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Vibrational Relaxation and Dephasing in Organic Solids†

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This paper presents a review of experimental studies conducted in the author's laboratory in the area of vibrational relaxation and dephasing in organic solids. The investigation utilizes temperature dependence of linewidths, lineshapes and frequencies in the Raman spectra. Theoretical background is presented on various anharmonic interactions for lattice phonons and internal vibrations in relation to their relaxations and dephasing. The effects of experimental conditions and disorders on linewidth are discussed. Some selected results of experimental investigations are discussed. It is found that for a lattice phonon transition the dephasing occurs by T_1-relaxations due to cubic anharmonic coupling. For an internal vibration the process responsible for dephasing depends on the frequency and the delocalization of the vibration. For a localized and low frequency internal mode, the dephasing occurs by an elastic phonon-scattering (T_2'-process) which does not destroy the excitation. For a delocalized internal vibration or for a high frequency internal vibration T_1-relaxations (but of different types) contribute to dephasing. The dominant contribution to the temperature dependence of vibrational frequencies for both phonons and internal vibrations are derived primarily from the thermal expansion of the lattice.

INTRODUCTION

Vibrational relaxation plays an important role in many physical and chemical processes which occur in the condensed phase. Vibrational relaxations occur due to anharmonic interactions between various vibrational modes of a solid.[1–3] The relaxations of an optically induced vibrational excitation can be classified into two types:[3,4]

i) T_1-relaxation in which an optically created vibrational excitation undergoes inelastic scattering and exchanges energy with other excitations resulting in energy dissipation as well as a loss in phase memory of this excitation;

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ii) T_2-relaxation, also known as dephasing, which simply results in a loss of phase memory.

Although T_1-relaxation contributes to T_2, there are processes other than T_1-relaxation which can provide the dominant mechanism for dephasing. These processes are pure dephasing processes (also referred to as T_2'-relaxation) which involve an elastic scattering of the excitation. This creates a fluctuation in the energy of the excitation, and thus a loss of phase memory. In the density matrix formalism T_1-relaxation corresponds to the relaxation of the diagonal term i.e. the occupation number of a given level. A pure dephasing process, on the other hand, gives rise to the relaxation of the off-diagonal term of the density matrix but leaves the occupation number unaffected. It is the dephasing process which has been a subject of considerable interest during recent years.[3–9]

Relaxation and dephasing of an optical excitation can be studied either by a coherent transient method using laser pulses[3,4] or by a study of linewidth of the optical transition.[5,8] Although the coherent transient methods are desirable because they provide direct measurements of both T_1 and T_2-relaxations, these methods require sophisticated and expensive instrumentations.[3,4] Linewidth measurements[5,8] provide an indirect measure of T_2-relaxation and T_1-relaxation only if T_1-relaxation is the sole contributor to T_2-relaxation. The advantage of this method is that it is simple, unsophisticated, and inexpensive. It is the line width measurement which has been used in our laboratory to study vibrational relaxations in organic solids.

This paper presents a review of the study of vibrational dephasing conducted in this laboratory using linewidth measurements in Raman spectra. First, a brief theoretical discussion is presented on various contributions to dephasing. This section is followed by an experimental section where a discussion is first presented on various experimental parameters which may influence linewidth measurements. Need for special data handling of line width measurements is discussed. Finally, some selected results of experimental studies of dephasing for phonons and internal vibrations are presented.

A. THEORETICAL DISCUSSIONS

The homogeneous full width ν at half-maximum (FWHM) derived from various scattering processes is related to the T_2-relaxation as follows: $\nu = 1/2\pi CT_2$ (our definition). In this section various theoretical models are discussed in relation to their prediction of the lineshape and the temperature dependence of FWHM. The experimental observations are then compared on these two bases to identify the mechanism of dephasing.

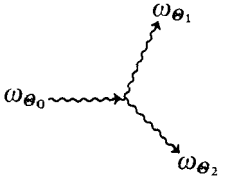
Both lattice phonons and internal vibrations are discussed. The source of T_1 and T_2-relaxations for a vibration in the crystal is the anharmonic interaction. This interaction for a vibration Θ_0 can be expressed as[8]

$$H_A^{\Theta_0} = \sum_{\theta_1,\theta_2} V_{\theta_0\theta_1\theta_2}\xi_{\theta_0}\xi_{\theta_1}\xi_{\theta_2} + \sum_{\theta_1,\theta_2,\theta_3} V_{\theta_0\theta_1\theta_2\theta_3}\xi_{\theta_0}\xi_{\theta_1}\xi_{\theta_2}\xi_{\theta_3} \quad (1)$$

