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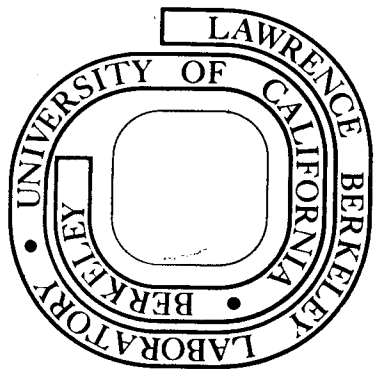**Publication Date**

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THE ORIGIN OF VIBRATIONAL DEPHASING OF

POLYATOMIC MOLECULES IN CONDENSED PHASES

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ABSTRACT

The vibrational dephasing of polyatomic moleucles in
condensed phases by intermolecular vibrational energy exchange
is treated theoretically. In the exchange model, dephasing
arises from random modulation of the vibrational frequency caused
by intramoleuclar anharmonic coupling to low frequency modes which
are undergoing intermolecular energy exchange with the bath.
The exchange rates are temperature dependent and as a consequence
manifest themselves experimentally as a temperature dependent
broadening and shift of the Raman spectral lineshape. Using a
reduced density matrix technique within the constraints of a
Markoff approximation, the theory allows the time dependence
introduced by the exchange process to be propertly accounted for,
and allows explicit expressions for the vibrational correlation

function and corresponding spectral lineshape functions to be derived and related to molecular parameters.

Application of the theory can have important consequences experimentally, since an analysis of the temperature dependence of the lineshape function allows the determination of the parameters which characterize the dephasing. These include the intermolecular energy exchange rates, the amplitude of the modulation which is in turn determined by the strength of intramolecular anharmonic coupling, and the effective activation energy for exchange which is related to the specific low frequency modes which participate in the dephasing process.

I. INTRODUCTION

Studies of spectral lineshapes can potentially reveal a great deal of information about dynamics of molecules in condensed phases. In particular, measurements of vibrational lineshapes and the corresponding dephasing and relaxation processes lead to an increased understanding of the interactions between a vibrating molecule and excitations of its surroundings. These interactions result in a finite correlation time for the vibration, which represents the time for loss of well-defined phase relationships among an ensemble of identically prepared excited molecules. This dephasing originates from a variety of mechanisms, which include inhomogeneous line broadening, vibrational energy relaxation and redistribution, as well as so-called "pure dephasing" which results from interactions which modulate the vibrational phase without causing energy redistribution. Gordon[1] showed that this decay is given by an autocorrelation function which is the Fourier transform of the Raman lineshape. This correlation function can be separated experimentally[2] (via the polarization of the scattered light) into contributions from the orientational relaxation of the molecules and the true vibrational correlation function. The observed spectral lineshape is then given as

$$I(\omega) \sim \int_{-\infty}^{\infty} \exp(-i\omega t) \langle [\vec{\varepsilon}_S \cdot \overleftrightarrow{\alpha}(0) \cdot \vec{\varepsilon}_I][\vec{\varepsilon}_S \cdot \overleftrightarrow{\alpha}(t) \cdot \vec{\varepsilon}_I] \rangle_o$$
$$\times \langle Q(0)Q(t) \rangle_v \, dt \tag{1}$$

where o and v denote the orientational and vibrational contributions.

$\alpha(t)$ is the Raman tensor for the transition of interest, $Q(t)$ is the normal coordinate, and ϵ_S and ϵ_I are the polarization vectors of the scattered and incident light. Recent experiments using picosecond laser excitation have succeeded in directly measuring the decay of the vibrational contribution to this correlation function.[3] In addition, these methods have been able to separately measure contributions to the decay due to population relaxation,[4] inhomogeneous broadening,[5] and pure homogeneous dephasing processes.

The basis for the interpretation of this data has been provided by theoretical models of vibrational relaxation and dephasing recently advanced by several authors.[6-12] These models have sought to define the relevant relaxation pathways and dephasing mechanisms, predict observed decay times, and understand the experimentally observed difference between T_1 times (population relaxation) and T_2 times (dephasing). The models which treat pure dephasing[9-11] represent the system as a harmonic oscillator weakly coupled to a reservoir of oscillators in thermal equilibrium. The off-diagonal part of this coupling results in decay of the vibrational energy into the reservoir modes (T_1), while the diagonal part is responsible for pure dephasing. The dephasing problem has also been treated semi-classically[12] using a model wherein the vibrational phase is modulated by random binary collisions.

Since interactions with other intramolecular modes are not included, these descriptions are most useful in the case of a diatomic molecule in

a monatomic solvent or matrix. In polyatomic systems, however, the situation is complicated by the presence of a number of intramolecular modes, some of which may interact more strongly with the vibration of interest than does the reservoir. Additionally, in a system which is made up of a collection of such molecules, resonant intermolecular transfer of vibrational energy can play an important role in the dephasing process. One might expect the dominant dephasing mechanism in systems such as these to result from modulation of the vibrational frequency due to energy exchange among low-frequency intramoleuclar vibrations.[13]

It should be pointed out that this approach[13] to dephasing processes is quite general. The key idea is the partitioning of the degrees of freedom of the molecule and surroundings (excluding the vibrational mode whose dephasing we are interested in, hereafter called mode A) into two groups, the exchanging modes and the reservoir. The exchanging modes are those modes which interact strongly with mode A such that their excitation shifts the frequency of mode A (e.g. from ω_o to $\omega_o + \delta\omega$). Thus, excitation and de-excitation of the exchanging modes by either resonant energy transfer from neighboring molecules or by interaction with the thermalized reservoir has the effect of modulating the vibrational frequency of mode A. Therefore, this approach takes into account (in part) not only the perturbation of vibrational spectra by intramolecular interactions (which will cause dephasing), but also includes dynamic effects, namely the modulation of these interactions by influences of the surroundings. It should also be noted that nothing in this theory requires that exchanging

modes be intramolecular vibrations, and they might, for example, be lattice vibrations or acoustic phonons depending on the system.

