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Triplet Excitions in Crystalline Trans-Stilbene I. Spectroscopy of the $S_0 \rightarrow T_1$ Transition

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Triplet Excitons in Crystalline Trans-Stilbene

I. Spectroscopy of the $S_0 \rightarrow T_1$ Transition

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The first singlet → triplet absorption of trans-stilbene has been studied between 10 and 300 K. The triplet exciton energy (energy of the lowest 0–0 line) is 17380 cm^{-1} at 10 K, and does not change significantly with temperature. Vibrational A_g modes of 206, 1250 and 1570 cm^{-1} are active. The Franck–Condon factor of the origin region is small. The low temperature spectra of the 0–0 and 206 cm^{-1} regions show a doublet structure with a splitting of 82 ± 1 cm^{-1} which is attributed to the site splitting. Further structure shown by the lines is discussed. The lines are approximately lorentzian. From curve fitting, line-widths and exciton-phonon coupling constants, increasing linearly with T, are deduced. Exciton-phonon coupling appears to be different on the two sites. The product of absorption coefficient at 4880 Å, α, by the total triplet–triplet interaction rate constant has been measured at 295 K: $\alpha\gamma = 2.3 \pm 0.3 \cdot 10^{-15}$ cm^2 sec^{-1}, corresponding for γ_{total} to a value of a few 10^{-12} cm^3 sec^{-1}.

1 INTRODUCTION

Crystalline trans-stilbene (TS) has been used for a long time as a scintillator.[1] However, its electronic properties are still poorly known, although the isomerization reaction of the molecule has been extensively investigated.[2] The crystal space group is the same as that of anthracene, but the packing is more complex.[3] The unit cell contains two asymmetric units, each made of two molecules, occupying centers of symmetry, and there is an orientational (presumably static) disorder on one type of site only. The peculiarities of the

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corresponding exciton band structure, and non-rigidity of the molecule, may lead to interesting new effects in the exciton transport properties.

An investigation of triplet exciton properties has thus been started, in our laboratory, and the first results are reported here.

Little information on triplet exciton properties was available at the start of the present work: the $S_0 \rightarrow T_1$ absorption had been barely observed,[4] and the exciton energy was only approximately known. Two components of the diffusivity tensor $\mathscr{D}$ also had been measured at 300 K:[5] $\mathscr{D}$ is nearly isotropic in the (a, b) plane with $\mathscr{D} \sim 8 \cdot 10^{-5}\ \mathrm{cm}^2\ \mathrm{sec}^{-1}$. In the present study, the whole $S_0 \rightarrow T_1$ transition region was first studied at low resolution between 80 and 300 K. This was followed by a high resolution study of the origin region only, due to spectral limitations imposed by the light source. A number of interesting questions are raised from the analysis of the observed spectra.

2 EXPERIMENTAL SETUPS

As in all aromatic hydrocarbon crystals, the $S_0 \rightarrow T_1$ absorption is extremely weak, and it was measured as the action spectrum of delayed fluorescence (see appendix). Since the fluorescence emission lies between 3500 and 4500 Å,[6] the method is limited, toward the short wavelengths, to about 4500 Å.

Crystals of various origins were used. Their room-temperature triplet lifetimes were generally around 10 ms. The buildup and decay of delayed fluorescence at 300 K follows the law expected for the annihilation of two free triplet excitons.[7] There is evidence of trapping at low temperature, but as for generation of delayed fluorescence at least one of the annihilating triplets must be free, it is expected that the $S_0 \rightarrow T_1$ absorption of the crystal is recorded at all temperatures.

Unpolarized low resolution ($\sim 50\ \mathrm{cm}^{-1}$) spectra were taken between 4500 and 6000 Å using the setup shown in Figure 1. The light from an XBO 450 Watts Xenon lamp is passed through a monochromator (Coderg M1) whose grating G is rotated by a stepping motor, then focussed on the sample which is either in air (at room T), or in a chamber filled with N_2 gas, its temperature being controlled between 80 and 300 K. The exciting light intensity is monitored by a RTC 150 UV PM and the fluorescence light by an EMI 9635 QB. Various filter combinations (F_1, F_2) were used depending on the wavelength region under study.

