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Vibronic relaxation in molecular mixed crystals: Pentacene in naphthalene and p-terphenyl

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Picosecond photon echo techniques are used to measure directly vibronic relaxation times in the first excited singlet state of pentacene in naphthalene and p-terphenyl. In regions of low (< 300 cm^{-1}) and high (> 1000 cm^{-1}) vibrational energy, relaxation is fast ($\tau < 2$ ps) due to direct phonon emsssion (low energy) and fast vibrational energy redistribution (high energy). In the intermediate region relaxation times vary drastically. Effects of isotope substitution of guest and host suggest intramolecular relaxation in this region. Changes in local environment are shown to influence the relaxation rate quite drastically, indicating large host-induced anharmonic coupling between different vibrations.

I. INTRODUCTION

In recent years a number of papers have been published reporting measurements of vibrational relaxation times in molecular mixed crystals.[1-4] The results showed the relaxation times to be shorter than a few tens of picoseconds in general. However, no clear picture emerged about the processes that determine the relaxation rates and the pathways through which equilibrium is restored.

Rebane and co-workers,[1] measuring the unrelaxed (hot) fluorescence from vibronic levels of perylene and anthracene in n-hexane, observed an increase in relaxation rate with increasing vibrational energy. They explained these results by an intramolecular relaxation process, the rate of which depends upon the density of final levels. Studies by Voelker and Macfarlane[2] and ourselves,[3] on the other hand, showed no relation between relaxation rate and excess energy. Hochstrasser and Nyi,[4] studying hot fluorescence from azulene in naphthalene, concluded that vibration–vibration energy transfer to the *host* is the dominant relaxation channel in that system.

In this paper, we present the results of a picosecond photon echo study on vibronic transitions of pentacene (PTC) in naphthalene (NT) and p-terphenyl (TP). In order to obtain information about the relaxation mechanism we investigated the effect of deuteration of the guest and host molecules. We focus attention on two questions: (1) Is the initial step in the vibrational relaxation dominated by an intramolecular process or by energy transfer to the host crystal and (2) If it is intramolecular, what is the role of the host crystal? In this respect it is important to mention the recent results of Amirav *et al.*[5] on the relaxation of isolated large molecules (tetracene, pentacene), cooled in a supersonic jet. They observed predominantly unrelaxed fluorescence from levels with less vibrational energy than ≈ 1200 cm^{-1}. This proves that a free molecule as large as pentacene, with 102 vibrations, does not have enough degrees of freedom to act as its own heat bath in the low vibrational energy range

The results presented in this paper suggest that in the systems studied the relaxation is dominated by an intramolecular process. We further show that the local environment of the guest molecule has a drastic effect on the relaxation rate of vibronic levels.

II. EXPERIMENTAL

The phase relaxation times reported in this paper were determined using the accumulated three pulse stimulated echo method.[6] The experimental setup and sample preparation have been described previously.[3] Pentacene-d_{14} was synthesized following the procedure given in Ref. 7. According to the optical spectra, approximately 70% of the pentacene was fully deuterated. Naphthalene-d_8 (Aldrich) was vacuum sublimed and subsequently zone refined (100 passes).

III. RESULTS AND DISCUSSION

In a previous paper,[3] we have shown that at low temperature (1.5 K) pure dephasing processes are negligible on a picosecond time scale. The photon echo decay times therefore are only determined by population relaxation processes ($T_2 = 2T_1$). In Tables I and II, we have summarized the decay times of the vibronic transitions studied. Indicated are the vibrational frequencies relative to the electronic origins found at 16 587.7 cm^{-1} (PTC-h_{14}/NT-h_8), 16 613.4 cm^{-1} (PTC-d_{14}/NT-h_8), 16 589.8 cm^{-1} (PTC-h_{14}/NT-d_8), 17 005.2 cm^{-1} (PTC-h_{14}/TP, site O_3), and 17 064.7 cm^{-1} (PTC-h_{14}/TP, site O_4). (All frequencies in this paper are given in vacuum cm^{-1}.) Relaxation times longer than 2 ps could be measured directly and were, within the error limits, exponential. Relaxation times shorter than 2 ps were obtained from the spectral linewidth with the aid of the tabulated values for the Voigt profile.[8] The width of the Gaussian inhomogeneous distribution was assumed to be equal to the width of the electronic origin (≈ 1 cm^{-1}). The Voigt profile fitted the absorption lines to a good approximation unless otherwise indicated. We studied as many vibronic bands as possible; however, a number of bands did not show enough absorption intensity, even in the most concentrated crystals, to perform an echo experiment.

