# Site Selection Spectroscopy in the Temperature Range 2 K and 300 K

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In this paper we show that there exist rather simple aromatic systems which show no line narrowing in their fluorescence at 2 K, when excited with narrow bandwidth. However, large inhomogeneous line broadening is detected via a shift of the fluorescence bands with excitation energy. This inhomogenous broadening is attributed to a quasi-continuous site splitting, which is present up to about 240 K. The influence of high excess energy on the inhomogenous broadening is discussed.

## Introduction

It was in 1972 when Personov and his coworkers [1] showed that the fluorescence bands of aromatic molecules in a glassy matrix are inhomogeneously broadened due to a quasi continous site splitting. Excitation with a narrow laser line in the region of the OO-transition yields very sharp emission lines, which were attributed to the zero phonon transition. On the low energy side, the sharp zero phonon transition is accompanied by a broad phonon wing. The intensity distribution between the wing and the zero phonon line was shown to depend strongly on the temperature of the matrix. While in the liquid-He temperature range a large amount of the intensity is in the zero phonon line, it vanishes at about 40 K and the total band intensity is left in the phonon wing. Since then, it has been found that line narrowing in the fluorescence upon laser exitation seems to be a common feature for a large variety of molecules [2–8]. Cunningham et al. [8] tried to find the line narrowing, which occurs in the fluorescence, in the phosphorescence. However, in this case, the bands remain very broad, even with laser excitation. These authors argued that this might be due to a local temperature shock or to a jumping between different sites resulting from the relaxing excess energy.

In this paper we present a study in which we compare Anthracene and Diphenylanthracene (DPA), the fluorescence of which was excited and detected with narrow bandwidth in the temperature range between 2 K and 300 K. The aim here is to show that there exist relatively simple, non-polar aromatic systems, which show no line narrowing even at very low temperatures. However, though the bands remain very broad, inhomogenous line broadening in such systems can be clearly detected, even up to temperatures high above the glass point of the matrix. Besides this, we have tried to determine the influence of the relaxing excess energy on the inhomogenous broadening.

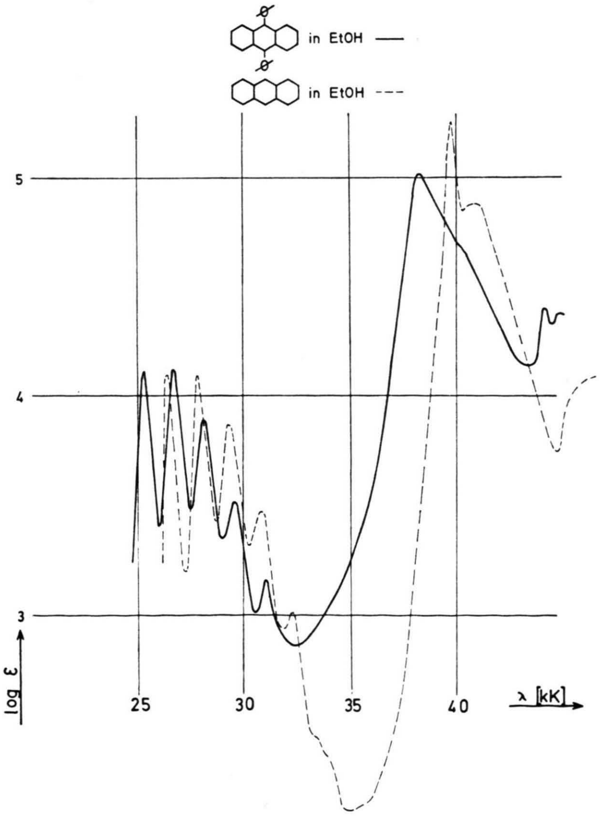

Fig. 1. Absorption of anthracene and DPA in EtOH at 77 K.

