

Fluorescence of supercooled molecules as a probe for intramolecular vibrational redistribution rates

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A theory is developed for the fluorescence spectra of supercooled polyatomic molecules in a jet. A single molecular mode (the "system") is assumed to be optically active and the other modes constitute a "bath" which induces line broadening and relaxation. Since the bath is finite and is initially cold, its motion is strongly correlated with that of the system. The correlated reduced dynamics of the system and bath is treated using the Mori projection operator technique. The present tetradic reduced description becomes useful especially in large statistical molecules where many molecular states are involved in the fluorescence. This is precisely the limit where the effective Hamiltonian formalism commonly used for the intramolecular dynamics in intermediate size molecules becomes very tedious and impractical. The fluorescence spectra in large statistical molecules may be interpreted in terms of simple rate equations and may be used to directly monitor the intramolecular vibrational redistribution of energy (IVR). We further compare the spectra predicted for statistical and intermediate size molecules with the existing experimental results in supersonic beams.

I. INTRODUCTION

Resonance fluorescence and near-resonance light scattering (RLS), both time resolved and frequency resolved, are well-known techniques for obtaining static (structural) and dynamical information on atomic and molecular systems. Recent RLS studies of molecules in the gas phase^{1,2} impurities in solid matrices or pure solids,^{3,4} and even biological systems⁵ have yielded valuable information regarding *intermolecular* interactions. In these studies it has been sometimes possible to resolve in the emission spectra a coherent narrow component (the so-called resonance Raman) and a broad, redistribution component which corresponds to incoherent photon scattering ("resonance fluorescence"). The coherent part results from a direct photon scattering from the initial to the final molecular levels and does not depend strongly on the nature of the intermediate molecular levels. The incoherent component, however, arises from a two-step scattering process of photon absorption to some intermediate level and a subsequent emission, and as such it depends directly on the nature of the intermediate molecular levels and on their relaxation properties. The ratio of the integrated intensities of the two components equals $\hat{\Gamma}/\Gamma_1$, where $\hat{\Gamma}$ is the proper dephasing rate of the transition and Γ_1 is the inverse lifetime of the intermediate molecular state.⁶⁻¹³

RLS studies of *isolated large molecules* (under collision-free conditions) are more difficult experimentally. Time-resolved studies of this type give useful information regarding the total lifetime of the intermediate levels and as such serve as a probe for intramolecular electronic to vibrational relaxation rates¹⁴⁻¹⁶ or radiative lifetimes. Frequency-resolved RLS studies of collisionless polyatomic molecules usually result in very

limited dynamical information. The resulting spectra are often inhomogeneously broadened (rotational envelopes, sequences) and their information content is limited to static (structural) characteristics of the molecules (rotational constants, vibrational frequencies, differences in potential surfaces). Recent progress in the studies of supercooled large molecules in a beam¹⁷⁻²⁰ has made it possible to carry spectroscopic studies of such molecules at 1-2 °K which makes it possible for the first time to use frequency-resolved and time-resolved RLS techniques as a probe for intramolecular processes.

In the theoretical treatment of intramolecular relaxations it is common to distinguish between the small, intermediate size, and the large (statistical) molecule limits.^{15,16} In the former case the density of molecular states is sufficiently low so that each state may be considered isolated. A RLS from such a molecule involves therefore only three states (the initial, intermediate and final states) and the molecule behaves like an atom. No dynamical information is then contained in the RLS spectra and they depend only on structural (static) information (level positions and transition dipoles). The intermediate case occurs when the density of molecular states increases (e.g., by considering larger molecules or higher vibrational energies). Here several molecular states are contributing to the RLS spectra which become more complicated (complex spectra in frequency-resolved RLS and combinations of oscillations and exponential decays in time-resolved spectra¹⁵). In this case the spectra contain more information. Theoretically this case may be handled very efficiently making use of the effective Hamiltonian formalism.¹⁵ The basic procedure is to diagonalize the molecular Hamiltonian and to use the exact molecular eigenstates to describe the RLS spectra. This is feasible as long as the number of molecular states involved is not too large. The effective Hamiltonian formalism is also very useful when the

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molecular dynamics is governed by few relevant states interacting with dense manifolds of other states where the experimental observables are connected only with the former.^{15,16} This is the usual case in the statistical limit of large molecules undergoing electronic to vibrational radiationless processes. Here typically the few relevant states belong to the first excited singlet whereas the dense manifolds correspond to other electronic states (the lowest triplet or the ground electronic state). Provided the density of states within the manifolds is large enough, their effect on the dynamics may be incorporated by the addition of an extra imaginary part to the effective Hamiltonian, corresponding to nonradiative relaxation rates. To summarize, the effective Hamiltonian formalism is useful when we include in our description all the relevant molecular states or when we want to eliminate certain groups of states (quasicontinua). If we consider intrastate relaxations, i.e., intramolecular vibrational redistribution (IVR) among the various vibrational degrees of freedom within the same electronic state due to anharmonicities, then the situation is much more complicated.^{21,22} We do not have the favorable situation where the molecular states may be divided into few relevant ones + continua. What we need then is a reduced formulation which will allow us to consider explicitly only few molecular degrees of freedom or few molecular dynamical variables and average over the rest. It is impossible to average over degrees of freedom or consider only few dynamical variables using the effective Hamiltonian formalism in Hilbert space and what we need then is to switch to Liouville space and develop a tetradic reduced description (TRD). Such a description enables us to adjust the level of input information to what is dictated by experimental resolution and it is the most appropriate way to handle the dynamics of highly vibrationally excited polyatomic molecules since we calculate directly the quantities of interest. A TRD was recently developed for the interpretation of molecular multiphoton processes in the infrared²⁴ and vibrational overtone spectra.²⁵ It should be emphasized that both the effective Hamiltonian formalism (EHF) and the TRD allow us to perform a dynamical reduction and consider explicitly only subdynamics of the entire system. The EHF allows us only to trace over irrelevant states whereas the TRD allows us a much more general type of reduction over degrees of freedom or to focus attention on few relevant dynamical variables. It is our purpose in this paper to develop a TRD for RLS in statistical molecules by considering the reduced molecular density matrix in Liouville space. We show how the dynamics reduces finally to simple rate equations so that RLS may be used to monitor the intramolecular vibrational redistribution rates (γ^{IVR}), which play a major role in the theories of unimolecular reactions and their magnitude is currently the subject of a lively debate.²¹ (It should be noted that recent studies of vibrational overtone spectroscopy and photoisomerization²⁵ and laser-induced fluorescence studies of optically pumped molecules²⁶ are yielding also valuable information related directly to γ^{IVR} .)

In Sec. II we present the basic molecular model and construct the Hamiltonian for RLS. In Sec. III we re-

view the conventional description of RLS in intermediate size molecules where we use the effective Hamiltonian formalism.¹⁵ In Sec. IV we make use of the tetradic scattering formalism^{27,28} and the Mori projection operator technique²⁹ to develop a TRD for RLS. The competition between IVR and the radiative relaxation is reflected in the γ matrix [Eq. (36)] which enters into the final expression and determines the ratio of the direct to the redistributed scattering processes. Finally, in Sec. V we study some limiting cases of our general expressions and discuss their range of validity and limitations. We further compare the molecular behavior in intermediate and in statistical molecules and make a few comments regarding the recent experimental results of supercooled spectra of alkyl-substituted benzenes.¹⁸

II. THE MODEL HAMILTONIAN

We consider a polyatomic molecule with two electronic states (the ground state $|g\rangle$ and an excited state $|e\rangle$) and $N+1$ vibrational modes. The molecule is assumed to be isolated in a supersonic beam and cooled to 0°K.¹⁷⁻²⁰ We shall ignore the rotational degrees of freedom as they do not play an important role in the experimental conditions to be considered. We further assume that only one vibrational mode ($\bar{\omega}_s$) is optically active in the absorption and emission processes between $|g\rangle$ and $|e\rangle$. This implies that only this mode has a relatively large configurational change between the two electronic states, whereas the rest of the modes are practically unaffected by the electronic excitation (apart from small, few percent, changes in frequencies). The absorption and emission spectra of our molecule thus consist of a progression of the optically active mode, and the other degrees of freedom perturb this progression causing line shifts and spectral broadening. In a RLS experiment, a weak monochromatic laser beam with frequency ω_1 is being scattered from the molecular beam and the scattered photons with frequency ω_2 are detected.

