

Picosecond-Duration Vibrational Relaxation Kinetics in the Excited S_1 State of Perylene and Anthracene Molecules

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We present and discuss the results of a direct observation of the picosecond range temporal behavior of vibronic lines in the luminescence spectrum of the matrix-isolated perylene and anthracene molecules. A novel subtractive dispersion mount of monochromators in conjunction with the synchroscan streak camera has been used. From spectrochronograms measured at different excitation wavelengths the vibrational energy relaxation times have been obtained. These are in the range of 20–30 ps and are most probably determined by the existence of the phonon bath of the matrix. A comparison of the measured relaxation constants with those estimated from the steady-state hot luminescence spectrum has been made.

INTRODUCTION

This paper is concerned with a study of vibrational relaxation in the S_1 electronic state of perylene and anthracene in solid matrices at liquid He temperature by means of a novel direct method of picosecond spectrochronography.^{1,2} The study is based on the steady-state hot luminescence (HL) research of the energy relaxation processes in impurity molecules³ (see also the latest review⁴) and serves as a further development of it. The questions of primary interest for us here are (i) how the absorbed energy is transferred within the molecule, (ii) which is the role of the solute and solvent thermal bath, and (iii) which is the precision of HL method for investigating vibrational relaxation processes.

As for the selection of the samples we rely on the following arguments. Anthracene and perylene molecules are spectroscopically (HL measurements included⁵) very well investigated model systems, they are widely believed to have just the right size for the ultrafast vibrational relaxation to take place owing to the intramolecular thermal bath, and recently some data have been available in literature, concerning the decay of laser-excited single vibronic level fluorescence of these molecules in isolated ultracold conditions.⁶

EXPERIMENTAL

Method Among other possible methods of studying vibrational relaxation processes in a multilevel emitting system, after a well-specified preparation of the initial state with a short light pulse, the method in which the spontaneous rise/decay-behavior of different spectral components is observed in time, seems to be a most direct and unambiguous one. If the emission occurs during energetic relaxation in an excited electronic state in condensed matter, it is HL. This approach, based on the detection of spontaneous emission and therefore dispensing with strong excitation as most nonlinear methods, has some evident advantages in case of very complicated and large molecules and molecular systems with liability to photodecomposition. According to Ref. 1, if the product of the used spectral and temporal resolutions, $\Delta\omega \cdot \Delta t$, approaches its transform-limited value, we record a quantity termed a "spectrochronogram." It can be shown⁷ that in the optical domain, where a measurement inevitably provides only partial information on the light waveform, the best one can do to determine all the essential features of nonstationary light emission is to measure spectrochronograms with appropriate shapes of the resolution cell in the ωt -plane.

Apparatus It is no easy and unambiguous task to work out an optimal key scheme and to choose the set of equipment to create an apparatus, which would enable one to resolve with a sufficient sensitivity the area in the ωt plane, approaching as near as possible the minimum value of $\Delta\omega \Delta t \approx 1$. The picosecond spectrochronograph used in this work (Figure 1) is based on a combination of a "Spectra Physics" mode-locked cw oxazine 1 dye laser (tuning range 685-