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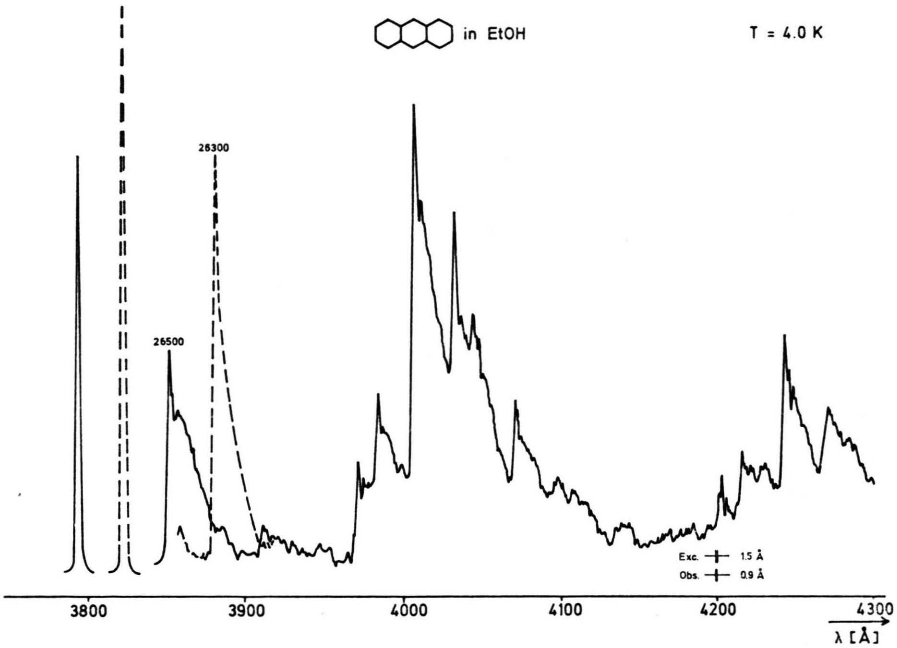

Fig. 2. Emission of anthracene in EtOH at 4 K. Two excitation lines are shown. For the excitation at 26300 $cm^{-1}$ only the short wavelength band of the fluorescence is drawn. The average bandpasses used are shown.

## Experimental

Anthracene and DPA were dissolved in EtOH. The concentration chosen was about $10^{-3}$ m. The sample was sealed in a quartz cuvette which was mounted in a Combi cryostat (Leybold), with a temperature range from 1.3 K up to 300 K. The temperature of the bath below 4 K was controlled by means of a He-pressure cell and a carbon resistor, above 4 K only the carbon resistor was used. The fluctuation of the temperature below 4.2 K was within 0.1 K. As an excitation source we used a