We now turn to the discussion of the results. Firstly, we consider the relaxation times of a specific

mixed crystal system, e.g. PTC-d_{14}/NT-h_8 for which the most data are available. In Fig. 1, the relaxation times are plotted as a function of vibrational energy. We can distinguish three regions of excess vibrational energy: a low excess energy ($E_v \lesssim 300$ cm^{-1}) region A, characterized by short relaxation times, an intermediate ($300 \lesssim E_v \lesssim 1000$ cm^{-1}) region B with relatively long living levels showing a large variation in relaxation times, and high excess energy ($E_v \gtrsim 1000$ cm^{-1}) region C in which relaxation is fast again. The +522 cm^{-1} transition in region B is a special case and will be discussed below.

The large relaxation rates in region A we explain by direct one or two phonon processes. The acoustic phonon branch extends to ≈ 150 cm^{-1} [9,10] so relaxation may occur by exchange of energy with two lattice phonons, a mechanism proposed by Bellows and Prasad[11] for the decay of librational phonons of naphthalene. Alternatively, these librational host phonons may also be *directly* involved in the relaxation path of the low frequency vibrations. A peculiar feature is the low relaxation rate of the +136 cm^{-1} mode of PTC-h_{14}/NT-d_8 as compared to the protonated host crystal. This could be an indication of an appreciable contribution to the relaxation from the librational phonons since their frequency changes significantly upon deuteration[12] while the acoustic phonons are expected to be less affected.

In region B this direct phonon process becomes less probable due to the larger energy gap. In this "sparse vibrational level" region the relaxation rate depends on the (unknown) structure of background states to which relaxation occurs.

In region C the density of background states becomes so high that it approaches a continuum. In this region, it is no longer justified to consider separate vibrations because mixing with other levels is very strong. This picture is consistent with the broad structured bands observed spectroscopically in this

region. Note that Amirav et al.[5] observed for tetracene in a supersonic jet that there is a strong intramolecular anharmonic mixing of vibrational levels starting at 1000 cm^{-1} excess energy.

We now turn to a more detailed discussion of the relaxation in energy region B and to the question of whether the relaxation in this region occurs via an intramolecular process or via direct energy transfer to the host. Note that both relaxation models are radiationless, implying that eventually all energy is transferred to the lattice. Therefore, we mean by intramolecular relaxation here only the *initial* process of breakup of a prepared vibration into other, lower frequency modes which subsequently can decay via phonon emission (cf. region A). Evidence for the occurrence of vibrational cascading in this system is obtained from the observation of fluorescence from levels other than the pumped ones.[13]

By inspection of the data in Table I that apply to region B, there appears to be a qualitative relation between the variation in relaxation rate and the change in frequency upon deuteration of the guest molecule. As shown in Fig. 2, vibrations that exhibit a larger than

TABLE II. Phase relaxation times at 1.5 K of the vibronic transitions of pentacene in p-terphenyl in the O_3 and O_4 sites.

O_3		O_4	
ν^a (cm^{-1})	$\frac{1}{2} T_2$ (ps)	ν^a (cm^{-1})	$\frac{1}{2} T_2$ (ps)
267.1	2.1 ± 0.5^b	267.8	2 ± 0.5^b
599.4	18 ± 3	599.4	10 ± 1
608.3	19 ± 3	606.9	32 ± 5
746.9	18 ± 3	744.9	31 ± 3

[a]Relative to the 0–0 band.
[b]From photon echo and linewidth measurements.

TABLE I. Phase relaxation times at 1.5 K of the vibronic transitions of pentacene in naphthalene.

PTC-h_{14}/NT-h_8		PTC-d_{14}/NT-h_8		PTC-h_{14}/NT-d_8	
ν^a (cm^{-1})	$\frac{1}{2} T_2$ (ps)	ν^a (cm^{-1})	$\frac{1}{2} T_2$ (ps)	ν^a (cm^{-1})	$\frac{1}{2} T_2$ (ps)
136.7	2.3 ± 0.4^b	131.7	1.5 ± 0.5^c	135.9	7.5 ± 2.5^c
260.4	2.4 ± 0.4^b	252.6	3.7 ± 0.1^b	259.7	3.5 ± 1^c
307.6	19 ± 2	288.7	14 ± 2	307.4	20 ± 2
346.4	8.5 ± 1	314.7	13 ± 1	344.3	14 ± 4
448.5	15 ± 1.5	415.4	30 ± 4	447.4	19 ± 2
521.6	1.5 ± 0.2^c	506.9	1.4 ± 0.2^c	520.3	1.7 ± 0.2^c
596.7	19.5 ± 1.3	574.7	13 ± 1.5	596.4	25 ± 2
609.1	59 ± 3	590.2	15 ± 1.5	608.0	47 ± 4
747.2	33 ± 1.5	715.1	26 ± 2	747.5	27 ± 2
		834	11 ± 2^d		
		960	10 ± 1.5		
		1197			
		1342			
		1367			
		1409	< 2		
		1418			
		1430			

