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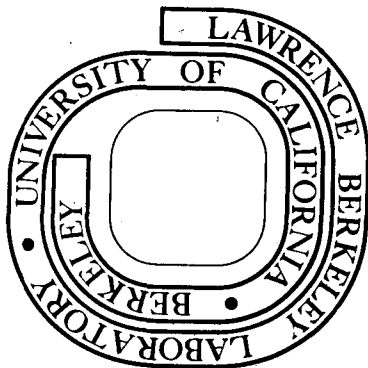
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Intermolecular Energy Exchange
as a Mechanism for Vibrational
Dephasing in Polyatomic Molecules

by

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ABSTRACT

Vibrational dephasing by intermolecular vibrational energy exchange is shown to be important for the case of polyatomic molecules in condensed phases. In this model, dephasing results from random modulation of the vibrational frequency due to exchange of energy by a low frequency mode. Analysis of the temperature dependence of Raman lineshapes in the intermediate exchange regime allows the determination of the parameters which characterize this dephasing process. These include the energy exchange rates, the amplitude of the modulation which is determined by intramolecular anharmonic coupling, and the effective activation energy for exchange. We outline the formalism and/the theory to the C-H stretching vibrations of 1,2,4,5-tetramethylbenzene (durene) and find that these activation energies correspond to individual low frequency intramolecular vibrations. It is shown that different C-H stretching modes are dephased by different but specific low frequency modes in solid durene.

I. Introduction

A wealth of information about the dynamics of molecules in condensed phases is available from an analysis of the vibrational autocorrelation function. This function has been experimentally obtained through Fourier analysis of Raman lineshape data and directly measured using picosecond spectroscopy. Several models¹ have been advanced which relate the experiments to the specific interactions responsible for the dephasing. Since these models treat the system as a harmonic oscillator weakly coupled to a reservoir of oscillators in thermal equilibrium, they are most appropriate for describing dephasing of diatomic molecules. 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. In this regard, we recently pointed out² that intermolecular energy exchange of low frequency modes plays an important role in the dephasing of high frequency vibrations. The key idea in this approach is the partitioning of the degrees of freedom of the molecule and surroundings into three groups: (i) the vibrational mode A whose dephasing we are investigating, (ii) the exchanging modes and (iii) the reservoir. The exchanging modes are those which interact strongly with mode A via the anharmonic portion of the vibrational potential, and are also capable of exchanging energy with reservoir degrees of freedom. These interactions introduce a time dependence into the Hamiltonian which can be thought of as a modulation of the frequency of mode A/^{and} which leads to a loss of vibrational phase coherence.

In this letter, we outline a formalism which treats this problem starting from the reduced density matrix and the Markoffian approximation and show how this approach offers a direct link between the theories of Kubo³ and Anderson⁴, and those arrived at from the modified Bloch equations⁵. Finally, we will demonstrate the relevance of this theory to the vibrational dephasing in 1,2,4,5-tetramethylbenzene (durene) by presenting the experimental results which confirm the salient features of the theory.

II. Exchange Theory of Vibrational Dephasing

The Hamiltonian which will be used to describe the molecule and reservoir takes the form

$$\mathcal{H} = H_A + H_B + H_P + H_R + H_I. \quad (1)$$

H_A and H_B are the zero order Hamiltonians for the high frequency mode and the low frequency exchanging modes respectively, H_P is the perturbation which couples mode A with the B modes, causing frequency shifts as discussed below and shown in fig. 1. H_R and H_I represent the zero order reservoir Hamiltonian and the interaction between the reservoir and the B modes. Since $[H_P, H_I] \neq 0$, the interaction or exchange term introduces a time dependence into the frequency of mode A via the perturbation Hamiltonian H_P . This time dependence can be displayed by use of the reduced density matrix, ρ^m , which has the equation of motion

$$\dot{\rho}^m = (-i/\hbar) \text{Tr}_R([\mathcal{H}, \rho]) \quad (2)$$

where ρ is the density matrix for the molecule plus reservoir and Tr_R is a trace over reservoir coordinates, i.e. $\rho^m = \text{Tr}_R(\rho)$. We will use the following form for \mathcal{H} :

$$H_A = \hbar\Omega_A (a^\dagger a + 1/2) \quad (3)$$

$$H_B = \sum_j \hbar\Omega_j (b_j^\dagger b_j + 1/2) \quad (4)$$

$$H_P = V_{anh} (a^+, a, b_j^+, b_j) \quad (5)$$

$$H_R = \sum_k \hbar \omega_k (\beta_k^+ \beta_k + 1/2) \quad (6)$$

$$H_I = \sum_{j,k} \hbar g_{jk} (b_j \beta_k^+ + \beta_k b_j^+). \quad (7)$$

a , b_j and β_k are annihilation operators for the A mode, B modes and reservoir modes respectively, and V_{anh} is the anharmonic coupling between A and B modes. By invoking the Markoffian approximation, the equation of motion (2) can be shown to reduce to

$$\begin{aligned} \dot{\rho}^m = & -i/\hbar [H_A + H_B + H_P, \rho^m] - 1/2 \sum_j \{ [b_j b_j^+ \rho^m - \rho^m b_j^+ b_j] \gamma_j \bar{n}(\Omega_j) \\ & - [b_j \rho^m b_j^+ - \rho^m b_j^+ b_j] \gamma_j (\bar{n}(\Omega_j) + 1) \\ & + \text{adjoint} \} \end{aligned} \quad (8)$$

where $\bar{n}(\Omega_j) = [\exp(\hbar \Omega_j / kT) - 1]^{-1}$

$\gamma_j = 2\pi \hbar^2 |g_{jk}(\omega_k = \Omega_j)|^2 D(\Omega_j)$, and $D(\omega)$ is the density of reservoir modes. The Markoffian assumption of no memory is included by taking correlation times of the reservoir to be much shorter than any time of interest for the evolution of ρ^m .