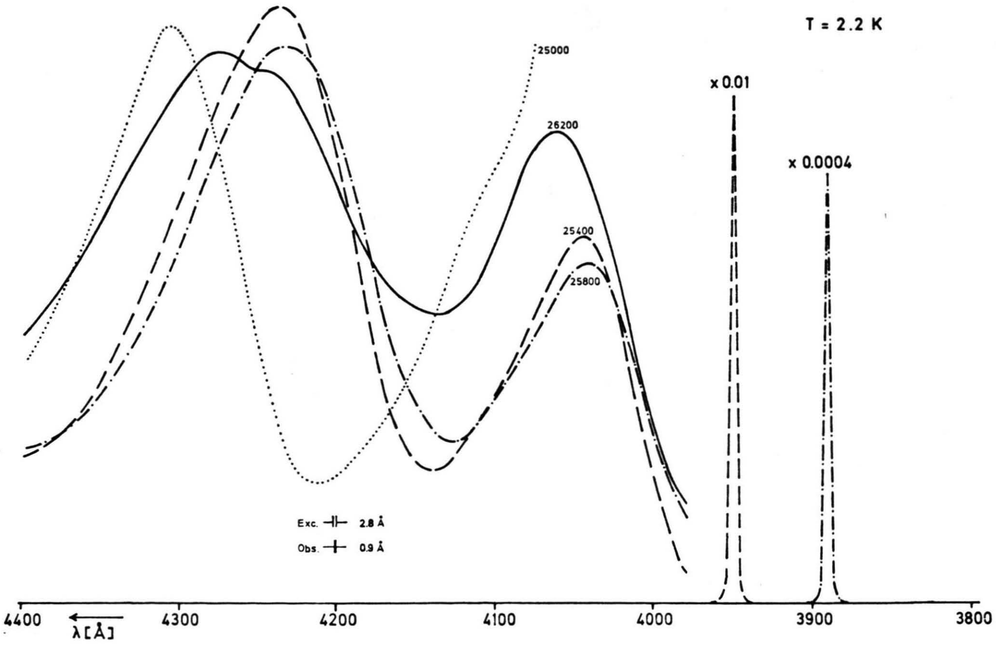

Fig. 3. Emission of DPA at 2.2 K excited at various points in the OO-band of $S_1$. Two excitation lines and the band passes used are shown. The numbers at the various emission spectra represent the wavenumber of excitation.

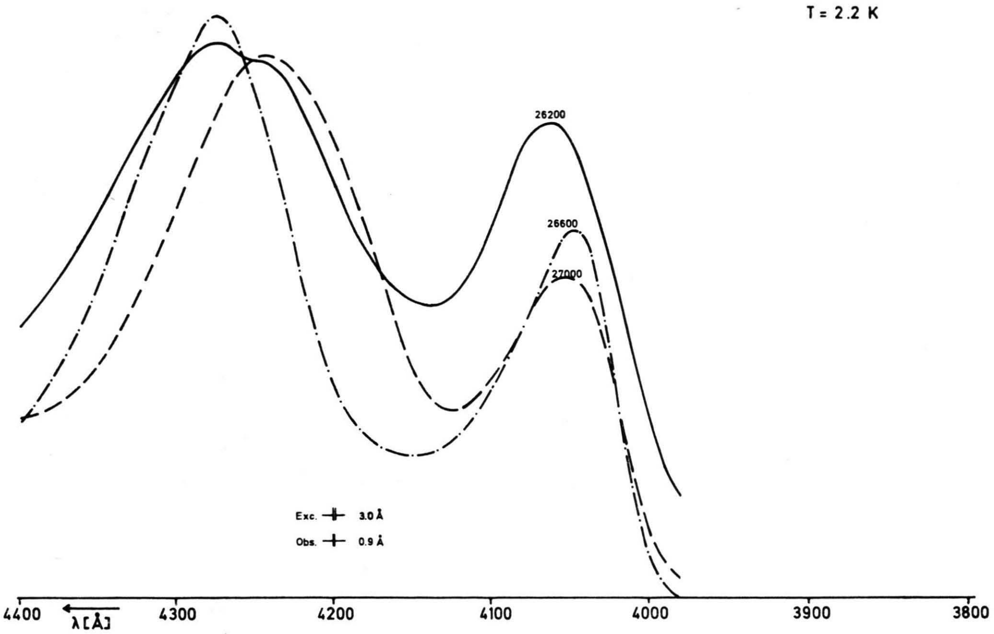

Fig. 4. Emission of DPA at 2.2 K, excited in the region of the first vibrational transition of $S_1$.

Xe-high pressure lamp together with a Zeiss-double monochromator. The bandwidths used varied from about 15 $cm^{-1}$, when excitation was in the OO-transition, to about 30 $cm^{-1}$ for $S_2$ excitation. The bandpasses used are shown in the figures.

To detect the signal we used a grating single monochromator (Chromatix CT 103) in 2nd order with a reciprocal linear dispersion of 3.75 Å/mm at 4000 Å. The slit widths used were about 250 $\mu$, with a corresponding bandpass of about 0.94 Å (6 $cm^{-1}$). The signal of the photomultiplier (EMI 9558 QB) was fed in a phase sensitive detector (PAR mod. 129) and recorded on a xy-recorder (HP 7045 A).