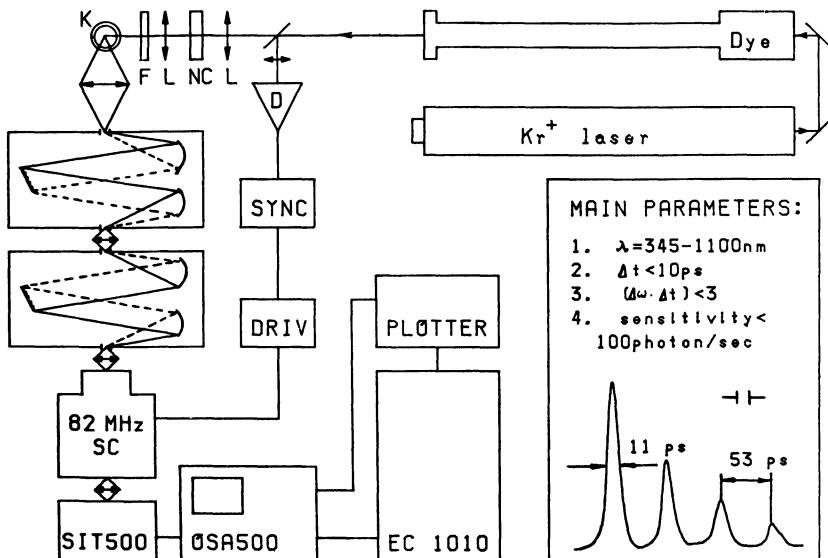


FIGURE 1 Picosecond spectrochronograph for studying time-resolved emission spectra with uncertainty-principle-limited resolutions. L, lens; NC, nonlinear crystal for second harmonic generation; F, filter; K, cryostat with samples immersed in liquid He; SC, synchroscan streak camera with a UMJ-93 image converter tube (multihalide photocathode, temporal resolution 2 ps); D, photodiode; SYNC, synchronization unit; DRIV, streak camera driver. As a spectrally resolving instrument a subtractive dispersion mount of two 40 cm-focal length high-luminosity (1:2.5) single-grating monochromators MDR-2 is used. The dispersion of MDR-2 with a 1200 grooves/mm grating is 2 nm/mm. On the right the current best parameters of the spectrochronograph and the time axis calibration picture, obtained by the laser beam passage through the Fabry-Perot interferometer (integration time $\sim 1\text{ s}$) showing fine temporal resolution, are displayed. FWHM of streak camera response in the static (without streaking) mode is also indicated.

805 nm, pulse duration 3 ps, average power up to 200 mw), synchronously pumped with 82 MHz by a krypton-ion laser, a double-grating spectrometer, and a streak camera. A subtractive dispersion mount of the spectrometer is used to narrow its pulse response with preserved luminosity up to the transform-limited value.⁸ An angle-tuned LiIO₃ frequency doubler enables an excitation with $\leq 1\%$ efficiency in the near UV 345–400 nm region. For data recording and processing a EC 1010-computer-controlled B&M Spektronik OSA 500 optical multichannel analyzer with a SIT vidicon is used.

Instead of commonly-used pulsed deflection of streak camera a continuous streaking in synchronism with the dye laser operation⁹⁻¹¹ is employed. We are convinced that at the current technical level this set-up enables a high quality of a set of important parameters (see Figure 1).

As far as the sensitivity of the system is one of the most critical parameters for the purposes of this work, some further comments are needed. The spectrochronograph unit signal level corresponds at best to ≈ 100 photons on the streak camera photocathode, depending severely on the specific tube characteristics. Owing to a relatively high noise level of the tube used in this work we cooled the photocathode with the liquid nitrogen vapour. As a result the average noise level was reduced nearly tenfold. Unfortunately, the sparse but high-amplitude noise component (probably due to the contaminant alkali ions) remains almost unchanged. Due to the lag phenomenon in the vidicon it finally causes a bad signal-to-noise ratio, which cannot be substantially improved by a long-term averaging procedure.

Samples Aromatic compounds were zone-refined, and *n*-heptane distilled. Species were prepared as a mixed crystal of anthracene in fluorene (concentration $\leq 10^{-5}$ M/l) and frozen solutions of anthracene ($\approx 10^{-3}$ M/l) and perylene ($\approx 10^{-4}$ M/l) in *n*-heptane. In the case of frozen solutions with high solute concentration (used to gain the signal) steady-state spectra were also measured to ensure the lack of the influence of associates and other adverse effects.

