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 preciscely 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 systems\(^{5}\) 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 \(\Gamma / \Gamma_1\), where \(\Gamma\) is the proper dephasing rate of the transition and \(\Gamma_1\) 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 rates\(^{14,15}\) 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 beam\(^{16-20}\) 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 spectra\(^ {15}\)). 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 limitation of the number of states involved is not too large.

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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. 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 (quasicontinuous). 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. 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 tetratic 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 infrared and vibrational overtone spectra. 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 ($\gamma_{IVR}$), which play a major role in the theories of unimolecular reactions and their magnitude is currently the subject of a lively debate. It should be noted that recent studies of vibrational overtone spectroscopy and photoisomerization and laser-induced fluorescence studies of optically pumped molecules are yielding also valuable information related directly to $\gamma_{IVR}$.

In Sec. II we present the basic molecular model and construct the Hamiltonian for RLS. In Sec. III we review the conventional description of RLS in intermediate size molecules where we use the effective Hamiltonian formalism. In Sec. IV we make use of the tetratic scattering formalism and the Mori projection operator technique to develop a TRD for RLS. The competition between IVR and the radiative relaxation is reflected in the $\gamma$ 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.

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. 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 ($\omega_\mu$) 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 $\omega_2$ being scattered from the molecular beam and the scattered photons with frequency $\omega_2$ 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 $|\omega_1\rangle$, a single photon in the final emission channel $|\omega_2\rangle$, or no photons at all (the vacuum state). $v$ denotes the vibrational state of $\omega_\mu$, whereas $a$ 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" (electron, the radiation field, and $\omega_\mu$) and the "bath" ($\gamma_{IVR}$).

Within the rotating wave approximation (RWA) which holds extremely well for optical frequencies, we need consider only the following types of states: $|g, \omega_1, 0, 0, 1, e, \text{vac}, \nu, \alpha\rangle$, 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

$$|	ext{g00}\rangle = |g, \omega_1, 0, 0\rangle,$$

$$|\text{e\alpha}\rangle = |e, \text{vac}, \nu, \alpha\rangle,$$

(1)
and

$$|f_{ua}\rangle = |g, \omega_2, u, a\rangle .$$

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

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

$$H = H_0 + U + V = H_1 + V ,$$

where

$$H_2 = |g\rangle \langle g| \omega_1 a a^\dagger a + \sum_{i=1}^{n} \omega_i b_i b_i^\dagger b_i + \sum_{i=1}^{n} \omega_i b_i b_i^\dagger b_i + i\gamma R \rangle$$

$$\times \langle e| + |f\rangle \langle e| + \sum_{i=1}^{n} \omega_i b_i b_i^\dagger b_i + i\gamma R \rangle,$$

$$= |g\rangle H_2(g) + |e\rangle H_2(e) + |f\rangle H_2(f) ,$$

$$U = |g\rangle U_{gke} |e\rangle U_{eke} + |f\rangle U_{fke} ,$$

$$U_{gke} = U_{eke} = F_1(Q_e)(a + a^\dagger),$$

$$V = \mu (|g\rangle \langle e| + |e\rangle \langle g|) + \mu, f\langle f| + |f\rangle \langle f|) ,$$

and

$$\langle g| H_2(g) = \omega_1 \langle g| ,$$

$$\langle e| H_2(e) = \omega_2 \langle e| ,$$

$$\langle f| H_2(f) = (\omega_1 - \omega_2) \langle f| .$$

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 $\omega_1$ and $\omega_2$ are such that the available molecular vibrational energy ($\omega_1 - \omega_2$) in the intermediate state $|e\rangle$ and $|f\rangle$ 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 documented 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 $H_2$). 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 are

$$H_1^{\text{ef}}|g\rangle = \omega_1 |g\rangle ,$$

$$H_1^{\text{ef}}|f\rangle = (E_f - \frac{i}{2} \gamma_f) |f\rangle ,$$

$$\langle g| H_2^{\text{ef}}|f\rangle = \langle g| (E_f - \frac{i}{2} \gamma_f) .$$

For $H_1^{\text{ef}}$ we have considered only one vibrational state (the ground state). Since $H_1^{\text{ef}}$ is complex we need consider its right- and left-hand eigenstates ($|J\rangle$ and $|\bar{J}\rangle$, respectively). Finally, the $|K\rangle$ states are the eigenstates of $H_2^{\text{ef}}$. Since $H_1^{\text{ef}}$ also includes the $\omega_1$ photon, we may write $E_F$ as $\omega_1 + \omega_2$. The states $|J\rangle$, $|\bar{J}\rangle$, and $|K\rangle$ are linear combinations of the harmonic states which are eigenstates of $H_2$ (Eq. (2a)). The resolution of the unity, using our new basis set is

$$I = |g\rangle \langle g| + \sum_{J} |J\rangle \langle J| + \sum_{K} |K\rangle \langle K| .$$

