)$$

$$S(\omega) = \frac{1}{\sqrt{2\pi}\Delta} \exp(-\omega^2/2\Delta^2) \quad (17b)$$

where σ_0 and I_0 are given by Eqs.(2) and (1). As κ is varied, the absorption line shape thus changes continuously from a Gaussian to a Lorentzian.

IV. Emission Lineshapes of Harmonic Molecules

In general the evaluation of Eq.(8), for example $T(t)$, still requires a summation over eigenstates i.e.,

$$T(t) = \sum_b V|b\rangle \exp(-i\epsilon_b t) \langle b|V \quad (18)$$

However for harmonic molecules this summation can be carried out formally. The expressions derived here for the matrix elements of $T(t)$ may be used to calculate the matrix elements of $\bar{T}(t)$ as well by simply changing D to $-\underline{S}^{-1}D$, \underline{S} to \underline{S}^{-1} and exchanging ω' and ω'' . $\bar{T}(t)$ may be evaluated using $\bar{T}(\tau)$ by substituting $\tau=t-i\beta$. It is therefore sufficient to consider only $T(t)$. Let us consider now a general harmonic molecule with the hamiltonian

$$H = |g\rangle H_g \langle g| + |e\rangle [H_e + \omega_{eg}^{-(1/2)\gamma}] \langle e|, \quad (19a)$$

$$H_g = \frac{1}{2} \sum_{j=1}^N \omega_j'' (p_j''^2 + q_j''^2) + \omega_0 \quad (19b)$$

$$H_e = \frac{1}{2} \sum_{j=1}^N \omega_j' (p_j'^2 + q_j'^2) \quad (19c)$$

with

$$\omega_0 = \frac{1}{2} \sum_{j=1}^N (\omega_j' - \omega_j'') \quad (19d)$$

We adopt the common spectroscopic notation, whereby we label ground-state quantities by a double prime and excited-state quantities by a single prime. The dimensionless momentum and coordinate corresponding to the j 'th excited state normal mode are denoted by p'_j and q'_j respectively:

$$p'_j = \left(\frac{1}{m_j \omega_j' \hbar} \right)^{1/2} p_j' \quad (20a)$$

$$q'_j = \left(\frac{m_j \omega_j'}{\hbar} \right)^{1/2} q_j' \quad (20b)$$

P'_j and Q'_j being the conjugate momentum and the normal coordinate, respectively, of the j 'th mode of the excited state. A similar transformation between p_j'' , q_j'' , and P_j'' , Q_j'' is defined by changing all ' indexes in Eq. (20) to ". ω_j' (ω_j'') and m_j are the frequency and the mass of the j 'th mode. The quantity ω_0 accounts for the zero point energy, and ω_{eg} is the fundamental (0-0) transition frequency. We shall now introduce a vector notation and define the N component column vectors \mathbf{q}' and \mathbf{q}'' whose components are q'_j and q''_j , $j=1, \dots, N$, respectively. The normal modes \mathbf{q}' and \mathbf{q}'' are not necessarily the same, and most generally they may be related by the transformation

$$\underline{q}' = \underline{S} \underline{q}'' + \underline{D} \quad (21)$$

where \underline{S} is the Dushinsky transformation matrix. \underline{D} is an N component vector whose components D_j denote the dimensionless displacements of the equilibrium positions between the two electronic states. In this section we shall introduce an additional simplifying assumption, namely, that the electronic dipole operator is weakly dependent on the nuclear coordinates, so that μ_{ij} becomes simply the Franck-Condon factor, i.e., $\mu_{ij} = \mu_{eg} \langle i|j \rangle$. This is the Condon

approximation. The eigenstates $|a\rangle$ and $|c\rangle$ will be denoted in this section by $|n\rangle$ and $|m\rangle$, respectively i.e.,