It is the effect of this frequency modulation on the temperature dependence of the vibrational lineshape and correlation function that is the subject of this paper. The application of these results to experimental lineshape data will be demonstrated in another publication.[14] In the present work,we present a theoretical treatment of the exchange mechanism of dephasing in the context of Markoffian coupling of the exchanging modes to the surroundings. The nature of this coupling will be discussed with regard to the requirements necessary to generate a time dependence of the vibrational frequency and thus cause dephasing. This approach properly takes into account any phase memory which is retained by the exchange process. Connections and comparisons of the results obtained for vibrational correlation functions and lineshapes with those from previous formulations[15-18] of the exchange theory will be made. With regard to the vibrational dephasing problem, we will also examine the important terms in the anharmonic potential which can give rise to the frequency shift, $\delta\omega$, and which might cause single exchanging modes to dominate dephasing processes, as is observed experimentally. Finally, it will be further shown that the application of the lineshape functions obtained here to the analysis of the temperature dependence of experimental lineshape data can give quantitative values of the frequency shift and thus a measure of the strength of the intramolecular coupling, and of the energy exchange rates.

II. THEORETICAL DISCUSSION

In this section the basic ideas introduced above are formalized and the resulting expressions for the vibrational correlation function are given. These expressions are valid when the excitation and de-excitation of the exchanging modes can be treated as a Markoffian process, that is, when the probabilities for these events to occur at a given time depend only on the state of the system at that time and not on its previous history. The application of this treatment and results to real systems is discussed. The importance of various terms in the anharmonic potential is discussed with regard to the origin of the frequency shift. Perturbation theory is used to estimate the contribution of various terms in the potential to $\delta\omega$.

A. Exchange Theory

The basic description of the vibrational exchange problem is given in terms of a zero order Hamiltonian, H_o, which is responsible for the basic energy level scheme of the molecule (i.e., it describes the energy levels of mode A and those of the exchanging modes); a perturbation, H_p, which couples these modes leading to the appearance of frequency shifts and additional spectral lines; and an exchange Hamiltonian, H_{ex}, which is capable of causing "transitions" among these various values of the vibrational frequency by modulating the strength of H_p. Ultimately, one hopes to calculate the resulting time dependence of the vibrational coordinate

of mode A, given by $Q_A = Q(a^+ + a)$ where a^+ is a creation operator for this mode. This then leads to an expression for the vibrational correlation function, $\langle Q_A(t) Q_A(o) \rangle$.

More specifically, suppose H_o is given by

$$H_o = H_A + H_B \tag{2}$$

$$= \hbar\Omega_A a_n^+ a_n + \hbar\Omega_B b_n^+ b_n$$

where only one exchanging mode is assumed to be present and b_n^+ is a creation operator for this mode. The n subscript refers to a particular molecule in the crystal or liquid sample. Further, let

$$H_p = C a_n^+ a_n b_n^+ b_n \tag{3}$$

and

$$H_{ex} = \sum_{j, i \neq j} J_{ij} (b_i^+ b_j) \tag{4}$$

where the sum is over all molecules. H_{ex} has the effect of causing excitation energy to be transferred among the exchanging modes of different molecules by resonant energy transfer, and H_p in this example corresponds to a portion of the $Q_A^2 Q_B^2$ term in the anharmonic vibrational potential of the molecule. One can now proceed to evaluate the equation

of motion for the positive frequency part of the vibrational amplitude

operator, $Q_{A+} \doteq Qa_n$, in the Heisenberg picture:

$$\dot{Q}_{A+}(t) = -(^i/\hbar)[Q_{A+}, H_o+H_p+H_{ex}]$$

$$= -(^i/\hbar)[Q_{A+}, H_A] - (^i/\hbar)[Q_{A+}, H_p]$$

(5)

$$= -i\Omega_A Q_{A+} - (^{iC}/\hbar)Q_{A+}b_n^+b_n,$$

since $[Q_{A+}, H_{ex}] = [Q_{A+}, H_B] = 0$. The first term represents oscilla-

tion of the vibration at frequency Ω_A, and the second term introduces

an additional "frequency shift" given by $(C/\hbar)b_n^+b_n$ which depends on the

occupation number of the exchanging mode. The important thing to note

is that H_{ex} is capable of introducing time dependence into this term,

since

$$\frac{d}{dt} H_p = (^{-i}/\hbar)[H_p, \mathcal{H}] = (^{-i}/\hbar)\left\{Ca_n^+a_n[b_n^+b_n, H_{ex}]\right\}$$

$$= (^{-i}/\hbar)\left\{Ca_n^+a_n\sum_{j\neq n}J_{jn}(b_n^+b_j-b_nb_j^+)\right\}$$

(6)

$$\neq 0$$

Thus, the number operator $b_n^+b_n$ is a time-dependent object. Physically,

the time dependence arises as a result of resonant energy transfer (de-

scribed by H_{ex}) among the exchanging modes of different molecules.