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)

$$I_{gk}(\omega_1, \omega_2) = \sum_{J} |\langle K| \langle J| \langle J| \rangle g| \rangle| \delta(\omega_1 - \omega_2 + \epsilon_{gk} .$$

The total RLS cross section is

$$I(\omega_1, \omega_2) = \sum_{K} I_{gk}(\omega_1, \omega_2) .$$

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 \( \omega_1 \) is near resonance with a single doorway state \( |e \beta \rangle \). We then have
\[
|J \rangle \rightarrow |e \beta \rangle = |e \alpha \rangle + \sum_{\alpha' \neq \beta} \gamma_{\alpha \alpha'} |e \alpha' \rangle .
\]
(6a)

Similarly, the \( |K \rangle \) states are
\[
|K \rangle \rightarrow |f \alpha \rangle = |f \alpha \rangle + \sum_{\alpha' \neq \alpha} \gamma_{\alpha \alpha'} |f \alpha' \rangle .
\]
(6b)

Upon substitution of Eq. (6) in (5) we get
\[
I(\omega_1, \omega_2) = \frac{1}{(\omega_1^2 + 2i\gamma_0)} \left( \sum_{\alpha, \beta} |\langle \langle \beta | \alpha \rangle |^2 \delta(\epsilon_{\alpha \beta} + \omega_1 + \omega_2) \right)
\times \int_0^t dt_1 \int_0^t dt_2 \phi(\tau_1) \phi(\tau_2) \exp(-iE_J - \frac{1}{2} \gamma_J) \exp[-iE_J - \frac{1}{2} \gamma_J] (t - \tau_1) \exp[(-iE_J - \frac{1}{2} \gamma_J) (t - \tau_2)] .
\]
(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 \( \ll \gamma_J \), we may put \( \phi(t) = \delta(t) \)
\[
(14)
\]
in Eq. (13) resulting in
\[
I(\omega_1, \omega_2) \propto \exp(-\gamma_J t) .
\]
(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. TETRATIC REDUCED DESCRIPTION OF RLS IN LARGE STATISTICAL MOLECULES

We shall now utilize the tetradic scattering formalism \(^{22,29}\) 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 \( T \) is defined as \(^{21,29}\)
\[
\tau(\epsilon) = \mathcal{V} + \mathcal{V} \mathcal{G}_d(\epsilon) \mathcal{V} ,
\]
(16)
where \( \mathcal{V} \) is the tetradic operator corresponding to \( V \), i.e.,
\[
\mathcal{V} = [V, ],
\]
(17)
and \( \mathcal{G}_d(\epsilon) \) is the complete tetradic Green's operator for the entire system and bath
\[
\mathcal{G}_d(\epsilon) = (\epsilon - \mathcal{L})^{-1} ,
\]
(18)
\( \mathcal{L}(L_0, L_1) \) being the Liouville operators corresponding to \( H(\{H_0, H_1\} \), i.e.,
\[
L = [H, ],
\]
(19)
The cross section for the photon scattering process (Fig. 1) is given by \(^{11,28}\)
\[
\sigma_{\alpha \beta}(\omega_1, \omega_2) = \frac{1}{\phi_r} I_{\alpha \beta}(\omega_1, \omega_2) ,
\]
(20)
where \( \phi_r \) is the incident photon flux and
\[
I_{\alpha \beta}(\omega_1, \omega_2) = \langle \langle \tau(0) \mathcal{V} \mathcal{G}_d(\epsilon) \mathcal{V} \rangle \rangle (\omega_1, \omega_2) .
\]
(21)
Here \( \langle \langle \cdots \rangle \rangle \) 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 \( \langle \langle i | j \rangle \rangle \) is denoted \( \langle \langle i | j \rangle \rangle \). \( p(\alpha) \) 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

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omit the averaging over initial states, resulting in
\[
I_{\omega}(\omega_1, \omega_2) = -i \sum_\beta \langle \psi_\beta, \psi_\beta | T(0) | \psi_\omega, \psi_\omega \rangle .
\]  
(22)

As we are interested in ordinary RLS using a weak excitation source we need consider only the contributions to \( T \) to lowest order in \( \psi \). Using Eq. (24) and Fig. 2, we note that we need to expand \( T \) to fourth order in \( \psi \), i.e.,
\[
T(\epsilon) \equiv \psi S(\epsilon) \psi S(\epsilon) \psi S(\epsilon) \psi ,
\]  
(23)

where
\[
S(\epsilon) = (\epsilon - L)^{-1} .
\]  
(24)