$$|a\rangle = |n\rangle = \prod_{j=1}^N |n_j\rangle \quad (22a)$$

$$|c\rangle = |m\rangle = \prod_{j=1}^N |m_j\rangle \quad (22b)$$

The final result is considerably simplified when the normal modes in the ground and the excited electronic states are identical, i.e., when the Dushinsky transformation matrix is diagonal

$$S_{ij} = (\omega_i'/\omega_j'')^{1/2} \delta_{ij} \quad (23)$$

We then have:

$$T_{mn}(t) = |\mu_{eg}|^2 G_{mn}(t) \quad (24a)$$

where

$$G_{mn}(t) = \prod_{j=1}^N G_{m_j n_j}(t) \quad (24b)$$

For simplifying the notation, we shall, hereafter, consider a single mode and omit all the j subscripts from ω_j' , ω_j'' , D_j , n_j , m_j . The total Green function can then be calculated using Eq.(24b). For a single mode, we get[18]

$$G_{mn}(t) = G_{00}(t) W_{mn}(t) \quad (25a)$$

where

$$G_{00}(t) = [\psi(t)]^{-1/2} \exp[D^2 f(t)] \quad (25b)$$

$$W_{mn}(t) = (m! n! 2^{m+n})^{-1/2} [\alpha(t)]^{m+n}$$

$$\sum_{k=0}^{k^*} \frac{(2k)!}{k!} \eta_{mnk} [\gamma(t)]^k H_{m+n-2k}[\lambda f(t)D/\alpha(t)] \quad (25c)$$

Here

$$\psi(t) = \frac{\omega_+^2}{4\omega'\omega''} [1 - (\omega_-/\omega_+)^2 \exp(-2i\omega't)] \quad (26a)$$

$$f(t) = -\frac{\omega''[1 - \exp(-i\omega't)]}{\omega_+ - \omega_- \exp(-i\omega't)} \quad (26b)$$

$$\alpha(t) = \left[\frac{\omega_- - \omega_+ \exp(-i\omega't)}{2\omega_+ - 2\omega_- \exp(-i\omega't)} \right]^{1/2} \quad (26c)$$

$$\gamma(t) = \frac{2\lambda^2 + i(\lambda^4 - 1) \sin \omega't}{2\lambda^2 - i(\lambda^4 - 1) \sin \omega't} \quad (26d)$$

$$\omega_{\pm} = \omega' \pm \omega'' \quad (26e)$$

$$\lambda = (\omega'/\omega'')^{1/2} \quad (26f)$$

$$\eta_{mnk} = \sum_{q=0}^{2k} (-1)^q \binom{m}{2k-q} \binom{n}{q} \quad (26g)$$

H_j are the Hermite polynomials. We have further defined

$$\binom{m}{l} = \begin{cases} \frac{m!}{l!(m-l)!} & \text{when } m \geq l \\ 0 & \text{when } m < l \end{cases} \quad (27)$$

and k^* is the integer part of $(m+n)/2$. For supercooled molecules at zero temperature we need only $n = 0$. Eq.(25c) then assumes the form:

$$W_{m0}(t) = (m! 2^m)^{-1/2} \beta^m(t) H_m[\lambda f(t)D/\beta(t)] \quad (28)$$

where

$$\beta(t) = \left\{ \frac{\omega_+ \omega_- [1 - \exp(-2i\omega' t)]}{\omega_+^2 - \omega_-^2 \exp(-2i\omega' t)} \right\}^{1/2} \quad (29)$$

When the frequencies ω' and ω'' are the same ($\omega = \omega' = \omega''$), we have $\lambda = 1$ and $\beta(t) = 0$. Eq.(29a) then reduces to the form:

$$\begin{aligned} W_{m0}(t) &= (m!2^m)^{-1/2} [2Df(t)]^m \\ &= (m!2^m)^{-1/2} D^m [\exp(-i\omega t) - 1]^m. \end{aligned} \quad (30)$$

The most general expression for $G_{nn}(t)$ including the Dushinsky rotation is given elsewhere^[18].