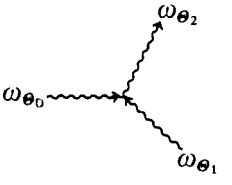
The symbol ξ_θ represents a displacement coordinate (normal coordinate) for the crystal mode θ. In case of a delocalized mode, θ labeling requires specification of the branch index and the wave vector index (q). If θ_0 represents a lattice phonon motion, important anharmonic interactions are due to lattice anharmonicity and all displacement coordinates ξ_{θ_1}, ξ_{θ_2}. . . refer to lattice displacements. The first term on the right hand side is a cubic anhormonic interaction term and it leads to a T_1-relaxation which is given as

$$\frac{1}{\pi T_1} = \frac{18\pi}{h^2}\sum_{\theta_1,\theta_2} |V_{\theta_0\theta_1\theta_2}|^2[(\eta_{\theta_1} + \eta_{\theta_2} + 1)\delta(\omega_{\theta_1} + \omega_{\theta_2} - \omega_{\theta_0}) + (\eta_{\theta_2} - \eta_{\theta_1})\{\delta(\omega_{\theta_1} - \omega_{\theta_2} - \omega_{\theta_0}) - \delta(\omega_{\theta_1} - \omega_{\theta_2} - \omega_{\theta_0})\}] \quad (2)$$

Here η_θ is the occupation number of the phonon mode θ of frequency ω_θ. The first term describes a down conversion process:



The second term describes an up conversion process in which a phonon of frequency ω_{θ_1} (or ω_{θ_2}) combines with the phonon θ_0 to produce a phonon of higher frequency as shown in the following diagram:



Quartic anharmonic terms of Eq. (1) lead to both T_1-relaxations and pure dephasing (T_2'-relaxations). A diagonal quartic anharmonic interaction consisting of terms like $V_{\theta_0\theta_0\theta_1\theta_1}$ has been suggested[5,7] to lead to an exchange modulation where the T_2'-relaxation is given as

$$\frac{1}{\pi T_2'} = e^{-\beta h\omega_\theta}(\delta\omega_{\theta_1})^2 T_{\theta_1}^*[1 + (\delta\omega_{\theta_1} T_{\theta_1}^*)^2]^{-1} \quad (3)$$

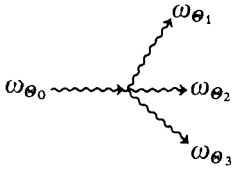
In Eq. (3) $\delta\omega_{\theta_1}$ is a change in frequency of the mode θ_1 due to the excitation of the phonon θ_0. $T_{\theta_1}^*$ is the T_1-relaxation time for the mode θ_1.

The off-diagonal quartic anharmonic interaction terms $V_{\theta_0\theta_1\theta_2\theta_3}$ lead to both a T_1-relaxation (T_1' to distinguish from the cubic T_1-process) and a pure dephasing (T_2' type process which we label for the present case as T_2''). These processes are given as[8]

$$\frac{1}{\Pi T_1'} = \frac{24\Pi}{h^2} \sum_{\theta_1,\theta_2,\theta_3} |V_{\theta_0\theta_1\theta_2\theta_3}|^2 \times \{(1 + \eta_{\theta_1} + \eta_{\theta_2} + \eta_{\theta_3})\delta(\omega_{\theta_1} + \omega_{\theta_2} + \omega_{\theta_3} - \omega_{\theta_0}) + (1 + \eta_{\theta_1})(1 + \eta_{\theta_2})\eta_{\theta_3}\delta(\omega_{\theta_1} + \omega_{\theta_2} - \omega_{\theta_3} - \omega_{\theta_0}) + (1 + \eta_{\theta_1})\eta_{\theta_2}\eta_{\theta_3}\delta(\omega_{\theta_1} - \omega_{\theta_2} - \omega_{\theta_3} - \omega_{\theta_0})\}. \tag{4}$$

$$\frac{1}{\Pi T_2''} = \sum_{\theta_1,\theta_2} |V_{\theta_0\theta_0\theta_1\theta_2}|^2 \eta_{\theta_1}(\eta_{\theta_2} + 1)\delta(\omega_{\theta_1} - \omega_{\theta_2}) \tag{5}$$

Eq. (4) contains the four phonon inelastic scattering processes such as



The process described by Eq. (5) leads to modulation of the energy of the phonon of frequency ω_{θ_0} but the occupation number of vibration does not change. The temperature dependence of these relaxation processes is contained in the occupation number η_θ. The temperature dependence can be expected to be different for each of these mechanisms. Also the 0°K residual linewidth is expected to be different for each case. For example, the up-conversion T_1-type process and the T_2'' type process do not predict any width [$\alpha(1/T_1)$ or $(1/T_2'')$] at 0°K. The lineshape predicted by all processes except for the T_2' is a thermally weighted Lorentzian in ω^2 assuming the relaxation is not frequency dependent. The lineshape is described as[8,10]

$$I_{\alpha\gamma\beta\lambda}(\omega) = \frac{1}{2\Pi}[\eta(\omega) + 1]\frac{4P_{\alpha\beta}^* P_{\gamma\lambda}\omega_0^2 \nu}{\{[\omega_0 + \Delta(T)]^2 - \omega^2\}^2 + 4\omega_0^2(\nu)^2} \tag{6}$$

