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THE INFLUENCE OF INITIAL CONDITIONS ON DYNAMICAL PROCESSES IN MOLECULAR SOLIDS

R.M. Hochstrasser
Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, U.S.A.

Résumé - Préparant par voie optique des excitations vibrationnelles dans les solides, nous proposons quelques idées nouvelles pour étudier les effets dynamiques qui en résultent. Nous avons prédit un effet significatif [voir référence 41. La compréhension des différentes contributions à la largeur de raie Raman permet d'obtenir la valeur des temps de relaxation vibrationnelle pour les modes actifs en Raman.

Abstract - Recent ideas on the effects of optical preparation on the dynamics of vibrational excitations in solids are presented. A significant effect is predicted [see reference 41. An understanding of the various contributions to the Raman linewidth in molecular crystals yields values for the vibrational relaxation times of the Raman active modes.

I - INTRODUCTION:

In this report I will summarize some of our recent work on vibrational energy relaxation and pure dephasing in molecular crystals. In particular I will confine my remarks to the case of the benzene crystal.

Our approach to studying vibrational relaxation in crystals has been to use the method of coherent anti-Stokes Raman scattering. In this technique the vibrational states (excitons) of the crystal are excited by two light fields whose frequency difference can drive an oscillating polarizability. This material oscillation may beat with a third field to generate coherent anti-Stokes light. Either the frequency dependence of the generated intensity, or the variation of signal intensity as a result of delaying the third pulse, can be employed to measure the vibrational coherence loss time. There can be many contributions to the coherence loss time but the situation for molecular crystals is greatly simplified as a result of the vibrational energy transfer, or band formation, causing an averaging out of the inhomogeneous distribution of transition frequencies /1-3/. The transitions that are observed are therefore essentially homogeneous and the linewidths or decay times yield interesting molecular properties directly.

Much of our work during the past few years was aimed at defining the various contributions to the Raman linewidth. The 992cm⁻¹, totally symmetric ring stretching mode, has received the most attention. For this mode the four factor group (k=0) levels span 8v=1cm⁻¹, with the A_g (factor group) component at the bottom of the band. The inhomogeneous distribution has a width of D = 0.1 cm⁻¹ as gauged from studies of isotopically mixed crystals /4/. Thus the effective inhomogeneous width /2/ that arises from averaging by exciton motion is (D/8)v³D= 10⁻⁴cm⁻¹. This corresponds to an effective decay halftime of ca. 50ns, but the decay is not exponential and these considerations are just guidelines. In any event, this contribution can be neglected in relation to picosecond timescale relaxation processes.

Another important contribution to the linewidth of vibrational transitions involves isotopic impurities. In recent work we showed that the C₁³ containing molecules in natural benzene crystals have significant effects on the vibrational relaxation rates.
Thus experiments must be carried out using isotopically pure material. So far, the monodeuterobenzene was not removed, but experiments which involved deliberate doping have suggested that the effect of C\textsubscript{6}H\textsubscript{5}D in natural crystals would not be significant. Experiments of this sort and those discussed in the previous paragraph have covered all known possible contributions to the linewidth and lead us to conclude that the effects of intrinsic vibrational energy relaxation can be deduced by this elimination.

II - DESCRIPTION OF THE DOORWAY STATE:

As was shown recently by Velisko and Hochstrasser /5/ the optical excitation of a crystal or a mixed crystal at sufficiently low temperatures yields a rather special initial state. The case of a neat crystal is well-known: The initial state is approximately a k=0 state for which by definition the excitation amplitudes are equal for all molecules. The mixed crystal is a somewhat more complex situation, but the result is the same: The initial state for a given configuration of impurity molecules has equal excitation amplitudes on all host molecules. This result is dependent on there being no dephasing of the initially created excitations and also on there being separated bands. Each of these approximations is discussed briefly below.

The existence of separated bands, as illustrated in Figure 1, implies that

\[ |A\rangle \quad \begin{array}{c|c|c|c|c} \hline \hline \omega_p & \hline \hline \end{array} \quad |B\rangle \quad \begin{array}{c|c|c|c|c|c|c|c} \hline \hline \omega_A & \hline \hline \end{array} \quad 10\rangle \]

Fig. 1 - Separated band pulsed excitation.

the excitation bands of the two components, host A and guest B, are not simultaneously excited by the frequency components of the light pulse of width \( \omega_p \). In order that the bands are not mixed significantly we must have their widths \( \varepsilon_A \) and \( \varepsilon_B \) considerably less than their separation \( \Delta \). In this situation a sufficiently long light pulse (\( \tau_p \gg \Delta / A \)) centered at the frequency \( \omega_A \) will interact in a first approximation only with A-band molecules.

