PICOSECOND DEPHASING AND RELAXATION IN VIBRONIC STATES
OF MOLECULES IN THE CONDENSED PHASE

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We demonstrate that picosecond photon-echo and absorption-recovery experiments can be used to determine the elastic and inelastic scattering contribution to the relaxation of vibronic transitions in molecules in solids. For pentacene in naphthalene we find that, up to 14 K, dephasing is only determined by vibrational relaxation. The observed exponential activation of this process is interpreted as a decay of the initial level, via a resonant phonon, into other molecular vibrations.

In recent years, considerable progress has been made in the study of optical dephasing in purely electronic transitions (zero-phonon lines) of molecules in the condensed phase. In a number of mixed crystal systems [1-3] it was found that at low temperature (ca. 1.5 K) the inelastic ($T_e$) scattering completely dominated the elastic ($T_g$) scattering contribution to the dephasing time ($T_2$) where $T_2^{-1} = (T_g^0)^{-1} + (2T_e)^{-1}$. At higher temperature (ca. 10 K) the reverse situation occurs and the homogeneous linewidth ($\delta_T$) is determined by elastic scattering. For vibronic transitions of molecules in the condensed phase, the importance of elastic and inelastic scattering to relaxation and the effect of temperature on these processes has not yet been assessed in a single case. The unraveling of these effects however is quite important if more is to be learned about the dynamics of vibronically excited states in molecular solids. Upper limits on some excited-state vibrational lifetimes ($T_1$) have recently been obtained from hot-band spectra [4] and photochemical hole-burning experiments [5,6]. From these experiments it is clear that picosecond techniques must be used to time-resolve the relaxation processes. We have recently shown [7] that picosecond photon echoes may be used to study ultra-fast optical dephasing processes.

In this letter we show that a combined picosecond photon-echo and absorption-recovery study leads, for the first time, to a determination of the elastic and inelastic scattering contribution to vibronic relaxation.

We have chosen to study vibronic relaxation in the $1B_{2u} - 1A_{1g}$ transition of pentacene in naphthalene. The optical absorption spectrum of this mixed crystal system, in the region of interest, is shown in fig. 1. The electronic origin, which is by far the most intense line in the spectrum, is located at 6026.8 Å [8,9]. The studied vibronic transitions at 261 and 748 cm$^{-1}$ above the origin are indicated in the spectrum. The origin has a linewidth of 1 cm$^{-1}$ at 1.3 K, which can almost entirely be attributed to inhomogeneous broadening, as the fluorescence lifetime is $19.5 \pm 1$ ns. The widths of the 261 and 748 cm$^{-1}$ bands are 2.1 and

![Absorption Spectrum](image)

Fig. 1. Absorption spectrum of pentacene in naphthalene at 1.3 K. The light was polarized along the naphthalene $b$-axis.
0.8 cm⁻¹ respectively, so the first appears to be partly homogeneously broadened.

The apparatus for measuring the absorption recovery is similar to that described by Ippen et al. [10]. In our experiments the entire intensity-stabilized [11] pulse train from a synchronously pumped Rh 6G dye laser is used.

Details about the generation and amplification of the pulses needed in the photon-echo experiments have been published previously [7]. Essential to the experiments reported here is the fact that the echo is generated using two non-collinear excitation pulses, which leads to a spatially separated echo [12], as shown in Fig. 2.

The echo is then time-resolved by optical mixing with a probe pulse and the upconverted signal is detected [7]. This configuration gives an excellent rejection of stray light even at the shortest pulse separations (25 ps), which enables us to measure echo decay times down to 10 ps! By giving the probe pulse twice the delay of the second excitation pulse, synchronization of probe pulse and echo is maintained and the photon-echo decay curve can be measured.

We now turn to the experimental results. A typical result from an absorption-recovery experiment on the 5767 Å vibronic band is shown in Fig. 3a. Also plotted in the figure is the autocorrelation of the pulses showing a width of 19 ps, which corresponds to a 13 ps gaussian pulse or a 10 ps single-sided exponential. These long pulses were intentionally generated by limiting the bandwidth of the laser to approximately the absorption linewidth. This is essential, for with shorter pulses too little absorption from the probe beam takes place for reliable (experimental) results. The pulse shape is not exactly known so only that part of the transient was analyzed in which correlation effects between pump and probe pulse [10] are negligible. At 1.3 K fitting of the decay to an exponent yields a relaxation time of 32 ± 2 ps. Not shown in the figure is the background on which the transient signal is superimposed. The lifetimes of the singlet and triplet state are longer than the repetition time of the experiment (12 ns) so the system has no time to equilibrate. This results in the observed background. A noticeable feature is the complete absorption recovery after ca. 150 ps. In view of the abovementioned bottlenecks this cannot be caused by complete relaxation of the system. We therefore conclude that in the excited state appreciable absorption occurs at the probe wavelength.