In this equation $\Delta(T)$ is the thermal line shift. The subscripts $\alpha\gamma\beta\lambda$ define the polarizations. $P_{\alpha\beta}$ is the $\alpha\beta$ component of the polarizability tensor. Equation (6) predicts an asymmetric Lorentzian in ω^2 and not a simple symmetric Lorentzian in ω. However, for a narrow line and especially at low temperature the lineshape is close to a Lorentzian in ω itself.[12]

It has been suggested that if T_2'-mechanism involving an exchange modulation is operative, the ratio of the temperature dependence of the linewidth and that of the frequency remains constant.[5] In this case the lineshape can be a Lorentzian or a Gaussian or more complex depending on the rate of modulation. This criterion may be used to determine the role of T_2'-type process. However, in order that the criterion of the ratio of temperature dependence of the vibrational frequency and that of the linewidth can be used, other contributions to temperature dependence of the vibrational frequency have to be considered.[8] In view of this fact various contributions to temperature dependence of vibrational frequencies are briefly discussed here.

The temperature dependence of the vibrational frequency is derived from thermal expansion of the lattice as well as from cubic and quartic anharmonic interactions other than those responsible for thermal expansion. These contributions are summarized as follows:[8]

$$\Delta_{\Theta_0}^{\text{T.E.}} = \omega_{\Theta_0}(0)\left[\exp\left\{-\gamma_{\Theta_0}\int_0^T \alpha(T)\,\mathrm{d}T\right\} - 1\right] \tag{7}$$

$$\Delta_{\Theta_0}^{3} = \frac{-18}{h^2}\sum_{\Theta_1,\Theta_2} |V_{\Theta_0\Theta_1\Theta_2}|^2 \left\{\frac{\eta_{\Theta_1}+\eta_{\Theta_2}+1}{(\omega_{\Theta_1}+\omega_{\Theta_2}+\omega_{\Theta_0})_p} + \frac{\eta_{\Theta_1}+\eta_{\Theta_2}+1}{(\omega_{\Theta_1}+\omega_{\Theta_2}-\omega_{\Theta_0})_p}\right.$$

$$\left. + \frac{\eta_{\Theta_2}-\eta_{\Theta_1}}{(\omega_{\Theta_1}-\omega_{\Theta_2}+\omega_{\Theta_0})_p} + \frac{\eta_{\Theta_2}-\eta_{\Theta_1}}{(\omega_{\Theta_1}-\omega_{\Theta_2}-\omega_{\Theta_0})_p}\right\} \tag{8}$$

$$\Delta_{\Theta_0}^{4} = \frac{12}{h}\sum_{\Theta_1} V_{\Theta_0\Theta_0\Theta_1\Theta_1}(2\eta_{\Theta_1}+1) \tag{9}$$

$$\Delta_{\Theta_0}^{4'} = \delta\omega_{\Theta_1} e^{-\beta h\omega_{\Theta_1}}\left[1 + (\delta\omega_{\Theta_1} T_{\Theta_1}^{*})^2\right]^{-1} \tag{10}$$

Equation (7) describes the contribution due to thermal expansion. In this equation $\gamma_{\Theta_0} = -(\partial \ln\omega_{\Theta_0}/\partial \ln V)$ is the Gruneisen parameter for the mode Θ_0 where V is the volume of the crystal. The Gruneisen parameter is derived from the compressibility data and from the pressure dependence of the vibration frequency.[8] The term $\alpha(T)$ is the thermal expansion coefficient which is a function of temperature, T. The term $\Delta_{\Theta_0}^{3}$ describes the contribution due to cubic anharmonic interaction which couples the vibration Θ_0 with two other vibrations Θ_1 and Θ_2. In the expressions of the right hand side the subscript p refers to the principal values of the terms. Equation (9) describes the contributions due to diagonal quartic anharmonic interactions. Equation (10), on the other hand is the contribution, again, due to diagonal quartic anharmonic interactions but it involves an exchange modulation mechanism.