Within the Condon approximation, the absorption lineshape at temperature T (Eq.(2)) is^[18]

$$\begin{aligned} \sigma(\omega_L) &= |u_{eg}|^2 \sum_n P(n) \operatorname{Im} G_{nn}(\omega_L - \omega_{eg} + \epsilon_n) \\ &= |u_{eg}|^2 \operatorname{Re} \int_0^\infty dt \exp[i(\omega_L - \omega_{eg})t] \sigma(t). \end{aligned} \quad (31)$$

In the absence of Dushinsky mixing, then Eq.(24b) holds. In this case we need only consider a single mode.

$$\sigma(t) = [\psi_T(t)]^{-1/2} \exp[D^2 f_T(t)] \quad (32a)$$

with

$$\psi_T(t) = \frac{1}{4\omega' \omega''} (\omega'' C_+ A_- + \omega' C_- A_+) (\omega' C_+ A_- + \omega'' C_- A_+) \quad (32b)$$

and

$$f_T(t) = - \frac{\omega'' C_- A_-}{\omega'' C_+ A_- + \omega' C_- A_+} \quad (32c)$$

where

$$C_\pm = 1 \pm \exp(-i\omega' t) \quad (33a)$$

$$A_\pm = (\bar{n} + 1) \pm \bar{n} \exp(i\omega'' t) \quad (33b)$$

$$\bar{n} = [\exp(\hbar\omega''/kT) - 1]^{-1} \quad (33c)$$

We shall now consider two limiting cases of Eq.(32). At zero temperature $\sigma(t)$ becomes identical to Eq. (25b), Eqs.(32b) and (32c) reduce to Eqs.(26a) and (26b), respectively, and $\sigma(t) = G_{00}(t)$.

When $\omega = \omega' = \omega''$, $\psi_T(t) = 1$, $f_T(t) = -1/2 C_{A-}$ and we get

$$\begin{aligned} \sigma(t) = & \exp(-\frac{1}{2}D^2 C_{A-}) = \exp\{\frac{1}{2}D^2 (\bar{n} + 1)[\exp(-i\omega t) - 1] \\ & + \frac{1}{2}D^2 \bar{n}[\exp(i\omega t) - 1]\} \end{aligned} \quad (34)$$

V. The Role of Intramolecular Vibrational Redistribution

So far we have considered purely harmonic molecules. The previous expressions apply to small molecules or to large polyatomic molecules with small amounts of vibrational energy. As the degree of excitation is increased the anharmonicities start to play a major role by inducing relaxation and line broadening. Anharmonic effects may be incorporated systematically in a perturbative way, starting with the previous expressions[19]. A simpler procedure for incorporating the effects of IVR processes on the emission lineshapes of supercooled molecules is provided by introducing an intramolecular vibrational redistribution (IVR) rate γ_{bd}^{IVR} whereby the doorway state $|d\rangle$ relaxes to

state $|b\rangle$. Once the system is in the $|b\rangle$ state, then the bath modes become hot since they absorb the excess vibrational energy ω_{db} . As a result the emission from the $|b\rangle$ state can be represented by our stochastic model whereby the parameters Δ and Λ (Eq.(4)) now depend on the amount of vibrational energy in the bath. For the doorway state $|d\rangle$, $\Delta=0$ and there is no broadening. We expect that the stochastic fluctuations amplitude Δ for emission from a given $|b\rangle$ state will increase as the available energy of the bath ω_{db} increases. The total emission thus consists of a progression of narrow lines originating from the doorway state and a series of broad emission lines corresponding to the redistributed emission. Our expression for the emission in this case is[19]:

$$I_d(\omega_S) = -\text{Im} [\bar{G}_{dd}(\epsilon_d - \omega_S + i \bar{\gamma}_d/2) + \sum_b \gamma_{bd}^{\text{IVR}} / \gamma \cdot \bar{K}_{bb}^{(0)}(\epsilon_b - \omega_S)] \quad (35)$$

where

$$\bar{\gamma}_d = \gamma + \sum_b \gamma_{bd}^{\text{IVR}} \quad (35a)$$

and

$$\bar{K}_{bb}^{(0)}(\omega) = -i \int_0^{\infty} d\tau \exp(i\omega\tau - \gamma\tau/2) J_0^{(b)}(\tau) \bar{G}_{bb}(\tau) \quad (35b)$$