The combined state of the molecule and the radiation field will be denoted by $|a, b, v, \alpha\rangle$, where $a=g, e$ stands for the electronic state of the molecule; $b=\omega_1, \omega_2, \text{vac}$ denotes the state of the radiation field which has either a single photon in the incident channel (ω_1), a single photon in the final emission channel ω_2 , or no photons at all (the vacuum state). v denotes the vibrational state of $\bar{\omega}_s$, whereas α comes for the collection of all other vibrational quantum numbers of the molecule. Only the first three quantum numbers may be resolved in the experiments to be considered. We shall thus partition our degrees of freedom into the "system" (electronic, the radiation field, and $\bar{\omega}_s$) and the "bath" ($\omega_\nu, \nu=1, \dots, N$).

Within the rotating wave approximation³⁰ (RWA) which holds extremely well for optical frequencies, we need consider only the following types of states: $|g, \omega_1, 0, 0\rangle$, $|e, \text{vac}, v, \alpha\rangle$, and $|g, \omega_2, u, \alpha\rangle$ for the initial, intermediate, and final states, respectively. For abbreviating the notation we shall hereafter replace the indices $g\omega_1, e\text{vac}$, and $g\omega_2$ by g, e , and f , respectively. Thus we put

$$\begin{aligned} |g00\rangle &\equiv |g, \omega_1, 0, 0\rangle, \\ |eva\rangle &\equiv |e, \text{vac}, v, \alpha\rangle, \end{aligned} \quad (1)$$

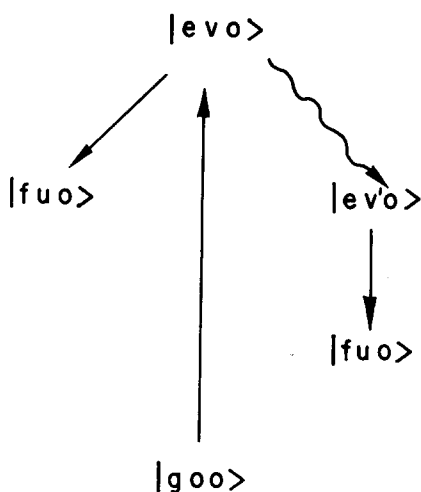


FIG. 1. Schematic representation of RLS from a polyatomic molecule consisting of a direct scattering and an indirect scattering process whereby an IVR process (wiggly line) occurs prior to the emission of the final photon.

and

$$|f u \alpha\rangle \equiv |g, \omega_2, u, \alpha\rangle.$$

The photon scattering process is represented schematically in Fig. 1.

The total Hamiltonian for the molecule and the radiation field, within the RWA³⁰ may be written in the form

$$H = H_0 + U + V \equiv H_1 + V, \quad (2)$$

where

$$\begin{aligned} H_0 = & |g\rangle(\omega_1 + \bar{\omega}_s a^\dagger a + \sum_{\nu=1}^N \bar{\omega}_\nu b_\nu^\dagger b_\nu) \langle g| + |e\rangle \\ & \times \left(\omega_{ge} + \bar{\omega}'_s a^\dagger a + \frac{1}{\sqrt{2}} \Delta_s (a + a^\dagger) + \sum_{\nu} \bar{\omega}'_\nu b_\nu^\dagger b_\nu - \frac{i}{2} \gamma_R \right) \\ & \times \langle e| + |f\rangle \left(\omega_2 + \bar{\omega}_s a^\dagger a + \sum_{\nu=1}^N \bar{\omega}_\nu b_\nu^\dagger b_\nu \right) \langle f| \\ \equiv & |g\rangle H_0^{(g)} \langle g| + |e\rangle H_0^{(e)} \langle e| + |f\rangle H_0^{(f)} \langle f|, \end{aligned} \quad (2a)$$

$$U = |g\rangle U_g \langle g| + |e\rangle U_e \langle e| + |f\rangle U_f \langle f|, \quad (2b)$$

$$\begin{aligned} U_g = & F_1(Q_\nu)(a + a^\dagger) + F_2(Q_\nu)(a + a^\dagger)^2 + \dots, \\ U_e = & F'_1(Q_\nu)(a + a^\dagger) + F'_2(Q_\nu)(a + a^\dagger)^2 + \dots, \end{aligned} \quad (2c)$$

and

$$V = \mu_{ge}(|g\rangle \langle e| + |e\rangle \langle g|) + \mu_{ef}(|e\rangle \langle f| + |f\rangle \langle e|), \quad (2d)$$

where we have denoted molecular vibrational frequencies by $\bar{\omega}$ and photon frequencies by ω . a^\dagger (a) and b_ν^\dagger (b_ν) are the creation (annihilation) operators for the optically active mode $\bar{\omega}_s$ and the other molecular modes $\bar{\omega}_\nu$. Δ_s is the dimensionless horizontal shift in the equilibrium position of $\bar{\omega}_s$ between the two electronic states $|g\rangle$ and $|e\rangle$, μ is the electronic transition dipole operator, and ω_{ge} is the fundamental electronic transition frequency. In Eq. (2) we have further partitioned H_1 into the pure harmonic Hamiltonian (H_0) and the anharmonic part (U). The latter is then expanded in a power series in $Q_s = (1/\sqrt{2})(a + a^\dagger)$ [Eqs. (2b) and (2c)]. For the sake of subsequent manipulations we further define

$$H_1^{(g)} \equiv H_0^{(g)} + U_g, \quad (2e)$$

$$H_1^{(e)} \equiv H_0^{(e)} + U_e, \quad (2f)$$

$$H_1^{(f)} \equiv H_0^{(f)} + U_f. \quad (2g)$$

III. RESONANCE LIGHT SCATTERING CROSS SECTION IN INTERMEDIATE SIZE MOLECULES—THE EFFECTIVE HAMILTONIAN FORMALISM (EHF)

When the molecule is not too large and the photon frequencies ω_1 and ω_2 are such that the available molecular vibrational energy ($\omega_1 - \omega_{ge}$ in the intermediate state $|e\rangle$ and $\omega_1 - \omega_2$ in the final state $|f\rangle$) is not too high, then the number of molecular states participating in the RLS experiment may be reasonably small (say less than a 100). In such a case we may use the conventional effective Hamiltonian formalism developed for the treatment of radiationless processes in intermediate size molecules, to describe RLS phenomena. Since this formalism is well documented¹⁵ we shall not rederive it here but merely quote the general results for the sake of comparison with the TRD to be developed hereafter. The basic idea here is to use the exact molecular eigenstates (i. e., the eigenstates of H_1). These may be found by diagonalizing the matrix corresponding to H_1 in the energy range of interest. (This matrix is relatively small in the intermediate case.) The resulting molecular eigenstates are¹⁵

$$H_1^{(g)} |g\rangle = \omega_1 |g\rangle, \quad (3a)$$

$$H_1^{(e)} |J\rangle = (E_J - \frac{1}{2} i \gamma_J) |J\rangle, \quad (3b)$$

$$\langle \bar{J} | H_1^{(e)} = \langle \bar{J} | (E_J - \frac{1}{2} i \gamma_J), \quad (3c)$$

and

$$H_1^{(f)} |K\rangle = E_K |K\rangle \equiv (\epsilon_K + \omega_2) |K\rangle. \quad (3d)$$

For $H_1^{(e)}$ we have considered only one vibrational state (the ground state). Since $H_1^{(e)}$ is complex we need consider its right- and left-hand eigenstates ($|J\rangle$ and $\langle \bar{J}|$, respectively).¹⁵ Finally, the $|K\rangle$ states are the eigenstates of $H_1^{(f)}$. Since $H_1^{(f)}$ also includes the ω_2 photon, we may write E_K as $\epsilon_K + \omega_2$. The states $|J\rangle$, $\langle \bar{J}|$, and $|K\rangle$ are linear combinations of the harmonic states which are the eigenstates of H_0 [Eq. (2a)]. The resolution of the unity, using our new basis set is¹⁵

$$I = |g\rangle \langle g| + \sum_J |J\rangle \langle \bar{J}| + \sum_K |K\rangle \langle K|. \quad (4)$$

Making use of these definitions, the RLS cross section for photon scattering where the molecule starts at $|g\rangle$ and ends up in $|K\rangle$ is given by (up to a proportionality constant)¹⁵

$$I_{Kg}(\omega_1, \omega_2) = \left| \sum_J \frac{\langle K | V | \bar{J} \rangle \langle \bar{J} | V | g \rangle}{\omega_1 - E_J + \frac{1}{2} i \gamma_J} \right|^2 \delta(\omega_1 - \omega_2 - \epsilon_K). \quad (5a)$$