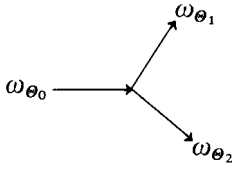
The dephasing derived from T_1-relaxation (Eq. (2)), T_1'-relaxation (Eq. (4)), and T_2''-relaxation (Eq. (5)) are additive, but T_2'-relaxation (Eq. (3)) cannot be assumed to be so.[4] If only T_1, T_1' and T_2'' processes occur, the overall

dephasing is described by a relaxation time T_2 given as

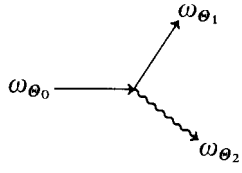
$$\frac{1}{T_2} = \left(\frac{1}{T_1} + \frac{1}{T_1'} + \frac{1}{T_2''}\right) \tag{11}$$

Now we consider how the relaxation processes apply to an internal vibration. An internal vibration can be localized or delocalized. Furthermore, interactions leading to T_1- or T_2'-relaxations for an internal vibration can arise from two types of anharmonic interations[11] which can be described in terms of Eq. (1). Here θ_0 represents an internal vibration. If θ_1 θ_2 (and θ_3 for Quartic anharmonic terms) represent internal vibrations, the anharmonic terms are due to internal anharmonicity and can be expected to show only small changes from liquid phase to solid phase. On the other hand, if any of θ_1, θ_2 (and θ_3) represent a lattice phonon, we are dealing with mixed mode anharmonicity referring to mixing between internal and external motions.[11] These terms would be highly dependent on the crystalline interactions.

For a high frequency internal vibration the density of vibrational states at frequencies required by an energy conservation can be high enough to allow T_1 and/or T_1'-type processes to occur either by internal anharmonicity or by mixed mode anharmonicity where at least one mode (θ_1, θ_2 or θ_3) is an internal mode). This process can be represented as

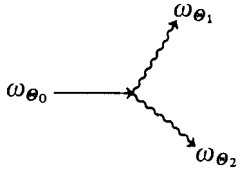


internal anharmonicity

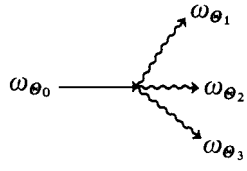


mixed mode anharmonicity

Here straight lines are used to represent an internal vibration and wiggly lines to represent a lattice phonon. On the other hand, for a low lying internal vibration, the T_1-relaxation can occur only by mixed mode anharmonicity as



if $\omega_{\theta_0} < 2\omega_D$

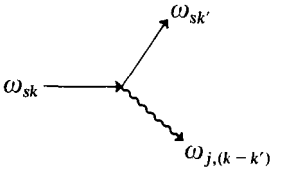


if $\omega_{\theta_0} < 3\omega_D$

Here ω_D is the Debye cut-off frequency for phonon bands. For an intermediate frequency vibration for which $\omega_{\theta_0} > 3\omega_D$, a bottleneck might appear due to the lack of vibrational density of states at energy required by the energy

conservation ($\omega_{\theta_0} = \omega_{\theta_1} + \omega_{\theta_2} + \omega_{\theta_3}$) for a T_1-type process. This situation could specially occur for a localized internal vibration. However, a pure dephasing mechanism as predicted by a T_2' or a T_2'' type process can occur since these processes do not require such an energy conservation.

There are additional processes which occur for a delocalized internal vibration. These processes are exciton-phonon interaction processes and are analogous to the electronic exciton-phonon interaction processes.[1] In this process θ_0 and θ_1 refer to the same vibrational mode (same branch index) but different wave vectors. These processes can be represented as



where $\omega_{sk} - \omega_{sk'} = \omega_{j,(k-k')}$

The indices k and k' refer to the wave vector, while s and j refer to branch indices.

B. EXPERIMENTAL STUDY

B1. Effect of experimental conditions

Slit width correction Vibrational transitions at low temperatures are considerably sharp. Some of these transitions at 2°K have a linewidth of approximately 0.05 cm^{-1}, which can be comparable to or even less than the band pass of the spectrometer.[8] This was certainly the case with our spectrometer (Spex Model 14018). In our Raman spectroscopic study we selected a set of slit widths of 15 μ.[8,12,13] This slit width corresponds to a band pass of approximately 0.3 cm^{-1}. In order to correct for the slitwidth one cannot simply subtract this amount from the observed width. The observed lineshape is related to the actual line shape by the following convolution:

$$I_{obs}(\omega_0) = \int s(\omega) I(\omega - \omega_0)\, d\omega \tag{12}$$

In this equation $I_{obs}(\omega_0)$ is the observed lineshape. $S(\omega)$ is the slit function, $I(\omega')$ is the actual line shape. The slit function $S(\omega)$ was obtained[8,12,13] from the digital form spectrum of the exciting laser line (5145 Å) in a single frequency mode (band with approximately 100 MHz) with the help of a temperature stabilized etalon. One may attempt to deconvolute Eq. (12)

to obtain the actual lineshape $I(\omega')$. We find it easier to use a computer simulation method to obtain $I(\omega')$. Various computer simulated shapes $I_{obs}(\omega)$ are obtained by assuming $I(\omega')$ to be either Lorentzian of Eq. (6), or a Gaussian of variable linewidth and convoluting it with $S(\omega)$. The simulated spectra are compared with the observed spectra and from the best fit, the actual line shapes and the line widths of the vibrational transitions are determined. This method has worked very well in all the cases we have investigated so far.[8,12–14]