It is illustrative to consider matrix elements of eq. (8). It will be assumed for simplicity that only one mode of frequency Ω_B is involved in the exchange. In this case only the four states $|V_A, V_B\rangle = |00\rangle, |01\rangle, |10\rangle$ and $|11\rangle$ need be considered.

One then finds that

$$\dot{\rho}_{00,10}^m = -i\omega_0 \rho_{00,10}^m - W_+ \rho_{00,10}^m + W_- \rho_{01,11}^m \quad (9)$$

$$\dot{\rho}_{01,11}^m = -i(\omega_0 + \delta\omega) \rho_{01,11}^m - W_- \rho_{01,11}^m + W_+ \rho_{00,10}^m \quad (10)$$

where $W_+ = \gamma_B \bar{n}(\Omega_B)$ and $W_- = \gamma_B (\bar{n}(\Omega_B) + 1)$. The frequency terms include frequency shifts due to H_p and are given by $\omega_0 = \Omega_A + (V_{10,10} - V_{00,00})/\hbar$ and $\omega_0 + \delta\omega = \Omega_A + (V_{11,11} - V_{01,01})/\hbar$ where $V_{ij,k\ell} = \langle ij | V_{anh} | k\ell \rangle$. The off-diagonal parts of V_{anh} have been ignored. These off-diagonal elements can be expected to lead to T_1 processes, since they can result in a redistribution of the vibrational excitation, however, to the extent that the exchange process occurs adiabatically; the neglect of off-diagonal elements of V_{anh} in equations (9) and (10) does not represent a serious restriction. These coupled density matrix equations are equivalent to the weak field modified Bloch equations.⁴ The molecule-radiation field interaction could also have been included in the Hamiltonian if desired.

To calculate the observed spectrum one needs the vibrational correlation function which is equivalent to the one-time average $\langle Q(t) \rangle$ where $Q = Q(a^\dagger + a)$ is the vibrational coordinate for mode A. This is given by

$$\langle Q(t) \rangle \sim \rho_{00,10}^m(t) + \rho_{01,11}^m(t) \quad (11)$$

These density matrix elements obey the coupled equations (9) and (10) which can be compactly expressed and solved using a matrix notation. We arrive at a result which is identical to Anderson exchange,⁴ namely

$$\frac{\langle Q(t) \rangle}{\langle Q(0) \rangle} = \underline{1} \cdot \exp[t(i\underline{\omega}_v + \underline{\Gamma})] \cdot \underline{W}. \quad (12)$$

$\underline{1}$ is a vector whose elements are all unity, $\underline{\omega}_v$ is a diagonal matrix and contains the vibrational frequencies including frequency shifts, and $\underline{\Gamma}$ gives the transition rates between these frequencies. \underline{W} is a column vector which gives the initial population distribution. The spectrum is the Fourier transform of (12) which, for the two frequency case (Eq. (9) and (10)) becomes:

$$I(\omega) = \frac{W_+(\delta\omega)^2 / (1 + W_+/W_-)}{[\omega'^2 - (\delta\omega/2)]^2 + [W_-(\omega' + \delta\omega/2) + W_+(\omega - \delta\omega/2)]^2} \quad (13)$$

where $\omega' = \omega - \omega_0 - \delta\omega/2$. This reduces to the low temperature approximation (Eq. (6) of reference 2) near $\omega = \omega_0$, and thus we see that this approach offers a direct link between the theories of Kubo,³ Anderson,⁴ McConnell⁵ and others.⁶

The important assumptions which have been made in the course of this development are the Markoff approximation, a diagonal perturbation Hamiltonian H_p , and the form taken for H_I . The first is probably very good for this problem and the second has already been discussed. The form of H_I could have been chosen differently to include, for example, multiple quantum transitions in the exchange with little complication.

We should note that the application of these equations to spontaneous Raman scattering or infrared spectroscopy leads to a knowledge of the exchange rates, W_+ , the lifetime of the low frequency mode, $(W_-)^{-1} \equiv \tau$, and the identification of the specific exchange mode B which is important in bringing about vibrational dephasing. In this model the dephasing results from random frequency modulation of the high frequency mode A by an amount $\delta\omega$ due to intermolecular exchange of the low frequency mode B. The magnitude of $\delta\omega$ is deter-

mined by the anharmonic potential which couples modes A and B; therefore, the dephasing can be highly selective in the sense that particular terms in the expansion of the potential may be dominant. To illustrate more explicitly the nature of this selectivity it is instructive to consider the relative importance of individual terms.