The evaluation of the necessary matrix elements of \( T \) [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\(^{3,4,5,31}\) 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\(^{5,4,3,31}\) 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 Zwanzig\(^{29}\) projection operator which projects onto the equilibrium state of the bath and makes the evaluation of Eq. (22) feasible.\(^{5,16}\) Similar ideas apply also for the treatment of collisional perturbations on RLS where the bath is provided by the translational degrees of freedom.\(^{3,11}\)

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 \( \mathbf{K} \) 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 Mori\(^{29}\) projection operator technique which was recently applied to molecular multiphoton processes in general\(^{11}\) (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\(^{24,25}\). 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:
\[
A_{\omega} = | \psi_\omega \rangle \langle \psi_\omega | ,
\]  
(25a)

\[
A_{\omega}^{(\text{op})} = \sum_\alpha | \psi_\alpha \rangle \langle \psi_\alpha | \delta(\omega_1 - \omega_2 - \omega_3 - E_\omega) ,
\]  
(25b)

and
\[
A_{\text{op}}^{(\text{ef})} = \sum_\alpha | \psi_\alpha \rangle \langle \psi_\alpha | \delta(\omega_1 - \omega_2 - \omega_3 - E_\omega) .
\]  
(25c)

The expectation values of these operators correspond to the total population of the \( | \psi_\omega \rangle \), \( | \psi_\omega^{\text{ef}} \rangle \), and \( | \psi_\alpha \rangle \) states. In addition to these operators we further introduce operators corresponding to optical coherences:
\[
A_{\text{ef}}^{\text{op}} = \langle \psi_\omega | \psi_\omega^{\text{ef}} \rangle ,
\]  
(25d)

\[
A_{\text{ef}}^{\text{op}} = \sum_\alpha \langle \psi_\alpha | \psi_\alpha^{\text{ef}} \rangle \delta(\omega_1 - \omega_2 - \omega_3 - E_\omega) ,
\]  
(25e)

\[
A_{\text{ef}}^{\text{op}} = | \psi_\omega \rangle \langle \psi_\omega | .
\]  
(25f)

We now define a Mori projection operator\(^{29}\) \( P \) onto the subspace spanned by our set of operators
\[
P = \sum_\nu A_\nu S^{-1}(A_\nu, B) ,
\]  
(26)

where \( S \) is the overlap matrix of our set of operators
\[
S_{\nu \nu} = \langle A_\nu | A_\nu \rangle
\]  
(27)

and \( B \) is any operator. \( \langle A_\nu, A_\nu \rangle \) is the scalar product in Liouville space of the two operators and is defined as
\[
\langle A_\nu, A_\nu \rangle = \text{Tr}(A_\nu^{\dagger} A_\nu) .
\]  
(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 \( \rho \) at time \( t \). The result is
\[
P \rho(t) = \sum_\nu \sigma_\nu(t) A_\nu ,
\]  
(29)

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

\[\text{FIG. 2. Liouville–space coupling scheme for RLS. There are six pathways which lead from } | \psi_\omega \rangle \text{ to } | \psi_\omega^{\text{ef}} \rangle \text{ in fourth order, four of which pass via } | \psi_\alpha \rangle \text{ and the other two are purely coherent components which pass via } | \psi_\omega^{(\text{op})} \rangle \text{ or } | \psi_\omega^{(\text{op})} \rangle .\]
\[ I_{ao} = iTr[A_{ao}^{(3)}T(0)A_{ao}^{(1)}] = iTr[A_{ao}^{(3)}P^T(0)PA_{ao}^{(1)}], \]  

(30)

in terms of the projection \( P^T P \). 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\(^{33,34}\)

\[ P^T(0)P = PUP, \]

(31a)

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

\[ \langle T(0) \rangle = \langle \psi \rangle \langle S(0) \rangle \langle \psi \rangle \langle S(0) \rangle \langle \psi \rangle \langle S(0) \rangle \langle \psi \rangle, \]

(31b)

where

\[ \langle \psi \rangle = PUP, \]

(33a)

and

\[ \langle S(0) \rangle = PUP, \]

(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 \( A_{ee}(1g g) \) to \( A_{ef}(1 f f) \) in fourth order. Making use of the Liouville conjugation symmetry\(^{28}\)

\[ S_{ee,ee}(\epsilon) = -S_{ee,ee}(\epsilon^*), \]