The total RLS cross section is

$$I(\omega_1, \omega_2) = \sum_K I_{Kg}(\omega_1, \omega_2). \quad (5b)$$

Let us consider the case where we have a weak anharmonic mixing of the harmonic states in the $|e\rangle$ and $|f\rangle$ states. We further assume that the true molecular states are sufficiently sparse and that the excitation fre-

quency ω_1 is near resonance with a single doorway state $|e\bar{v}0\rangle$. We then have

$$|J\rangle - |e\bar{v}0\rangle = |ev0\rangle + \sum_{\nu\alpha} \beta_{\nu\alpha}^{\alpha\alpha} |ev'\alpha\rangle. \quad (6a)$$

Similarly, the $|K\rangle$ states are

$$|K\rangle - |f\bar{u}\alpha\rangle = |fu\alpha\rangle + \sum_{u'\alpha'} \gamma_{u'u'}^{\alpha\alpha'} |fu'\alpha'\rangle. \quad (6b)$$

Upon substitution of Eq. (6) in (5) we get

$$I(\omega_1, \omega_2) = \frac{|\langle ev0|V|g00\rangle|^2}{(\omega_1 - E_{v0})^2 + \frac{1}{4}\gamma_v^2} \times \sum_{u,\alpha} |\langle f\bar{u}\alpha|V|e\bar{v}0\rangle|^2 \delta(\epsilon_{u\alpha} + \omega_2 - \omega_1), \quad (7)$$

i. e.,

$$I(\omega_1, \omega_2) = \frac{|\langle ev0|V|g00\rangle|^2}{(\omega_1 - E_{v0})^2 + \frac{1}{4}\gamma_v^2} \left(\sum_{u=0}^{\infty} |\langle v|u\rangle|^2 \delta(\epsilon_u + \omega_2 - \omega_1) + \sum_{u=1}^{\infty} \sum_{k=1}^{\infty} \sum_{\alpha} |\langle v-k|u-k\rangle \beta_{v-k, u-k}^{\alpha} - \langle v|u\rangle \gamma_{u, u-k}^{\alpha}|^2 \times \delta(\epsilon_{u-k, \alpha} + \omega_2 - \omega_1) \right) \quad (8)$$

(where $\beta=0$ if $v-k < 0$ and $\gamma=0$ if $u-k < 0$). The first term in Eq. (8) is the RLS in the harmonic limit and consists of a progression of narrow lines corresponding to the $\bar{\omega}_s$ mode. The second term is a redistributed spectrum due to intensity borrowing via the anharmonic mixing terms β and γ . Equations (5) and (8) are the basic expressions for frequency-resolved RLS spectra in intermediate size molecules. In order to consider time-resolved experiments we put in Eq. (2d),¹⁵

$$\mu_{g\epsilon} = \phi(t) \sum_J [|g\rangle\langle J| + |\bar{J}\rangle\langle g|], \quad (9)$$

where $\phi(t)$ is the incident radiation field amplitude [$|\phi(t)|^2$ is the incident flux]. We assume that $\phi(t)$ is finite around $t=0$ so that $\phi(-\infty) = \phi(+\infty) = 0$. We may now solve the time dependent Schrödinger equation for the molecular wave function where we take $\psi(-\infty) = |g\rangle$. The solution to first order in $\mu_{J\epsilon}$ is

$$C_J(t) \equiv \langle \bar{J} | \psi(t) \rangle = \mu_{J\epsilon} \int_{-\infty}^t d\tau \phi(\tau) \exp[(-iE_J - \frac{1}{2}\gamma_J)(t-\tau)]. \quad (10)$$

In order to define the emission rate to the final state $|N_K\rangle$ we define the corresponding doorway state $|N_K\rangle$ as

$$|N_K\rangle = \frac{1}{\delta_K} \sum_J \mu_{JK} |J\rangle, \quad (11)$$

where

$$\delta_K^2 = \sum_J |\mu_{JK}|^2$$

is a normalization constant. The emission rate will be

$$I_{K\epsilon}(t) \propto |\langle N_K | \psi(t) \rangle|^2 = \sum_{J,J'} C_J(t) C_{J'}^*(t) \mu_{JK} \mu_{KJ'}. \quad (12)$$

Upon substitution of Eq. (10) in (12), we finally get¹⁵

$$I_{K\epsilon}(t) \propto \sum_{J,J'} (\mu_{gJ} \mu_{JK} \mu_{KJ'} \mu_{J'\epsilon}) \times \int_{-\infty}^t d\tau_1 \int_{-\infty}^{\tau_1} d\tau_2 \phi(\tau_1) \phi(\tau_2) \exp[(-iE_J - \frac{1}{2}\gamma_J)(t-\tau_1)] \times \exp[(iE_{J'} - \frac{1}{2}\gamma_{J'})(t-\tau_2)]. \quad (13)$$

If the molecular states $|J\rangle$ are sufficiently sparse we may assume that only one state $|J\rangle$ contributes to Eq. (13). If in addition we take a short excitation pulse whose duration is $\ll \gamma_J^{-1}$, we may put

$$\phi(t) = \delta(t) \quad (14)$$

in Eq. (13) resulting in

$$I_{K\epsilon}(t) \propto \exp(-\gamma_J t). \quad (15)$$

This concludes our review of RLS spectra (both time and frequency resolved) in supercooled collisionless intermediate molecules. These results will be used in Sec. V for comparison with our TRD or RLS.

IV. TETRADIC REDUCED DESCRIPTION OF RLS IN LARGE STATISTICAL MOLECULES

We shall now utilize the tetradic scattering formalism^{27,28} to provide a reduced description for RLS in large molecules. This approach is based on formulating scattering theory in terms of density matrices in Liouville space (rather than wave functions in Hilbert space) and is particularly convenient for performing averages over irrelevant degrees of freedom. The tetradic T matrix \mathcal{T} is defined as^{27,28}

$$\mathcal{T}(\epsilon) = \mathcal{V} + \mathcal{V} \mathcal{G}_c(\epsilon) \mathcal{V}, \quad (16)$$

where \mathcal{V} is the tetradic operator corresponding to V , i. e.,

$$\mathcal{V} = [V,], \quad (17)$$

and $\mathcal{G}_c(\epsilon)$ is the complete tetradic Green's operator for the entire system and bath

$$\mathcal{G}_c(\epsilon) \equiv (\epsilon - L)^{-1}, \quad (18)$$

$L(L_0, L_1)$ being the Liouville operators corresponding to $H(H_0, H_1)$, i. e.,

$$L = [H,], \text{ etc.} \quad (19)$$

The cross section for the photon scattering process (Fig. 1) is given by^{11,28}

$$\sigma_{u-o}(\omega_1, \omega_2) = \frac{1}{\phi_g} I_{uo}(\omega_1, \omega_2), \quad (20)$$

where ϕ_g is the incident photon flux and

$$I_{uo}(\omega_1, \omega_2) = -i \langle \mathcal{T}(0)_{fufu, gog\alpha} \rangle = -i \sum_{\alpha\beta} P(\alpha) \langle \langle fu\beta, fu\beta | \mathcal{T}(0) | go\alpha, go\alpha \rangle \rangle. \quad (21)$$

Here $\langle \dots \rangle$ denotes a thermal average of a tetradic operator over the bath degrees of freedom (averaging over all possible initial bath states and summing over all final bath states), and we are using here the double bracket notation,²⁸ where the Liouville space analog of $|i\rangle\langle j|$ is denoted $|ij\rangle$. $P(\alpha)$ is the initial distribution of bath states. Since the molecule is initially cold at 0°K, all occupation numbers are initially zero. We can thus

omit the averaging over initial states, resulting in

$$I_{uo}(\omega_1, \omega_2) = -i \sum_{\beta} \langle\langle fu\beta, fu\beta | \mathcal{T}(0) | goo, goo \rangle\rangle. \quad (22)$$

As we are interested in ordinary RLS using a weak excitation source we need consider only the contributions to \mathcal{T} to lowest order in ϵ . Using Eq. (2d) and Fig. 2, we note that we need to expand \mathcal{T} to fourth order in \mathcal{U} , i. e.,

$$\mathcal{T}(\epsilon) \cong \mathcal{U} \mathcal{S}(\epsilon) \mathcal{U} \mathcal{S}(\epsilon) \mathcal{U} \mathcal{S}(\epsilon) \mathcal{U}, \quad (23)$$

where

$$\mathcal{S}(\epsilon) = (\epsilon - L_I)^{-1}. \quad (24)$$

The evaluation of the necessary matrix elements of \mathcal{T} [Eq. (22)] is not at all trivial. Formally, the present Hamiltonian (2) appears very similar to that of an impurity molecule in a solid matrix^{3,4,9,31} and the treatment of the RLS should be similar. However, in the latter problem the number of the bath degrees of freedom is infinite ($N \rightarrow \infty$) and as a result the motion of the system (under quite general types of conditions) may be considered *uncorrelated* with that of the bath (i. e., the system is too small to affect the bath in a significant way). The common treatments^{3,4,9,31} of RLS from impurities in solids make use of this property and assume that the bath is always in thermal equilibrium regardless of what happens to the system. It is then possible to define a Zwanzig³² projection operator which projects onto the equilibrium state of the bath and makes the evaluation of Eq. (22) feasible.^{9,10} Similar ideas apply also for the treatment of collisional perturbations on RLS where the bath is provided by the translational degrees of freedom.⁶⁻¹¹