To continue the analysis and arrive at an expression for the vibrational correlation function, one can make the assumption that this time dependent vibrational frequency can be expressed in terms of a Markoffian random function, $\Delta\omega(t)$. If the transition probabilities which characterize this function are known, one can proceed to calculate the desired correlation function and Raman lineshape. Under what conditions then, is the energy transfer process resulting from the presence of H_{ex} described by a Markoffian random function?

The problem of coherence or lack of coherence in resonant energy transfer has been addressed by many authors.[19-21] The randomness arises due to interaction of the vibrational excitations with other degrees of freedom (e.g., lattice vibrations in a solid) which have been denoted here as "reservoir modes". The degree of coherence in the energy transfer can be described[20] in terms of a "memory function" which decays due to the excitation-reservoir interactions. When this decay becomes rapid compared to the time required for energy transfer over a distance comparable to the intermolecular spacing (and therefore rapid compared to the time dependence of $b_n^+ b_n$), the memory function can be replaced by a delta function (the Markoff approximation) and the energy transport is Markoffian. It can then be described in terms of a master equation:

$$\frac{\partial P_n}{\partial t} = \sum_i \left\{ F_{in} P_i - F_{ni} P_n \right\} \tag{7}$$

where P_n and P_i represent the probability that an excitation is present on molecule n and on molecule i, respectively. Of course, in a more disordered liquid phase system, any coherent contribution to energy transfer would be disrupted not only by molecular motion, but also due to the lack of intermediate to long range order or translational symmetry.

Returning to the exchange problem, it can be seen that under these conditions the time dependence introduced by H_{ex} can be treated as a Markoffian random modulation of the frequency of mode A caused by excitation and de-excitation of the exchanging mode by resonant energy transfer. It is reasonable to assume Markoffian energy transfer in the case of the low frequency intramolecular modes which would be potential exchanging modes. Although no definitive experimental evidence exists, one expects relatively strong interactions with lattice modes to effectively disrupt coherent transfer. Since a further effect of the molecule-reservoir interactions is to bring the average excited population of the exchanging mode to its thermal equilibrium value, the frequency modulation can be characterized by rates of excitation and de-excitation given by $W_+ = \tau^{-1} \exp[-\hbar\Omega_B/kT]$ and $W_- = \tau^{-1}$ respectively. W_+ represents the probability that a thermally generated excitation is transferred to some particular molecule, and τ is the average lifetime of the excitation on this molecule.

Since the rates W_+ and W_- fully characterize the random function $\Delta\omega(t)$ (as long as the problem only contains two possible values of the vibrational frequency), one could proceed at this point to evaluate the

desired correlation function. It should be noted, however, that the simple interpretation of the exchange process as a random frequency modulation depended on the diagonal form chosen for H_p. In the following portion of this section, a model is developed which incorporates the basic ideas described above in a way which allows the salient features of the exchange model to be easily displayed. This model explicitly includes the role of the reservoir and allows insight into the features required to make the modulation Markoffian, and into the possible role of off-diagonal parts of H_p.

The basic model to be explored is that of a molecule interacting with a reservoir of simple harmonic oscillators. The total Hamiltonian takes the form:

$$\mathcal{H} = H_A + H_B + H_P + H_R + H_I = H_M + H_R + H_I$$

H_A and H_B are the zero order Hamiltonians for mode A and for the exchanging modes, and H_P is the perturbation which couples mode A with the B modes thus causing frequency shifts as discussed above. H_R and H_I represent the zero order reservoir Hamiltonian and the interaction between the reservoir and the B modes. H_I takes the place of H_{ex} in the above discussion and serves to modulate the vibrational frequency of mode A. Since it was the reservoir which introduced the random nature of this modulation, we expect this direct molecule-reservoir interaction to

give a reasonable description of the random frequency modulation model of exchange theory.

The time dependence will be displayed by use of the reduced density matrix,[22,23] ρ^M, which has the equation of motion

$$\dot{\rho}^M = (^{-i}/\hbar)\mathrm{Tr}_R \{[\mathcal{H},\rho]\} \tag{9}$$

where ρ is the density matrix for the molecule plus reservoir and Tr_R is a trace over reservoir coordinates, i.e., $\rho^M = \mathrm{Tr}_R\{\rho\}$. This tracing operation represents an average over the reservoir distribution. We will use the following form for $\mathcal{H}$:

$$H_A = \hbar\Omega_A(a^+a+1/2) \tag{10}$$

$$H_B = \sum_j \hbar\Omega_j(b_j^+b_j+1/2) \tag{11}$$

$$H_P = V_{anh}(a^+,a,b_j^+,b_j) \tag{12}$$

$$H_R = \sum_k \hbar\omega_k(\beta_k^+\beta_k+1/2) \tag{13}$$

$$H_I = \sum_{j,k} \hbar g_{jk}(b_j\beta_k^+ + \beta_k b_j^+) \quad . \tag{14}$$

a^+, b_j^+, and β_k^+ are creation operators for the A mode, the j-th exchanging mode, and the k-th reservoir mode respectively, and V_{anh} represents the intramolecular anharmonic coupling between the A mode and the B modes.