(34)

we get

\[ \langle T(0) \rangle_{ff,ee} = 4 \langle m_{ff,ee} \rangle \langle n_{ee,ee} \rangle \langle S_{ee,ee} \rangle \langle S_{ee,ee} \rangle \langle S_{ee,ee} \rangle \langle S_{ee,ee} \rangle \]

\[ \times \langle \psi \rangle \langle S_{ee,ee} \rangle \langle S_{ee,ee} \rangle \langle S_{ee,ee} \rangle \langle S_{ee,ee} \rangle \langle S_{ee,ee} \rangle \langle S_{ee,ee} \rangle \langle S_{ee,ee} \rangle \langle S_{ee,ee} \rangle \langle S_{ee,ee} \rangle \]

\[ \times \langle \psi \rangle \langle S_{ee,ee} \rangle \langle S_{ee,ee} \rangle \langle S_{ee,ee} \rangle \langle S_{ee,ee} \rangle \langle S_{ee,ee} \rangle \]

(35)

The first term in Eq. (35) arises from the four pathways (Fig. 2) which pass through \( A_{ee}(1e e) \), whereas the second term arises from the other two pathways which pass via \( A_{ef}(1f f) \).

\[ \langle S_{ee,ee} \rangle \]

is the \( T_2 \) relaxation matrix in the excited electronic state. It has a contribution from the anharmonicities (IVR processes \( \gamma^{IVR} \)) as well as from other interstate relaxation (e.g., radiative lifetimes \( \gamma^R \)). For the Hamiltonian (2), we have

\[ \langle S_{ee,ee} \rangle_{vv,uu} = -i(\gamma^{IVR} + \gamma^R)_{vv,uu} = \gamma^R_{vv,uu}, \]

(36a)

where

\[ Y^R_{vv,uu} = \begin{cases} -Y_{vv,uu}, & v' = v, \\ 0, & u = u', \\ \sum_{u' = u, v' = v} Y_{vv,uu}, & u' = u. \end{cases} \]

(36b)

and

\[ \gamma^R_{vv,uu} = \gamma^R_{uu,uu}. \]

(36c)

Similarly, we can define an analogous relaxation matrix for the ground electronic state \( \langle S_{ee,ee} \rangle \), where we take \( \gamma^R = 0 \), i.e.,

\[ \langle S_{ee,ee} \rangle_{vv,uu} = -iY_{vv,uu}, \]

(37a)

\[ \bar{Y}_{vv,uu} = \begin{cases} -\bar{Y}_{vv,uu}, & u = u', \\ 0, & u = u', \\ \sum_{u' = u, v' = v} \bar{Y}_{vv,uu} = \bar{Y}_{vv,uu}, & u = u', \end{cases} \]

(37b)

\[ \bar{Y}_{vv,uu} = \bar{Y}_{uu,uu}. \]

(37c)

The IVR rates (to lowest order in \( U_e \) and \( U_e^2 \)) are given by

\[ \gamma^{IVR}_{vv,uu} = 2\pi \sum_{\alpha} P_{\alpha}(\alpha) \langle |v\alpha| U_e |u\beta\rangle \delta(E_{\alpha\alpha} - E_{\nu\beta}), \]

(37d)

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

\[ P_1(\alpha) \propto \delta(E - H_0), \]

(38a)

which depends on the total initial energy of the bath \( E_1 \) for the \( v - v' \) (\( u - u' \)) relaxation processes, i.e.,

\[ E_v = \omega_v - \omega_v - i\omega_v, \]

(38b)

and

\[ E_u = \omega_u - \omega_u - i\omega_u. \]

(38c)

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

\[ \gamma^{IVR}_{vv,uu} = \frac{\gamma^{IVR}_{vv,uu}}{\gamma^{IVR}_{uu,uu}} \]

(39a)

and

\[ \gamma^{IVR}_{uu,uu} = \frac{\gamma^{IVR}_{vv,uu}}{\gamma^{IVR}_{uu,uu}}. \]

(39b)

\[ \gamma^{IVR}_{uu,uu} = \frac{\gamma^{IVR}_{uu,uu}}{\gamma^{IVR}_{uu,uu}} \]

where \( \rho(\epsilon) \) is the density of states in the bath with energy \( \epsilon \). Substitution of the expansion (2c) in Eqs. (36e) and (37d) shows that the main contribution to \( \gamma^{IVR}_{uu,uu} \) comes from the odd powers in the expansion \( F_1, F_3, \) etc., \( F_1, F_3, \ldots \), etc.