The basic theoretical difficulty in our problem of intramolecular line broadening in RLS is that although we have a natural partitioning of our degrees of freedom into a system and a bath, since the bath is finite and since initially it is at 0°K then its motion is *strongly correlated* with that of the system. Energy conservation alone dictates that any relaxation in the system will result in a significant change in the energy (and motions) of the bath. This basic problem may be overcome by making use of the Mori²⁹ projection operator technique which was recently applied to molecular multiphoton processes in general²⁴ (here we are interested in the special case of two-photon processes). Within this formalism we focus attention on few relevant molecular (system and bath) operators to provide a reduced description of the photon scattering process and no assumption regarding the equilibrium state of the bath need to be made. The procedure goes as follows^{24,29}: We first have to identify a set of molecular operators which play a major role in the RLS and which are expected to be "slow" relative to all other molecular operators. We start with the following set:

$$A_{gg} = |goo\rangle\langle goo|, \quad (25a)$$

$$A_{ee}^{(v)} = \sum_{\alpha} |ev\alpha\rangle\langle ev\alpha| \delta(\omega_1 - \omega_{ge} - v\bar{\omega}_s - E_{\alpha}), \quad (25b)$$

and

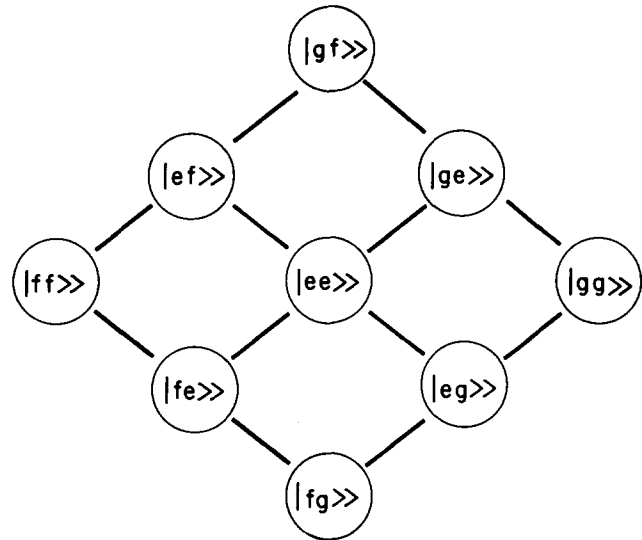


FIG. 2. Liouville-space coupling scheme for RLS. There are six pathways which lead from $|gg\rangle\rangle$ to $|ff\rangle\rangle$ in fourth order, four of which pass via $|ee\rangle\rangle$ and the other two are purely coherent components which pass via $|gf\rangle\rangle$ or $|fg\rangle\rangle$.

$$A_{ff}^{(u)} = \sum_{\alpha} |fu\alpha\rangle\langle fu\alpha| \delta(\omega_1 - \omega_2 - \bar{\omega}'_s u - E_{\alpha}). \quad (25c)$$

The expectation values of these operators correspond to the total population of the $|g\rangle$, $|ev\rangle$, and $|fu\rangle$ states. In addition to these operators we further introduce operators corresponding to *optical coherences*:

$$A_{ge}^{ov} = |goo\rangle\langle evo|, \quad (25d)$$

$$A_{fe}^{uv'} = \sum_{\alpha} |fu\alpha\rangle\langle ev'\alpha| \delta(\omega_1 - \omega_2 - u\bar{\omega}'_s - E_{\alpha}), \quad (25e)$$

$$A_{gf}^{ou} = |goo\rangle\langle fuo|. \quad (25f)$$

We now define a Mori projection operator²⁹ P onto the subspace spanned by our set of operators

$$PB = \sum_{\nu} A_{\nu} S^{-1}(A_{\nu}, B), \quad (26)$$

where S is the overlap matrix of our set of operators

$$S_{\mu\nu} = (A_{\mu}, A_{\nu}) \quad (27)$$

and B is any operator. (A_{ν}, A_{μ}) is the scalar product in Liouville space of the two operators and is defined as

$$(A_{\mu}, A_{\nu}) \equiv \text{Tr}(A_{\mu}^{\dagger} A_{\nu}). \quad (28)$$

The definition of the Mori projection operator P is the crucial step in achieving a successful reduced description for any physical phenomena. In order to get a feeling for the significance of Eq. (26) let us operate with P on the total density matrix ρ at time t . The result is

$$P\rho(t) = \sum_{\nu} \sigma_{\nu}(t) A_{\nu}, \quad (29)$$

where $\sigma_{\nu}(t)$ are C numbers which give the expectation values of A_{ν} at time t . Thus when P operates on ρ it causes a considerable reduction of information and retains only information regarding our dynamical quantities of interest— A_{ν} . The RLS expression (22) may now be recast in the form

$$I_{u0} = i\text{Tr}[A_{ff}^{(u)}\mathcal{T}(0)A_{gg}^{(0)}] = i\text{Tr}[A_{ff}^{(u)}P\mathcal{T}(0)PA_{gg}^{(0)}], \quad (30)$$

in terms of the projection $P\mathcal{T}P$. If our chosen set of operators (25) (which define the projection P) form a complete set of slow variables, we can further invoke the factorization assumption and write^{11,33,34}

$$P\mathcal{T}(0)P \cong P\mathcal{U}P\mathcal{G}(0)P\mathcal{U}P\mathcal{G}(0)P\mathcal{U}P\mathcal{G}(0)P\mathcal{U}P, \quad (31)$$

or alternatively (since $P^2 = P$)

$$\langle\mathcal{T}(0)\rangle = \langle\mathcal{U}\rangle\langle\mathcal{G}(0)\rangle\langle\mathcal{U}\rangle\langle\mathcal{G}(0)\rangle\langle\mathcal{U}\rangle\langle\mathcal{G}(0)\rangle\langle\mathcal{U}\rangle, \quad (32)$$

where

$$\langle\mathcal{G}\rangle \equiv P\mathcal{G}P \quad (33a)$$

and

$$\langle\mathcal{U}\rangle \equiv P\mathcal{U}P. \quad (33b)$$

The problem is thus reduced to the evaluation of a product of matrices whose size is determined by our chosen set of operators (25). From Fig. 2 we note that there are six pathways which lead from $A_{gg}(|gg\rangle\rangle)$ to $A_{ff}(|ff\rangle\rangle)$ in fourth order. Making use further of the Liouville conjugation symmetry²⁸

$$\mathcal{G}_{ab,cd}(\epsilon) = -\mathcal{G}_{ba,dc}^*(\epsilon^*), \quad (34)$$

we get

$$\begin{aligned} \langle\mathcal{T}(0)_{ff,gg}\rangle &= 4\langle\mathcal{U}_{ff,fe}\rangle(\text{Im}\langle\mathcal{G}_{fe,fe}\rangle)\langle\mathcal{U}_{fe,ee}\rangle\langle\mathcal{G}_{ee,ee}\rangle\langle\mathcal{U}_{ee,ee}\rangle \\ &\quad \times (\text{Im}\langle\mathcal{G}_{ee,ee}\rangle)\langle\mathcal{U}_{ee,ee}\rangle + 2\text{Re}\langle\mathcal{U}_{ff,fe}\rangle\langle\mathcal{G}_{fe,fe}\rangle\langle\mathcal{U}_{fe,fg}\rangle \\ &\quad \times \langle\mathcal{G}_{fg,fg}\rangle\langle\mathcal{U}_{fg,ee}\rangle\langle\mathcal{G}_{ee,ee}\rangle\langle\mathcal{U}_{ee,ee}\rangle. \end{aligned} \quad (35)$$

The first term in Eq. (35) arises from the four pathways (Fig. 2) which pass through $A_{ee}(|ee\rangle\rangle)$, whereas the second term arises from the other two pathways which pass via $A_{fg}(|fg\rangle\rangle)$ and $A_{gf}(|gf\rangle\rangle)$.