The excitation density I was kept low, and the delayed fluorescence flux ϕ was $\propto I^2$. After passing through operational amplifiers, the signals were fed in a laboratory-made circuit with an output $Y = \phi^{1/2}/I$, that is, proportional to the absorption coefficient α.[8] The data were accumulated in a DIDAC

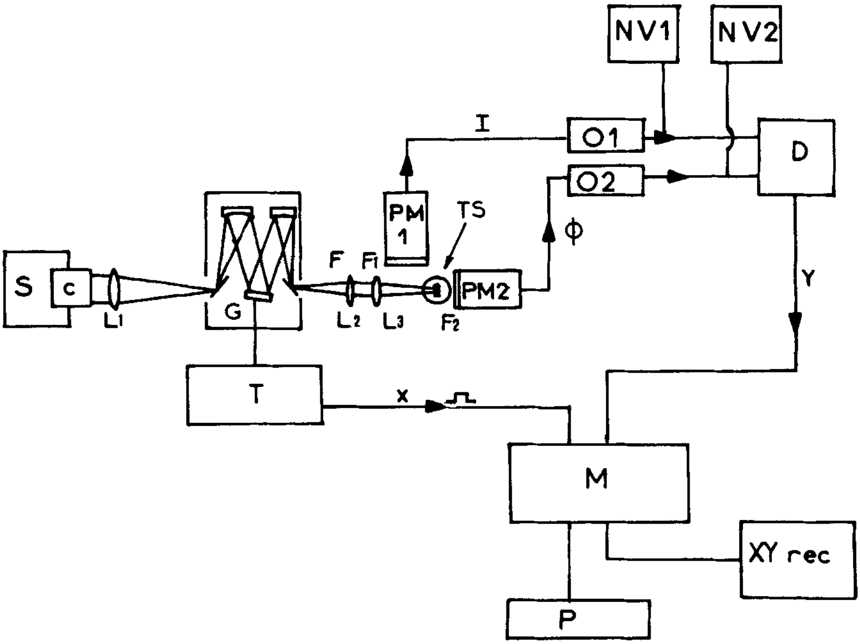

FIGURE 1 Experimental setup used for obtaining low-resolution spectra S:XBO 450 W Xenon arc, focussed using condenser C and lens L_1 onto the entrance slit of a monochromator (resolution 24 Å/mm). Its output is passed through filters F (BG18 + GG455 or OG515) and focussed on the trans-stilbene crystal TS. The exciting light is attenuated by neutral filters F_1 as needed and monitored by PM1 (150 UVP), and fluorescence light is filtered by F_2 (Corning 7.60 or 5.58) and detected by PM2 (9635 QB). Their outputs I and ϕ respectively, are passed through identical operational amplifiers O1 and O2 (Tektronix type O), read on numerical voltmeters NV1 and NV2 to check that conditions such that $\phi \propto I^2$ are met, then sent into a divider D performing the operation $Y = \phi^{1/2}/I$. Y is sent into a multiscaler M (DIDAC 4000) triggered by pulses sent by the system T which also energizes the stepping motor rotating the grating G. Output of M can be analogic on an XY recorder or digital on a printer P.

4000 multi-channel analyzer used as a multiscaler, with an acquisition time of 40 μs. The grating remained 200 ms in each position, and during this time 5000 measurements at the corresponding wavelength were made and stored. The results were either analogically displayed on an XY tracer (see Figure 2) or printed in digital form.

For the high (0.4 cm^{-1}) resolution study, the lamp and monochromator were replaced by a dye laser (Spectra Physics 370, using Rhodamin 6 G and pumped at 5145 Å), limited to about 5600 Å toward short wavelengths. The sample was placed under vacuum in a cryostat (Air Products) which could maintain any temperature above 10 K.