The \( \langle S_{ee,ee} \rangle, \langle S_{ef,ef} \rangle, \) and \( \langle S_{ef,ee} \rangle \) matrices correspond to intramolecular dephasing (\( T_1 \) processes) and are taken to be diagonal\(^{13}\) so that their only nonvanishing matrix elements are

\[ \langle S_{ee,ee} \rangle_{vv,uu} = (\omega_v + i\omega_v - \omega_v - \Delta_{uu} + i\Gamma_{uu}), \]

(40a)

\[ \langle S_{ef,ef} \rangle_{vv,uu} = (\omega_v - \omega_u - i\omega_v - \Delta_{uu} + i\Gamma_{uu}), \]

(40b)

\[ \langle S_{ef,ee} \rangle_{vv,uu} = (\omega_v - \omega_u - \omega_v - \Delta_{uu} + i\Gamma_{uu}), \]

(40c)

where

\[ \Gamma_{uu} = \frac{1}{2} \left( \gamma_v + \gamma_u + \gamma^{(dr)}_{uu} \right) = \frac{1}{2} \left( \gamma_v + \gamma_u + \frac{1}{2} \gamma^{(dr)}_{uu} \right). \]

(41)

Here \( \gamma \) is the contribution of \( T_2 \) to \( T_2 \) and \( \gamma^{(dr)}_{uu} \) stands for a proper dephasing rate which is dynamical in nature\(^{27-29,31,32}\) even if the two potential surfaces \( U_e \) and \( U_e^2 \) are identical and it has to do with the anharmonics. Using the well-known expressions from the theory of line broadening we have (to lowest order in \( U_e - U_e^2 \))\(^{27,28,35,38}\),

\[ \gamma^{(dr)}_{uu} = \pi \sum_{\nu} \left| \langle u\beta | U_e | u\alpha \rangle - \langle u\beta | U_e | v\alpha \rangle \right|^2 \times P(\alpha) \delta(E_e - E_u), \]

(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 \( \gamma^{(dr)}_{uu} \) comes from the even powers of \( U_e \) and \( U_e^2 \) (i.e., \( F_2, F_4, \ldots, F_2, F_4, \ldots \), etc.). It is also clear from Eq. (42) that \( \gamma^{(dr)}_{uu} \) vanishes when the bath is cold. Furthermore, \( \gamma_e = 0 \) so that the \( vv \) and \( uu \) dephasing rates arise only from the lifetime of the excited state

\[ \gamma_{ee} = \frac{1}{2} \gamma_v, \]

(43a)

\[ \Gamma_{ee} = \frac{1}{2} \gamma_v. \]

(43b)

\[ \Gamma_{uu} = \frac{1}{2} \gamma_u. \]

(43b)
The $\Delta_{uv}$, $\tilde{\Delta}_{uv}$, and $\tilde{\Delta}_0$ terms are level shifts associated with the same relaxation mechanisms contributing to $\Gamma_{uv}$, $\tilde{\Gamma}_{uv}$, and $\tilde{\Gamma}_{uv}$, respectively. Substitution of Eqs. (38)–(43) into (35) and rearranging terms results in

$$
I_{uv} = 4 \frac{|\mu_{uv}|^2 \tilde{\Gamma}_{uv}}{\omega_1 + \nu \tilde{\omega}_s - \omega_{ee} - \Delta_{uv}^2 + \tilde{\Gamma}_{uv}^2 \gamma_s^2} \omega_1 - \omega_{ee} - \Delta_{uv}^2 + \tilde{\Gamma}_{uv}^2 \gamma_s^2 + 4 \sum_{\nu' \neq \nu} |\mu_{uv'}|^2 \tilde{\Gamma}_{uv'} \omega_1 - \omega_{ee} - \Delta_{uv}^2 + \tilde{\Gamma}_{uv'}^2 \gamma_s^2 + 2 |\mu_{uv}|^2 |\mu_{uv'}|^2 \gamma_s^2 
\times \text{Im}[(\omega_1 + \nu \tilde{\omega}_s - \omega_{ee} - \Delta_{uv} + i\tilde{\Gamma}_{uv})/(\omega_2 - \omega_{ee} - \Delta_{uv} + i\tilde{\Gamma}_{uv})]^{1/2} \approx I_{uv}^{(1)} + I_{uv}^{(2)} + I_{uv}^{(3)},
$$

(44)

where

$$
|\mu_{uv}| \approx |\mu_{uv}(\nu)| ,
$$

(45)

($\nu$) being the Franck-Condon overlap factor of the $Q_\nu$ mode, which is determined by its frequency in frequency ($\Delta_\nu$) and in equilibrium position $\Delta_{uv}$ between the $U_\nu$ and $U_\nu'$ electronic surfaces.37

Typically, we expect the proper dephasing rates $\tilde{\Gamma}$ to be much faster than the IVR $\tilde{\Gamma}_{uv}$, $\tilde{\Gamma}_{uv} \ll \tilde{\Gamma}_{uv}$. The first term in Eq. (44) thus represents a progression of narrow lines ($\tilde{\Gamma}$ width, no $\tilde{\Gamma}$) which arise from a direct scattering from $|\phi_0\rangle$ via $|\nu\nu'e\rangle$ to $|\phi_{nu}\rangle$ without any vibrational redistribution. The second term represents a progression of broad band ($\tilde{\Gamma}$ width) redistributed lines, whereas the third term represents an additional contribution to the narrow progression along from the two pathways of Fig. 2 which do not pass through $|\nu\nu'e\rangle$.