Effect of inhomogeneities or structural disorders Real crystals invariably contain structural imperfections and defects. Also there are crystals (example: *p*-bromochlorobenzene) which contain orientational disorder in order to generate a statistically averaged center of symmetry. These disorders also contribute to line broadening. The contribution due to disorder has to be corrected in order that one can relate the line broadening to a T_2-relaxation due to anharmonic interactions. Very often the residual line width (0°K limit) of a localized vibrational transition may be entirely due to the disorder. While it is possible that certain imperfections may show a temperature dependence behavior due to anealing, in most cases one can safely assume the line width derived from disorder or inhomogeneities to be temperature independent. The line width due to disorder and that due to anharmonic interactions are not always additive. The actual line shape of a vibrational transition is given as

$$I(\omega') = \int I^A(\omega' - \omega) I^D(\omega)\, d\omega \tag{13}$$

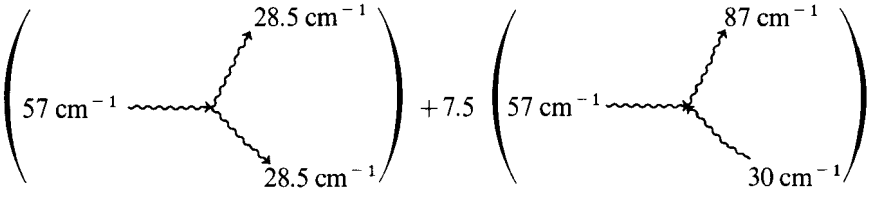
Here I^A and I^D are line shapes derived from anharmonic interactions and disorders, respectively. The line widths are additive, only if I^A and I^D are both Lorentzians. If I^A and I^D are both Gaussians, then $\nu^2_{total} = \nu^2_A + \nu^2_D$. On the other hand, if I^A and I^D are of different forms, no such simple relation holds. Our theoretical analysis[12] of a highly delocalized phonon motion reveals a line shape for I^D similar to the one predicted by Eq. (6). Thus, for a narrow band width phonon transition, I^A and I^D are both Lorentzians and the two linewidths can be expected to be additive. For a highly localized vibration such as many internal modes, I^D represents a statistical distribution of states and is a Gaussian. Thus, for an internal vibration I^A can be a Lorentzian and I^D a Gaussian. In this case we again have used a computer simulated convolution method to obtain I^A. Various forms (with varying widths) of I^A are convoluted with I^D and the resulting line shape $I(\omega)$ compared with the experimentally observed $I(\omega)$. From the best fit, the line shape I^A and the homogeneous width ν is obtained.

Crystal quality Crystal quality does not appear to have as pronounced of an effect on vibrational line widths as it has on line widths of electronic transitions.[1] Phonon bands seem to be extremely insensitive to crystal qualities. The reason is that Raman phonons in molecular crystals sample short range interactions and, thus, order in local structure. As the phonon motions are highly delocalized, changes in distribution of inhomogeneities from one sample to another do not affect the linewidth of phonon transitions. On the other hand, a localized internal vibrational transition has been found to exhibit variations in the 2°K line width (predominantly due to inhomogeneities) from one sample to another.[13]

Polarization effects Although in principle linewidth and lineshape measurements should be made in polarized spectra, we have found that in most cases the lineshapes and the linewidths show very little variation from one polarization to another. However, one should determine the polarization effects for each case before using data obtained from unpolarized spectra.

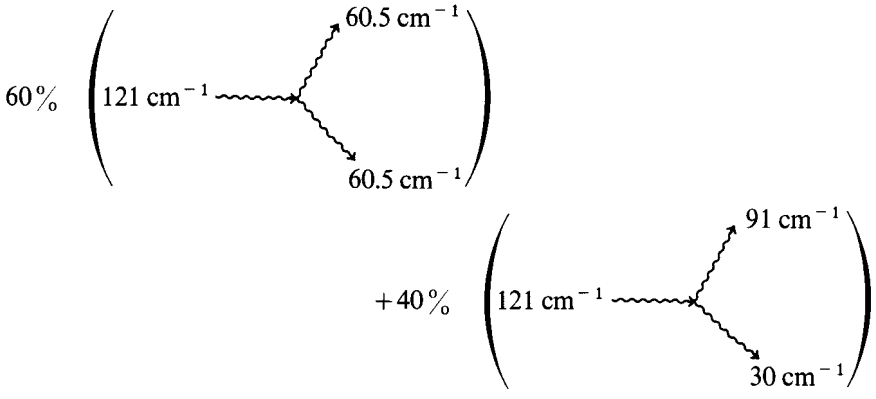
B2. Results of experimental investigation