The anharmonic potential is expanded into cubic and quartic terms as:

$$V_{\text{anh}} = \sum_{ijk} C_{ijk} Q_i Q_j Q_k + \sum_{ijkl} C_{ijkl} Q_i Q_j Q_k Q_l + \dots \quad (14)$$

In this expression, the C's are real coefficients while the Q's represent vibrational normal coordinates in the harmonic approximation. Starting with harmonic oscillator base states, the contribution to $\delta\omega$ from each of these terms has been estimated to second order and is listed in Table I. The only first order or diagonal contribution is from terms of the form $C_{1122} Q_1^2 Q_2^2$ where Q_1 is the coordinate of the high frequency mode and Q_2 that of a low-frequency mode. This contribution may be of either sign depending on the sign of the coefficient. The second order contributions are off-diagonal and can give rise to T_1 processes as well as T_2 processes. The table is meant only to show the order of magnitude the effects of various terms in the anharmonic coupling have in introducing frequency shifts.

Several important points emerge. First, V_{anh} possesses the full molecular symmetry and thus restrictions are imposed on the symmetry type of the exchange modes depending on the symmetry of A. In general, the direct product $\Gamma_i \times \Gamma_j \times \Gamma_k \times \Gamma_l$ must be totally symmetric. Because of the off-diagonal nature of most of the coupling channels this may be important for T_1 processes. Sec-

only, from table I, the diagonal $(Q_1^2 Q_2^2)$ terms appear to be dominant in determining the important dephasing channels. Physically, $Q_1^2 Q_2^2$ represents the product of the RMS amplitude of Q_1 overlapping the RMS amplitude of Q_2 . In this context, we would expect to be able to interpret the dephasing in terms of intermolecular steric effects. Experimentally we find that different high frequency modes are dephased by different but specific low frequency modes in durene. Although there may be several low frequency modes which could easily be thermally excited in a given temperature range, the anharmonic coupling seems to strongly couple a particular mode A to only one B mode.

III. Interpretation of the Vibrational Dephasing in 1,2,4,5-Tetramethylbenzene (durene)

The Raman spectrum of durene in the C-H stretching region provides an excellent example of the application of exchange theory to vibrational dephasing. This example possesses the advantage that individual low frequency methyl group motions appear to dominate the dephasing of the high frequency C-H stretches, and thus the interpretation of the data is straightforward.

The Raman spectrum of durene between 2850 cm^{-1} and 3050 cm^{-1} is shown in Fig. 2. The five bands above 2920 cm^{-1} display a marked broadening and shift of apparent vibrational frequency as the temperature is increased. We can interpret this temperature dependence in terms of the exchange model presented above. From experimental lineshape data, the modes which are important in the dephasing process can be identified in the following manner.

Since the exchange rate W_+ and the lifetime τ satisfy detailed balance, their temperature dependence is given by the Boltzmann factor,

$$W_+ \tau = \exp(\epsilon_i/kT) \quad (15)$$

where ϵ_i is the energy of the low-frequency mode involved in the dephasing process. If τ is independent of temperature over the temperature range studied, the exchange rates are given by $W_- = 1/\tau$ and $W_+ = (1/\tau)\exp(-\epsilon_i/kT)$, and the experimental lineshape data can be fit to the resulting temperature-dependent exchange theory expressions. In addition, temperature-independent dephasing channels, T_2' , can be accounted for by multiplying the correlation function in equation (11) by $\exp(-t/T_2')$. The resulting expression for the lineshape contains five parameters. τ , $\delta\omega$ and ϵ_i describe the exchange process, and T_2' and ω_0 give the linewidth and frequency in the low-temperature limit. The parameters are adjusted for the best fit to approximately 125 data points which represent the observed lineshape at ten different temperatures. The resulting values for the five lines in the durene spectrum are given in Table 2. Typical lineshape data and the corresponding fitted function are shown in Fig. 3 for the 3027 cm^{-1} transition.

From an experimental point of view the most significant feature of the spectrum is that all the Raman transitions are in intermediate exchange. This occurs when $\delta\omega$, the difference between the C-H vibrational frequencies with and without the low frequency excitation, and τ , the lifetime of the low frequency mode, satisfy the condition

$$(\delta\omega)(\tau) \approx 1 \quad (16)$$

A second feature which is important to note is that both positive and negative frequency shifts with temperature are observed. This is to be expected from the exchange model, since the quartic terms $Q_i^2 Q_j^2$ of the anharmonic potential will represent an attractive interaction for some pairs of modes Q_i, Q_j , and a repulsive interaction for other pairs. The quantities $\delta\omega$ and τ represent the effects of that part of the Hamiltonian which embody the interactions between the observed vibrational mode and the exchanging mode and between the exchanging mode and

reservoir. A good approximation to the product $\delta\omega \cdot \tau$ can be obtained by dividing the temperature dependent contribution to the linewidth due to exchange by the temperature dependent shift of the apparent vibrational frequency. This quantity is plotted as a function of temperature in Fig. 4. $\delta\omega\tau$ is constant for each transition over the temperature range, supporting the assumption of constant τ . Both positive and negative values of $\delta\omega\tau$ are found and they are on the order of unity for all five lines in the durene spectrum. It is this latter feature which characterizes the "intermediate exchange" regime.