The problem of finding the time dependence of ρ^M is simplified by two key assumptions.[22] First, it is assumed that the reservoir is so large that the interaction, H_I, has little effect on it, and that ρ^R, the reservoir reduced density matrix, is therefore constant and given by a thermal distribution. The second assumption is the Markoff approximation. Under this approximation, autocorrelation functions involving reservoir operators are replaced by δ-functions. Although we can then not expect to describe the effect of coherence in the molecule reservoir interaction (which would be important for times on the order of reservoir correlation times), the solution of the equations of motion is greatly simplified.

Since the method of derivation of the equation of motion of the reduced density matrix has been described quite lucidly by others,[22,23] the procedure is only outlined here. By eliminating the dependence in eq. (9) on the full density matrix a simplified equation of motion is obtained:

$$\dot{\rho}_I^M(t) = (-1/\hbar^2) \int_0^t dt' \text{Tr}_R \left\{ V_I(t) V_I(t') \rho_I^M(t') \otimes \rho_I^R(0) \right.$$
$$\left. - V_I(t) \rho_I^M(t') \otimes \rho_I^R(o) V_I(t') \right\} + \text{hermitian adjoint} \qquad (15)$$

where $\otimes$ represents an outer product, and

$$V_I(t) = \sum_{j,k} \hbar g_{jk} \left\{ b_j \beta_k^+ \exp[-i(\Omega_j - \omega_k)t] \right.$$

$$\left. - \beta_k b_j^+ \exp[i(\Omega_j - \omega_k)t] \right\} \qquad (16)$$

is the interaction picture version of H_I. ρ_I^M and ρ_I^R are also in the interaction picture. By introducing the density of reservoir modes, $D(\omega)$, the sum over these modes is converted to an integral over ω. This frequency integral over the exponential factors in eq. (16) causes the integrand in the time integral of eq. (15) to be negligible except for $t' \approx t$ (assuming that $D(\omega_k)$ and $g_{jk}(\omega_k)$ are slowly varying functions). The time interval for which this integrand is non-negligible corresponds to a reservoir correlation time for $V_I(t)$. If this time is small compared to the time required for $\rho_I^M(t)$ to change appreciably, we can set $\rho_I^M(t')$ = $\rho_I^M(t)$. This substitution is the Markoff approximation and is equivalent to assuming δ-function correlation functions for the reservoir. Performing the integrals and transforming back to the Schroedinger picture, one obtains:

$$\dot{\rho}^M = (-i/\hbar)[H_M\, \rho^M] - (1/2)\sum_j \left\{ [b_j b_j^+ \rho^M \right.$$

$$- b_j^+ \rho^M b_j]\gamma_j \bar{n}(\Omega_j)$$

$$- [b_j \rho^M b_j^+ - \rho^M b_j^+ b_j]\gamma_j\, (\bar{n}(\Omega_j)+1) \qquad (17)$$

$$\left. + \text{hermitian adjoint} \right\}$$

or

$$\dot{\rho}^M = \mathcal{B}\rho^M \qquad (18)$$

where $\bar{n}(\Omega_j) = [\exp(\hbar\Omega_j/kT)-1]^{-1}$ is the average number of reservoir excitations of frequency Ω_j and $\gamma_j = 2\pi\hbar^2|g_{jk}(\omega_k=\Omega_j)|^2 D(\Omega_j)$. $\mathcal{B}$ is the equivalent "superoperator". The formal result for the decay of the vibrational amplitude (which for these purposes is equivalent to the vibrational correlation function) is

$$\langle Q_A(t) \rangle = \mathrm{Tr}_M \left\{ Q_A \exp(t\mathcal{B})\rho^M(o) \right\}. \tag{19}$$

Thus, a full solution amounts to determination of this exponential operator.

It is illustrative to consider matrix elements of eq. (17). It will be assumed that only one exchanging mode of frequency Ω_B is coupled to mode A by V_{anh} and that the temperature is low enough that only the four states $|V_A V_B\rangle = |00\rangle, |10\rangle, |01\rangle, |11\rangle$ need be considered. One then finds

$$\dot{\rho}^M_{00,10} = -i\omega_o\rho^M_{00,10} -W_+ \rho^M_{00,10} +W_- \rho^M_{01,11}$$

$$+(i/\hbar)\sum_{n,m}' (V_{00,nm}\rho_{nm,10} - \rho_{oo,nm}V_{nm,10}) \tag{20}$$

$$\dot{\rho}^M_{01,11} = -i(\omega_o+\delta\omega)\rho^M_{01,11} +W_+\rho_{00,10} -W_-\rho^M_{01,11}$$

$$\tag{21}$$

$$+(i/\hbar)\sum_{n,m}' (V_{01,nm}\rho_{nm,11} - \rho_{01,nm}V_{nm,11})$$

where $W_+ = \gamma_B \bar{n}(\Omega_B)$ and $W_- = \gamma_B(\bar{n}(\Omega_B)+1)$. In the limit of $kT \ll \hbar\Omega_B$

these exchange rates take the form $W_+ = \gamma_B \exp[-\hbar\Omega_B/\hbar\tau]$ and $W_- = \gamma_B$.