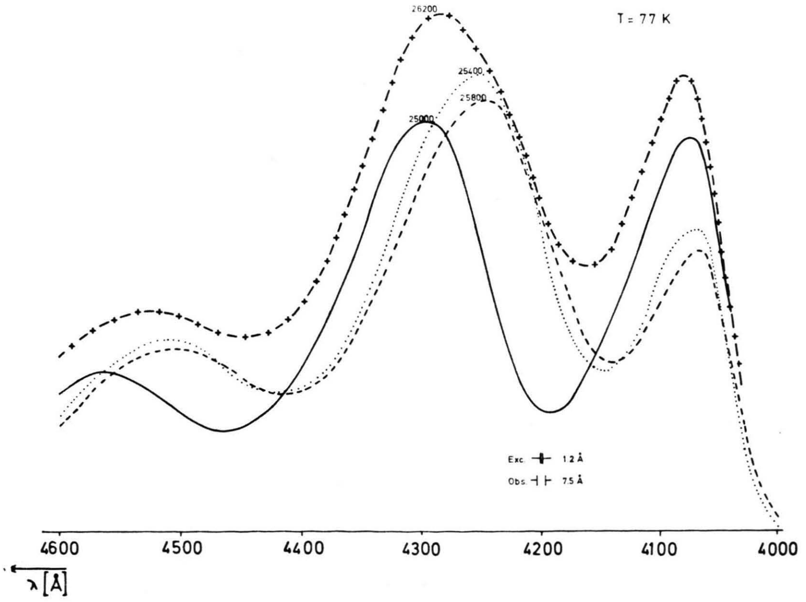

Fig. 5. Emission of DPA at 77 K, excited in the region of the OO-band of $S_1$.

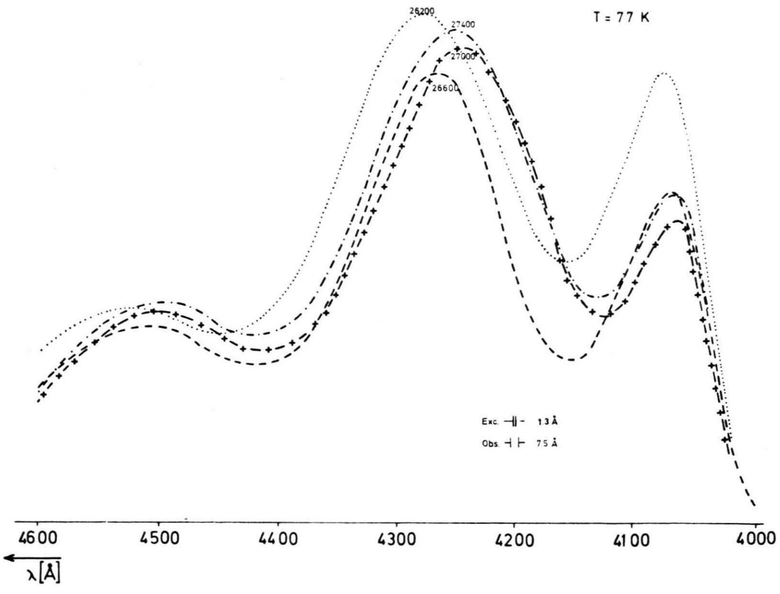

Fig. 6. Emission of DPA at 77 K, excited in the first vibrational transition of $S_1$.