It is very interesting (Table 2) that the activation energies ϵ_i correspond very closely (with one exception) to observed bands in the low frequency vibrational spectrum of durene.⁷ This correspondence is indicated in the column labelled "Dephasing Mode" in Table 2, along with the symmetry of these modes in the point group D_{2h} . The observed fundamental frequencies for these modes are 187 cm^{-1} and 197 cm^{-1} for the torsion, 282 cm^{-1} for the methyl rock, and 354 cm^{-1} for the out-of-plane bend. The experimental results/^{presented here} demonstrate that the interaction responsible for dephasing via a coupling to the low frequency modes is very selective. This is perhaps the most surprising result of the study.

In conclusion, we have outlined an approach to vibrational dephasing in condensed phases based on energy exchange which is potentially applicable to many experimental cases. This formalism has been applied to the analysis of the Raman spectrum of durene in the C-H stretching region. It was found that single low frequency methyl group modes provide the dominant dephasing channels via intermolecular energy exchange, and analysis of the temperature dependent lineshape in the intermediate exchange range allowed the determination of intermolecular energy exchange rates, lifetimes, and frequency shifts. This information is useful in elucidating the nature of the interactions responsible for the dephasing processes and points out the importance the anharmonic part of the potential plays in the dephasing process. Finally, it should be pointed out that the exchange formalism is very versatile. Indeed, it has recently

0 0 11 0 5 0 0 0 0 1 7
been applied in a similar manner to dephasing processes in other branches of optical spectroscopy.⁸ The approach provides a fuller understanding of the information contained in spectral lineshapes and yields a considerable amount of information on the dynamics of molecular interactions which contribute to the lineshape autocorrelation function in a variety of fields.

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Table I. Contributions to $\delta\omega$, from various terms in the anharmonic potential.

Term	Symmetry Rule	$\delta\omega^a$	Relative ^b Magnitude	Sign
$Q_1^2 Q_2$	$\Gamma_2 = a_g$	$-\left[\frac{4}{2\omega_1 + \omega_2} + \frac{4}{2\omega_1 - \omega_2} \right] C_{112} ^2$	1.3×10^{-3}	-
$Q_1 Q_2^2$	$\Gamma_1 = a_g$	$-\left[\frac{4}{\omega_1 + 2\omega_2} - \frac{4}{\omega_1 - 2\omega_2} \right] C_{122} ^2$	5.5×10^{-4}	+
$Q_1^3 + Q_1 Q_2^2$	$\Gamma_1 = a_g$	$-\left[\frac{4}{\omega_1 + 2\omega_2} - \frac{4}{\omega_1 - 2\omega_2} \right] C_{122} ^2 - \frac{24C_{122}C_{111}}{\omega_1}$	7.4×10^{-3}	+/-
$Q_2^3 + Q_1^2 Q_2$	$\Gamma_2 = a_g$	$-\left[\frac{4}{2\omega_1 + \omega_2} + \frac{4}{2\omega_1 - \omega_2} \right] C_{112} ^2 - \frac{24C_{112}C_{222}}{\omega_2}$	8.1×10^{-2}	+/-
$Q_1 Q_2^3$	$\Gamma_1 \times \Gamma_2 = a_g$	$-\left[\frac{18}{\omega_1 + 3\omega_2} - \frac{18}{\omega_1 - 3\omega_2} + \frac{54}{\omega_1 + \omega_2} - \frac{54}{\omega_1 - \omega_2} \right] C_{1222} ^2$	7.6×10^{-3}	+
$Q_1^3 Q_2$	$\Gamma_1 \times \Gamma_2 = a_g$	$-\left[\frac{18}{3\omega_1 + \omega_2} + \frac{18}{3\omega_1 - \omega_2} + \frac{54}{\omega_1 + \omega_2} + \frac{54}{\omega_1 - \omega_2} \right] C_{1112} ^2$	4.1×10^{-2}	-
$Q_1^2 Q_2^2$	None	$4C_{1122} - \left[\frac{16}{\omega_1} + \frac{16}{\omega_2} + \frac{8}{\omega_1 + \omega_2} \right] C_{1122} ^2$	3.9	+/-

^a Calculated using second order perturbation theory

^b These quantities represent $\delta\omega$ in cm^{-1} for a situation where all C-coefficients are equal to 1 cm^{-1} , $\omega_1 = 3000 \text{ cm}^{-1}$ and $\omega_2 = 300 \text{ cm}^{-1}$.

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Table II. Exchange Parameters for the Raman Active C-H Stretches in 1,2,4,5-tetramethylbenzene (Durene)

Raman Active C-H Stretch		Low Frequency Dephasing Channels.			
ω_0 (cm ⁻¹)	Mode ^a	Dephasing Mode	ϵ_1 (cm ⁻¹)	$\delta\omega$ (cm ⁻¹)	τ (ps)
2929.0	b _{3g}	b _{3g} - torsion	194 ± 10	+13.6	0.36
2957.7	b _{2g}	-----	229 ± 21	+10.5	0.86
2970.3	b _{1g}	b _{1g} , a _{1g} - Methyl Rock	265 ± 6	-24.2	0.19
2987.3	a _g	b _{3g} , b _{2g} - out-of-plane Methyl Bend	341 ± 13	-20.6	0.25
3027.5	a _g	b _{1g} , a _g - Methyl Rock	263 ± 19	-21.2	0.36

^a Symmetry labels refer to D_{2h} point group.