The results for W_+ and W_- are traceable to the form chosen for H_I.

Additional interactions could have been included to represent double-quantum

transitions, etc., as required by a particular physical situation. The

primes on the sums in eqs. (20) and (21) indicate that only off-diagonal

elements of V_{anh} appear. The diagonal contributions are included in the

frequency terms which are given by $\omega_o = \Omega_A + (V_{10,10} - V_{00,00})/\hbar$ and $\omega_o + \delta\omega$

$= \Omega_A + (V_{11,11} - V_{01,01})/\hbar$ where $V_{k\ell,nm} = \langle k\ell | V_{anh} | nm \rangle$. If the off-diagonal

contributions of V_{anh} are ignored, eq. (20) and (21) are coupled only to

each other and their solution is greatly simplified. However, it is clear

that the off-diagonal parts lead to important contributions to dephasing

and to a partial redistribution of vibrational energy among the exchanging

modes. The dephasing contribution can be taken into account in a partial

and approximate fashion by calculating the shift in the energy levels due

to these off-diagonal elements and incorporating the result into the

value of $\delta\omega$. This procedure is nonrigorous, and it may ignore important

effects, especially when energy denominators are small enough to allow

appreciable mixing of zero order states to be induced by these off-diagonal

parts of V_{anh}.

To calculate the vibrational correlation function, one notes that

for this simple two-frequency exchange problem,

$$\langle Q_A(t) \rangle \sim \rho^M_{00,10}(t) + \rho^M_{01,11}(t) \tag{22}$$

and that eq. (20) and (21) can be written in a matrix form (neglecting the off-diagonal terms in V_{anh}):

$$\dot{\underset{\sim}{P}}_{01}(t) \equiv \begin{bmatrix} \dot{\rho}^M_{00,10}(t) \\ \dot{\rho}^M_{01,11}(t) \end{bmatrix}$$

$$= \begin{bmatrix} i\omega_o - W_+ & W_- \\ W_+ & -i(\omega_o + \delta\omega) - W_- \end{bmatrix} \begin{bmatrix} \rho^M_{00,10}(t) \\ \rho^M_{01,11}(t) \end{bmatrix}$$

$$\equiv (i\underset{\approx}{\omega}_V + \underset{\approx}{\mathbb{I}}) \cdot \underset{\sim}{P}_{01}(t) \tag{23}$$

Thus,

$$\frac{\langle Q_A(t) \rangle}{\langle Q_A(o) \rangle} = [1 \ 1] \cdot \begin{bmatrix} \rho^M_{00,10}(t) \\ \rho^M_{01,11}(t) \end{bmatrix} = \underset{\sim}{1} \cdot \exp[t(i\underset{\approx}{\omega}_V + \underset{\approx}{\mathbb{I}})] \cdot \underset{\sim}{W}_o \tag{24}$$

where $\underset{\sim}{W}_o = \underset{\sim}{P}_{01}(o)$ is the initial population distribution. This result is a matrix representation of eq. (19) for this simple case of diagonal V_{anh}.

To summarize, a general expression [eq. (24)] for the decay of the vibrational correlation function has been obtained for the case of a vibrational mode which interacts through the anharmonic potential of the molecule with other modes which undergo energy exchange. Although this result was derived for the example of a single exchanging mode in a low temperature limit, additional exchanging modes and harmonics can easily

be accommodated by including the appropriate frequency shifts and
exchange rates in $\underset{\approx}{\omega}_V$ and $\underset{\approx}{\Pi}$. The results obtained here are valid for
Markoffian modulation of the vibrational frequency. To be more specific,
the approach taken here applies when the correlation time of the interaction
which causes the energy exchange (whether due to resonant energy transfer
or interaction with a "reservoir") is short compared to the time
dependence of $\rho^M(t)$. We have ignored off-diagonal elements of V_{anh},
but have indicated how their effect on the dephasing might be included
by incorporating the appropriate energy level shifts into $\delta\omega$. This
might be done, for example, using a perturbation expansion (see below).
The error introduced by this procedure and the contribution of the
off-diagonal terms to the vibrational relaxation time, T_1, remains
unaccounted for.

However, these errors might be expected to be quite minimal in the
case of well-separated vibrational levels. In the case of the vibrational
exchange problem presented here, the exchange rate W_+ is expected to have
an exponential temperature dependence with an activation energy equal
to the frequency of the exchanging mode. W_- is approximately constant
and is given by the inverse lifetime of an exchanging mode excitation.

B. Role of the Anharmonic Potential, V_{anh}

One can see that application of these ideas to experimental examples
in the intermediate exchange regime can lead to knowledge of the exchange
rates and identification of the exchanging modes which are important in

bringing about vibrational dephasing. In addition, a determination of $\delta\omega$ can give increased understanding of the anharmonic potential responsible for the coupling between mode A and the exchanging modes. To illustrate this, the anharmonic vibrational potential is expanded as a power series in the normal coordinates of the molecule:

$$V_{anh} = \sum_i k_i Q_i^2 + \sum_{i,j,k} c_{ijk} Q_i Q_j Q_k + \sum_{i,j,k,\ell} c_{ijk\ell} Q_i Q_j Q_k Q_\ell \tag{25}$$

$$+ \dots$$

In Table I, the contributions to $\delta\omega$ are computed in second order for cubic and quartic terms involving at most two coordinates. As above, the quantity $\delta\omega$ refers to the difference in frequency of the $|01\rangle \to |11\rangle$ transition as compared to the $|00\rangle \to |10\rangle$ transition. The zero order frequencies used in the numerical estimates are typical for a C-H stretching mode (mode A) and a low frequency mode of an aromatic methyl group (exchanging mode).