RESULTS

Perylene

It is convenient to start with the reproduction (see also Ref. 1) of the three-dimensional spectrochronogram of the resonant secondary emission (RSE) of perylene molecules in the *n*-heptane matrix at 4.2 K under excitation to the level $\nu_9 + \nu_7$, which is by ~ 2800 cm⁻¹ higher than the 0-0 transition energy (Figure 2). To the right from the change of the intensity scale four slowly-decaying (with 5-6 ns time constant) ordinary (i.e., vibrationally relaxed) luminescence (OL) lines are seen. On the left one can observe four short-living HL lines arising due to the radiative transitions from the excited levels of two

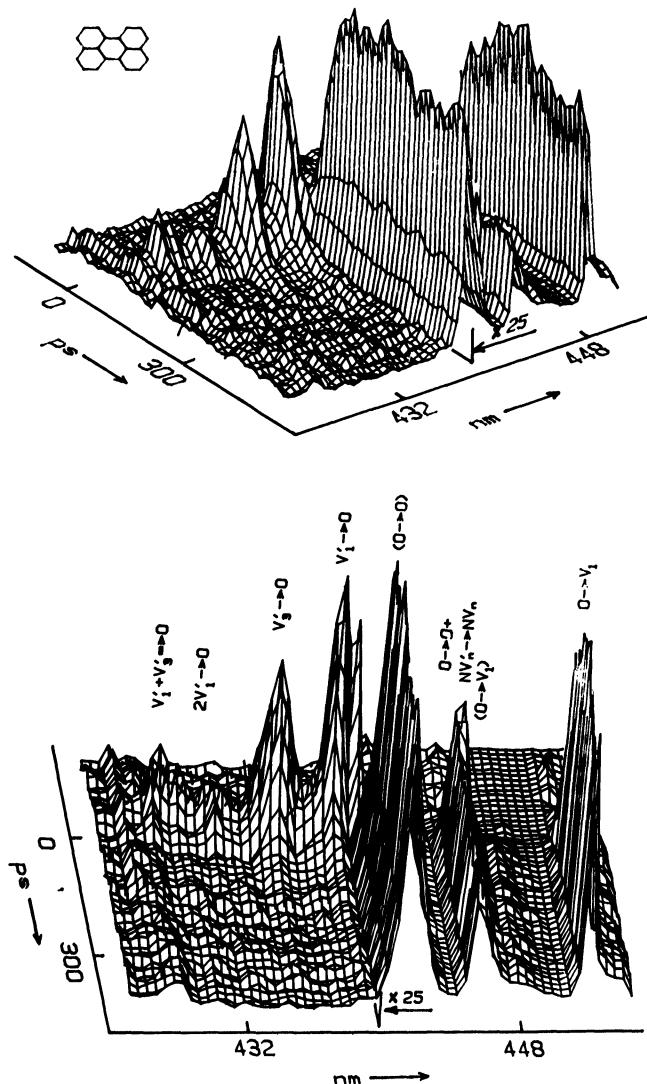


FIGURE 2 Two views of the spectrochronogram of the fluorescence of perylene molecules (near 0-0 transition region) in the *n*-heptane matrix at 4.2 K. The spectral width of the intermediate slit is 31 cm^{-1} . At $t=0$ an excitation by tightly-focused nearly transform-limited (3 ps long and 5 cm^{-1} spectrally wide) frequency-doubled laser pulses (average power density $6\text{--}30\text{ W/cm}^2$) at $\lambda = 393.8\text{ nm}$ populate a selected high-lying intramolecular vibrational level of S_1 manifold.

lowest totally symmetric vibrational modes of the perylene molecule populated in the course of the excitation energy relaxation process in S_1 state. The transitions are assigned by indicating the initial and final vibrational levels in the excited and ground electronic states, respectively.[†]

In addition to a broad quasi-continuous distribution of guest molecules in the Shpolskii systems^{12,13} there ordinarily exist also some distinct groups of inhomogeneous centers, having on the whole similar spectra but different transition frequencies. In the present case one can see two series of OL lines, which correspond to two—"red" and "blue" (marked with brackets in Figure 2)—types of perylene guests. All HL lines belong to the "red" centers which have considerably higher density as is evident from the comparison of the $0 \rightarrow \nu_1$ vibronic line intensities (the 0-0-line of the "red" centers is suppressed by reabsorption).