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Figure Captions

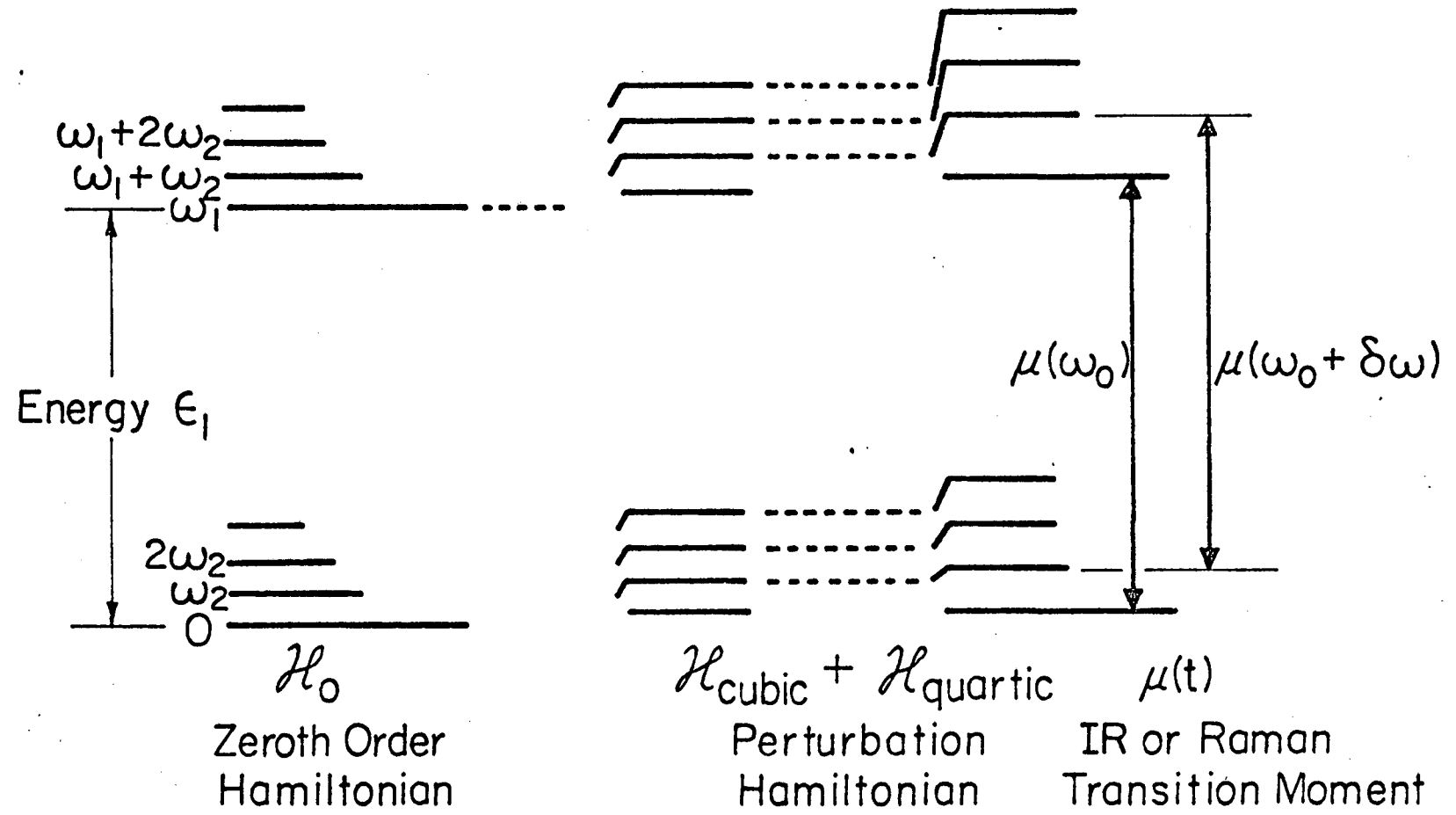
Fig. 1. Energy level scheme for two coupled vibrational modes. The zero order Hamiltonian describes two normal modes with frequencies ω_1 and ω_2 . When the anharmonic perturbations which couple these modes are included, the levels shift such that a number of vibrational frequencies are possible for the high frequency mode, depending on the occupation of the low frequency mode. Excitation and relaxation of the low frequency mode can now cause dephasing of the high frequency mode through modulation of its vibrational frequency.

Fig. 2. The five Raman bands whose dephasing is discussed in the text are those between 2920 cm^{-1} and 3050 cm^{-1} . The four between 2920 cm^{-1} and 3000 cm^{-1} are assigned as C-H stretching modes of the methyl group protons, and the line at 3027 cm^{-1} as the aromatic proton C-H stretch. The bands between 2850 cm^{-1} and 2920 cm^{-1} are harmonics of C-H bending vibrations of methyl protons ("scissors" modes). The arrows in the lower panel indicate the magnitude of frequency shifts which occur when the sample is warmed to room temperature.

Fig. 3. Typical fits to experimental lineshape data for the 3027 cm^{-1} line in the durene Raman spectrum for three typical temperatures. In (a) a Lorentzian approximation to the exchange lineshape (see ref. 2) is also shown (curve #2). For the lower temperature in (b) and (c) the approximate curve would be essentially coincident with the more exact function.