From experimental results which will be presented in another publication,[14] one particularly interesting characteristic of the dephasing process emerges; in some cases the dephasing can be accounted for over a fairly large temperature range by an exchange mechanism wherein only a single exchanging mode is important. In other words, although there may be several low frequency modes which could easily be thermally excited, the anharmonic coupling seems to strongly couple a particlar A mode to only one possible exchanging mode.

With this somewhat surprising result in mind, there are several important features to be noted from Table I. First, some of the terms in V_{anh} always give a positive contribution to $\delta\omega$ while others are always negative, but some can give a contribution of either sign. Thus, the experimentally determined sign of $\delta\omega$ may offer some clue as to which terms are important. Second, the requirement that V_{anh} possess the full molecular symmetry sets definite restrictions on the symmetry type of possible exchanging modes, depending on the symmetry of mode A. This may be an important source of the selectivity observed in the experiments. Finally, the largest contribution to $\delta\omega$ seems to come from the only term with a diagonal portion, namely the $C_{1122}Q_1^2Q_2^2$ term. This term can give a value of $\delta\omega$ of either sign, and no restrictions due to symmetry apply. It is important to keep in mind that the actual contributions from the various terms depend on the magnitudes of the C-coefficients, which are difficult to estimate. In addition, in situations where more than one exchanging mode is in fact important, coupling terms like $C_{123}Q_1Q_2Q_3$ would conceivably play a role. We reiterate, however, that these are basically higher order effects and that $Q_1^2Q_2^2$ gives the lowest order diagonal contribution and is likely to have a dominant effect. Thus, although it may be intuitively clear in some situations that only one or two modes can effectively act as exchanging modes, this selectivity appears to be contained in the relative magnitudes of the anharmonicity coefficients in the expansion of V_{anh} [eq. (25)]. In such cases, experimental spectra can be quite easily analyzed in terms of the formalism which has been presented here.

C. Comparison to Previous Results

Before proceeding to calculate the spectral lineshape expected from the correlation function derived above, it is worthwhile to make the connection between these results and the previous formulations of exchange theory due to Anderson[15] and Kubo,[16] to McConnell,[17] and to Cohen-Tannoudji.[18] As mentioned above, the exchange probabilities given by W_+ and W_- (and others if more than two frequencies are involved) serve to characterize the random function $\Delta\omega(t)$. This function represents the fluctuations in the vibrational frequency caused by the exchange process. Anderson[15] uses the properties of such Markoffian random functions to arrive at a result for the vibrational correlation function which is identical with our eq. (24). This result was obtained here as a solution of coupled density matrix equations [eqs. (20) and (21)] which are essentially equivalent to the phenomenological coupled Bloch equations of McConnell.[17] Although in our formulation of the problem an external radiation field does not appear, it could have been included semi-classically in H_M in eq. (17). Solutions of the resulting density matrix equations with the field included lead to an approximate result[24] for the dephasing time and spectral shift which can be cast in the form of a Lorentzian lineshape function. This approximate form is valid in the slow to intermediate exchange regime $(W_+, W_- \lesssim \delta\omega)$, wherein the major effect of the exchange is a broadening and shift of the spectral line associated with mode A. As shown in the next section, this approximate result can also be obtained from more general lineshape functions.

Thus, the formalism adopted here embodies features present in both the random function approach and the modified Bloch approach. The time dependence resulting from the basic commutation relation of the various parts of the Hamiltonian and the operator Q_A is displayed by the reduced density matrix $\rho^M(t)$. This approach offers a link between the previous theories. It also has a physical appear in that the detailed assumptions leading to the Markoff approximation, the possible role of off-diagonal elements of H_p, and the forms for the exchange rates W_+ and W_- become somewhat clearer.

D. Lineshape Functions

Given the results obtained above for the form of the vibrational correlation function, one can proceed to calculate the expected spontaneous Raman lineshape when exchange is important. Aside from other contributions to the correlation function, the lineshape function is given by:

$$I(\omega) \sim \int_{-\infty}^{\infty} \exp(-i\omega t) \left\{ \underset{\sim}{1} \cdot \exp[t(i\underset{\approx}{\omega}_V + \underset{\approx}{\Pi})] \cdot \underset{\sim}{W}_0 \right\} dt$$
$$= \text{Re} \left\{ \underset{\sim}{1} \cdot \underset{\approx}{A}^{-1} \cdot \underset{\sim}{W}_0 \right\} \tag{26}$$

where $\underset{\approx}{A} = i(\underset{\approx}{\omega}_V - \omega\underset{\approx}{I}) + \underset{\approx}{\Pi}$, and $\underset{\approx}{I}$ is the identity matrix. For the two-

frequency exchange problem [eq. (23)], the following explicit form is obtained:

$$I(\omega) = \frac{W_+(\delta\omega)^2/(1+W_+/W_-)}{[\omega'^2-(\delta\omega/2)^2]^2 + [W_-(\omega'+\delta\omega/2)+W_+(\omega'-\delta\omega/2)]^2}$$