$\langle\mathcal{G}_{ee,ee}\rangle$ is the T_1 relaxation matrix in the excited electronic state. It has a contribution from the anharmonicities (IVR processes γ^{IVR}) as well as from other inter-state relaxation (e.g., radiative lifetimes γ_v^R). For the Hamiltonian (2), we have

$$\langle\mathcal{G}_{ee,ee}\rangle_{v'v',vv} \equiv -i(\gamma^{IVR} + \gamma^R)_{v'v'}^{-1} \equiv \gamma_{v'v'}^{-1}, \quad (36a)$$

where

$$\gamma_{v'v'}^{IVR} \equiv \begin{cases} -\gamma_{v'v}, & v' \neq v, \\ \sum_{v'' \neq v} \gamma_{v''v}, & v' = v \end{cases} \quad (36b)$$

$$\quad (36c)$$

and

$$\gamma_{v'v}^R \equiv \gamma_v^R \delta_{vv'}. \quad (36d)$$

Similarly, we can define an analogous relaxation matrix for the ground electronic state ($\mathcal{G}_{gg,gg}$), where we take $\gamma_{\bar{v}}^R = 0$, i.e.,

$$\langle\mathcal{G}_{gg,gg}\rangle_{u'u',uu} \equiv -i\bar{\gamma}_{u'u}^{-1}, \quad (37a)$$

$$\bar{\gamma}_{u'u} \equiv \begin{cases} -\bar{\gamma}_{u'u}, & u \neq u', \\ \sum_{u'' \neq u} \bar{\gamma}_{u''u} \equiv \bar{\gamma}_u, & u = u'. \end{cases} \quad (37b)$$

$$\quad (37c)$$

The IVR rates (to lowest order in U_g and U_e) are given by

$$\bar{\gamma}_{u'u} = 2\pi \sum_{\alpha\beta} P_u(\alpha) |\langle u\alpha | U_g | u'\beta \rangle|^2 \delta(E_{u\alpha} - E_{u'\beta}), \quad (37d)$$

$$\gamma_{v'v}^{IVR} = 2\pi \sum_{\alpha\beta} P_v(\alpha) |\langle v\alpha | U_e | v'\beta \rangle|^2 \delta(E_{v\alpha} - E_{v'\beta}), \quad (36e)$$

where $P(\alpha)$ is the microcanonical distribution of bath states

$$P_i(\alpha) \propto \delta(E_i - H_0), \quad i = v, u, \quad (38)$$

which depends on the total initial energy of the bath (E_i) for the $v \rightarrow v'$ ($u \rightarrow u'$) relaxation processes, i.e.,

$$E_v = \omega_1 - \omega_{ge} - v\bar{\omega}_s \quad (38a)$$

and

$$E_u = \omega_1 - \omega_2 - u\bar{\omega}'_s. \quad (38b)$$

Using Eqs. (36e) and (37d) we note that the IVR rates satisfy the microscopic reversibility conditions, i.e.,

$$\frac{\gamma_{vv'}}{\gamma_{v'v}} = \frac{\rho(\omega_1 - \omega_{ge} - v\bar{\omega}_s)}{\rho(\omega_1 - \omega_{ge} - v'\bar{\omega}_s)} \quad (39a)$$

and

$$\frac{\bar{\gamma}_{uu'}}{\bar{\gamma}_{u'u}} = \frac{\rho(\omega_1 - \omega_2 - u\bar{\omega}'_s)}{\rho(\omega_1 - \omega_2 - u'\bar{\omega}'_s)}, \quad (39b)$$

where $\rho(\epsilon)$ is the density of states in the bath with energy ϵ . Substitution of the expansion (2c) in Eqs. (36e) and (37d) shows that the main contribution to γ^{IVR} ($\bar{\gamma}^{IVR}$) comes from the odd powers in the expansion F_1, F_3, \dots , (F'_1, F'_3, \dots , etc.).

The $\langle g_{fe,fe} \rangle$, $\langle g_{ee,ee} \rangle$, and $\langle g_{fg,fg} \rangle$ matrices correspond to intramolecular dephasing (T_2 processes) and are taken to be diagonal⁶⁻¹³ so that their only nonvanishing matrix elements are

$$\langle g_{fe,fe} \rangle_{uv,uv} = (\omega_2 + u\bar{\omega}'_s - v\bar{\omega}_s - \omega_{ge} - \Delta_{uv} + i\Gamma_{uv})^{-1}, \quad (40a)$$

$$\langle g_{ee,ee} \rangle_{ov,ov} = (\omega_1 - \omega_{ge} - \bar{\omega}_s v - \bar{\Delta}_{ov} + i\bar{\Gamma}_{ov})^{-1}, \quad (40b)$$

$$\langle g_{fg,fg} \rangle_{uo,uo} = (\omega_2 + u\bar{\omega}_s - \omega_1 - \bar{\Delta}_{uo} + i\bar{\Gamma}_{uo})^{-1}, \quad (40c)$$

where

$$\Gamma_{uv} = \frac{1}{2}(\gamma_v + \bar{\gamma}_u) + \hat{\Gamma}_{uv}^{(dyn)} \equiv \bar{\Gamma}_{uv} + \hat{\Gamma}_{uv}^{(dyn)}. \quad (41)$$

Here $\bar{\Gamma}$ is the contribution of T_1 to T_2 and $\hat{\Gamma}_{uv}^{(dyn)}$ stands for a proper dephasing rate which is dynamical in nature.^{27,28,31} $\hat{\Gamma}_{uv}^{(dyn)}$ exists even if the two potential surfaces U_g and U_e are identical and it has to do with the anharmonicities. Using the well-known expressions from the theory of line broadening we have (to lowest order in $U_g - U_e$)^{27,28,35,36}:

$$\begin{aligned} \hat{\Gamma}_{uv}^{(dyn)} &= \pi \sum_{\alpha\beta} |\langle u\beta | U_g | u\alpha \rangle - \langle v\beta | U_e | v\alpha \rangle|^2 \\ &\quad \times P(\alpha) \delta(E_\alpha - E_\beta), \end{aligned} \quad (42)$$

where again $P(\alpha)$ is the microcanonical distribution of bath states [Eq. (38)].

It is clear from Eqs. (42) and (2c) that the main contribution to $\hat{\Gamma}_{uv}^{(dyn)}$ comes from the even powers of U_g and U_e (i.e., $F_2, F_4, \dots, F'_2, F'_4, \dots$, etc.). It is also clear from Eq. (42) that $\hat{\Gamma}_{uv}^{(dyn)}$ vanishes when the bath is cold. Furthermore, $\bar{\gamma}_0 = 0$ so that the ov and uo dephasing rates arise only from the lifetime of the excited state

$$\Gamma_{ov} = \bar{\Gamma}_{ov} = \frac{1}{2}\gamma_v, \quad (43a)$$

$$\Gamma_{uo} = \bar{\Gamma}_{uo} = \frac{1}{2}\bar{\gamma}_u. \quad (43b)$$

The Δ_{uv} , $\bar{\Delta}_{ov}$, and $\bar{\Delta}_{uo}$ terms are level shifts associated with the same relaxation mechanisms contributing to

Γ_{uv} , $\bar{\Gamma}_{ov}$, and $\bar{\Gamma}_{uo}$, respectively. Substitution of Eqs. (36)–(43) into (35) and rearranging terms results in

$$I_{uo} = 4 \frac{|\mu_{uv}|^2 \bar{\Gamma}_{uv}}{(\omega_2 + u\bar{\omega}_s - v\bar{\omega}'_s - \omega_{ge} - \bar{\Delta}_{uv})^2 + \bar{\Gamma}_{uv}^2} \gamma_{vv}^{-1} \frac{|\mu_{ov}|^2 \bar{\Gamma}_{ov}}{(\omega_1 - \omega_{ge} - v\bar{\omega}_s - \bar{\Delta}_{ov})^2 + \bar{\Gamma}_{ov}^2} + 4 \sum_{v' \neq v} \frac{|\mu_{uv'}|^2 \Gamma_{uv'}}{(\omega_2 + u\bar{\omega}_s - v'\bar{\omega}'_s - \omega_{ge} - \Delta_{uv'})^2 + \Gamma_{uv'}^2} \gamma_{v'v}^{-1} \frac{|\mu_{ov}|^2 \bar{\Gamma}_{ov}}{(\omega_1 - \omega_{ge} - v\bar{\omega}_s - \bar{\Delta}_{ov})^2 + \bar{\Gamma}_{ov}^2} + 2 |\mu_{ov}|^2 |\mu_{uo}|^2 \times \text{Im}[(\omega_2 + u\bar{\omega}_s - v\bar{\omega}'_s - \omega_{ge} - \bar{\Delta}_{uv} + i\bar{\Gamma}_{uv})(\omega_1 - \omega_{ge} - v\bar{\omega}_s - \bar{\Delta}_{ov} + i\bar{\Gamma}_{ov})(\omega_2 - \omega_1 + u\bar{\omega}_s - \bar{\Delta}_{uo} + i\bar{\Gamma}_{uo})]^{-1} \equiv I_{uo}^{(1)} + I_{uo}^{(2)} + I_{uo}^{(3)}, \quad (44)$$

where

$$\mu_{uv} \equiv \mu_{ge} \langle u | v \rangle, \quad (45)$$

$\langle u | v \rangle$ being the Franck–Condon overlap factor of the Q_s mode, which is determined by its change in frequency ($\bar{\omega}_s - \bar{\omega}'_s$) and in equilibrium position Δ_s between the U_g and U_e electronic surfaces.³⁷