3 LOW RESOLUTION SPECTRA, 4500–5800 Å

The spectra were taken with the setup described above, between 80 and 300 K. Below 80 K, the instrument bandwidth becomes larger than the effective linewidths. Results at 83 and 295 K are shown on Figure 2.

The energy of the triplet exciton, taken as the energy of maximum absorption in the first band, is near 17400 cm^{-1}, and, to the accuracy of the experiment, is independent of temperature (to $\pm$ 10 cm^{-1}).

The linewidths being large, only three internal vibrations appear: 205 cm^{-1}, 1300 $\pm$ 50 cm^{-1} (the energy is uncertain since only shoulders are seen), and 1570 cm^{-1}. These modes are those appearing in singlet-singlet absorption at 208, perhaps 1337, and 1599 cm^{-1} and in the fluorescence spectrum at 212, 1337 and 1635 cm^{-1}.[4] According to the theoretical analysis of Warshel,[9] these three A_g modes are all related to the central ethylenic double bond: respectively, phenyl bending around C=C, H bending around the same bond, and C=C stretching.

Clearly, this is not enough for a complete vibronic analysis. A few remarks are however in order. Warshel has not considered the triplet state but he calculates that the line $\nu = 1$, 208 cm^{-1} should have an intensity about half that of the 0–0 line. Earlier $S_0 \rightarrow S_1$ spectra could not give accurate values of the relative intensities, which can be done here with photoelectric detection. It is found that the 206 cm^{-1} line has indeed (see also Figure 3) half the intensity of the 0–0 line. The situation is rather different for the C=C stretching mode. Warshel calculated for $S_0 \rightarrow S_1$, $I_{10}/I_{00} = 0.85$ and $I_{20}/I_{00} = 0.35$,[9] corresponding to a relatively large change in C=C bond length. Actually, from experimental spectra $I_{10}/I_{00} > 1$. In the triplet state one finds $I_{10}/I_{00} > 2$ and $I_{20}/I_{00} > 6$ (Figure 2). This latter value is surprising. Either the central carbon–carbon bond lengthens much more in the triplet than in the singlet excited state, or part of the oscillator strength below 5000 Å comes from another source. There may be a congestion of combination mode lines in the 2×1570 cm^{-1} region, or a second triplet state may underly the $S_0 \rightarrow T_1$ absorption. High resolution spectra of this region will help to solve the problem.

Since the whole energy range of the transition could not be scanned, and since another transition may be present at higher energies, a precise value of the Franck-Condon factor of the origin region cannot be given. It is certainly smaller than 0.1 and may be as small as 0.02, in contrast with the situation in anthracene and similar materials. Since in the weak coupling limit, certainly valid here, matrix elements and factor group (Davydov) splitting energies are multiplied by the FC factors, we expect the Davydov splitting of the origin line, of great importance in the theory of exciton transport, to be small.

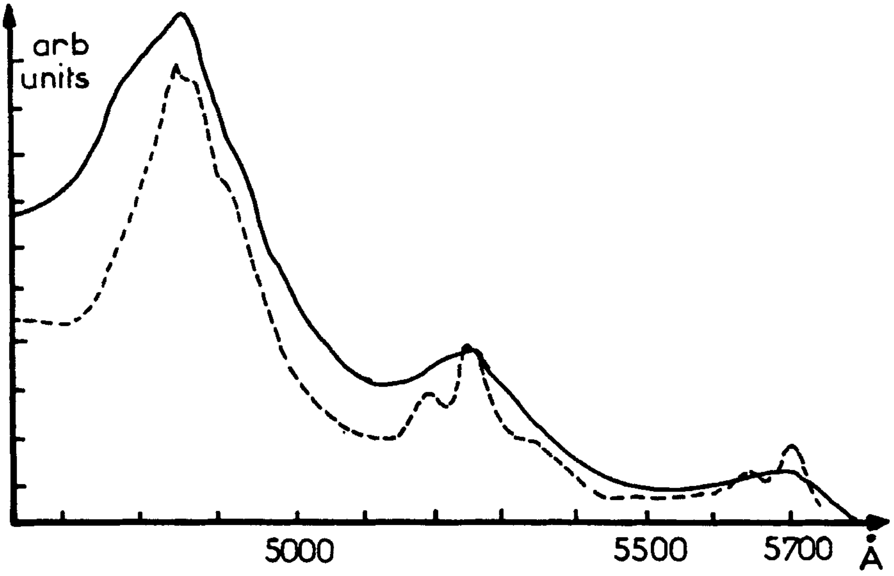

FIGURE 2 Absorption coefficient (arbitrary units) in the $S_0 \rightarrow T_1$ transition of trans-stilbene. Solid line: 295 K. Dashed line: 83 K.