The decay times of the hot lines obtained by the one-exponential least-squares fit of experimental curves with allowance made for the temporal response function of the spectrochronograph are gathered in Table I. The computer treatment consists also in data correction owing to the changes in sensitivity as a function of the position (time) in the streak camera tube and vidicon.

TABLE I
Lifetimes τ (ps) for the lowest vibronic levels in S_1 state of perylene molecules in *n*-heptane at 4.2 K

Vibrational energy (cm^{-1})	Assignment to vibrational modes	τ (this work)	τ (Ref. 5)
1580	ν'_9		10 ± 3
1380	ν'_8		5 ± 2
1300	ν'_7		14 ± 3
900	$\nu'_1 + \nu'_3$	15.7 ± 2.5	
710	$2\nu'_1$	21.0 ± 1.4	
550	ν'_3	26.0 ± 2.2	
360	ν'_1	25.0 ± 0.5	35 ± 5

[†] As to the assignment, one has to bear in mind that depending on the experimental conditions and the difference of vibrational frequencies in the actual electronic states, the $N\nu'_n \rightarrow (N-1)\nu_n$ -type transitions can overlap with the transitions $\nu'_n \rightarrow 0$ and the $N\nu'_a \rightarrow N\nu_b$ -type ones with $\nu_a \rightarrow \nu_b$. Other combinations in the complex organic molecules with small Stokes losses are less probable.

Anthracene

N-heptane host In this case we have succeeded in tuning the excitation almost over the whole $S_0 \rightarrow S_1$ absorption band and monitoring the relaxation of different amounts of excess vibrational energy at selective excitation. In Figure 3 the spectrochronogram of anthracene molecules at the excitation to the 1400 cm^{-1} vibrational Franck-Condon level is shown. As a whole the picture is similar to that of perylene. The only remarkable differences are that HL lines are even weaker than in the previous case, and the inhomogeneous distribution of centers is essentially broader due to an extremely high guest concentration. A varying of excitation to the higher energy side causes only small changes in this picture.

In Figure 4 the time axis cuts of the spectrochronogram at the $0-0$, $\nu'_1 \rightarrow 0$, and $\nu'_0 \rightarrow \nu_4$ transition wavelengths are given. As one can see, their shapes are quite complicated. In the case of curve A this is due to the overlapping of the rapidly decaying $N\nu'_n \rightarrow N\nu_n$ -type hot transitions to the $0-0$ one as intramolecular vibrational quanta of aromatics differ only slightly in S_0 and S_1 electronic states. In other cases the reason is the weak OL contribution from the inhomogeneous centers. As the tip on $0-0$ line gives information about the decay of all (in the selected cases single) actual vibrational levels, it is worth full attention. The same peculiarity was observed in case of matrix-isolated perylene¹ and, probably, of tetracene.¹⁴ An analogous feature is expected also on top of the $0 \rightarrow \nu_n$ OL lines (see the discussion on the Franck-Condon factors of anthracene in Ref. 15), but this has not been confirmed by experiment.[†]

Fluorene host For comparison analogous measurements were performed in a mixed crystal — anthracene in fluorene. Two excitation frequencies were used, corresponding to the excitation up to the $2 \times \nu'_1 \approx 780\text{ cm}^{-1}$ and $\nu'_7 \approx 1500\text{ cm}^{-1}$ vibrational Franck-Condon levels. As was expected in the first case (Figure 5a), only one HL line ($\nu'_1 \rightarrow 0$) is detected. In the second case (for steady state HL spectrum at this excitation see Ref. 5) one additional HL line ($\nu'_6 \rightarrow 0$) is seen (Figure 5b).

[†] Let us note that this peculiar time profile of $0-0$ line can serve as a good indicator for unambiguous assignment, which is very useful when broad inhomogeneous spectra are investigated.