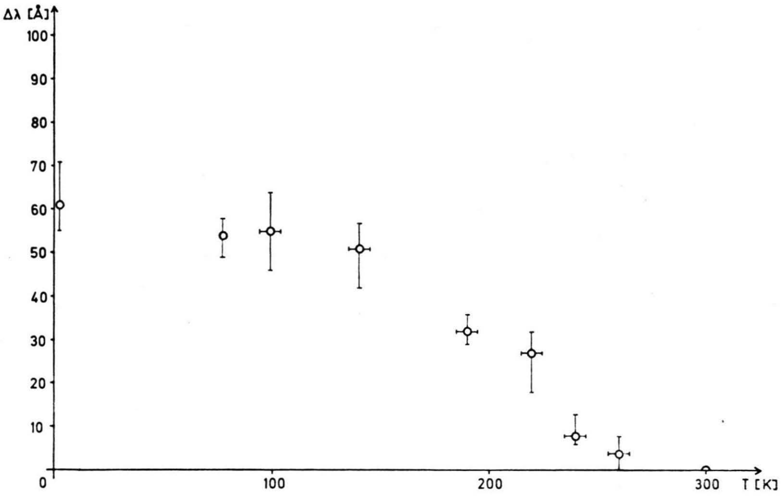

Fig. 7. The shift of the first vibronic transition of the fluorescence spectrum as a function of the temperature.

## Results

In this section we summarize some outstanding results of our experiments:

(1) Comparing Fig. 2 with 3 and 4 we see that on the one hand, there occurs no line narrowing in DPA when we excite the OO-transition of $S_1$. The fluorescence bands remain very broad even down to 2 K, and the line shape hardly changes from that at 77 K (Figs. 5 and 6). On the other hand, it is easily possible to get narrow lines in the case of anthracene at 4.2 K.

(2) Though there is no line narrowing in DPA at 2.2 K, we do see that the position of the fluorescence vibronic bands strongly depend on the position of excitation. We see that the shift of the vibronic bands is much more pronounced than that of the OO-transition.

(3) Figures 5 and 6 show that this shift of the fluorescence vibronic bands with the excitation wavenumber is still present at 77 K. Moreover, far above the glasspoint of the solvent at about 200 K, we still observe a shift of the fluorescence bands with respect to the excitation wavelength (Figure 7). At about 250 K this shift tends to vanish and is clearly absent at room temperature (Figure 8).

(4) Scanning the 2nd vibrational band of $S_1$ with narrow bandwidth excitation (Figs. 4 and 6)

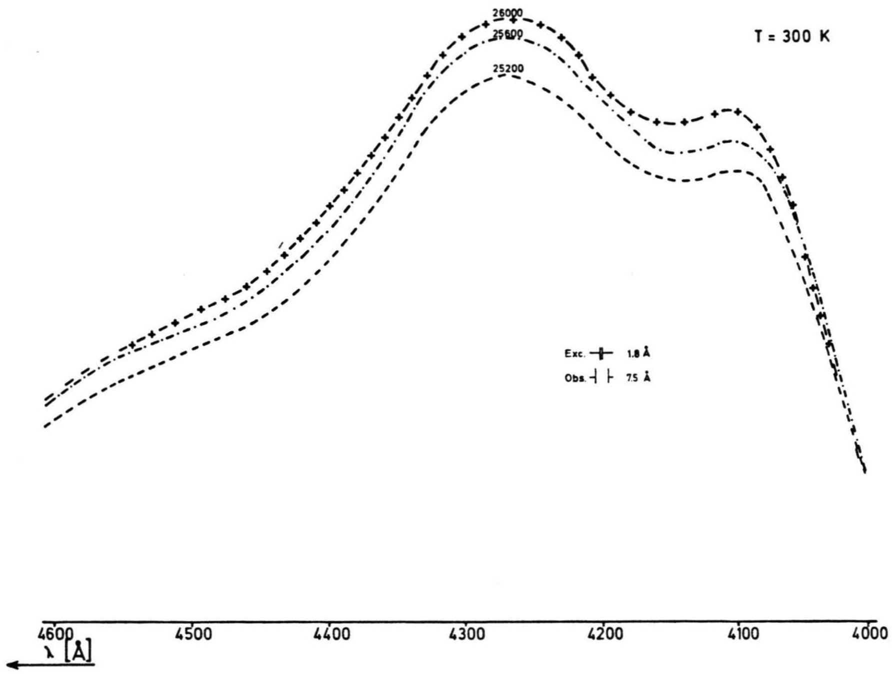

Fig. 8. Emission of DPA at room temperature, excited at various positions in the OO-Band of $S_1$.

the shift is still present; however, it becomes somewhat smaller with increasing excess energy. Exciting the $S_2$-state, there is no longer any shift observable (Figure 9). With respect to these observations the situation does not change between 2 K and 77 K.

