

APPENDIX

LIST OF PUBLICATIONS AND REPRINTS

1. K.G.Mandal and T.N.Misra,
Spectroscopic investigation on the effect of gas adsorption on all-trans β -carotene solid film,
Ind.J.Pure & Appl. Phys. 10, 86 (1972)
2. K.G.Mandal and T.N.Misra,
Spectroscopic investigation on the effect of gas adsorption on solid films of polyenes: evidence of a low-lying forbidden electronic transition,
Chem.Phys. Letters 27, 57 (1974)
3. K.G.Mandal, B.Mallick and T.N.Misra,
The electronic spectra of some polyenes: evidence of a low-lying forbidden electronic transition,
(To be published)
4. K.G.Mandal and T.N.Misra,
The electronic spectra of α, ω -di-1 and α, ω -di-2-naphthylpolyenes in solution and in solid state,
(To be published)
5. K.G.Mandal and T.N.Misra,
The electronic spectra of α, ω -di-1-anthrylpolyene in solution and in solid state,
Bull.Chem.Soc. Japan 00, 00 (1975)
6. K.G.Mandal, K.A.M.Panicker and T.N.Misra,
Donor - Acceptor complexes between vitamin A (alcohol) and some electron acceptors: its biological implications,
Ind.J.Biochem.Biophys. 9, 328 (1972)

7. K.G.Mandal and T.N.Miera,
Stability constants of donor-acceptor complexes between
vitamin A and some electron acceptors, Ind.J.Biochem.
Biophys. 11, 175 (1974)

8. K.G.Mandal and T.N.Miera,
Delayed emission from organic mixed crystals:
Phosphorescence spectrum of biphenyl guest-carbazole
host mixed crystal,
J.Chem.Phys. 59, 2409 (1973)

9. K.G.Mandal and T.N.Miera,
Delayed emission from organic mixed crystal:
decay and rise characteristics of phosphorescence
from a biphenyl guest - carbazole host mixed crystal,
J.Chem.Phys. 61, 292 (1974)

Spectroscopic Investigation on the Effect of Gas Adsorption on All-*trans* β -Carotene Solid Film

KRISHNAGOPAL MANDAL & T. N. MISRA*

Department of Physics, North Bengal University
Darjeeling

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The effect of adsorption of gases on the absorption spectra of all-*trans* β -carotene film has been investigated. It has been observed that both ${}^1A \rightarrow {}^1B$ and ${}^1A \rightarrow {}^1D$ transitions in the visible and ultraviolet regions respectively show large red shift. It has been suggested that due to vapour adsorption, reaggregation of β -carotene in the film occurs and the excited state potential surfaces are strongly perturbed.

In an earlier publication¹ we have reported the effect of adsorption of a few gases on the ${}^1A \rightarrow {}^1B$ transition of all-*trans* β -carotene in the visible. We have extended our investigation to the other band system due to transition ${}^1A \rightarrow {}^1D$ in the ultraviolet. The experiments were motivated by the desire to test a hypothesis concerning the change in semiconduction currents in crystalline powder of β -carotene due to various gas adsorptions² which in turn has been proposed to explain the olfactory transduction mechanism³. High purity all-*trans* β -carotene was obtained from E. Merck of Germany. A 'Spectromom 202' ultraviolet spectrophotometer of Hungarian Optical Works was used to record the spectra.

In Fig. 1 we reproduce the absorption spectra of all-*trans* β -carotene under various experimental conditions. A tentative vibrational analysis of spectra is given in Table 1. At 18°C, the solution spectra in diethylether exhibit three main absorption bands in the visible, and the bands are separated by 1330 cm^{-1} . In solution spectrum, the band system in the ultraviolet region is broad and no vibrational structure is resolved. This solution