Fig. 4. This graph plots the portion of the line broadening due to exchange divided by the frequency shift. This quantity gives an approximation to the quantity $\delta\omega\tau$, and indicates that this product is constant as a function of temperature over the temperature range studied.

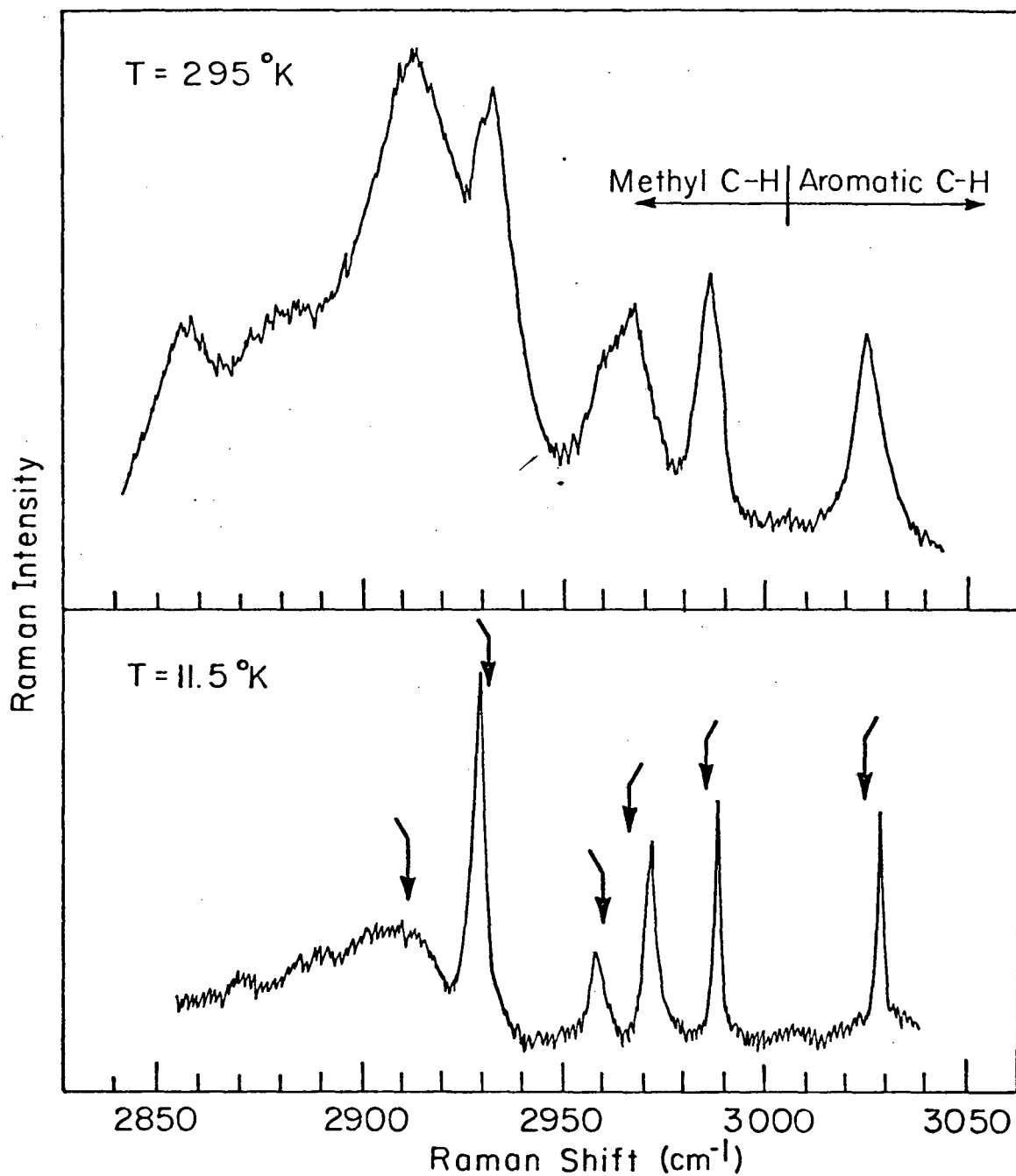
A SCHEMATIC REPRESENTATION OF VIBRATIONAL ENERGY LEVELS IN AN ANHARMONIC OSCILLATOR