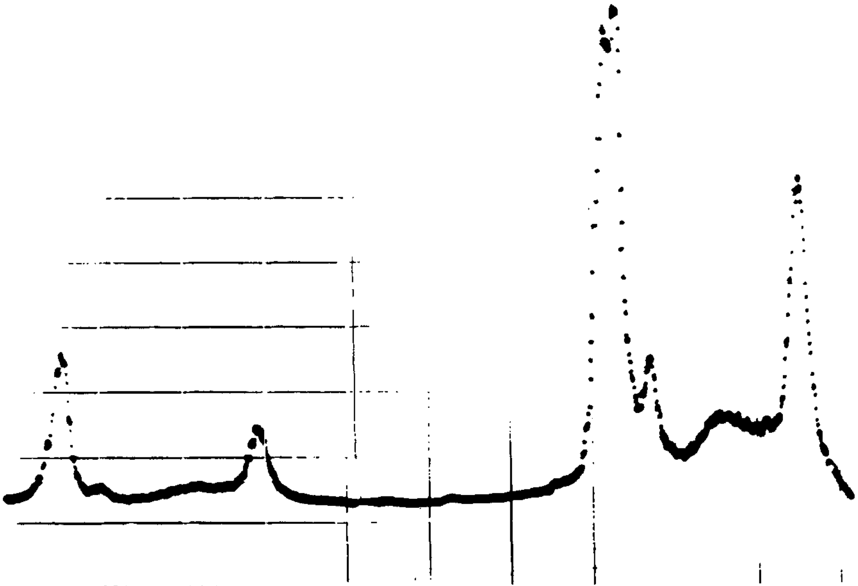

FIGURE 3 Absorption coefficient in the low-energy region of the transition at 10 K. Resolution 0.4 cm^{-1}. Origin region and 206 cm^{-1} phonon region. Energies increase from right to left.

As shown on Figure 2, the lines are very broad. We shall see in Section 4 that they are in fact multiplets, so that an accurate determination of the widths is not easy. They are $\Gamma \gtrsim 200\ \text{cm}^{-1}$ at 300 K and still $\sim 80\ \text{cm}^{-1}$ at 100 K, varying roughly linearly with T. For comparison, the widths are, at room temperature, about $100\ \text{cm}^{-1}$ in anthracene,[10] and around $200\ \text{cm}^{-1}$ in pyrene.[8] The conjunction of large widths and small Davydov splitting suggests that the so-called "non-local" scattering should, in trans-stilbene, be much larger than the "local" one to account for the experimental value of $\mathscr{D}$,[5] although the equations relating, in the case of anthracene, $\mathscr{D}$ to the spectral properties[10] cannot be used as such in the present case.

4 HIGH RESOLUTION SPECTRA

The first $300\ \text{cm}^{-1}$ of the $S_0 \rightarrow T_1$ absorption have been studied at $0.4\ \text{cm}^{-1}$ resolution in linearly polarized light at several temperatures from about 10 K to 80 K. In this region, four main bands are seen centered at 17380, 17462, 17586 and $17668\ \text{cm}^{-1}$, or if the first one is taken as origin, at 0, 82, 206 and $206 + 82\ \text{cm}^{-1}$.

The $206\ \text{cm}^{-1}$ interval is the energy of the already mentioned A_g internal mode,[9] building a short progression. The ratio of the intensity of this band to that of the origin one seems to decrease slightly with T and is at 10 K only 0.3.