Typically we expect the proper dephasing rates $\hat{\Gamma}$ to be much faster than the IVR $\bar{\Gamma}_{ov}$, $\bar{\Gamma}_{uo} \ll \Gamma_{uv}$. The first term in Eq. (44) thus represents a progression of narrow lines ($\bar{\Gamma}$ width, no $\hat{\Gamma}$) which arise from a direct scattering from $|go\rangle$ via $|ev\rangle$ to $|fu\rangle$ without any vibrational redistribution. The second term represents a progression of broad band (Γ width) redistributed lines, whereas the third term represents an additional contribution to the narrow progression coming from the two pathways of Fig. 2 which do not pass through $|ee\rangle$. Using contour integration it is easy to show that

$$\int d\omega_2 I_{uo}^{(3)} = 0, \quad (46)$$

so that the main effect of $I_{uo}^{(3)}$ is to modify the line shapes of the narrow lines without affecting their integrated intensity. If we are interested only in the gross features

of the RLS spectra (the various components and their relative intensities) we may thus safely ignore $I_{uo}^{(3)}$ altogether. We should bear in mind, however, that a detailed study of the narrow line shapes will require the inclusion of $I_{uo}^{(3)}$. We should further note that in the solid state or collisional broadening in RLS,^{1–13} where similar narrow and broad components appear, $I_{uo}^{(3)}$ is very important in determining the relative integrated ratio of both components. The difference lies in the fact that in our case the bath is initially cold and $I_{uo}^{(3)}$ is not dephased at all (no $\hat{\Gamma}$ contributions to $I_{uo}^{(3)}$). We thus have

$$I_{uo} = 4 \left(\frac{|\mu_{uv}|^2 \bar{\Gamma}_{uv}}{(\omega_2 + u\bar{\omega}_s - v\bar{\omega}'_s - \omega_{ge} - \bar{\Delta}_{uv})^2 + \bar{\Gamma}_{uv}^2} \gamma_{vv}^{-1} + \sum_{v' \neq v} \frac{|\mu_{uv'}|^2 \Gamma_{uv'}}{(\omega_2 + u\bar{\omega}_s - v'\bar{\omega}'_s - \omega_{ge} - \Delta_{uv'})^2 + \Gamma_{uv'}^2} \gamma_{v'v}^{-1} \right) \times \frac{|\mu_{ov}|^2 \bar{\Gamma}_{ov}}{(\omega_1 - \omega_{ge} - v\bar{\omega}_s - \bar{\Delta}_{ov})^2 + \bar{\Gamma}_{ov}^2}. \quad (47)$$

Introducing the definition

$$\chi(\epsilon, \Gamma) \equiv \Gamma / [(\epsilon - \omega_{ge})^2 + \Gamma^2], \quad (48)$$

we get, for the fluorescence spectrum,

$$I(\omega_1, \omega_2) \equiv \sum_u I_{uo}(\omega_1, \omega_2) = 4 \left(\sum_{k=v}^{\infty} |\mu_{v+k,v}|^2 \chi[\omega_2 + (v+k)\bar{\omega}_s - v\bar{\omega}'_s - \Delta_{v+k,v}, \bar{\Gamma}_{v+k,v}] \gamma_{vv}^{-1} + \sum_{v'=0}^{v-1} \sum_{k=v'}^{\infty} |\mu_{v'+k,v'}|^2 \chi[\omega_2 + (v'+k)\bar{\omega}_s - v'\bar{\omega}'_s - \Delta_{v'+k,v'}, \Gamma_{v'+k,v'}] \gamma_{v'v}^{-1} \right) |\mu_{ov}|^2 \chi(\omega_1 - v\bar{\omega}_s - \Delta_{ov}, \bar{\Gamma}_{ov}). \quad (49)$$

Equation (49) is our general result for the homogeneously broadened RLS spectra of supercooled polyatomic molecules. However, there exists another static (inhomogeneous) line-broadening mechanism which was not incorporated in (49). This mechanism exists even if both U_g and U_e surfaces are harmonic and is due to the slight frequency changes in the bath modes $\bar{\omega}_\nu \neq \bar{\omega}'_\nu$ which turns any $u-v$ transition into a distribution of $u\alpha-v\alpha$ transitions with slightly different frequencies. Since this mechanism is connected with the distribution of the bath α states, it is ineffective when the bath is cold so that it does not affect the $o-v$ transition. In order to incorporate this effect into the line shape we have to define a function $\eta_{v'+k,v'}(\xi)$ which describes the static distribution of molecular frequencies for the $v' \rightarrow v' + k$ transition. η may be calculated from the Hamiltonian

(2) by counting states and taking into account Franck–Condon factors, using a microcanonical distribution of bath states of the type (38).²⁶ The RLS spectrum will then be given by (49) with the substitution

$$\chi[\omega_2 + (v'+k)\bar{\omega}_s - v'\bar{\omega}'_s - \Delta_{v'+k,v'}, \Gamma_{v'+k,v'}] - \int d\xi \chi(\xi, \Gamma_{v'+k,v'}) \eta_{v'+k,v'}(\xi). \quad (50)$$

For the sake of simplicity we may take

$$\eta_{v'+k,v'}(\xi) = \frac{1}{\pi} \frac{\hat{\Gamma}^{(\text{stat})}}{[\xi - \omega_2 - (v'+k)\bar{\omega}_s + v'\bar{\omega}'_s + \Delta_{v'+k,v'}]^2 + \hat{\Gamma}^{(\text{stat})^2}}. \quad (51)$$

Upon substitution of Eqs. (50) and (51) in Eq. (49) we

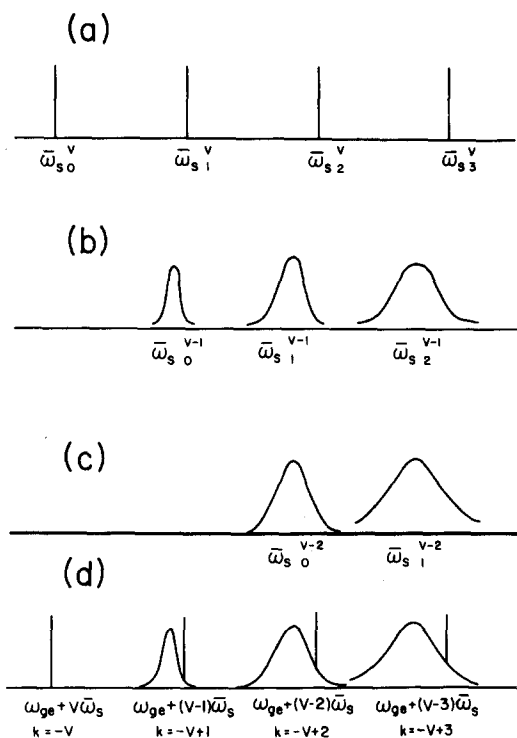


FIG. 3. Fluorescence spectra of a supercooled polyatomic molecule with one optically active mode. The top row (a) is a sequence of direct emission lines from the initially pumped state v . The bath is cold and the lines are narrow. The next row (b) represents the redistributed emission from $v-1$, etc. The observed spectrum (d) (bottom line) is the sum of all possible $v-v+k$ transitions.

note that Eq. (49) retains its form with the only modification

$$\Gamma_{v'+k, v'} = \tilde{\Gamma}_{v'+k, v'} + \hat{\Gamma}_{v'+k, v'}, \quad (52)$$

where $\tilde{\Gamma}$ was defined in Eq. (41) and

$$\hat{\Gamma}_{v'+k, v'} = \hat{\Gamma}_{v'+k, v'}^{(\text{dyn})} + \hat{\Gamma}_{v'+k, v'}^{(\text{stat})}. \quad (53)$$