(5) The position of the fluorescence bands with respect to $S_2$ excitation is on the high energy side of the spectral region which is covered by the band shift (Figure 10).

(6) From Figs. 3, 4, 5 and 6 we see that the fluorescence bands do not shift further if we excite the high energy side of the OO-transition of $S_1$. If the radiation source is centered exactly in the valley between the OO-band and the 1st vibronic band (at 26200 $\mathrm{cm}^{-1}$), the bands in the fluorescence become very broad and cover nearly the whole spectral region where the shift occurs. If we irradiate the molecule at a few hundred wavenumbers farther to the high energy side, the emission bands suddenly become narrower again and shift to the low energy side. Scanning the 1st vibronic band, the situation concerning the fluorescence shift is nearly the same as already discussed for the OO-transition, except that the shifts are somewhat smaller. Though the observations are essentially temperature independent between 77 and 2 K, we see that at 2.2 K there occurs a small dip in the very broad band which we get by exciting exactly between the two transitions (Figs. 3 and 4).

## Discussion

While in anthracene the zero phonon-lines, followed by their phonon wings on the low energy side are clearly resolved, in DPA the zero phonon-line is absent (Figs. 2 and 3). Because of this lack of any line narrowing in DPA we have to conclude that the fluorescence bands are homogenously broadened either (1) because of very dense intrinsic rotational vibrational states of the phenyl groups or (2) because of a very strong impurity phonon interaction. In the latter case the intensity of the zero phonon-line is given by [9]

$$G_0 = \exp\{-\bar{S}\}\exp\{-8\bar{S}[T/\Theta]^2\}.$$

$\bar{S}$ is a parameter describing the strength of the impurity phonon coupling. In the case of anthracene in a Shpolskii matrix, this parameter is in the order of 1 [9]. However, as is known from spectroscopic work on F-centers in inorganic crystals, $\bar{S}$ may assume values even up to 20 [9]. In this case $\exp\{-\bar{S}\} \approx 10^{-9}$ and there is no zero phonon-line even at very low temperatures. Though we favour the first possibility (see discussion below) we can not definitly decide, at the moment, which of the two cases accounts for the broad lines of DPA in EtOH.

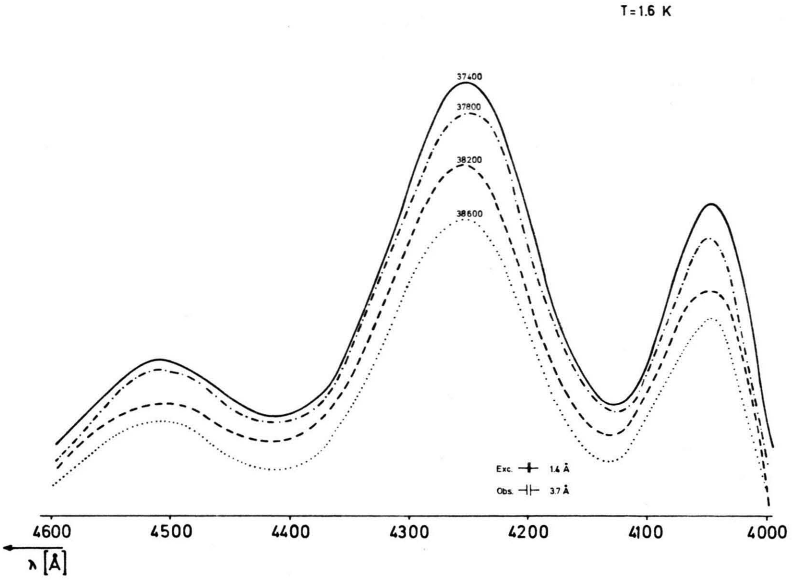

Fig. 9. Emission of DPA at 1.6 K when excited at several positions in the $S_2$-state.