Here $J_0^{(b)}$ is given by Eq.(7) but the bath parameters Δ and

Λ are taken to be dependent on $|b\rangle$. We have applied Eqs.(35) towards the calculation of the emission spectra of ultracold Anthracene[19]. A comprehensive supersonic beam study of this molecule was conducted recently by Zewail and coworkers[4]. Our results are displayed in Figures 2-5. Anthracene has 17 modes which are directly coupled to the electronic transition. The parameters of these modes used on our calculation are summarized in Table I. Fig. 2 demonstrates that for excess vibrational energy of 1168 cm^{-1} IVR processes already play an important role in the emission since the purely harmonic emission (bottom figure) clearly fails to reproduce the broad background as shown in the experimental spectrum (top figure). The middle figure which introduced IVR via our stochastic model reproduces the experimental spectrum quantitatively. This effect becomes more dramatic as the excess vibrational energy is increased to 1792 cm^{-1} as shown in Fig. 3. Both figures 2 and 3 were calculated in the fast modulation (Lorentzian) limit. The effect of κ is demonstrated in Fig. 4. A Lorentzian ($\kappa=\infty$), intermediate ($\kappa=1$) and a Gaussian ($\kappa=0$) lineshapes with the same full width at half maximum are compared. Finally Fig. 5 shows the emission spectrum of vibrationally hot anthracene at three temperatures. This calculation was made in the harmonic limit setting $\gamma^{\text{IVR}}=0$. The present calculations demonstrate the simplicity in which this model can be used to interpret the spectra of large polyatomic molecules. The amount of computational effort does not increase dramatically as the molecular size increases. This is in sharp contrast to conventional expressions which are based on summations over eigenstates, which are intractable for large molecules.