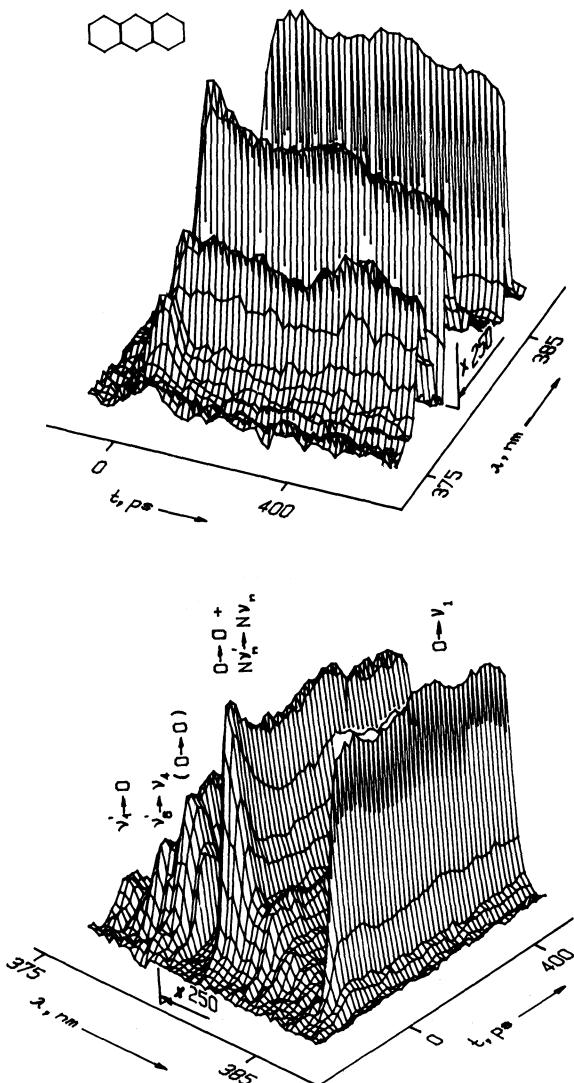


FIGURE 3 Two views of the spectrochronogram of the fluorescence of anthracene molecules in the *n*-heptane matrix at 4.2 K. Excitation wavelength is 362.5 nm (or $0-0 + 1400 \text{ cm}^{-1}$). The spectral width of the intermediate slit is 22 cm^{-1} to the lower energy side and 64 cm^{-1} to the higher energy side from the change of the intensity scale. The intensity scale is not corrected on the apparatus sensitivity.

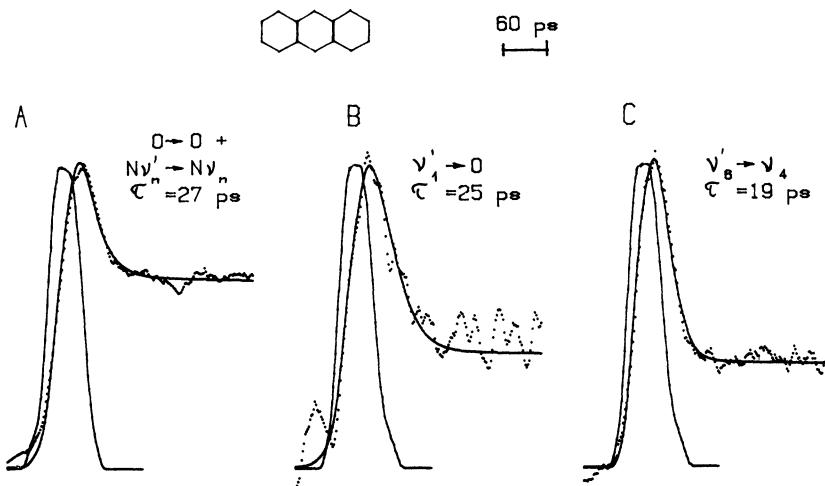


FIGURE 4 The time axis cuts of the spectrochronogram shown in Figure 3 at $\lambda \approx 382 \text{ nm}$ (a), $\lambda \approx 375 \text{ nm}$ (b), and $\lambda \approx 377 \text{ nm}$ (c) (the intensity scale is not preserved). Solid lines represent the least-squares fit of the dotted experimental curves. The temporal response function of the spectrochronograph, indicating the zero time point, is also shown. The given lifetimes are averaged over a number of measurements. Note the substantial part of slow OL resulting from inhomogeneous centers at each wavelength.