A reasonable estimate for $\hat{\Gamma}_{uv}^{(\text{stat})}$ is

$$(\hat{\Gamma}_{uv}^{(\text{stat})})^2 \cong \sum_{\alpha} P(\alpha) [\bar{\omega}_{uv}(\alpha) - \bar{\omega}_{uv}^0]^2, \quad (54)$$

where $\bar{\omega}_{uv}^0$ is the mean uv transition frequency and $P(\alpha)$ is the microcanonical distribution of bath states at the appropriate energy E , i. e.,

$$P(\alpha) = \delta(E - H_0) / \text{Tr} \delta(E - H_0). \quad (55)$$

The following remarks should be made at this stage:

(i) $\hat{\Gamma}_{uv}^{(\text{stat})}$ (like $\hat{\Gamma}_{uv}^{(\text{dyn})}$) vanishes when the bath is cold. Thus the $o-v$ and $v-v+k$ transitions in Eq. (49) are not broadened and their widths are due to T_1 ($\tilde{\Gamma}$). (ii) Physically we expect $\hat{\Gamma}_{uv}^{(\text{stat})} \gg \hat{\Gamma}_{uv}^{(\text{dyn})}$. This makes the difference between the broad and narrow components in Eq. (44) even more pronounced and provides a further justification for the neglect of $I_{uo}^{(3)}$.

V. DISCUSSION

In the preceding sections we have developed a general reduced theory for RLS from collisionless supercooled

polyatomic molecules in the statistical limit. The molecular dynamical information affecting the RLS spectra [Eq. (49)] is contained in the T_1 (γ and $\bar{\gamma}$) relaxation matrices [Eqs. (36) and (37)] and in the T_2 dephasing rates Γ [Eqs. (42) and (52)–(54)]. Our general result [Eq. (49)] contains two terms. The first describes a progression of narrow emission lines $v-v+k$ resulting from photon absorption and subsequent emission prior to intramolecular energy redistribution, whereas the second term describes a progression of broad emission lines resulting from energy redistribution prior to photon emission. In Fig. 3 we give a schematic plot of the predicted RLS spectra. It should be noted that for the sake of clarity in the notation, we have included only one single mode $\bar{\omega}_s$ in the system. The inclusion of several modes is a trivial generalization which will not affect the form of Eq. (49) but merely increase the size of the γ and Γ matrices to include all possible progressions and combination bands of the system. Our final result (49) may be obtained from a simple kinetic scheme involving rate equations:

$$\begin{aligned} |go\rangle &\xrightarrow{K_{gv}} |ev\rangle, \\ |fu\rangle &\xleftarrow{\gamma_{uv}^R} |ev\rangle \xrightarrow{\gamma_{v'v}^R} |ev'\rangle \xrightarrow{\gamma_{uv'}^R} |fu\rangle. \end{aligned} \quad (56)$$

The corresponding kinetic equations are

$$\frac{dP_v}{dt} = K_{vg} P_g + \sum_{v' \neq v} \gamma_{vv'}^{IVR} P_{v'} - \gamma_{vv} P_v, \quad (57a)$$

$$\frac{dP_u}{dt} = \sum_{v'} \gamma_{uv'}^R P_{v'}, \quad (57b)$$

where

$$\gamma_{vv} = \gamma_v^{IVR} + \gamma_v^R \quad (57c)$$

and

$$\gamma_v^R = \sum_u \gamma_{uv}^R, \quad (57d)$$

where P_g , P_v , and P_u are the populations of the $|go\rangle$, $|ev\rangle$, and $|fu\rangle$ levels, respectively. Assuming steady state we set

$$P_g^{(ss)} = 1 \quad (58a)$$

and

$$\frac{dP_v^{(ss)}}{dt} = 0 \quad (58b)$$

in Eqs. (57). We then get

$$P_{v'}^{(ss)} = \gamma_{v'v}^{-1} K_{vg}, \quad (59)$$

and the emission rate to the $|fu\rangle$ state is

$$\begin{aligned} I_{uo} &= \sum_{v'} \gamma_{uv'}^R P_{v'}^{(ss)} \\ &= \gamma_{uv}^R \gamma_{vv}^{-1} K_{vg} + \sum_{v' \neq v} \gamma_{uv'}^R \gamma_{v'v}^{-1} K_{vg}. \end{aligned} \quad (60)$$

Equation (60) coincides with Eq. (47) if we take the radiative rates γ_{uv}^R , $\gamma_{uv'}^R$, and K_{vg} to be the Lorentzian functions appearing in (47) with widths $\tilde{\Gamma}_{uv}$, $\Gamma_{uv'}$, and $\tilde{\Gamma}_{ov}$, respectively, corresponding to the appropriate emission and absorption line shapes.

The rate equations (57) could be derived directly from the Hamiltonian [Eq. (2)] by using the projection operator (26) to derive reduced equations of motion (rather than evaluate the tetradic T matrix). This was done recently in other related contexts.²⁴ The rate equations (57) may be used to solve for the time evolution of the emission. Taking for example a very short excitation $\delta(t)$ [Eq. (14)] we have to solve Eqs. (57) with the initial condition

$$P_v(0) = 1 \quad (61a)$$

and the emission will be

$$I_{uv'}(t) = \gamma_{uv'}^R \cdot P_{v'}(t), \quad (61b)$$

with $P_{v'}(t)$ being the solution of Eqs. (57). Denoting the right and left eigenvalues of γ by $|\lambda_i\rangle$ and $\langle\lambda_i|$, respectively, with eigenvalue λ_i i. e.,

$$\gamma |\lambda_i\rangle = \lambda_i |\lambda_i\rangle \quad (62a)$$

and

$$\langle\lambda_i| \gamma = \lambda_i \langle\lambda_i|, \quad (62b)$$

we have^{38,39}

$$I_{uv'}(t) = \gamma_{uv'}^R \sum_i \langle v' | \lambda_i \rangle \langle \lambda_i | v \rangle \exp(-\lambda_i t). \quad (63)$$

This emission pattern could be very different than the corresponding intermediate case expression [Eqs. (13)–(15)].

We shall now analyze our results [Eqs. (49) and (63)] under several limits of physical interest.

A. Slow vibrational redistribution

When

$$\gamma_R \gg \gamma_{v'v}, \quad (64)$$

we have

$$\gamma_{v'v}^{-1} \cong (1/\gamma_V^R) \delta_{v'v} \quad (65)$$

In this limit the second term in large parentheses in Eq. (49) vanishes and we get only a progression of narrow emission lines corresponding to direct photon scattering (no redistribution before emission)

$$I(\omega_1, \omega_2) = \frac{4}{\gamma_V^R} \sum_{k=v}^{\infty} |\mu_{v+k,v}|^2 \chi(\omega_2 + k\bar{\omega}_s - \Delta_{v,v+k}, \bar{\Gamma}_{v+k,v}). \quad (66)$$

In a time-resolved experiment, if we adopt the rate equations (57) we then get

$$P_v(t) = \exp(-\gamma_V^R t), \quad (67a)$$

$$P_{v'}(t) \cong 0 \quad (67b)$$

and

$$I_{uv}(t) = \gamma_{uv}^R \exp(-\gamma_V^R t), \quad (68a)$$

$$I_{uv'}(t) \cong 0. \quad (68b)$$

B. Fast vibrational redistribution

We shall now consider the limit

$$\gamma_{v'v} \gg \gamma_V^R. \quad (69)$$

In order to evaluate the RLS spectrum we need to con-

sider the matrix γ^{-1} . In general we have^{38,39}

$$\gamma^{-1} = \sum_i \frac{|\lambda_i\rangle\langle\lambda_i|}{\lambda_i}, \quad (70)$$

where $|\lambda_i\rangle$ and $\langle\lambda_i|$ are the right and left eigenvectors of γ . A direct consequence from the detailed balance condition (39) is^{38,39} that γ^{IVR} has one eigenvalue $\lambda_0 = 0$ with the eigenvectors

$$|\lambda_0\rangle = \sum_v P_v^{(\text{MC})} |v\rangle, \quad (71a)$$

$$\langle\lambda_0| = \sum_v \langle v|, \quad (71b)$$

where $P_v^{(\text{MC})}$ is the equilibrium microcanonical population of the v level, i. e.,

$$P_v^{(\text{MC})} = \rho(\omega_1 - \omega_{ge} - v\bar{\omega}_s) / \sum_v \rho(\omega_1 - \omega_{ge} - v\bar{\omega}_s). \quad (72)$$