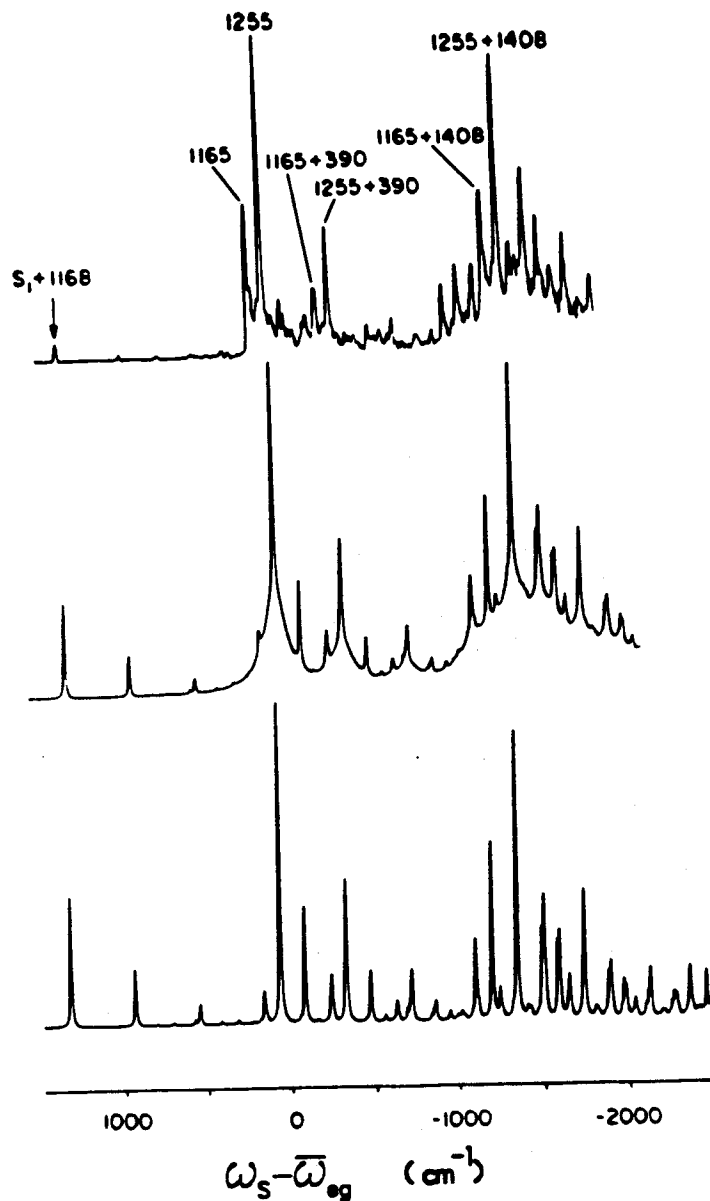


Figure 2. The $7\frac{1}{2}$ dispersed fluorescence of ultracold Anthracene in a supersonic beam. The available vibrational energy is 1168 cm^{-1} . The parameters of the optically active modes are given in Table I. The top figure is the experimental spectrum[4]. The bottom figure is the emission in the harmonic approximation ($\gamma_{bd}^{IVR}=0$) using the first term in Eq.(35). The calculation clearly fails to reproduce the broad redistributed emission. The middle figure was calculated with IVR. (Eqs.(35)) with Eq.(25)). Only one $|b\rangle$ state (the ground vibrational state $|b\rangle=|0\rangle$) was used. $\gamma_{bd}^{IVR}/\gamma=5$. The relaxed emission was calculated in the fast modulation limit (Eq.(16)) with $\Gamma=35 \text{ cm}^{-1}$.