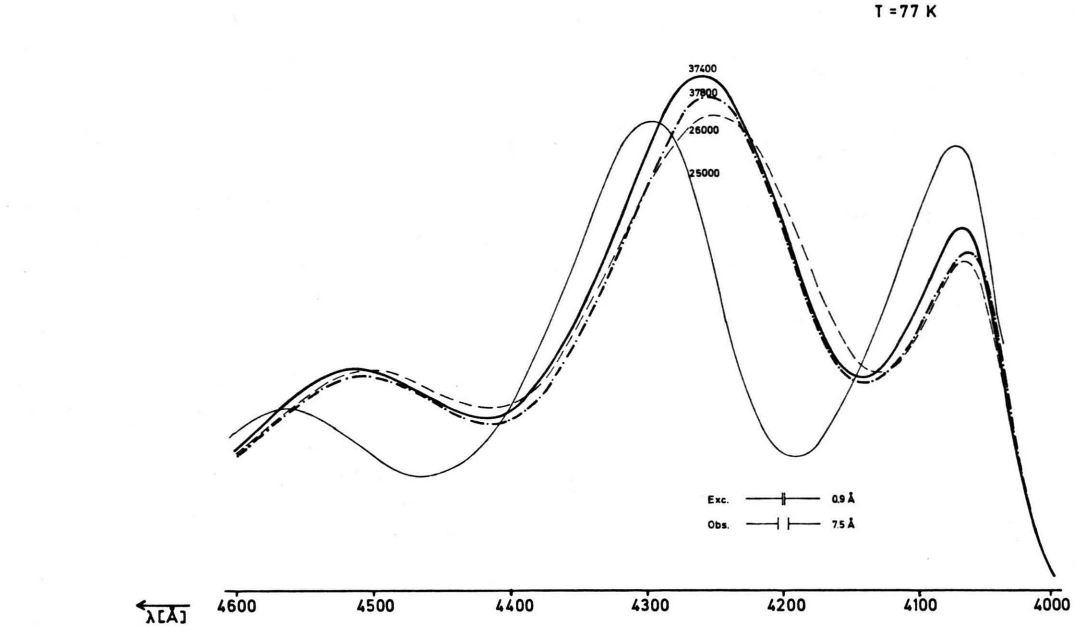

Fig. 10. Fig. 10 shows the position of the fluorescence bands when excited in the $S_2$-state compared to the fluorescence bands when excited in the $S_1$-state.

Though there is no line narrowing, we see that a large amount of inhomogenous broadening is present. Because of this inhomogenous broadening the fluorescence bands shift with the excitation energy, if we excite the molecule in the region of the OO-transition at various points with a narrow width of a few wavenumbers. As originally proposed by Personov[1], we attribute this shift to the excitation of various sites selected by means of the narrow band-width radiation. This quasicontinous site splitting, which results in the inhomogenous broadening, is due to a comparatively large interaction of the excited impurity with the surrounding glass molecules.

As already stated, there is no further shift if we excite the high energy side of the OO-transition (or the 1st vibronic state). The lack of any shift and the large broadening we get when we excite in the "valley" between the states results from the fact that in the upper state we excite a molecule in the low energy site, and in the lower state one in a high energy site with the same probability. The low site of the upper state relaxes to the low site of the vibrational groundstate (Figure 11). That is, we have simultanously the emission from the high and from the low site which results in the very broad band. What seems to support our interpretation is the fact that at 2 K it is possible to reveal a small dip on the top of the broad band (Figure 3).