(27)

where $\omega' = \omega - \omega_o - \delta\omega/2$. The temperature dependence of this lineshape is shown in Fig. 1. The parameters chosen for $\delta\omega$, γ_B, and Ω_B are typical of those expected for vibrational spectra. In this particular illustration two well-defined peaks are observed at $\omega' = \pm\delta\omega/2$ (i.e., at $\omega=\omega_o$ and $\omega=\omega_o+\delta\omega$) in the low temperature limit. However, it is quite possible and is often observed (for example when $(\gamma_B)^{-1}<1psec$) that the smaller peak is essentially invisible or appears as an extended wing of the larger peak. Thus, the two-peak structure may be difficult to observe experimentally. It should also be noted that for typical parameters and a reasonable range of temperatures, the slow to intermediate exchange regime can be experimentally investigated for many molecules in condensed phases. At higher temperatures, Fig. 1 shows the appearance of strong spectral narrowing as the fast exchange ($W_+,W_->>\delta\omega$) regime is entered. It should be born in mind, however, that as the temperature increases contributions from additional higher frequency exchanging modes and from harmonics will most likely prevent this narrowing from being observed in a real system.

In the slow to intermediate exchange regime, an approximate Lorentzian lineshape which is valid near $\omega=\omega_o$ can be obtained by setting $\omega'-\delta\omega/2\approx -\delta\omega$ in eq. (27):

$$I(\omega) \approx \frac{W_+\tau^2(\delta\omega)^2/[D(1+W_+\tau)]}{(\omega'+\delta\omega/2-W_+\delta\omega\tau/D)^2+W_+^2[(\delta\omega)^2\tau^2]^2/D^2} \tag{28}$$

where $D = 1+(\delta\omega)^2\tau^2$ and $\tau = (W_-)^{-1}$ is approximately constant over the temperature range where this equation is valid. Thus, one expects to observe an effective Raman frequency

$$\omega^{eff} = \omega_o+W_+\delta\omega\tau/1+(\delta\omega)^2\tau^2) \tag{29}$$

and an effective dephasing time

$$(T_2^{eff})^{-1} = W_+(\delta\omega)^2\tau^2/(1+(\delta\omega)^2\tau^2)+(T_2')^{-1} \tag{30}$$

where additional relaxation processes can be included via the relaxation time T_2'. These results are identical to those obtained by solution of the modified Bloch equations with the radiation field included.[24] They are especially useful in visualizing the effect of phase memory in the exchange process. Specifically, when $\delta\omega\tau \ll 1$ the vibration retains all memory of its phase prior to the excitation of the exchanging mode, and both the frequency shift and line broadening effects vanish. In fact, whenever $\delta\omega\tau \lesssim 1$, partial retention of phase memory occurs, and one observes a narrower line than might be expected on the basis of the rate W_+, since the exchange contribution to the linewidth is always less than W_+. On the other hand, when $\delta\omega\tau \gg 1$ all phase memory is lost during a single exchange event. In this case the frequency shift vanishes and the contribution to the dephasing rate is simply W_+. Thus, it is the tempera-

ture dependent linewidth and frequency shift which is present when par-
tial phase memory is retained that provides experimental evidence for
vibrational exchange.

When eqs. (29) and (30) are appropriate, the values of $\delta\omega$, τ, and
the activation energy which corresponds to the frequency of the ex-
changing mode can be obtained by plotting the frequency of the Raman line
and its width vs. the inverse temperature. We have found that this pro-
cedure often gives very good results in the case of vibrational spectra.
Alternately, the lineshape given by eq. (27) can be least-squares fit to
the experimentally determined lineshape function to determine these para-
meters.[14] Additional relaxation processes represented by T_2' can be in-
cluded in the fitting process by using a lineshape function which consists
of a convolution of a Lorenzian of width $1/T_2'$ with eq. (27). It is
hoped that once these parameters have been determined, this information
will prove very useful in understanding the vibrational dynamics of the
system being investigated.

One such dynamical question that is touched upon by the ideas pre-
sented here is the role of inhomogeneous broadening in vibrational
spectra. Recent picosecond measurements indicate that the $2942 cm^{-1}$
Raman band of liquid methanol is inhomogeneously broadened at room
temperature. This broadening was attributed to a range of molecular
environments caused by quasistatic hydrogen-bonded structures in this
liquid which persist for times longer than the experimental timescale. Under
certain conditions, the exchange mechanism might provide a degree of
understanding of such spectra in that they can be viewed as the result

of interactions between the vibration and degrees of freedom which are in the slow exchange limit. For example, the two peaks in the spectral lineshape in Fig. 1 for the low temperature limit represent two "molecular environments" in the sense that some molecules possess thermally excited exchanging modes while others do not. The question of inhomogeneity versus homogeneity is really a matter of the rate of interconversion of these "environments" compared to the strength of the interaction which causes a distribution of frequencies to appear.

III. SUMMARY AND CONCLUSIONS

In this paper we have sought to demonstrate the applicability of
an energy exchange mechanism to the phenomenon of vibrational dephasing
in condensed phase systems. The basic premise of this mechanism is that
dephasing is caused by random modulation of the vibrational frequency.
This modulation arises due to interactions between the vibrational mode
of interest and other degrees of freedom which undergo excitation and
de-excitation via energy exchange. Physically, the excitation and de-
excitation rates are related to the rate of intermolecular resonant en-
ergy transfer or to the interaction of the molecule with degrees of free-
dom of the macroscopic system (i.e., the "reservoir").