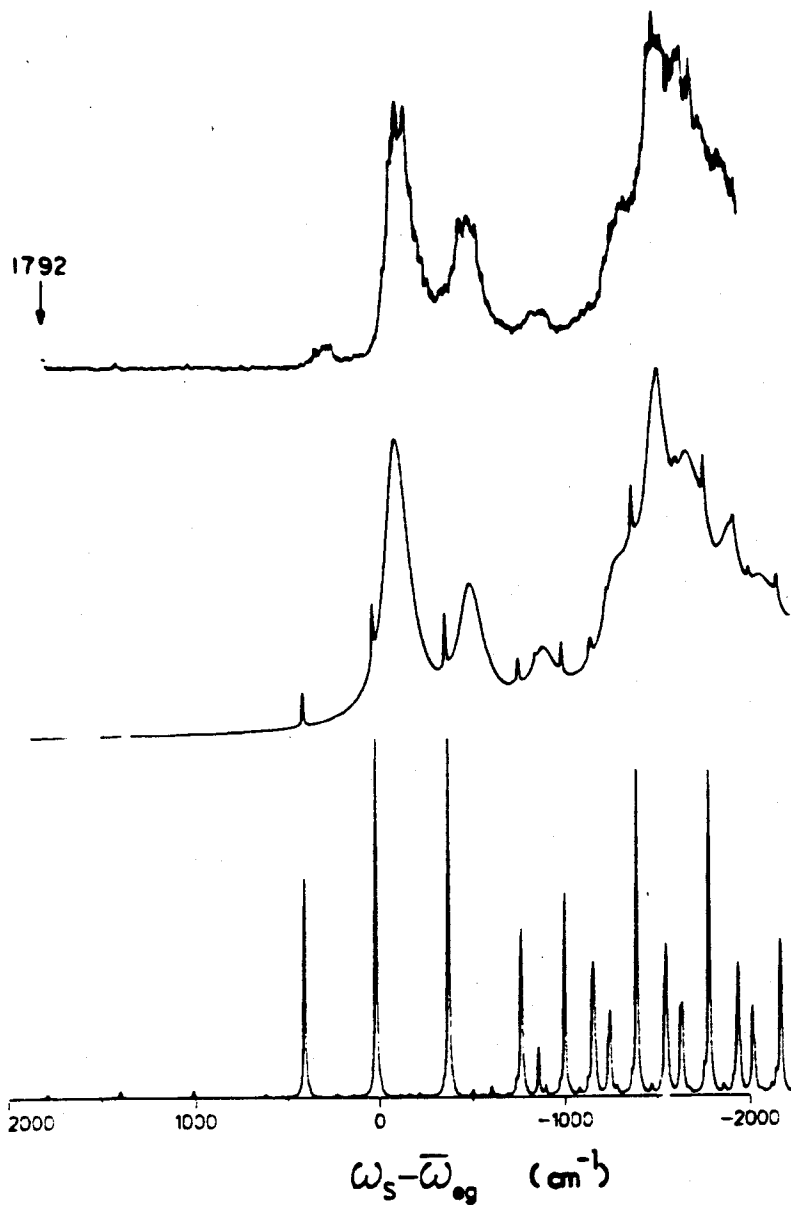


Figure 3. The same as Fig. 2 but for the combination $5_0^1 12_0^1$ dispersed fluorescence spectrum with 1792 cm of excess vibrational energy. $\Gamma = 75 \text{ cm}^{-1}$, $\gamma_{bd}^{IVR} / \gamma = 40$.

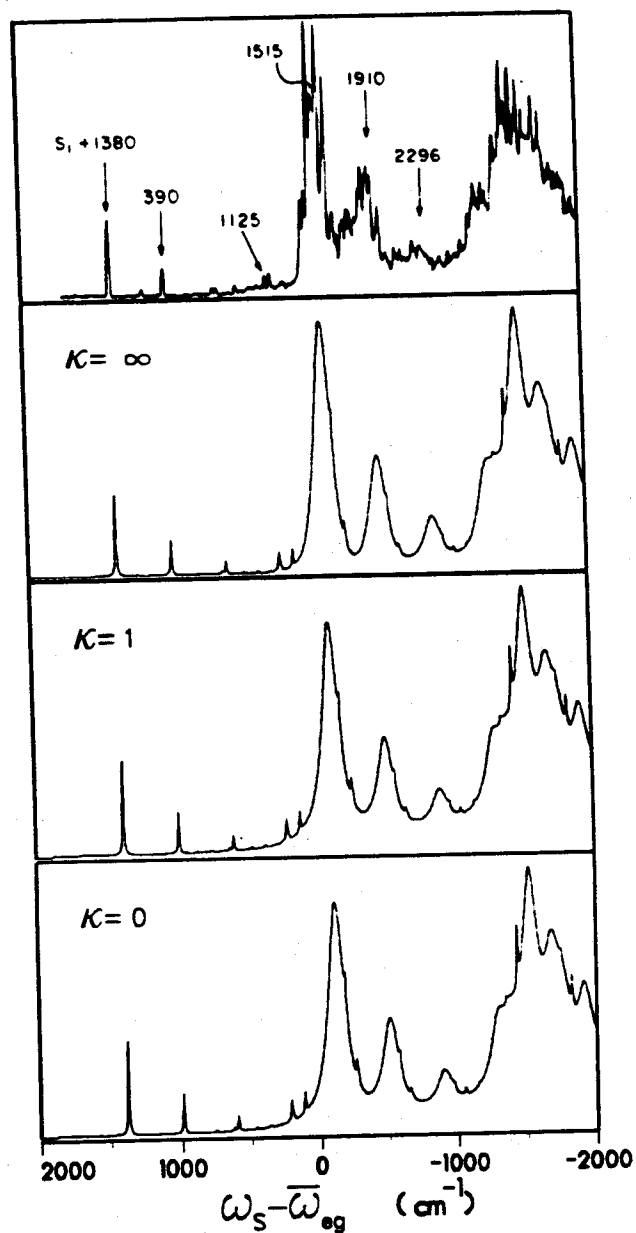


Figure 4. The same as Fig. 2 but for the 6_1^1 dispersed fluorescence with 1380 cm^{-1} of excess vibrational energy. $\gamma_{\text{bd}}^{\text{IVR}}/\gamma = 30$. The calculations demonstrate the variation of

the emission with the stochastic parameter κ . $\kappa = \infty$, 1 and 0 correspond respectively to Lorentzian, intermediate, and Gaussian broadening. The $\kappa = \infty$ curve has $\Gamma = 65 \text{ cm}^{-1}$. In the other calculation Δ and Λ were chosen such that the stochastic lineshape has the same full width at half maximum.