Using contour integration, it is easy to show that

$$
\int d\omega_2 I_{uv}^{(3)} = 0 ,
$$

(46)

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

$$
I(\omega_1, \omega_2) = \sum_{\nu} I_{\nu\nu}(\omega_1, \omega_2) = 4 \left( \sum_{\nu} |\mu_{uv\nu}|^2 \chi(\omega_2 + \nu + k) \tilde{\omega}_{\nu'} - \nu \tilde{\omega}_s - \Delta_{uv\nu|\nu'} \tilde{\Gamma}_{uv\nu|\nu'} \gamma_s^2 \right) + \sum_{\nu' \neq \nu} \left( \sum_{\nu} |\mu_{uv\nu'}|^2 \chi(\omega_2 + \nu' + k) \tilde{\omega}_{\nu'} - \nu' \tilde{\omega}_s - \Delta_{uv\nu'|\nu'} \tilde{\Gamma}_{uv\nu'|\nu'} \gamma_s^2 \right) |\mu_{uv}|^2 \chi(\omega_1 - \nu \tilde{\omega}_s - \Delta_{uv} \tilde{\Gamma}_{uv})
$$

(49)

Equation (49) is our general result for the homogeneous broadening 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 $U_\nu$ and $U_\nu'$ surfaces are harmonic and is due to the slight frequency changes in the bath modes $\tilde{\omega}_{\nu'}$ which turns any $u-v$ transition into a distribution of $u-a-v$ transitions with slightly different frequencies. Since this mechanism is connected with the distribution of the bath $a$ 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 $\eta_{\nu\nu'|\nu'}(\xi)$ which describes the static distribution of molecular frequencies for the $\nu'-v' + k$ transition. $\eta$ 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).36 The RLS spectrum will then be given by (49) with the substitution

$$
\chi(\omega_2 + \nu + k) \tilde{\omega}_{\nu'} - \nu \tilde{\omega}_s - \Delta_{uv\nu|\nu'} \tilde{\Gamma}_{uv\nu|\nu'} \gamma_s^2 + \int d\xi \chi(\xi, \Gamma_{uv\nu|\nu'}) \eta_{\nu\nu'|\nu'}(\xi).
$$

(50)

For the sake of simplicity we may take

$$
\eta_{\nu\nu'|\nu'}(\xi) = \frac{1}{\pi} \Gamma^{(\text{stat})} \tilde{\Gamma}^{(\text{stat})} \xi^2 + \tilde{\Gamma}^{(\text{stat})} \xi^2 .
$$

(51)

Upon substitution of Eqs. (50) and (51) in Eq. (49) we
polyatomic molecules in the statistical limit. The molecular dynamical information affecting the RLS spectra [Eq. (49)] is contained in the $T_1$ ($\gamma$ and $\tilde{\gamma}$) relaxation matrices [Eqs. (36) and (37)] and in the $T_2$ dephasing rates $\Gamma$ [Eqs. (42) and (52)–(54)]. Our general result [Eq. (49)] contains two terms. The first describes a progression of narrow emission lines $v \sim v + k$ 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 $\bar{\omega}$ 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 $\gamma$ and $\Gamma$ 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:

$$
|go\rangle \frac{K_{fv}}{\gamma_{sv}} |ev\rangle,
$$

$$
|fu\rangle \frac{\gamma_{sv}^{R}}{\gamma_{sv}} |ev\rangle \frac{\gamma_{sv}^{R}}{\gamma_{sv}} |fu\rangle.
$$

The corresponding kinetic equations are

$$
\frac{dP}{dt} = K_{sf} P_{s} + \sum_{v} \gamma_{sv}^{R} P_{v} - \gamma_{sv} P_{s},
$$

and

$$
\frac{dP}{dt} = \sum_{v} \gamma_{sv}^{R} P_{v},
$$

where

$$
\gamma_{sv} = \gamma_{sv}^{IR} + \gamma_{sv}^{R}
$$

and

$$
\gamma_{sv}^{R} = \sum_{l} \gamma_{sv}^{l},
$$

where $P_{s}$, $P_{v}$, and $P_{s}$ are the populations of the $|go\rangle$, $|ev\rangle$, and $|fu\rangle$ levels, respectively. Assuming steady state we set