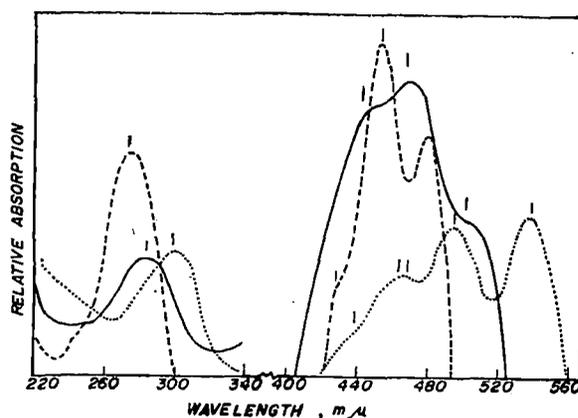


Fig. 1 — Absorption spectra of all-*trans* β -carotene [---, solution in diethylether; —, solid film; and , solid film after adsorption of CCl_4 vapour. The ultraviolet band system has been shown 2.5 times stronger in the diagram]

spectrum is similar to that reported earlier⁴. The spectrum due to solid state film is structurally similar to that in solution but the bands are broad and the spectrum is red shifted; the shift for the band system in the visible is 820 cm^{-1} and that for the ultraviolet is only 280 cm^{-1} . These shifts of the two transitions are roughly in the ratio of their intensity. The dotted lines in Fig. 1 show the spectrum when CCl_4 vapour is adsorbed on the surfaces of the crystallites in the film. The adsorption of vapour changes the visible band quite markedly — the first intense band in the system is now observed at 18510 cm^{-1} and also the intensity distribution among the vibronic bands changes. A tentative analysis of the band system has been made (Table 1). The frequency 1650 cm^{-1} has been observed in the solid film spectrum only after adsorption of gases.

We have extended the investigation to more vapours. In Table 2 the positions of the two band systems are shown under conditions of different vapour adsorption. The shifts of the band systems do not seem to have any relation with the ionization potentials of the vapours adsorbed indicating that

*Present address: Department of Physics, Birla Institute of Technology & Science, Pilani, Rajasthan.

TABLE — 1 ABSORPTION BANDS OF ALL-*trans* β-CAROTENE

Solution spectrum of β-carotene crystals at 291°K		Solid state film of β-carotene crystals at 291°K before adsorption		Solid state film of β-carotene crystals at 291°K after adsorption of CCl ₄ vapour	
Wavenumber cm ⁻¹	Assignment	Wavenumber cm ⁻¹	Assignment	Wavenumber cm ⁻¹	Assignment
VISIBLE BAND SYSTEM ¹ A→ ¹ B					
20740 (VS)	0	19920 (S)	0	18510 (VS)	0
22070 (VS)	0+1330	21370 (VS)	0+1450	20160 (VS)	0+1650
23400 (W)	0+2×1330	22520 (W)	0+1450+1150	21310 (Sb)	0+1650+1150
				21610 (Sb)	0+1650+1450
				22760 (Wb)	0+1650+1150+1450
					0+1650+1450+1150
ULTRAVIOLET BAND SYSTEM ¹ A→ ¹ D					
36490 (S)	0	35210 (S)	0	33440 (S)	0

 TABLE 2 — EFFECT OF GAS ADSORPTION ON THE 0,0 BAND OF ALL-*trans* β-CAROTENE CRYSTAL FILM

Gas adsorbed	Ionization potential eV	¹ A→ ¹ B transition wavelength (0,0 band before gas absorption is at 502 mμ)	¹ A→ ¹ D transition wavelength (0,0 band before gas adsorption is at 284 mμ)
Aniline	7.69	540	299
Benzyl alcohol	8.56	542	300
Toluene	9.20	537	294
Cyclohexane	9.51	538	295
Acetaldehyde	10.20	539	296
Carbon tetra-chloride	11.47	540	299

these spectral changes are not due to donor-acceptor-complex formation.

Examination of the ¹A→¹D transition in the ultraviolet clearly shows that the shape of the band system is distinctly retained even after vapour

adsorption and that the band system shows a shift of about 1771 cm⁻¹. This conclusively proves that the strong band at 18510 cm⁻¹ is not a new band being allowed due to different vapour adsorption but the band system is shifted towards red.