All the derived relaxation constants concerning anthracene are gathered in Table II (constants for $\nu'_1 \rightarrow 0$ and $\nu'_6 \rightarrow \nu_4$ transitions under different excitation conditions coincide within experimental error). Note that in case of fluorene host we had used a two-exponential approximation with nearly equal rise and decay times. Yet the precision of the data in Table II leaves room for improvement because of a rather low signal and poor signal-to-noise ratio.

DISCUSSION

Vibrational energy relaxation in matrix-isolated molecules

In monitoring the molecular HL we follow in fact the population decay of the corresponding Franck-Condon levels. The emission decays with the rate, which is the sum of the rates of the radiative,

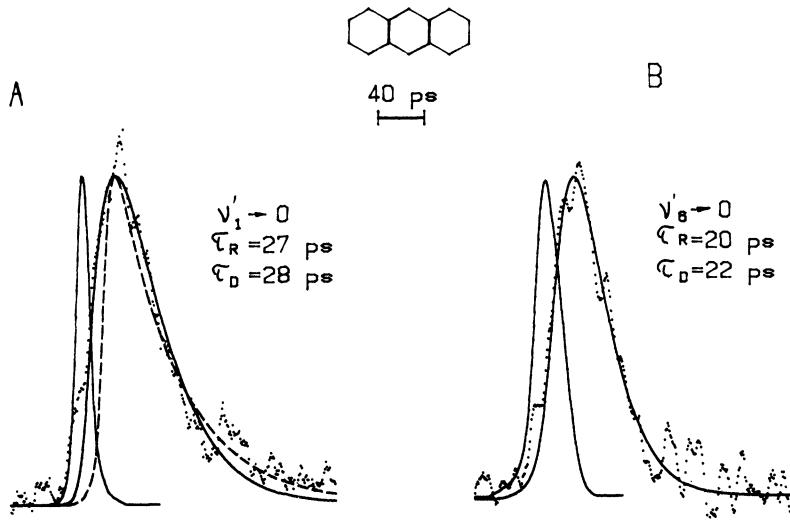


FIGURE 5 The time axis cuts of the fluorescence spectrochronogram of anthracene in fluorene: (a) at 380 nm (excitation at 373.4 nm or $0-0 + 2 \times 390 \text{ cm}^{-1}$); (b) at 369 nm (363.8 nm , $0-0 + 1500 \text{ cm}^{-1}$). τ_R and τ_D denote the rise and decay times, respectively. The dashed curve represents the best one-exponential fit of the experimental curve. Other details are the same as in Figure 4.

electronic radiationless, and all kinds of vibrational relaxation processes. Due to a very low intensity the role of hot radiative transitions is evidently negligible. The same can be said about the electronic radiationless processes as far as the quantum efficiency of our systems

TABLE II
Time constants (ps) for the lowest vibronic levels in S_1 state of anthracene molecules in fluorene and *n*-heptane at 4.2 K. Experimental error $\pm 15\%$

Vibrational energy (cm^{-1})	Assignment to vibrational modes	Fluorene			τ (Ref. 5)
		τ_R	τ_D	N -heptane	
1500	ν'_7				6 ± 1^f
1400	ν'_6	20	22	19	3.5 ± 1.5^f
780	$2\nu'_1$			22	
390	ν'_1	25	28	25	18 ± 3^n

^f In fluorene.

ⁿ In Ne.

at the given excitation frequencies does not change significantly and is near to 1. Consequently, we can draw a conclusion that the lifetimes of the vibronic states measured are nearly completely determined by the vibrational redistribution of the excitation energy in the S_1 state of molecules.