Phonons Dephasing of Raman-active phonons in several crystals have been investigated in this laboratory. For the cases studied so far,[8,12,14] we find that the dephasing of a phonon transition occurs by a T_1-relaxation mechanism (Eq. (2)) where by the optical phonon exchanges its energy with two other phonons through cubic anharmonic interactions. The line shapes are of the form predicted by Eq. (6). Two crystals will be specifically discussed here. These are naphthalene and *p*-bromochlorobenzene. The low frequency phonons of naphthalene (57 cm^{-1} and 68 cm^{-1} phonons) have 2°K line widths $< 0.05\ cm^{-1}$. This value corresponds to $T_2(=T_1) > 1.06 \times 10^{-10}$ sec which is considerably slower than the usually assumed picosecond values for vibrational relaxations. The temperature dependence of the line width of these low frequency phonons is explained by a combination of the up-conversion and the down conversion processes.[8] For example the temperature dependence of the 57 cm^{-1} phonon is explained by using the following combination[8]



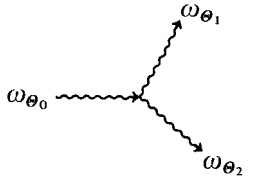
Down Conversion Up Conversion

Here, the up-conversion processes appear to be more efficient than the down conversion processes. The reason may be the increased density of states at higher frequencies which makes the up-conversion more efficient. The phonon density of states[15,16] of naphthalene have peaks around 90 cm^{-1} and 97 cm^{-1}. The high frequency ~ 121 cm^{-1} and 141 cm^{-1} phonons of naphthalene show T_2-relaxations ($= T_1$) which, even at 2°K, are at least an order of magnitude shorter than that for the low frequency phonons. This appears to be a general trend in systems studied so far in our laboratory. The temperature dependence of line width of the 121 cm^{-1} phonon transition is explained by a combination of two types of down conversion processes as presented below



The efficient relaxation in the case of high frequency phonons can be explained by peaks in phonon density of state[15,16] of naphthalene at half frequencies (60.5 cm^{-1} and 70.5 cm^{-1}).

The *p*-bromochlorobenzene crystal is orientationally disordered.[17] Thus, the total line width is derived from scattering due to both disorder and anharmonic interactions. A temperature dependence of the line width of the 26 cm^{-1} (2°K value) phonon of this crystal is shown in Figure 1. The figure also shows the 2°K line shape of this Raman-active phonon transition as well as the theoretically computed line shape using Eq. (6). The agreement between the experimental curve and the theoretical curve is excellent.[12] We attempted to fit the temperature dependence of the line width assuming the T_1-relaxation of Eq. (2) as the contributor of dephasing.[12] In the theoretical computation, temperature dependence of the line width due to T_1-process of the type