$$
P_{s}^{(ss)} = 1
$$

and

$$
\frac{dP_{s}^{(ss)}}{dt} = 0,
$$

in Eqs. (57). We then get

$$
P_{s}^{(ss)} = \gamma_{s}^{-1}, K_{sf},
$$

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

$$
I_{uv} = \sum_{v} \gamma_{uv}^{R} P_{v}^{(ss)}.
$$

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

V. DISCUSSION

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

$$P_v(0) = 1$$

and the emission will be

$$I_{\nu \nu}(t) = \gamma^R_{\nu \nu} \cdot P_{\nu}(t),$$

with $P_{\nu}(t)$ being the solution of Eqs. (57). Denoting the right and left eigenvectors of $\gamma$ by $|\lambda_i\rangle$ and $\langle \lambda_i |$, respectively, with eigenvalue $\lambda_i$ i.e.,

$$\gamma |\lambda_i\rangle = \lambda_i |\lambda_i\rangle,$$

and

$$\langle \lambda_i | \gamma = \lambda_i \langle \lambda_i |,$$

we have\(^{28,30}\)

$$I_{\nu \nu}(t) = \gamma^R_{\nu \nu} \sum_i \langle \nu' | \lambda_i \rangle \langle \lambda_i | \nu \rangle \exp(- \lambda_i t).$$

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

$$\gamma_R \gg \gamma_{\nu' \nu},$$

we have

$$\gamma^{-1}_{\nu' \nu} \approx (1/\gamma^R_{\nu' \nu}) \delta_{\nu' \nu}.$$  

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)

$$I(\omega_1, \omega_2) = \frac{4}{\gamma^R_{\nu' \nu}} \sum_{\nu' = v} |\mu_{\nu' \nu}|^2 |\chi(\omega_2 + k\overline{\omega}_s - \Delta_{\nu' \nu}, \overline{\Gamma}_{\nu' \nu},)\rangle.$$

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

$$P_{\nu}(t) = \exp(- \gamma^R_{\nu \nu} t),$$

$$P_{\nu'}(t) \approx 0$$

and

$$I_{\nu \nu}(t) = \gamma^R_{\nu \nu} \exp(- \gamma^R_{\nu \nu} t),$$

$$I_{\nu \nu}(t) \approx 0.$$

**B. Fast vibrational redistribution**

We shall now consider the limit

$$\gamma_{\nu' \nu} \gg \gamma^R_{\nu' \nu}.$$

In order to evaluate the RLS spectrum we need to consider the matrix $\gamma^{-1}$. In general we have\(^{28,30}\)

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

where $|\lambda_i\rangle$ and $\langle \lambda_i |$ are the right and left eigenvectors of $\gamma$. A direct consequence from the detailed balance condition (39) is\(^{28,30}\) that $\gamma_{\nu' \nu}$ has one eigenvalue $\lambda_0 = 0$ with the eigenvectors

$$|\lambda_0\rangle = \sum v P^{(MC)}_v |v\rangle,$$

$$\langle \lambda_0 | = \frac{1}{\sum v |v\rangle \langle v |}$$

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

$$P^{(MC)}_v = \rho(\omega_1 - \omega_{ee} - v\overline{\omega}_s) / \sum \rho(\omega_1 - \omega_{ee} - v\overline{\omega}_s).$$

The other eigenvalues of $\gamma_{\nu' \nu}$ will be $O(\gamma_{\nu' \nu})$, i.e.,

$$\lambda_i = O(\gamma_{\nu' \nu}), \quad i = 1, 2, \ldots$$

When condition (69) holds, we may use first order perturbation theory to evaluate the eigenvalues of $\gamma = \gamma_{\nu' \nu} + \gamma^R_{\nu' \nu}$ by treating $\gamma^R_{\nu' \nu}$ as a perturbation. As a result we get

$$\lambda_j \approx \sum v P^{(MC)}_v \gamma^R_{\nu \nu},$$

$$\lambda_i = O(\gamma_{\nu' \nu}) + O(\gamma^R_{\nu' \nu}) \approx O(\gamma_{\nu' \nu}), \quad i = 1, 2, \ldots,$$

whereas the eigenvectors remain unchanged (to lowest order in $\gamma^R_{\nu' \nu}$). Equations (74) together with (69) imply the existence of *separation of eigenvalues* in the problem, i.e.,

$$\lambda_j \ll \lambda_i, \quad i = 1, 2, \ldots,$$

so that $\gamma^{-1}_j$ will have the dominant contribution to $\gamma^{-1}$, i.e.,

$$\gamma^{-1} \approx |\lambda_0\rangle \langle \lambda_0 | / \lambda_0,$$

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

$$I(\omega_1, \omega_2) = 4 \left( \sum_{\nu' = v} |\mu_{\nu' \nu}|^2 \chi(\omega_2 + (v + k)\overline{\omega}_s - \Delta_{\nu' \nu}, \overline{\Gamma}_{\nu' \nu},) \right. \left. + v\overline{\omega}_s - \Delta_{\nu' \nu}, \overline{\Gamma}_{\nu' \nu}, \right) P^{(MC)}_{\nu' \nu}$$

$$+ (v + k)\overline{\omega}_s - v\overline{\omega}_s - \Delta_{\nu' \nu}, \overline{\Gamma}_{\nu' \nu}, \right) P^{(MC)}_{\nu' \nu}. $$