[a]Relative to the 0–0 band.
[b]From linewidth and photon echo experiments.
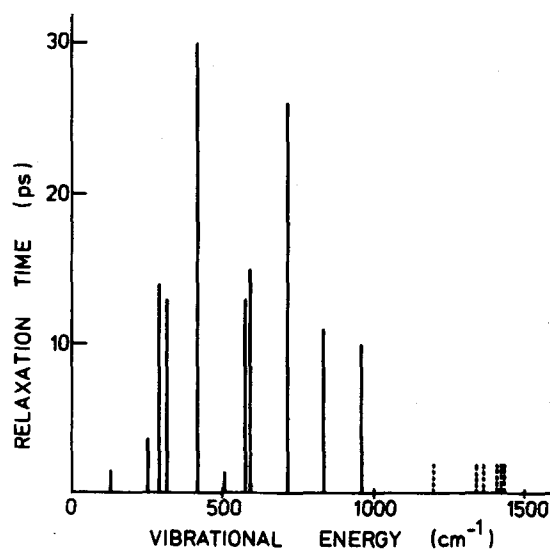[c]From linewidth measurements.
[d]Decay showing the beat pattern.

FIG. 1. Relaxation times ($\frac{1}{2} T_2$) of PTC-d_{14}/NT-h_8 at 1.5 K as a function of vibrational energy. Dashed lines indicate an upper limit to the relaxation times.
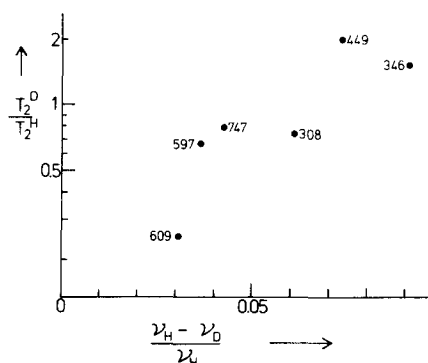
FIG. 2. Ratio of the relaxation times at 1.5 K of several vibronic bands in PTC-h_{14}/NT-h_8 (T_2^H) and PTC-d_{14}/NT-h_8(T_2^D) plotted as a function of the relative frequency shift upon deuteration. Indicated at each point are the vibrational frequencies (in cm^{-1}) of PTC-h_{14}/NT-h_8.

average *reduction* in frequency show a *decrease* in relaxation rate and *vice versa*. This behavior can be explained if we assume predominantly intramolecular relaxation. In this picture the relaxation occurs via phonon induced anharmonic interactions between different vibrational modes. We assume that a given level is coupled to a number of others, implying occurrence of branching. The relaxation rate of a state depends on the number of levels to which relaxation can occur as well as the coupling strengths. The deuteration effect of Fig. 2 then can originate from the fact that a vibration that shows a larger than average frequency shift upon deuteration loses some of its relaxation channels, since a number of possible accepting states are now at a higher frequency. This description is to some extent analogous to that of relaxation processes whose rates are governed by the density of background states (Fermi golden rule). The difference is, however, that in our model we consider a phonon assisted process. Therefore, all levels within ≈ 150 cm^{-1} (a typical value for the Debye frequency) can be involved. We also should keep in mind that we are still in the sparse level region.

We can roughly estimate the number of vibrational levels below a given frequency by extrapolating data from benzene, naphthalene, and anthracene to pentacene. From the former three molecules experimental data and calculations on the frequencies of the normal vibrations[14,15] are available. We then find for pentacene the following estimates for the total number of modes (including overtones): ≈ 25 ($E < 300$ cm^{-1}), ≈ 50 ($E < 500$ cm^{-1}), and ≈ 100 ($E < 700$ cm^{-1}). In view of these numbers, the above mentioned branching seems feasible.

Information can also be obtained by comparing the effects of deuteration on guest and host (Table I). If the relaxation is mostly intramolecular, we expect a large influence of guest deuteration, since the entire vibronic structure changes, while effects of host deuteration are expected to be minor. From Table I it is clear that deuteration of guest *and* host both have a quite drastic effect. However, the effect of host deuteration amounts only to a $\approx 20\%$ change in relaxation rate, while guest deuteration induces changes of this

quantity with as much as a factor of 4. This once more indicates a large contribution from the intramolecular process. The role of the host in this picture is the furnishing of phonons to make up the energy difference between initial and final states and the inducing of anharmonic interactions between the guest vibrational modes.