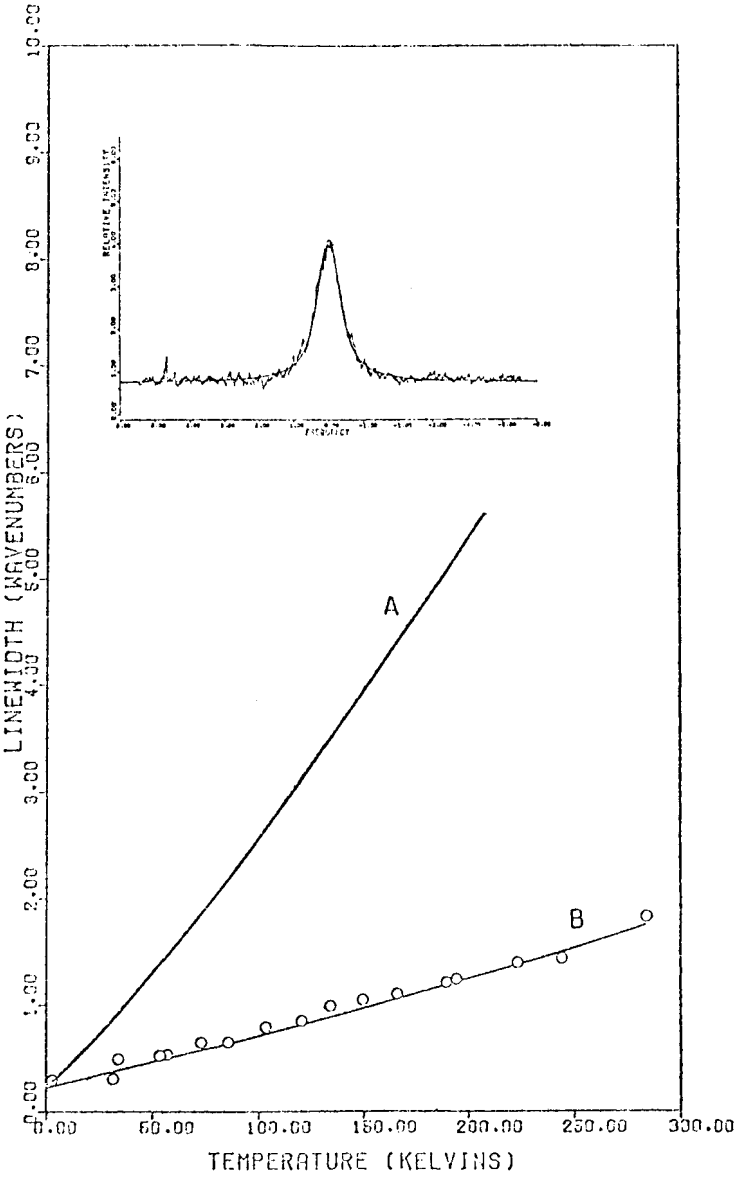


FIGURE 1 For 26 cm^{-1} Raman-active phonon of *p*-bromochlorobenzene, experimentally observed lineshape at 2°K is compared with the theoretically simulated line shape (solid curve). The figure also exhibits temperature dependence of the line width. Experimentally observed data points are represented by circles. Curve A is the theoretically calculated temperature dependence using the observed total width at 2°K as the width due to T_1-relaxation. Curve *B* is the theoretically calculated temperature dependence obtained with v^4 $(T = 0) = 0.05\ cm^{-1}$.

can be reduced to:

$$\nu^A(T) = \nu^A(T = 0)\{1 + \eta_{\theta_1} + \eta_{\theta_2}\}. \tag{14}$$

Furthermore the zero temperature line width $\nu^A(T = 0)$ can be approximated by $\nu^A(T = 2°\text{K})$. This line width determines the slope of the temperature dependence curve. When the observed total width at 2°K is taken as ν^A due to T_1-anharmonic processes, curve A is obtained for $\omega_{\theta_1} = \omega_{\theta_2} = \frac{1}{2}\omega_{\theta_0}$. This curve rises much faster than the one predicted by experimental data. It is found that any combination of ω_{θ_1} and ω_{θ_2} yields a much faster temperature dependence than the one experimentally observed. The higher order processes (quartic) would lead to even a greater temperature dependence. These observations suggest a contribution of disorder to the total line width. In accordance with our theoretical predictions, the lineshape is still close to a Lorentzian (Eq. (6)) even though the contribution due to disorder is present. One can then expect the line width contributions, ν^D due to disorders and ν^A due to anharmonic interactions to be additive. In the calculation we take,[12] $\nu = \nu^D + \nu^A$ with ν^D as an adjustable parameter. We find that when $\nu^D = 0.55\ \text{cm}^{-1}$ (that leaves ν^A at 2°K to be $0.05\ \text{cm}^{-1}$) and we assume ν^D to be independent of temperature, the curve B is obtained again for $\omega_{\theta_1} = \omega_{\theta_2} = \frac{1}{2}\omega_{\theta_0}$. The fit between the experimental data points and the theoretical curve is excellent. Thus, for the lowest frequency Raman active phonon in *p*-bromochlorobenzene, the contribution to 2°K line width is predominantly due to disorder. Yet the line shape is close to a Lorentzian and the linewidth contributions due to disorder and that due to anharmonic interactions are additive.

An analysis of the temperature dependence of phonon frequencies requires the knowledge of the optical Gruenisen parameters γ. This information is available only for the naphthalene crystals. We find that the temperature dependence of the phonon frequencies for the naphthalene crystal is derived predominantly from the thermal expansion of the lattice. Hence, the major contributor to the line width and that to the frequency shift are different.

Internal vibrations Several internal vibrations of the naphthalene crystal have been investigated in our laboratory. The $760\ \text{cm}^{-1}$ interval vibration of naphthalene falls beyond the range of $3\omega_D$. For this mode the internal vibrational density of states is not sufficiently dense to allow a T_1-relaxation involving internal anharmonicity. Furthermore, isotopic mixed crystal technique reveals that this vibration is localized. This vibration has been studied in detail.[13] The temperature dependences of its line shape and line width are shown in Figure 2. The 2°K line shape for this transition is a Gaussian representing an inhomogeneous broadening. At higher temperatures the lineshape is inbetween a Lorentzian and a Gaussian. The data