Thus, our present investigation confirms that the excited state potential energy surfaces are perturbed due to gas adsorption on all-*trans* β-carotene film and large red shift of both the transitions takes place indicating strong interaction between molecules in the reaggregated form.

The authors wish to thank Prof. S. N. Sen, Head of the Department, for kindly providing the necessary laboratory facilities.

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SPECTROSCOPIC INVESTIGATION ON THE EFFECT OF GAS ADSORPTION ON SOLID FILMS OF POLYENES: EVIDENCE OF A LOW-LYING FORBIDDEN TRANSITION

Krishnagopal MANDAL and T.N. MISRA

Department of Physics, North Bengal University, Darjeeling, India

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Optical absorption spectra of a few polyenes in the crystalline state have been studied. On adsorption of certain gases on the crystallite surfaces of polyenes, a new band appears on the low energy side of the long wavelength bands of these polyenes. The position of this band is 536, 537 and 375 $m\mu$ for all-*trans* β -carotene, 15,15'-*cis* β -carotene and retinyl compounds, respectively. A good mirror image relationship between the new absorption bands and the well known emission bands for these molecules indicates that this new band may be due to a weak transition to a low-lying π -electron state. This transition corresponds to a forbidden state below the strongly allowed (1B_u) state. The adsorbed gas molecules introduce the perturbation required for the enhancement of a low-lying forbidden transition.

1. Introduction

Investigations on the electronic spectra of linear conjugated polyenes have shown that the maxima of absorption and emission bands in the visible region have very little or no overlap [1]. This has led to the speculation that the absorption and emission bands in these molecules are severely Franck-Condon forbidden, which, taking account of the 0-0 band of a very strong absorption having a high extinction coefficient, as is the case with the intense absorption band of polyenes, is not easy to rationalise.

Recently, Hudson and Kohler [2] have presented some experimental evidence that there exists a low-lying forbidden state below the well-defined lowest π -electron state in α,ω -diphenyloctatetraene. This experimental evidence has also been supported by the theoretical treatment of Schulten and Karplus [3]. They have demonstrated that the inclusion of doubly excited configurations in semi-empirical and a priori calculations of polyenes leads to the existence of a low-lying weak π -electron state which has 1A_g symmetry in the all-*trans* form. The transition from the ground state to this low-lying π -electron state is for-

bidden. This low-lying state is present in other isomers as well [3]. Transition to this state has not been detected so far due to its very weak intensity.

In earlier communications [4, 5] we have reported the effect of gas adsorption spectra of all-*trans* β -carotene solid film. Adsorption of certain gas molecules on the crystallite surface changes the visible absorption spectrum: an intense band appears on the long wavelength side. In the light of recent works of Schulten and Karplus [3] it was thought worthwhile to extend the investigation to other polyenes so as to see whether this new band is due to the transition to a low-lying π -electron state.

2. Experimental

The polyenes employed in the present work are all-*trans* β -carotene, 15,15'-*cis* β -carotene, all-*trans* vitamin A alcohol and all-*trans* vitamin A acetate. These compounds of high quality have been obtained from Hoffman-La Roche Co., Switzerland. They have been used without further purification. Thin films of polycrystals of the polyenes have been made on the quartz surface