XBL 777-5846

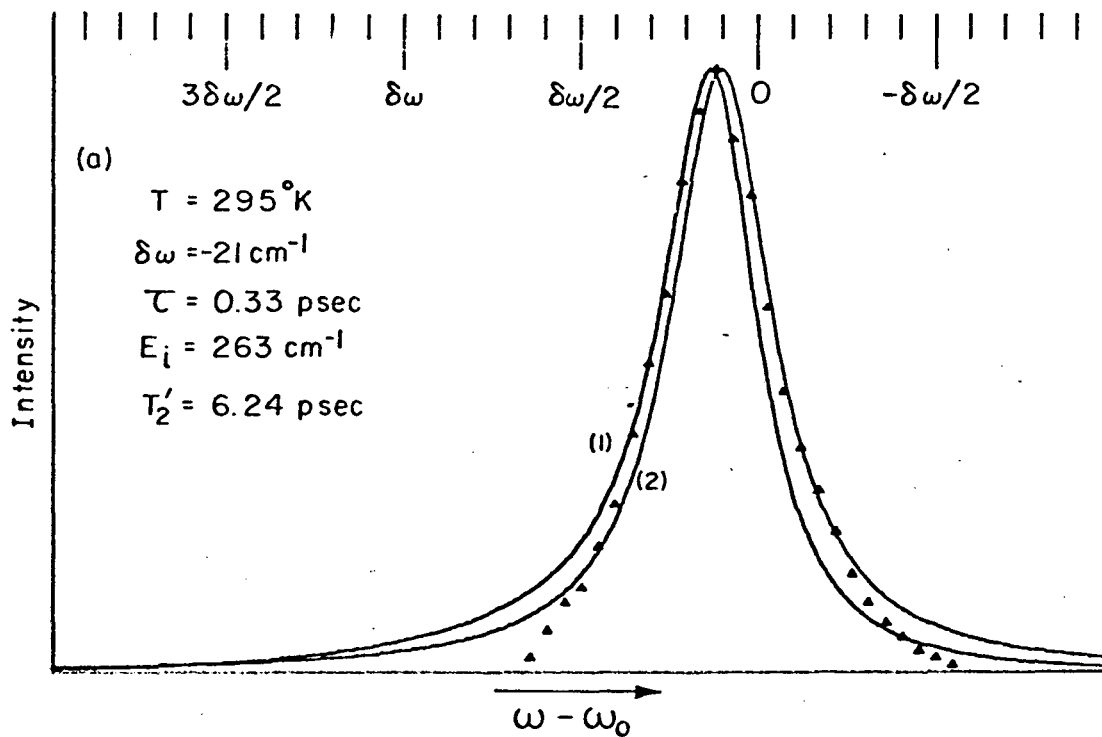
Figure 1

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SPONTANEOUS RAMAN SPECTRUM: C-H STRETCHING REGION
1,2,4,5-TETRAMETHYL BENZENE (SOLID)

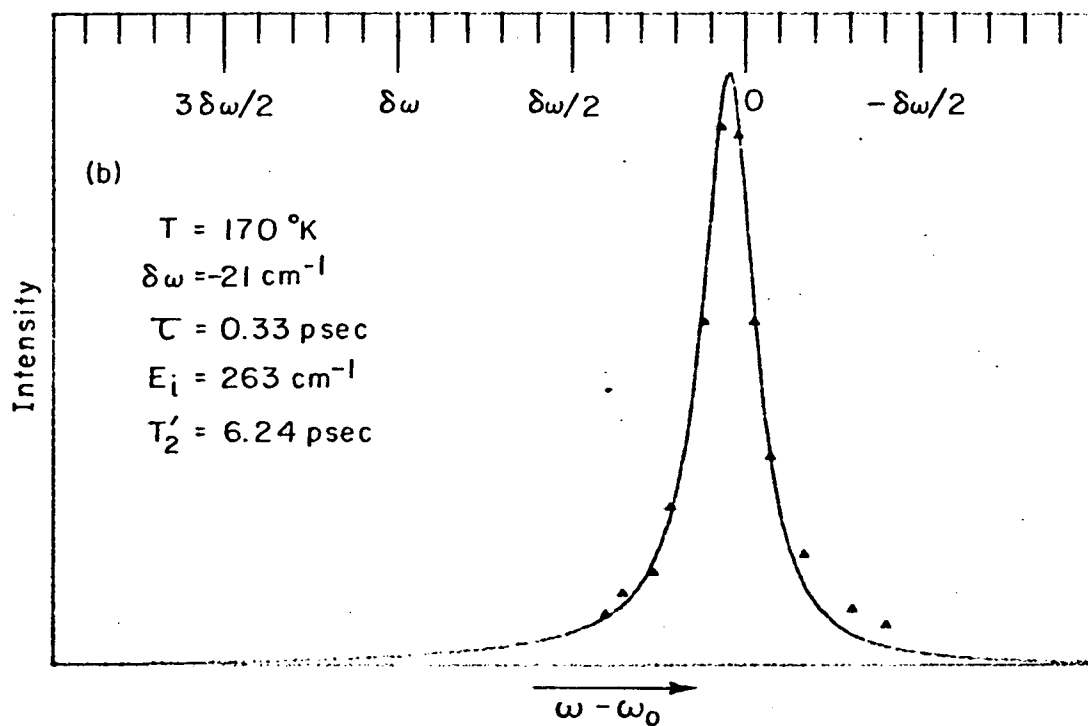
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Figure 2