This induced anharmonicity could explain the influence of host deuteration. The unit cells of naphthalene-h_8 and -d_8 have slightly different dimensions.[16,17] Therefore, the distortion of the guest molecule will also be different (especially with respect to the C–H bonds which are expected to be influenced most). This changes the relaxation rates, since a distortion of a given part of the molecule will mix the normal modes that contribute appreciably to the motion of those atoms. It is noteworthy that the frequencies of all vibrations, except the 747 cm^{-1}, decrease upon deuteration of the host (Table I), indicating a decreasing influence of the host crystal. This correlates qualitatively with the observation of a decrease in relaxation rates of all vibronic levels, except those at +609 and +747 cm^{-1}. We can therefore tentatively conclude that the effect of host deuteration on the relaxation arises from a host induced change in anharmonic interactions. The +609 cm^{-1} band forms an exception to the correlation mentioned above. We have to realize, however, that this band has an extremely low relaxation rate (in NT-h_8) and is therefore expected to be very sensitive to small variations in interaction, while the above reasoning is only roughly, indicating a trend.

The influence of the crystalline environment on vibrational relaxation is demonstrated more clearly by the results on pentacene in p-terphenyl (Table II). Here the differences between the two sites O_3 and O_4 are appreciable, while the vibrational frequencies are approximately equal. Furthermore, the host phonon branches and host vibron frequencies are of course identical for both sites. The results therefore indicate a strong medium induced anharmonicity of the guest vibrations.

In region B there is one vibronic band (+522 cm^{-1}) that does not fit the overall picture because of its short lifetime. We can explain this feature by assigning this band as the overtone of the +260 cm^{-1} mode assuming a slightly anharmonic potential energy well. The shortening of the relaxation time when more quanta are excited is roughly in agreement with the theory of Fisher[18] for a harmonic molecule subjected to a linear coupling with a phonon bath. He predicts a linear increase in relaxation rate with the number of quanta excited.

A final point to be mentioned is the nonexponential decay of the +834 cm^{-1} band of PTC-d_{14}/NT-h_8 as shown in Fig. 3. This quantum beat arises from the splitting in the absorption spectrum, also shown in Fig. 3. From the 14 ps period we calculate an energy spacing of 2.4 cm^{-1}, in good agreement with the observed 2.2 cm^{-1} splitting. Of course, no new physical information is obtained from the oscillatory pattern, since the splitting can, in this case, be observed directly in the spectrum. On the other hand, it reflects once more the *coherent* excitation of a large part of the inhomo-
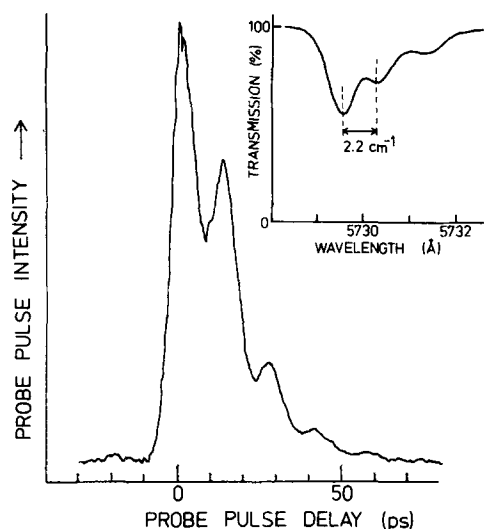
FIG. 3. Decay curve of the accumulated 3PSE on the +834 cm^{-1} band of PTC-d_{14}/NT-h_8. The absorption spectrum of this band is shown in the insert.

geneous distribution. This is remarkable in view of the 2.1 cm^{-1} spectral width (FWHM) of the laser.

IV. CONCLUSIONS

In the systems studied the vibrational relaxation is very fast ($\tau \lesssim 2$ ps) for low frequency modes, where direct phonon emission is possible, and for high frequency transistions where strong anharmonic mixing is present. In the intermediate region the relaxation rate is lower and varies drastically with vibrational frequency in a seemingly random fashion.

The effects of isotope substitution of guest and host molecules indicate a large intramolecular contribution to the relaxation process and a strong matrix-induced anharmonicity.

The results presented in this paper further show that the photon echo method can be successfully applied to the study of fast vibrational relaxation in the excited electronic state of large molecules. In this respect it complements the time resolved Raman techniques applied, e.g., by Laubereau and Kaiser[19] to study ground state vibrational relaxation.

Information about the relaxation path cannot be obtained by measuring relaxation times only. For that purpose it should be fruitful to combine measurements of relaxation times with hot fluorescence studies. It seems advantageous, however, to choose a system which has fewer internal degrees of freedom. Also, knowledge of the fundamental vibrational frequencies should be very helpful.

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