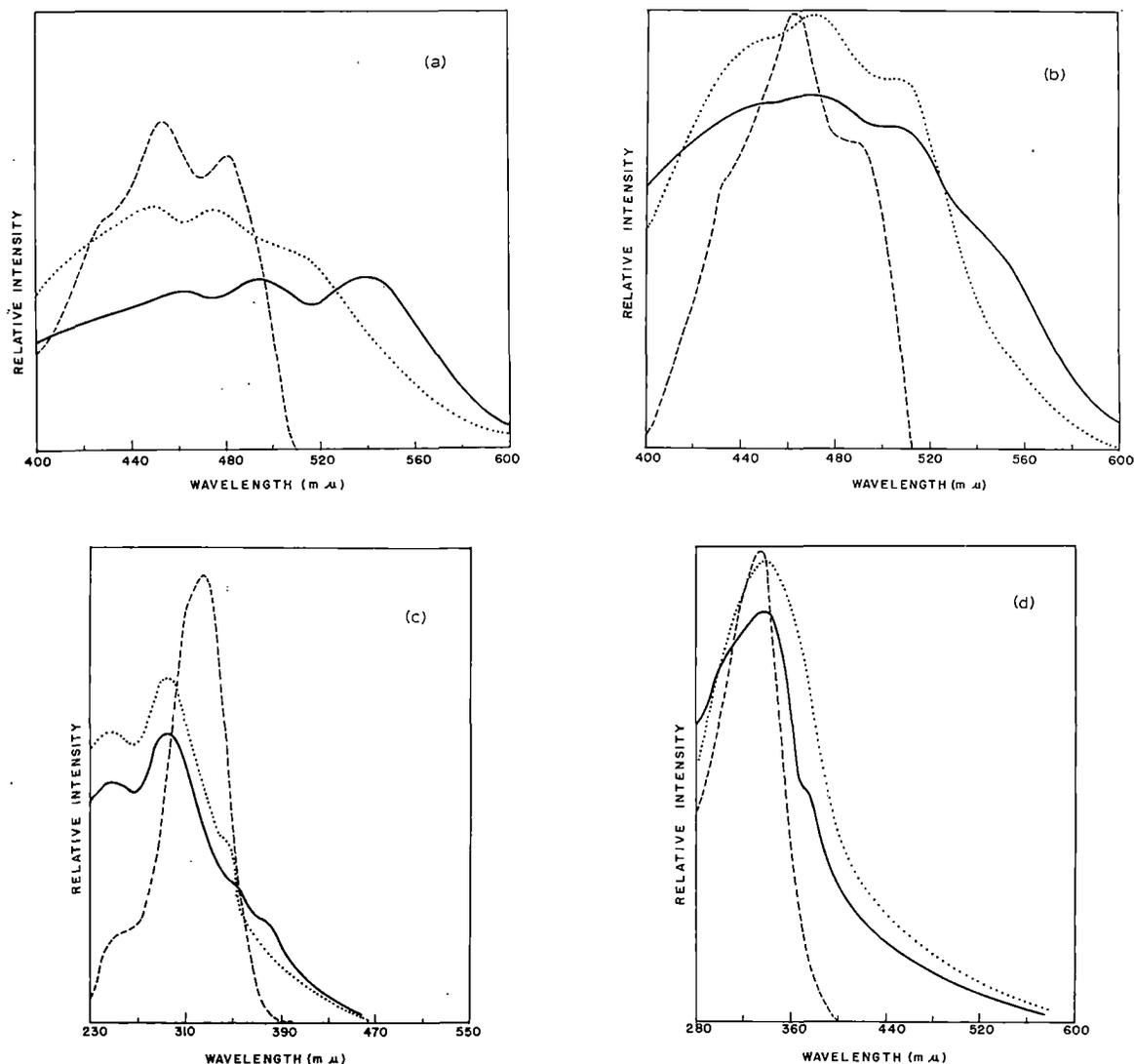


Fig. 1. (a) Absorption spectrum of all-*trans* β-carotene at room temperature (25°C). ---, solution spectrum in diethyl ether; . . . , solid film spectrum; —, solid film spectrum after CCl₄ vapour adsorption. (b) Absorption spectrum of 15,15'-*cis* β-carotene at room temperature. ---, solution spectrum in CCl₄; . . . , solid film spectrum; —, solid film spectrum after pyridine vapour adsorption. (c) Absorption spectrum of all-*trans* vitamin A alcohol at room temperature. ---, solution spectrum in ethyl alcohol; . . . , solid film spectrum; —, solid film spectrum after CCl₄ vapour adsorption. (d) Absorption spectrum of all-*trans* vitamin A acetate at room temperature. ---, solution spectrum in CCl₄; . . . , solid film spectrum; —, solid film spectrum after dimethylaniline vapour adsorption.

by gently rubbing the material. From the absorption spectrum, the thickness of the film has been estimated to be about 500 Å.