Going beyond the valley with the excitation energy to the low energy side of the following vibronic transition, the probability of exciting the molecule in the low site increases rapidly. This is due to the rapidly increasing absorption. That is, the band shifts back to the low site and becomes narrower again.

As seen in Fig. 9 it is not possible to get any shift of the fluorescence bands upon irradiation in the $S_2$-state. The question arises, if it is possible to select single sites in the higher electronic states, which have, due to very fast radiationless relaxation, a larger homogenous width than the lowest excited electronic state. Besides this, the number of vibronic states may be high enough to overlap each other. However, if this would be the case for DPA, the width of the fluorescence bands had to become very broad. As we see from Fig. 9 this possibility is ruled out. The same broadening must occur if the impurities change the sites very quickly because of the relaxing excess energy as discussed by Cunningham et al.[7]. Moreover, even a local temperature shock cannot account for the facts observed, since, as discussed below, we have a shift of the fluorescence bands up to about 250 K. Besides we know from the work of Bauer et al.[10] that several thousand wavenumbers of excess energy yield a temperatur increase of only a few degrees.

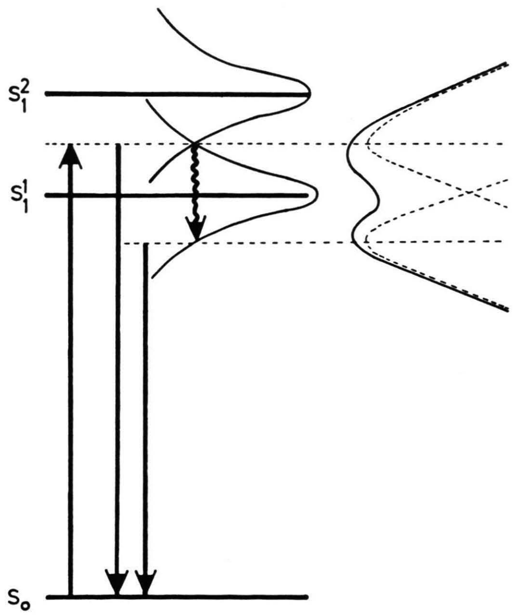

Fig. 11. Schematic level diagram which explains the simultaneous excitation of a "high" and a "low site" fluorescence emission as observed in DPA.

We prefer to explain the lack of any shift in the fluorescence bands upon excitation with high excess energy by a dynamical destruction of the solvent cage. The relaxing excess energy creates a highly vibrating molecule which alters its microscopic surroundings. Since the impurity relaxes very fast and the solvent cage is assumed to relax very slowly, the interaction of the impurity with the matrix becomes smaller and the energy of the $S_1$-state tends to assume the energy of the free molecule. Therefore, when excited with large excess energy, the fluorescence bands tend to lie on the high energy site (see Fig. 10), which is indeed the case. This interpretation seems to favor possibility (1) for explaining the line-broadening in DPA (see discussion above).

Comparing Figs. 3 and 4 with 5 and 6, there is no significant difference between 77 K and 2 K. Inhomogenous line broadening is still detectable from the fluorescence shift. However, what is more surprising, above 77 K and even above the glass temperature of EtOH it is possible to select single sites, as can be seen from the shift, which vanishes at about 240 K and is clearly absent at room temperature. There again several explanations exist:

(1) On the one hand these results may indicate that below 240 K the diffusion rate between different sites is much slower than the fluorescence decay rate. At 240 K, both processes have the same order of magnitude. Above 240 K the diffusion rate between different sites is much larger than the decay rate, and site selection clearly is no longer possible.

(2) On the other hand one may argue that the temperature dependent homogenous line broadening becomes so large that it dominates the inhomo-

genous width. In this case, too, site selection is impossible.

From Fig. 8 it is seen that, indeed, at 300 K the fluorescence lines are very broad. This supports (2) above although we still cannot rule out possibility (1).

## *Acknowledgement*

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