COMPARISON OF CALCULATED EXCHANGE LINESHAPE AND OBSERVED LINESHAPE
DURENE 3027 cm^{-1} VIBRATION

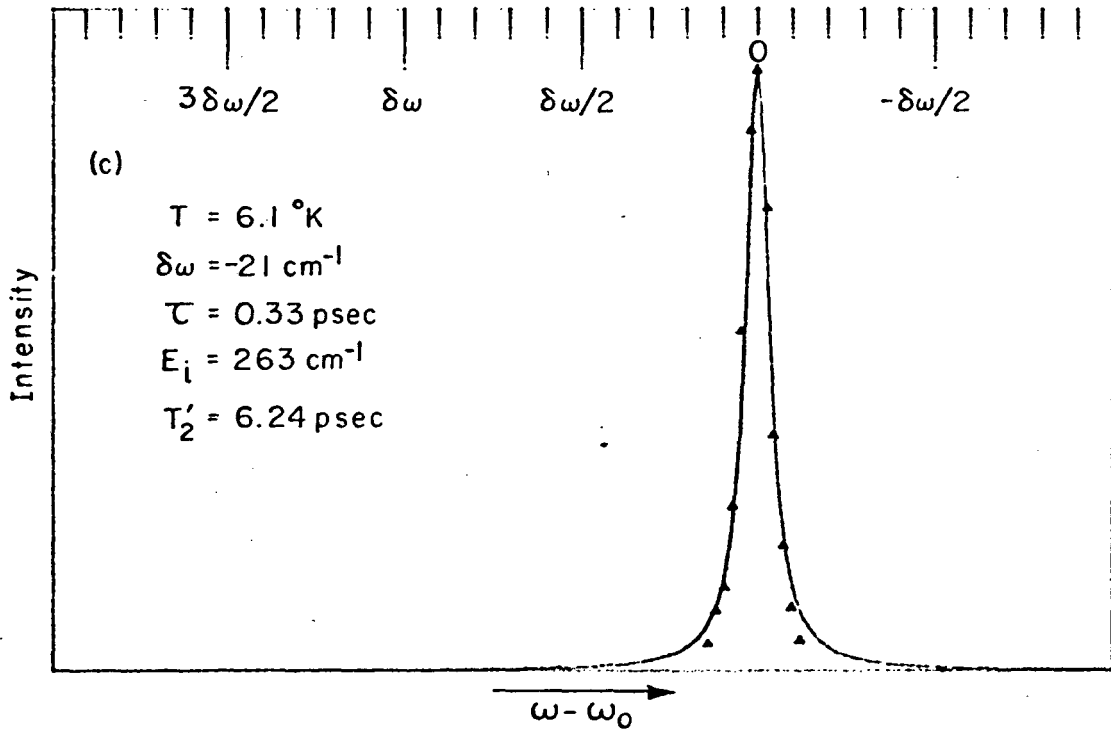
XBL 7711-6471

Figure 3 a

COMPARISON OF CALCULATED EXCHANGE LINESHAPE AND OBSERVED LINESHAPE
DURENE 3027 cm^{-1} VIBRATION

XBL7711-6472

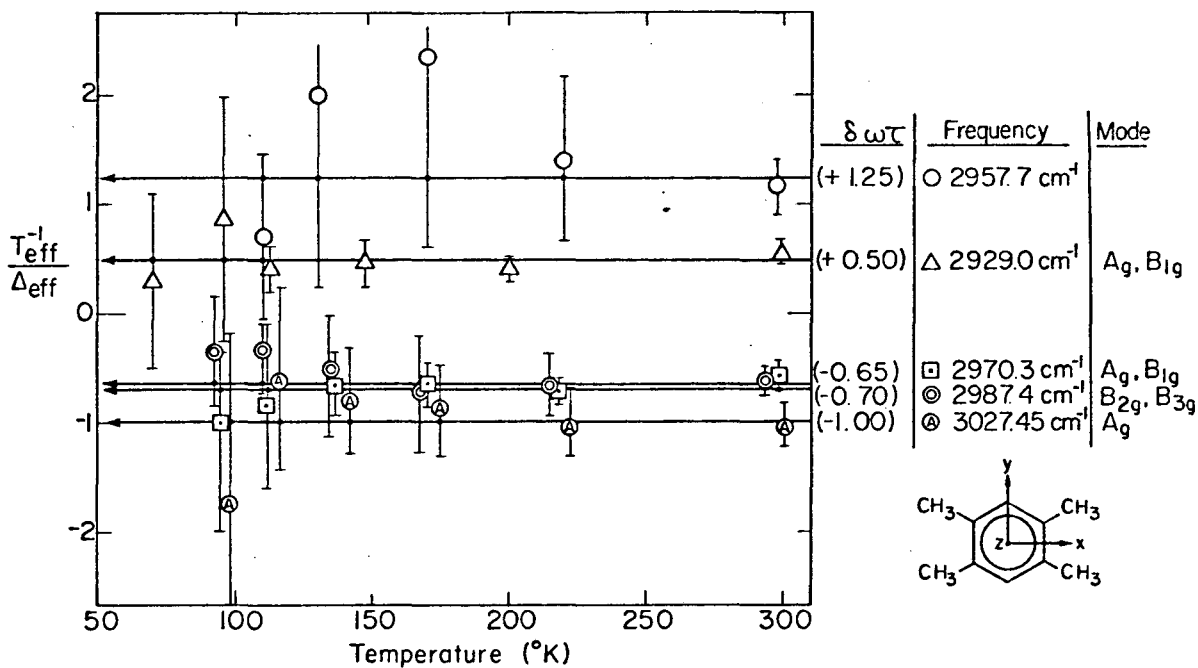
Figure 3 b

COMPARISON OF CALCULATED EXCHANGE LINESHAPE AND OBSERVED LINESHAPE
DURENE 3027 cm^{-1} VIBRATION

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Figure 3 c

RATIO OF THE TEMPERATURE DEPENDENT PORTION OF THE LINEWIDTH AND FREQUENCY SHIFT IN THE RAMAN TRANSITIONS OF TETRAMETHYLBENZENE (DURENE)



XBL777-5840A

Figure 4

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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