There is a striking difference between the relaxation picture in the mixed crystal and Shpol'skii systems. In the case of perylene and anthracene in *n*-heptane the HL level population processes are very fast, which is expressed in the exciting-pulse-limited rise time of HL lines (Figure 4). On the contrary, the HL lines in the system with anthracene in fluorene have a finite rise time (Figure 5). As can be seen from Table II, the time of the $\nu'_1 \rightarrow 0$ HL line rise coincides within a 15% experimental error with the $\nu'_6 \rightarrow 0$ line decay time. It seems as if in the case of a mixed crystal under low excess vibrational excitation energy the most important relaxation pathways go essentially through Franck-Condon levels, which have rather long decay times and give rise to the bottleneck effect for the rise times of HL lines. This effect should be expressed also in the retardation of the OL rise time but in practice it is hardly noticeable on the background of the OL rise. Probably this is due to the differences in matrix phonon systems, as there is a competition between the absorptions to the specific impurity Franck-Condon level and to the others, which are in near resonance with this state owing to the participation of phonons. It is possible that the different inhomogeneity of the systems plays also some role although there is no other experimental confirmation to that.

Up to now we have avoided the question whether the vibrational relaxation is intramolecular in nature or it is induced by the presence of the lattice modes superimposed on molecular modes. There is very little experimental evidence to answer this basic question. From the fact that the estimated vibrational lifetimes of anthracene and perylene were practically independent in four matrices (*n*-hexane, *n*-heptane, fluorene, Ne), which is in agreement with this work, the authors (see Refs. 4 and 5) concluded that the energy redistribution kinetics is mainly determined by coupling between intrinsic modes, whereas the role of external bath is to complete the relaxation. Yet, a comparison of the $\nu'_6 \rightarrow \nu_4$ hot band (our notation) decay time 8.1 ns on the anthracene molecules cooled by a supersonic jet expansion⁶ with that in Table II, leads to the necessity of emphasizing the role

of lattice thermal bath. One should compare also the analogous data for tetracene.^{14,16} This role consists in supplying sufficient density of effectively coupled levels for the fast irreversible vibrational relaxation to take place⁴ (see also Ref. 17). The observed practical independence of the matrix may be the result of the "effective resemblance" of the matrices.[†]

As for perylene molecules it was reported²⁰ that the OL rise time in the low-pressure vapour phase is less than 30 ± 10 ps. This is in agreement with our data but, taking into account the different experimental conditions (temperature, laser power, etc.), this can be accidental.

Comparison with HL data

It is interesting to compare the measured relaxation constants with those estimated from the steady-state HL spectrum⁵ and reproduced in the last column of the Tables. One can notice quite large mismatch, especially in case of anthracene. To elucidate the possible source(s) of those discrepancies one has to analyze the approximations made in deriving the basic formula of HL method (adiabatic and Condon) and the precision of experimentally measured parameters (relative integral intensities of hot bands, Franck-Condon factors for these hot transitions on the basis of OL and absorption spectra, the decay time of OL) (for details see Refs. 4 and 5). Although these moments may evolve some errors, it seems to us that their role is not decisive. The main reason is probably analogous to the one mentioned in the previous section in connection with the fast risetime of HL lines: not accounting the possible competing phonon-assisted relaxation channels. The relaxation mechanisms with the participation of non-totally symmetric molecular vibrations¹⁷ as well as some non-linear ones¹⁹ should also be considered. For understandable reasons one can expect that the actuality of those channels grows with the growth of excess vibrational energy.

[†] Immediately after the excitation pulse one should consider also the kind of relaxation caused not by perturbations but by the dispersion of the wavepacket created by the excitation.¹⁸ It causes the decay of the energy localized at the impurity center in time. A possible role of some peculiar nonlinear relaxation mechanisms¹⁹ cannot be overlooked either.

CONCLUSIONS

It has been shown that in low temperature matrices the energy relaxation time of some low-lying vibronic levels is S_1 state of two rather complex aromatic molecules, anthracene and perylene, is in the range of 20–30 ps. The same range of time has been shown for tetracene¹⁴ and it is not in contradiction with the measurements of homogeneous vibronic linewidths. This time is most probably determined by the existence of the phonon bath of the matrix formally much like in case of two- and three-atomic molecules (see, e.g., Ref. 21). A more detailed study of relaxation mechanisms requires measurements at different temperatures.

Acknowledgements

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