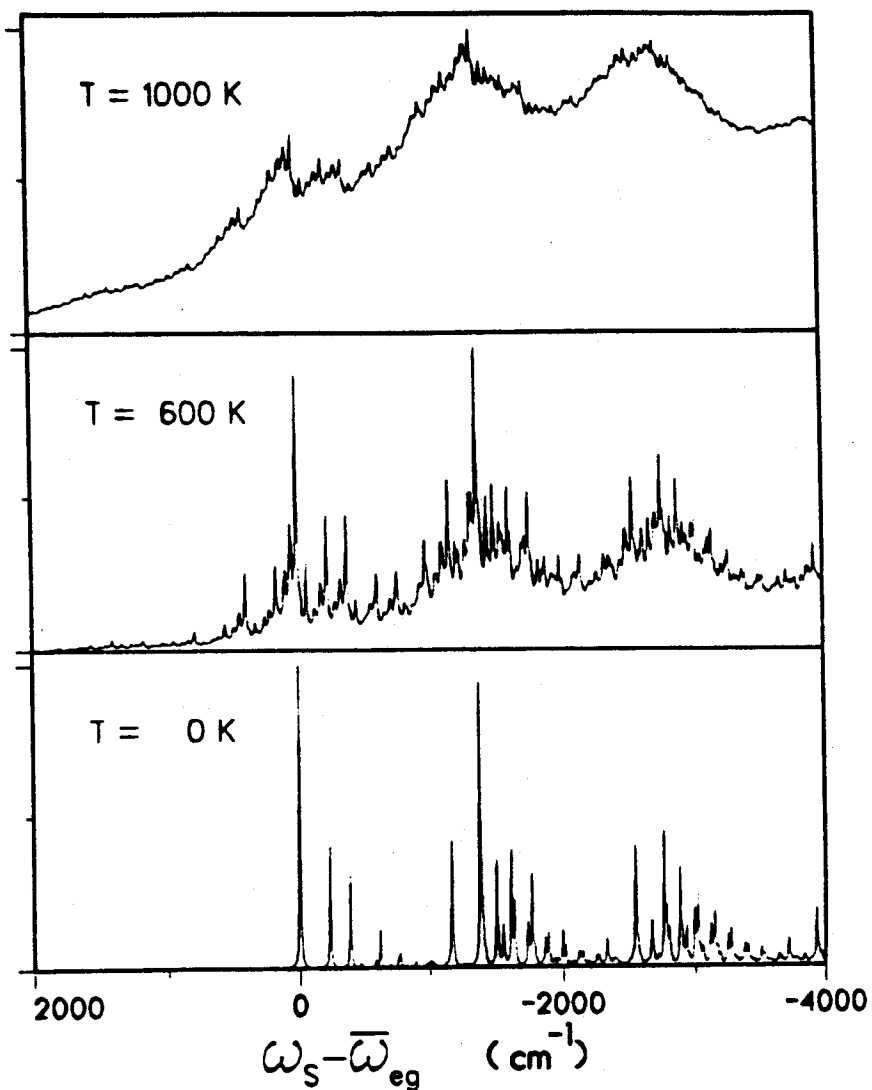


Figure 5. The total emission spectrum of Anthracene at finite temperatures, taking the electronically excited state to be in thermal equilibrium at three different temperatures. The calculation was made using Eqs. (31) and (32) in the absence of IVR. The linewidth $\gamma=10 \text{ cm}^{-1}$.