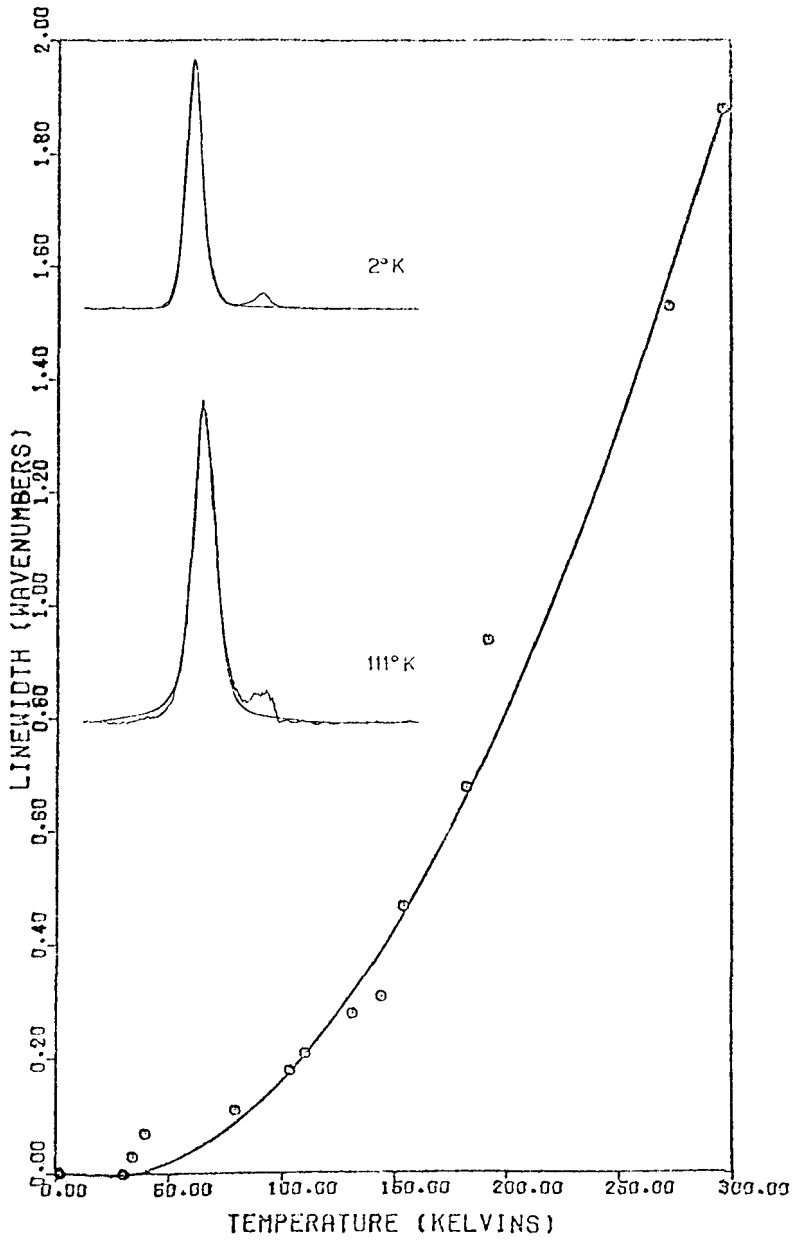


FIGURE 2 Experimentally observed lineshapes for the 764 cm^{-1} Raman active internal vibration of naphthalene at 2°K and 111°K are compared with theoretically simulated lineshapes (solid curves). The figure also shows the temperature dependence of the homogeneous linewidth of this mode. The homogeneous linewidths (v^4) derived from computer simulations are represented by circles. The solid curve is the theoretically calculated temperature dependence using a mixed-mode off-diagonal quartic anharmonic interaction with 140 cm^{-1} phonons.

points represent the homogeneous line width ν^A derived from the computer simulation method described earlier. The temperature dependence of this homogeneous line width is explained by the dephasing mechanism involving a T_2''-process (Eq. (5)) due to an off-diagonal mixed mode quartic anharmonic interaction with 140 cm^{-1} phonons. The theoretical curve obtained with this model is also shown in Figure 2. The observed temperature dependence of the vibrational frequency is explained by a large contribution from thermal expansion and a small contribution of opposite sign from a diagonal quartic interaction with the 140 cm^{-1} phonon.

The 390 cm^{-1} internal vibration of naphthalene is delocalized. It exhibits a factor group splitting of approximately 5 cm^{-1}. For this vibration, exciton-phonon interaction can lead to scattering within the band. We find that the vibrational transition has an asymmetric Lorentzian line shape at 2°K even though the vibration frequency is $>2\omega_D$. This result may indicate the importance of the exciton-phonon scattering. This aspect is currently being further explored in our laboratory. Some limited study has also been conducted on high frequency internal vibrations. The 3062 cm^{-1} C-H stretching Raman active mode of naphthalene has a Lorentzian lineshape even at 2°K. Also this transition is considerably broader than the 390 cm^{-1} mode and the 764 cm^{-1} mode, even though the C-H stretching mode is highly localized. This result indicates a favorable T_1-relaxation due to increased vibrational density of states at higher energies.

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