The other interval is more difficult to understand. The line at $+82\ \text{cm}^{-1}$ (or at $+206 + 82\ \text{cm}^{-1}$) is slightly more intense than the origin line (or the $+206\ \text{cm}^{-1}$), but there is no line at $2 \times 82\ \text{cm}^{-1}$: the absorption there is at most 1% of the absorption at $82\ \text{cm}^{-1}$ (this region has also been examined at much higher sensitivity than on Figure 3). This observation excludes the possibility of a vibronic band built by an a_g or b_g mode on a B_u triplet,† as well as of a progression vibronically induced through an ungerade mode coupled to a (hypothetical) gerade electronic state.‡ Factor group splittings cannot account for the spectrum either, since they should scale according to FC factors in the origin and $206\ \text{cm}^{-1}$ region. In addition, a $82\ \text{cm}^{-1}$ factor group splitting for the 0–0 band alone would imply a total splitting of several thousands cm^{-1} for the whole $S_0 \rightarrow T_1$ transition.

The crystal structure of TS allows the existence of a site splitting, since the unit cell (space group $P2_1/a$) contains two units of two molecules (occupying

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[†] The Raman spectrum of TS crystal recorded by us at 5 K shows no line between 74 and $87\ \text{cm}^{-1}$. Our spectra agree with the spectra at 77 K[11].

[‡] The possibility that both lines at 0 and $82\ \text{cm}^{-1}$ are false origins built on the same orbitally forbidden origin by two *u* internal modes with energies differing by $82\ \text{cm}^{-1}$ cannot be excluded now. Study of the (very weak) phosphorescence could test this assumption.

two "sites") not related by any interchange symmetry operation,† as is the case of 1-4 dibromonaphthalene (DBN) where site splitting occurs both in triplet and singlet states.[12] As pointed out by Castro and Hochstrasser[12] site splittings correspond to differences in Coulomb integrals, not in exchange integrals, so that splittings of the order of 10^2 cm^{-1} are normally expected both in the triplet and singlet states. We propose that a site splitting of 82 cm^{-1} is seen here in the triplet exciton spectrum of TS. It should indeed be independent of FC factor, provided it is small enough compared to internal phonon energies.

It is worth mentioning that site splitting in TS may well have a different origin from that in DBN. In the latter material, there is no evidence that molecules at different sites have different geometry (although no symmetry rule forbids such a difference), but different sites have clearly different environments, so that the difference in the two site energies is essentially due to different van der Waals interactions (band shifts) on the two sites. In TS on the contrary, the geometries of molecules on either site are different enough to be measurable by X-ray crystallography:[3] both are non planar, but with different tilt angles. Study of the isomerization of stilbene[2] leads to potential energy curves showing that both ground state and triplet state energies vary quite rapidly with the tilt angle, so that a tilt difference of a few degrees easily accounts for an energy difference of 82 cm^{-1} or $<5\%$ of the transition energy; site splitting would then come at least in part from differences in single (gas phase) molecule excitation energies on the two sites, a contribution which is neglected in DBN.[12]

The remainder of the discussion will be limited to the first 100 cm^{-1} of the absorption spectrum since the region of the 206 cm^{-1} phonon behaves very similarly.

At 20 K and above, the 0–0 band can be accounted for by a single lorentzian of width $\Gamma_0 \propto T$ with a phonon sideband extending to 50 cm^{-1}. An analysis of the lines (see Figure 5) gives a Debye-Waller factor which predicts an exciton-photon coupling constant increasing linearly with T (Figure 6). Above 50 K, the zero-phonon line merges into the phonon sideband, and the whole absorption strongly overlaps the absorption at 82 cm^{-1}, making the analysis inaccurate. As seen in the example given in Figure 5, in the 20–50 K temperature range, the absorption at 82 cm^{-1} can be accounted for by two lorentzian lines separated by 5 ± 1 cm^{-1} and having a width $\Gamma_{82} \simeq \frac{1}{2}\Gamma_0$ which is $\propto T$. Above 50 K, $\frac{1}{2}\Gamma_{82} \gg 5$ cm^{-1} and the two lines merge into one. Up to 80 K there is only a very weak tail (above the lorentzian

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† The structure has not been determined at 4 K, but the possibility of cycling single crystals from 300 K to 4 K and back without fracture, and the similarity of Raman spectra at all temperatures show that no phase change occurs.