In the separated band limit the full crystal Hamiltonian has eigenstates that are essentially of A and B type and the relaxations of A molecules is governed by the potential

\[ V = V_{AA} + V_{AB} = \sum_{j,k} (|A_j\rangle \langle A_k| + |A_j\rangle \langle A_k| \sum_{\xi_j \xi_k} (\xi_j \langle A_j| \xi_k \langle A_k| + \xi_j \langle A_j| \xi_k \langle A_k|) (\xi_j \langle A_j| \xi_k \langle A_k| + \xi_j \langle A_j| \xi_k \langle A_k|) B_{\xi_j \xi_k}) \]

where \( V_{AA} \) (or \( V_{AB} \)) refer to the coupling of an A molecule at site \( j \) and in some
vibrational state to an A (or B) molecule in some other vibrational state at site \( k \). The indicator functions for A or B occupancy at the \( j \)th site are \( \xi_j \) and \( 1 - \xi_j \), and \( V_{jk} \) is the lattice coordinate dependent intersite potential. The vibrational relaxation occurs through both \( V_{AA} \) and \( V_{AB} \) pathways, with the former corresponding to vibrational energy reorganization amongst A molecules and the latter to trapping of a host vibrational energy by B molecules.

The vibrational energy redistribution occurring in a neat crystal involves relaxation at a single site as well as relaxation which requires the creation of vibrational excitations at different sites. Since the molecules of the lattice are all related by symmetry, it is not possible to distinguish these pathways. However by introducing small amounts of isotopic impurities, it should become possible to distinguish the various relaxation mechanisms.

The state of a crystal at time \( t \), \( |\psi(t)\rangle \), resulting from the ground state, \( |\Phi_0\rangle \), interacting with excited states through the additional potential \( V(t) \) is given by:

\[
|\psi(t)\rangle - |\psi(0)\rangle = \sum_j |\Phi_j\rangle e^{-i\omega_j t} \int_0^t dt' e^{i\omega_j t'} \langle \Phi_j | V(t') | \Phi_0 \rangle
\]

(2)

where \( \omega_j = \omega_{j0} - \omega_0 \), and \( |\Phi_j\rangle \) are the eigenfunctions of the crystal. The additional potential in optical experiments is \(-E(t)\mu\) for linear excitations, \(-E_1(t)E_2(t)\alpha\) for quadratic excitations, and so on. When the Fourier transforms of the fields are introduced, the nature of the prepared state can be written in the familiar form:

\[
|\psi(t)\rangle - |\psi(0)\rangle = \sum_j |\Phi_j\rangle e^{-i\omega_j t} F(\omega_{j0} - \omega^{(n)}) \langle \Phi_j | d_n | \Phi_0 \rangle
\]

(3)

where \( \omega_n \) is the appropriate combination of field frequencies used to drive the system and \( d_1 = \mu \), \( d_2 = \alpha \), \( d_3 = \gamma \), etc., where \( \mu \) is the dipole moment, \( \alpha \) polarizability, \( \gamma \) the hyperpolarizability operator and so on. The quantity \( F(\omega_{j0} - \omega^{(n)}) \) is in general an \( n \)th order convolution of the spectra of the fields. In the linear case this is just the magnitude of the driving field spectrum at the resonance, \( E(\omega_{j0} - \omega) \). In many of our experiments aimed at vibrational relaxation we use a Raman interaction \((d_2)\), in which case:

\[
F(\omega_{j0}) = \int_0^{\infty} d\omega' E_1(\omega') E_2 (\omega_{j0} - \omega^{(2)} - \omega')
\]

(4)

with \( \omega^{(2)} = \omega_1 - \omega_2 \), where \( \omega_1 \) and \( \omega_2 \) are the center frequencies of the two driving fields of a CARS experiment. Equation (3) expresses the fact that a change in the wavefunction occurs only for those transitions for which \( d_n \) and a field frequency component exists.

In experiments with light pulses that persist for times short compared with the dynamical evolution of the system, we can consider that the pulse prepares a state which then evolves under the influence of the system Hamiltonian. The prepared state, or doorway state, for the Raman interaction is:

\[
|S\rangle = a^{(A)} |\Phi_0\rangle F (\omega_A)
\]

(5)

To obtain \( |S\rangle \) we assumed the pulse convolution to have a uniform frequency distribution over the A-band but no frequency components at the B-band such as is the case in CARS experiments. It follows that if each A site has the same matrix element of \( a \), the doorway state is given up to a constant by:

\[
|S\rangle = \sum_j |j\rangle \xi_j
\]

(6)
III - EFFECT OF INITIAL STATE ON RELAXATION:

It was seen above that the doorway state in the first approximation, equation (6) corresponds to one in which the excitation is equal on all host molecules even in the presence of many B molecules within the excitation volume. The energy relaxation of host molecules can now occur through the terms $V_{AA}$ and $V_{AB}$. Obviously the presence of B molecules implies the absence of A molecules in this relevant volume so that $A$ to $A$ transfer is changed by adding $B$. Similarly $A$ to $B$ transfer now depends on the specific topology of the disordered $A$ lattice. This way of looking at energy trapping is somewhat unusual since we are not considering the flow of energy to traps via some wavepacket in the host lattice, but instead that the doorway state collapses into a particular configuration of $B$ molecules. The predicted rate of relaxation is then the average of the rates for many different nearest neighbor configurations. This model predicts a nonmonotonic variation of the rate of trapping as a function of the concentration of $B$ molecules /5/ which is consistent with the preliminary results for relaxation in $C_6H_5/C_6D_6$ mixtures /3,4/.