We have formalized these ideas within the context of the Markoff
approximation. In other words, it is assumed that the coherence time
of the interaction responsible for the exchange is short compared to the
exchange rates. Within this approximation, the theory allows expressions
for the vibrational correlation function and spectral lineshape to be
derived using a reduced density matrix technique. These results appear
in a form which can easily be applied to the analysis of experimental
vibrational lineshapes. When one applies such an analysis, it is pos-
sible in favorable circumstances to determine quantitative values for
the exchange rates and the frequency shift which arises due to the inter-
actions between the vibrational mode of interest and the degrees of free-
dom which undergo energy exchange.

In the case of polyatomic molecules in condensed phases the role of exchanging mode seems to be played by low frequency intramolecular vibrations. These modes interact with higher frequency vibrational modes via anharmonic terms in the vibrational potential of the molecule so that when they exchange energy with other molecules or degrees of freedom the vibrational frequency of the high frequency mode is modulated and dephasing results. The study of this dephasing process in such systems thus provides an important source of knowledge of the anharmonic coupling and of vibrational energetics and dynamics in condensed phases.
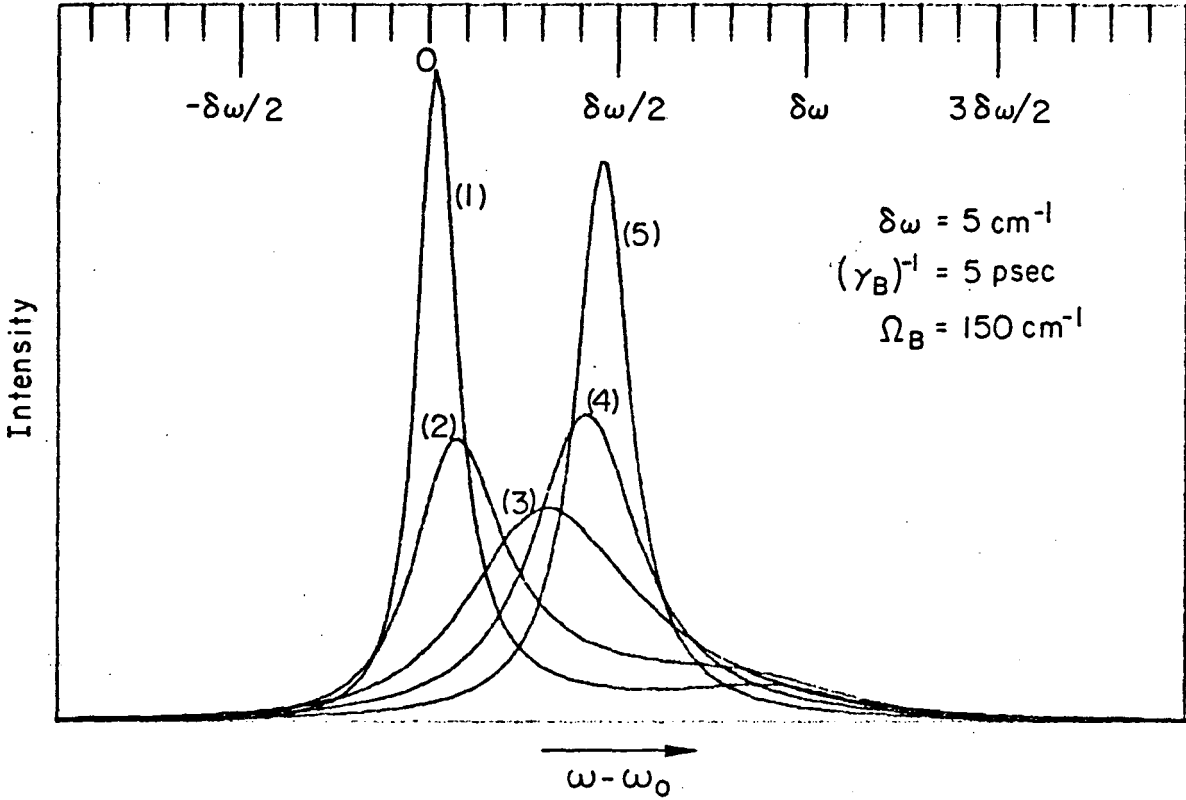
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Figure Caption

Figure 1. The temperature dependence of the exchange lineshape (eq. 27) for typical values of the parameters $\delta\omega$, γ_B and Ω_B. The curves shown correspond to the following temperatures: Curve #1 = 150°K; Curve #2 = 250°K; Curve #3 = 500°K; Curve #4 = 800°K; and Curve #5 = 1500°K. The exchange rates for this calculation were given by $W_+ = \gamma_B \; (n \; (\Omega_B))$ and $W_- = \gamma_B \; (n \; (\Omega_B) + 1)$.

TEMPERATURE DEPENDENCE OF EXCHANGE LINESHAPE

$\delta\omega = 5 \text{ cm}^{-1}$

$(\gamma_B)^{-1} = 5 \text{ psec}$

$\Omega_B = 150 \text{ cm}^{-1}$

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Figure 1