The other eigenvalues of γ^{IVR} will be $O(\gamma_{v'v})$, i. e.,

$$\lambda_i = O(\gamma_{v'v}), \quad i = 1, 2, \dots \quad (73)$$

When condition (69) holds, we may use first order perturbation theory to evaluate the eigenvalues of $\gamma = \gamma^{\text{IVR}} + \gamma_V^R$ by treating γ_V^R as a perturbation. As a result we get

$$\lambda_0 \cong \sum_v P_v^{(\text{MC})} \gamma_V^R, \quad (74a)$$

$$\lambda_i = O(\gamma_{v'v}) + O(\gamma_V^R) \cong O(\gamma_{v'v}), \quad i = 1, 2, \dots, \quad (74b)$$

whereas the eigenvectors remain unchanged (to lowest order in γ_V^R). Equations (74) together with (69) imply the existence of *separation of eigenvalues* in the problem, i. e.,

$$\lambda_0 \ll \lambda_i, \quad i = 1, 2, \dots, \quad (75)$$

so that λ_0^{-1} will have the dominant contribution to γ^{-1} , i. e.,

$$\gamma^{-1} = |\lambda_0\rangle\langle\lambda_0|/\lambda_0, \quad (76)$$

where $|\lambda_0\rangle$, $\langle\lambda_0|$, and λ_0 are given by Eqs. (71a), (71b), and (74a), respectively. Substitution of (75) in (49) results in

$$I(\omega_1, \omega_2) \propto 4 \left(\sum_{k=v}^{\infty} |\mu_{v+k,v}|^2 \chi[\omega_2 + (v+k)\bar{\omega}_s - v\bar{\omega}'_s - \Delta_{v+k,v}, \bar{\Gamma}_{v+k,v}] P_v^{(\text{MC})} + \sum_{v'=0}^{v-1} \sum_{k=v}^{\infty} |\mu_{v'+k,v'}|^2 \chi[\omega_2 + (v'+k)\bar{\omega}_s - v'\bar{\omega}'_s - \Delta_{v'+k,v'}, \bar{\Gamma}_{v'+k,v'}] P_{v'}^{(\text{MC})} \right). \quad (77)$$

Thus the emission spectrum is completely redistributed and reflects the microcanonical distribution of molecular states. {The integrated emission from the $|v'\rangle$ level is proportional to the microcanonical probability $P_{v'}^{(\text{MC})}$ [Eq. (72)].} Regarding the time-resolved experiments then what happened is that after a short time $t = 0(\lambda_0^{-1}) \ll \lambda_0^{-1}$ there is an equilibration in the excited states so that

$$P_{v'}(t) = \langle v' | \lambda_0 \rangle \exp(-\lambda_0 t) = P_{v'}^{(\text{MC})} \exp(-\lambda_0 t) \quad (78a)$$

and

$$I_{uv}(t) = \gamma_{uv} P_v^{(MC)} \exp(-\lambda_0 t) . \quad (78b)$$

Thus the emission rate from $|v\rangle$ is proportional to its microcanonical distribution $P_v^{(MC)}$.

C. Two intermediate states ($\nu = 1$)

If the initial excitation is to the $\nu = 1$ state of $|e\rangle$, i. e.,

$$\omega_1 \cong \omega_{gs} + \bar{\omega}_s , \quad (79)$$

then the γ matrix is 2×2 involving only the $\nu = 0, 1$ states

$$\gamma = \begin{pmatrix} \gamma_R & -\gamma^{IVR} \\ 0 & \gamma_R + \gamma^{IVR} \end{pmatrix} , \quad (80)$$

so that

$$\gamma_{11}^{-1} = 1/(\gamma^{IVR} + \gamma_R) \quad (81a)$$

and

$$\gamma_{01}^{-1} = \gamma^{IVR}/\gamma_R(\gamma^{IVR} + \gamma_R) , \quad (81b)$$

and we get one narrow and one broad progression, i. e.,

$$I(\omega_1, \omega_2) = \frac{4}{\gamma^{IVR} + \gamma_R} \left(\sum_{k=1}^{\infty} |\mu_{1+k,1}|^2 \chi(\omega_2 + (1+k)\bar{\omega}_s - \bar{\omega}'_s - \Delta_{1,1+k}, \tilde{\Gamma}_{1,1+k}) + \frac{\gamma^{IVR}}{\gamma_R} \sum_{k=0}^{\infty} |\mu_{k0}|^2 \chi(\omega_2 + k\bar{\omega}_s - \Delta_{k0}, \Gamma_{k0}) \right) \times |\mu_{01}|^2 \chi(\omega_1 + \bar{\omega}_s - \Delta_{0v}, \tilde{\Gamma}_{0v}) . \quad (82)$$

In the neighborhood of the origin $\omega_2 \cong \omega_{gs}$ ($k=0$) we have a narrow component $\bar{\omega}_{s1}^{-1}$ with area S_N and a broad component $\bar{\omega}_{s0}^{-1}$ with area S_B , where

$$\frac{S_N}{S_B} = \frac{|\mu_{11}|^2}{|\mu_{00}|^2} \frac{\gamma_R}{\gamma^{IVR}} \cong \frac{\gamma_R}{\gamma^{IVR}} , \quad (83)$$

where the last equality holds if the diagonal Franck-Condon factors are near unity. Knowledge of the radiative lifetime γ_R and the area ratio S_N/S_B gives us therefore a direct measurement of γ^{IVR} . In the time domain we have in this case

$$P_1^{(MC)} = 0 , \quad (84a)$$

$$P_0^{(MC)} = 1 , \quad (84b)$$

and

$$\lambda_0 = \gamma_R , \quad (84c)$$

so that

$$I_{u0}(t) = \gamma_{u0} \exp(-\gamma_R t) . \quad (84d)$$

In conclusion we note the following

(i) We have developed here a convenient framework for the description of RLS spectra from large statistical molecules where many molecular states are involved in the intramolecular line broadening. The final results [Eqs. (49) and (63)] may be interpreted in terms of the simple rate equations (57) provided the Markovian assumptions hold. If the number of relevant states is not large enough then the factorization assumption (32) will break down, the coherent term [second term in Eq. (35)] may have a significant contribution, and the broadening factors Γ may become frequency dependent.⁴⁰ In intermediate size molecules we may then adopt the effective

Hamiltonian formalism of Sec. III.

(ii) In the statistical limit, the intramolecular information may be put in the form of T_1 and T_2 (dephasing) relaxation matrices. In the intermediate case we are talking in terms of the mixing coefficients [β and γ in Eq. (6)]. It should be noted, as was already stressed²³ that the intrastate T_1 and the T_2 relaxations result from our *reduced description* and they do not show up in the effective Hamiltonian formalism.

(iii) *Frequency resolved RLS*: Our predicted spectra in statistical molecules consist of narrow and broad emission lines whose relative contribution depends on γ^{IVR}/γ_R . The spectra in the intermediate case [Eq. (8)] may be much more complicated, consisting of many lines with interference. It may happen, however, that in intermediate case molecules with low resolution the spectra will look like Eq. (49). [The narrow and broad components arising from the first and second terms in Eq. (8).] The broad component is due to mixing of the true molecular states and not due to irreversible relaxation.

The exact nature of the molecule (whether intermediate or statistical) may be revealed by improving the experimental spectral resolution. The absence of structure may indicate that the molecule is statistical.

(iv) *Time-resolved RLS*: The time resolved spectra consist of sums of exponentials [Eq. (63)] in statistical molecules and of complicated interference patterns [Eq. (13)] in intermediate size molecules.¹⁵ If we observe in the frequency resolved spectra broad and narrow components as shown in Fig. 3, then in statistical molecules this means that γ^R and γ^{IVR} are comparable [see Eq. (83)]. The time-resolved patterns of the broad and narrow lines are then expected to be different [Eq. (57)]. The narrow emission will occur immediately following the excitation whereas the broad one will be delayed (relaxation before emission). In intermediate size molecules with a single doorway state, the time evolution of both components is expected to be the same [Eq. (15)].

Note added in proof. The recent experimental data on the series of alkyl substituted benzene molecules¹⁸ contain broad and narrow components (Fig. 3) when excitation was made in the 6^1_{g0} and 12^1_{g0} lines. The time evolution of both components was recently resolved in the nanosecond region [J. B. Hopkins, D. E. Powers, and R. E. Smalley, *J. Chem. Phys.* (to be published)], and was found to be similar. This is compatible with the intermediate case expressions [Eqs. (8) and (15)] and not with the simple rate equations.⁵⁷

We expect that for larger molecules and with higher energies the molecular behavior will correspond to the statistical case.

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