It is of great interest to consider the effect on relaxation of changes in the nature of the prepared state $|S\rangle$. One of the assumptions in defining $|S\rangle$ is that the dephasing of the excitations is slow compared with the preparation time. Certain general aspects of the other limit where dephasing is rapid compared with the energy relaxation, can be seen without calculation with reference to Figure 2.

![Illustration of phased and dephased trapping processes.](image)

The situation described so far involves `phased trapping' where the final states, $|f\rangle$ corresponding to combinations of internal and external degrees of freedom, are reached directly from a well defined distribution of excitation amplitudes, whose oscillations at each site are exactly predictable.

In the other limit the doorway state decays rapidly into its dephased replica where now the amplitudes on different host sites are random phased, signified by the parameter $a_1$ in Figure 2. Now the energy relaxation is a `dephased trapping' into the set of final states $|f\rangle$. It appears as if the rate of relaxation should be different for these two limits. Furthermore, since dephasing mechanisms involving phonons are temperature dependent, we predict that the energy trapping will also be temperature dependent. Studies of such effects will not be straightforward using coherent spectroscopic methods, because the pure dephasing introduced by increases in temperature also contributes to the Raman linewidth.
It is worth noting that methods of excitation other than optical need not necessarily produce the initial states discussed here. For example, if a vibrational state became populated as a result of a spontaneous relaxation process the subsequent relaxation could begin from quite different states whose character would depend on the mechanism of the relaxation.

IV - VIBRATIONAL RELAXATION RESULTS:

As indicated elsewhere /4/ the vibrational relaxation times of the fundamentals of benzene do not correlate well with the number of available relaxation channels. This has suggested that there are specific mode couplings involved. For example, the coupling of the 991cm⁻¹ C-C stretch with the 854cm⁻¹ C-H out-of-plane bend /6,7/. However the rates generally increase with the total vibrational energy content as summarized in Figure 3.

Fig. 3 - Vibrational relaxation rates of some Raman active modes in benzene. The dashed line is intended to draw the eye to the two regions of behavior of rate versus total vibrational energy. (Data from Ref. [4])

The benzene crystal is sufficiently harmonic that we might expect Δν = ±1 selection rules to determine the relaxation pathways, where Δν indicates changes in both the internal and the external, relative motional, degrees of freedom. If this is correct, then the variations of rate with energy in Figure 3 have an obvious interpretation in terms of the internal anharmonicities of the benzene modes.

The anharmonicity of the benzene vibrations must increase with increasing energy content. Thus it could be considered that at low energy, say less than 1000 cm⁻¹, the modes are essentially harmonic on the relevant timescales of relaxation. In this "restricted access" region the existence of Δν = ±1 possibilities is not sufficient for a rapid relaxation, and a significant coupling must also be sought. In the higher energy, or "free access" region, coupling may occur to many of the levels that are separated by less than one lattice vibrational quantum, as a result of the
molecular anharmonicities becoming significant. At a certain state density still in the region of the fundamentals, the internal harmonic modes might be sufficiently mixed to allow relaxation into many channels while still maintaining the \( \Delta v = 1 \) selection rule for external modes. Internal mode mixing was previously invoked to describe the relaxation of CH modes in liquids /8/ specifically in that case in terms of their coupling to CH bending motions.

It will be interesting to discover by studies of the infrared active modes of benzene whether the trend of Figure 3 is upheld. The basic ideas proposed here might carry over into other types of molecules. Of course significant differences may be expected in the energy at which the anharmonic effects become dominant. For example in larger molecules where there are many lower frequency modes than found for benzene the onset of the free access region may be at quite low total energy. The lowest frequency modes may then be too close to the lattice modes for there to be a significant restricted region. In such cases one may actually observe a minimum in the rates at some intermediate energy where the modes are freed from significant lattice involvement. It is interesting that the trends indicated here for benzene crystals are not remarkably different from those seen for benzene molecules undergoing collisions with isopentane /9/. In that case the excitation of some of the combinations involving \( v_6, v_{16} \) and \( v_1 \) in the electronically excited state yields relaxation times that are not very sensitive to mode type or to total energy content. In fact one could imagine a similar curve drawn through these gas phase data as is drawn as a dashed line in Figure 3. It would be of great interest to have results for ground state relaxation resulting from benzene-benzene collisions, and for liquid benzene.

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References