Thus the emission spectrum is completely redistributed and reflects the microcanonical distribution of molecular states. {The integrated emission from the $\nu \nu'$ level is proportional to the microcanonical probability $P^{(MC)}_{\nu' \nu}$ [Eq. (72)].} Regarding the time-resolved experiments then what happened is that after a short time $t = 0(\lambda_0^2)\ll \lambda_0^2$ there is an equilibration in the excited states so that

$$P_{\nu'}(t) = \langle \nu' | \lambda_0 \rangle \exp(- \lambda_0 t) \equiv P^{(MC)}_{\nu' \nu} \exp(- \lambda_0 t)$$

and

J. Chem. Phys., Vol. 73, No. 9, 1 November 1980
\[ I_{\nu r}(t) = \gamma_{\nu r} P_{\nu r}^{MC} \exp(-\lambda_{\nu} t). \]  

(78b)

Thus the emission rate from \( \nu \) is proportional to its microcanonical distribution \( P_{\nu r}^{MC} \).

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

If the initial excitation is to the \( \nu = 1 \) state of \( |e\)\), i.e.,
\[ \omega_1 \approx \omega_{1e} + \bar{\omega}_1, \]  

(79)

then the \( Y \) matrix is 2 \( \times \) 2 involving only the \( \nu = 0, 1 \) states
\[ Y = \begin{pmatrix} \gamma_R & -\gamma_{1VR} \\ 0 & \gamma_R + \gamma_{1VR} \end{pmatrix}, \]  

(80)

so that
\[ \gamma_{11}^1 = 1/(\gamma_{1VR} + \gamma_R) \]  

(81a) and
\[ \gamma_{01}^1 = \gamma_{1VR}/(\gamma_{1VR} + \gamma_R), \]  

(81b)

and we get one narrow and one broad progression, i.e.,
\[ I(\omega_1, \omega_2) = \frac{4}{\gamma_{1VR} + \gamma_R} \sum_{k=1}^{\infty} |\mu_{1+k,1}|^2 \chi(\omega_2 + (1 + k)\bar{\omega}_1 - \bar{\omega}_1^*) \times \frac{\Delta_c}{\Gamma_1 - \Gamma_2^*} \]  

(82)

In the neighborhood of the origin \( \omega_2 \approx \omega_{1e} \) \( (k = 0) \) we have a narrow component \( \omega_1^1 \) with area \( S_B \) and a broad component \( \omega_1^0 \) with area \( S_B^* \) where
\[ \frac{S_B}{S_B^*} = \frac{\mu_{1,1}^2 \gamma_{1VR}}{\Gamma_1 - \gamma_{1VR}}, \]  

(83)

where the last equality holds if the diagonal Franck-Condon factors are near unity. Knowledge of the radiative lifetime \( \gamma_R \) and the area ratio \( S_B/S_B^* \) gives us therefore a direct measurement of \( \gamma_{1VR} \). In the time domain we have in this case
\[ P_1^{MC} = 0, \]  

(84a)

\[ P_0^{MC} = 1, \]  

(84b)

and
\[ \lambda_0 = \lambda_R, \]  

(84c)

so that
\[ I_{0r}(t) = \gamma_0 \exp(-\lambda_R t). \]  

(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 \( \Gamma \) may become frequency dependent. 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 \( \Gamma_1 \) and \( \Gamma_2 \) (dephasing) relaxation matrices. In the intermediate case we are talking in terms of the mixing coefficients \( \gamma \) and \( \alpha \) in Eq. (8). It should be noted, as was already stressed\(^{23}\) that the intrastate \( \Gamma_1 \) and the \( \Gamma_2 \) 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 \( \gamma_{1VR}/\gamma_R \). 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 of 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.\(^{16}\) If we observe in the frequency resolved spectra broad and narrow components as shown in Fig. 3, then in statistical molecules this means that \( \gamma_R \) and \( \gamma_{1VR} \) 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 alky substituted benzene molecules\(^{18}\) contain broad and narrow components (Fig. 3) when excitation was made in the \( 6_{14} \) and \( 12_{12} \) 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. (6) 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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