A pump-probe experiment was also performed on the 261 cm⁻¹ vibronic band, now using shorter pulses (autocorrelation width 4.3 ps). The measured relaxation time is 2.8 ± 1 ps. From the spectral bandwidth, assuming a 1 cm⁻¹ gaussian inhomogeneous contribution, we calculate with the tabulated values of the Voigt profile [13], a homogeneous lorentzian component of 1.6 cm⁻¹, corresponding to a 3.3 ps lifetime. We can thus conclude that the homogeneous width of this transition is completely determined by the population relaxation time. For pentacene in p-terphenyl we found for the corresponding vibrations relaxation times of 15 ± 4 ps (747 cm⁻¹) and 2 ± 1 ps (267 cm⁻¹).
Note that this last value is two orders of magnitude shorter than an earlier published one [14].

We now turn to the photon-echo measurements performed on the longest living vibronic state: the 748 cm\(^{-1}\) band of pentacene in naphthalene. A typical echo decay curve is shown in fig. 3b. The echo decay time at 1.3 K is \(33 \pm 1.5\) ps, so \(T_2 = 66 \pm 3\) ps, corresponding to a homogeneous linewidth \((\pi T_2)^{-1}\) of 0.16 cm\(^{-1}\). From the fact that, at low temperature, the echo decay time is identical to the population relaxation time, we conclude that pure dephasing processes (at this temperature) are negligible. At higher temperature the echo decay time shortens, as shown in fig. 4. The solid line in this figure is a best fit to the photon echo results with

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T_2^{-1}(T) = (\Delta T_0)^{-1} + T_{\infty}^{-1} \exp(-\Delta E/kT) ,
\]

whereby \(\Delta E = 16.6 \pm 1.5\) cm\(^{-1}\), \(T_{\infty} = 5.4 \pm 1.5\) ps and \(T_0 = 33\) ps. To determine the inelastic contribution to the dephasing process we measured the absorption recovery times as a function of temperature and the results are also given in fig. 4.

Several conclusions can be drawn. Firstly the results show that there is no difference between the relaxation times measured in the photon-echo and in the absorption-recovery experiments at any temperature. So up to 14 K pure dephasing processes are negligible.

Secondly the fact that the relaxation times are equal also indicates that only interactions in the excited state cause the photon-echo decay. For the photon echo is sensitive to fluctuations in both the ground and the excited state while in the absorption recovery only excited-state relaxations play a role. Thirdly the data can be well described by an exponential activation of \(T_2(T)\) over the whole temperature range. We note here that the data do not fit a \(T^7\) behaviour for \(T_2(T)\) as would be expected if Raman type processes involving acoustic phonons were active.

Several theories have been developed to describe the temperature dependence of \(T_2\), as recently discussed by de Bree and Wiersma [15]. The observed exponential activation can be explained, as we do, in terms of scattering to a phonon state localized at the impurity site [1,15]. A peaked structure in the electron-phonon coupling can also give an exponential activation [16] and on the basis of the available data we cannot exclude this latter mechanism.

An interesting point to note is that comparison between the vibronic and the purely electronic transition [17] shows that the same scattering process is involved in both states, since the same activation energy and only a small difference in pre-exponential constant was found. Surprisingly however, in the electronic origin it induces a pure phase relaxation while in the vibronic state it results in population relaxation. For the vibronic state this means that once the system is in the phonon state, it couples so strongly with other levels that it has only a small chance of returning to the originally prepared state. The states to which relaxation occurs can be of two types: (1) other vibrations of the pentacene molecule which, via internal conversion, can decay fast, in a phonon-assisted process, to the vibrationless electronic state; (2) vibrational states of the naphthalene host. Hochstrasser and Nyi [18] conclude from hot-band emission intensities that the last process is dominant in the azulene/naphthalene system. Preliminary measurements of the fluorescence intensity as a function of temperature with the laser tuned to the vibronic transition indicate that in the pentacene/naphthalene system internal conversion plays an important role; however a small contribution from photon-induced relaxation into host levels cannot be excluded.

Summarizing we have shown that picosecond...
photon-echo combined with absorption-recovery experiments can give detailed information on ultra-fast elastic and inelastic scattering processes that occur in vibronic states of molecules in the condensed phase. Our experiments show that at low temperature the vibronic homogeneous lineshape is completely determined by vibrational relaxation, as assumed in the interpretation of a recent photochemical hole-burning experiment [6]. The observed exponentially activated process of vibrational relaxation poses some interesting questions on the interplay between the molecular and crystal modes in inducing vibrational relaxation in electronically excited states.

Finally the picosecond photon echo as a probe of vibronic dephasing complements the coherent anti-Stokes Raman technique [19,20] developed for the study of vibrational dephasing in the electronic ground-state.

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Note added in proof

Additional support for the vibrational relaxation model proposed in this paper was recently obtained from temperature dependent picosecond three-pulse stimulated photon echo (3PSE) decay measurements on the 5767 Å band of pentacene in naphthalene. Up to 13 K it was found that the initial decay of the 3PSE was identical to that of the two-pulse echo, which shows that the loss of excited state population proceeds via two channels, one of which is phonon assisted. We further wish to note that in addition to a fast (≤32 ps) decay, the 3PSE also exhibits a long (most likely 19.5 ns) decay component. The origin of this echo will be described in a forthcoming paper and is related to the one recently reported by us [21].

References