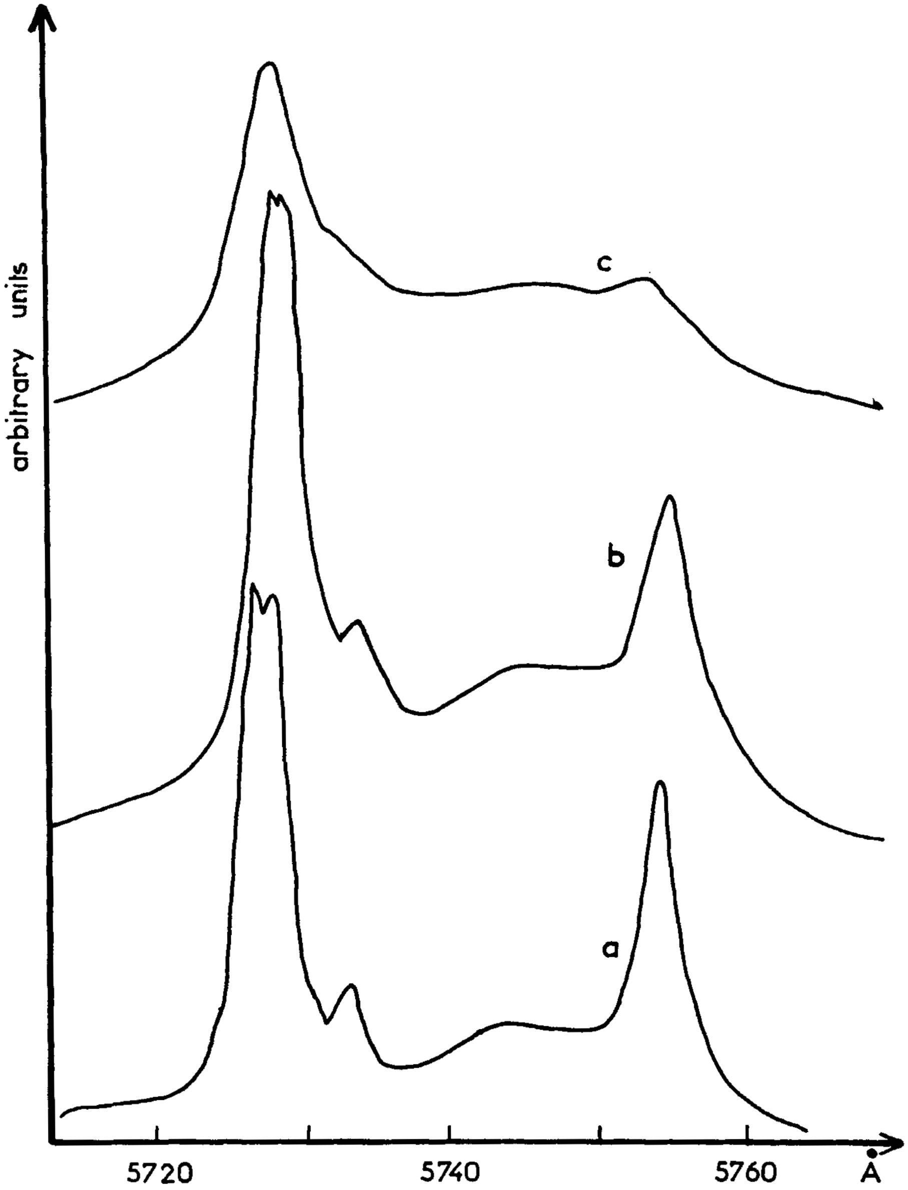

FIGURE 4 Absorption of the origin region: (a) at 20 K, (b) at 30 K, (c) at 50 K.