Solid films thus made have been exposed to vapours of CCl₄, acetone, cyclohexane, aniline, methanol, pyridine and dimethylaniline. The exposure has been

made by holding the films for about 5 minutes in a beaker containing the chemicals of spectrograde quality. The films have thus been exposed at the saturated vapour pressure of various chemicals at room temperature (25°C).

Absorption spectra were recorded immediately

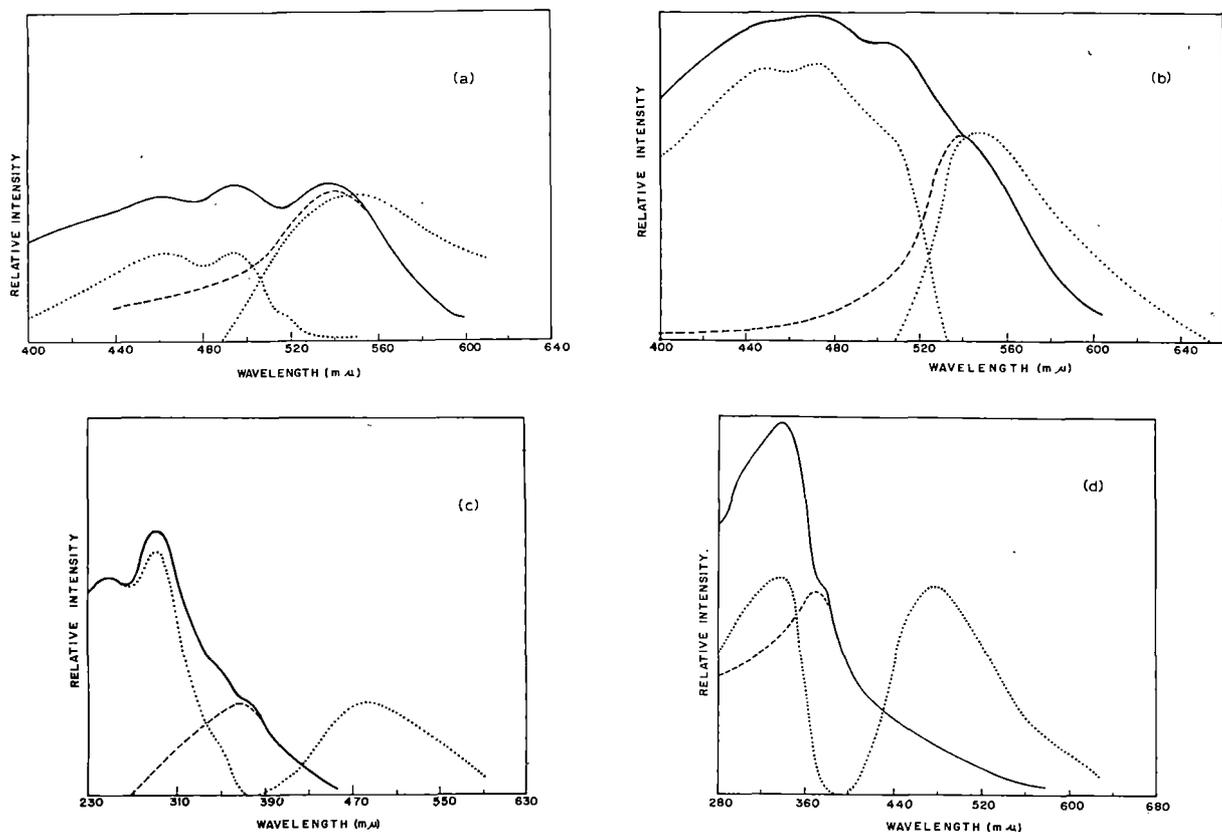


Fig. 2. (a) Absorption and emission spectra of all-*trans* β -carotene. —, absorption spectrum for the solid film after CCl_4 vapour adsorption. Resolution of the total absorption spectrum: . . ., band of the solid film; ---, new band; . . ., emission spectrum in solution. (b) Absorption and emission spectra of 15,15'-*cis* β -carotene. —, absorption spectrum for the solid film after pyridine vapour adsorption. Resolution of the total absorption spectrum: . . ., band of the solid film; ---, new band; . . ., emission spectrum in solution. (c) Absorption and emission spectra of all-*trans* vitamin A alcohol. —, absorption spectrum for the solid film after CCl_4 vapour adsorption. Resolution of the total absorption spectrum: . . ., band of the solid film; ---, new band; . . ., emission spectrum in solution. (d) Absorption and emission spectra of all-*trans* vitamin A acetate. —, absorption spectrum for the solid film after dimethylaniline vapour adsorption. Resolution of the total absorption spectrum: . . ., band of the solid film; ---, new band; . . ., emission spectrum in solution.

after exposure by a Perkin-Elmer Recording Spectrophotometer-202 at room temperature.

3. Results

The room temperature absorption spectra of the polyenes under investigation are shown in figs. 1 and 2. With all the vapours studied the effect is similar except that with certain of these the effect is more pronounced than with others. CCl_4 vapour adsorption on all-*trans* β -carotene and vitamin A alcohol affect the

absorption spectra intensely whereas pyridine and dimethylaniline vapours have a strong effect for *cis* β -carotene and vitamin A acetate, respectively.