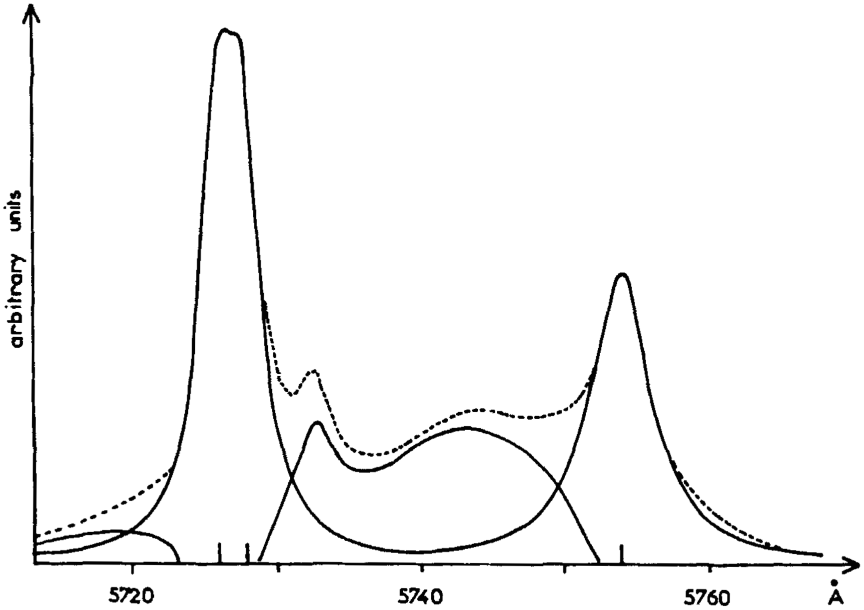

FIGURE 5 Analysis of the 30 K spectrum (dotted line). Lorentzian zero-phonon lines plus phonon sidebands.

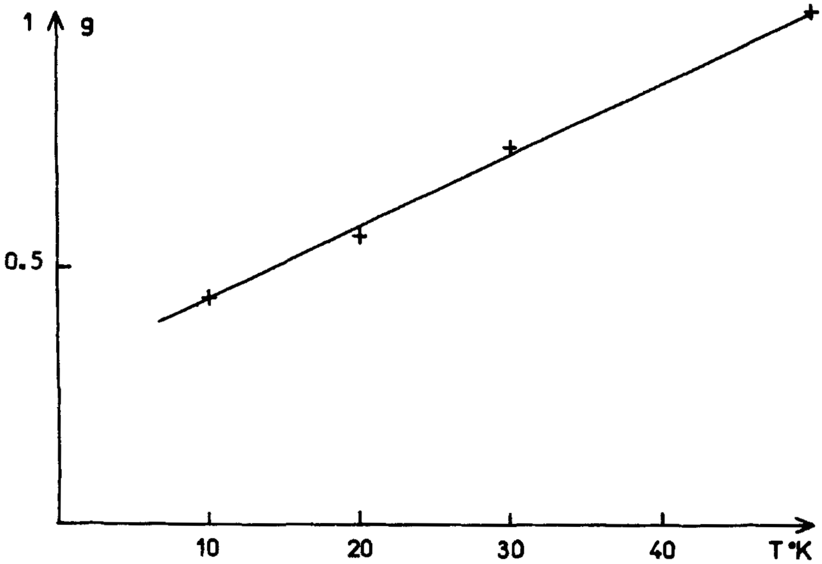

FIGURE 6 Temperature dependence of the exciton-phonon coupling constant g of the 17380 cm^{-1} line.

wing) on the high energy side of this band, and if this is interpreted as a side band, the Debye-Waller factor is >0.9 at all temperatures. These results are summarized on Table I.

Below 20 K, the temperature is not accurately known, being outside the calibration range of our thermocouple. At a temperature estimated to be slightly above 10 K, there is indication that the spectrum, and especially the origin line, become more structured. However, a small modulation of our laser intensity by our wavelength driving unit of about 2 cm^{-1} period could not be completely eliminated, and prevents a meaningful analysis of this structure.

The 5 cm^{-1} splitting of the 82 cm^{-1} band, and the corresponding 2 cm^{-1} splitting of the 206 + 82 cm^{-1} band, scale with FC factors as one would expect for a Davydov splitting, but some other observations make such an assignment doubtful: a 5 cm^{-1} DS splitting on the 82 cm^{-1} implies a total splitting on the corresponding site of 100 to 500 cm^{-1} which seems too large compared to other, known, triplet exciton DS splittings;[13] the relative magnitude of the two components of the 82 cm^{-1} depends on the direction of polarization for light propagating $\|$b axis, incident $\perp$ to (ac) plane. In addition, our results as they stand do not show a clear evidence of a splitting of the origin line.

If the polarization ratio of the two components is ~ 1, the DS must be $<\frac{1}{2}\Gamma_0$ at the lowest T studied, that is less than 1 cm^{-1}. If on the other hand the two components are uniquely polarized, the DS must be less than the uncertainty in our photon energy calibration, which is again about 1 cm^{-1}. This would be compatible with a total DS for the transition of 20 to 100 cm^{-1}, a reasonable order of magnitude.

Therefore, either the 5 cm^{-1} splitting at 82 cm^{-1} is not DS splitting, or the two sites have very different total splittings. One feature which should be

TABLE I

	Origin band			82 cm^{-1} band		Intensity ratio
T	Γ_0	DW factor α	g^a	Γ^{82}	DW factor α	I_0/I_{82}
~ 10	$<10^b$	0.82 ± 0.02	0.44	<6		
20	11	0.57 ± 0.02	0.56	6	>0.95	1.4
30	16	0.48 ± 0.02	0.73	9		1.4
50	28	0.37 ± 0.01	1	16	~ 0.92	1.4
300	>150 cm^{-1c}					

[a] Exciton-phonon coupling strength calculated by the relation $\alpha = \exp(-g)$

[b] Higher bound.

[c] Rough estimation. The lines cannot be resolved above 80°K.

included in the interpretation is the static disorder on one site, which obviously affects the corresponding exciton band. Further experiments, especially at 2 K and in other spectral regions, are planned to elucidate this question.

5 FINAL REMARKS

The present work raised a fundamental question, on the mechanism of triplet exciton motion in trans-stilbene: the observed spectroscopic properties could suggest a small triplet exciton diffusivity. Yet the measured room temperature value $\mathscr{D}_{aa} \sim 9 \cdot 10^{-5}\ \mathrm{cm}^2\ \mathrm{sec}^{-1}$ is comparable to the diffusivity in the (*ab*) plane of anthracene, where the DS is 18 cm^{-1}: $\mathscr{D} \sim 1.5 \cdot 10^{-4}\ \mathrm{cm}^2\ \mathrm{sec}^{-1}$.[10] The measured $\mathscr{D}_{aa}$ is also consistent with the measured value of $\alpha\gamma_{\mathrm{tot}}$ (see appendix). Hence, the room temperature diffusivity in trans-stilbene might well be completely determined by the "non-local" scattering.[14] Research on this interesting material is actively continued in this laboratory.

Acknowledgements

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Appendix Rate constant for triplet annihilation

To ascertain quantitatively the intensity of delayed fluorescence, and to gain further information on the triplet transport properties, the product $\alpha\gamma$ of the (unpolarized) absorption coefficient α at the 4880 Å Argon laser line (near the peak of the most intense band on Figure 2) by the total triplet–triplet annihilation rate constant γ, was measured at 300 K, using the phase method[15,16]. One finds

$$\alpha\gamma = 2.3 \pm 0.5 \cdot 10^{-15}\ \mathrm{cm}^2\ \mathrm{sec}^{-1}$$

which is comparable to the values found in anthracene or pyrene at 5145 Å.[15]

This implies that, at 295 K, γ is 10^{-12} to $10^{-11}\ \mathrm{cm}^3\ \mathrm{sec}^{-1}$, a value compatible with the measured value of $\mathscr{D}^5$.

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