The absorption spectrum of all-*trans* β -carotene in diethylether solution exhibits three main absorption bands at 482, 453 and 427 μm (fig. 1a). The bands are separated by about 1330 cm^{-1} . The spectrum in the solid state as shown in fig. 1a looks structurally similar to that in solution but the bands are broad and red-shifted. In figs. 1a and 2a we reproduce the absorption spectrum of all-*trans* β -carotene when CCl_4 vapours are adsorbed on the solid film. When various

vapours are adsorbed on the surfaces of the crystallites in the film, a marked change in the β -carotene spectrum is observed. On being exposed in CCl_4 vapour as shown in fig. 1a the first intense band appears at $536 \text{ m}\mu$. The intensity distribution among the vibronic bands also changes.

The absorption spectrum of 15,15'-*cis* β -carotene in CCl_4 consists of three bands at 485, 463 and $435 \text{ m}\mu$ (fig. 1b). In the solid state film the spectrum is broad and red-shifted. After exposure to various vapours the solid state spectrum shows a pronounced change in that a new band appears at $537 \text{ m}\mu$. The other bands show little change on gas adsorption. The absorption spectrum of the solid film when exposed to pyridine vapour is shown in figs. 1b and 2b.

The absorption spectra of all-*trans* vitamin A alcohol and all-*trans* vitamin A acetate are shown in figs. 1c and 1d, respectively. When exposed to different vapours, in both these polyenes a new weak band appears at $375 \text{ m}\mu$ along with the bands observed before vapour adsorption. The other bands do not show any shift after vapour adsorption. The absorption spectrum of vitamin A alcohol in ethanol has two bands, one at $250 \text{ m}\mu$ and the other, which is very intense, is at $325 \text{ m}\mu$. There is a weak hump at $309 \text{ m}\mu$. The crystal spectrum shows three main absorption bands at 250, 294 and $345 \text{ m}\mu$.

4. Discussion

4.1. A low-lying forbidden electronic transition

Our experimental results show that in all the polyenes studied a new band appears when certain vapours are adsorbed on the surface of polyene crystals. The intensity of this new band depends on the polyenes and also on the vapour adsorbed. In all-*trans* β -carotene this new band at $536 \text{ m}\mu$ appears intense and in other polyenes this band is relatively weak. There is a large overlap between the well-studied long wavelength band system and the new band. It is difficult to locate exactly the position of this new band. In order to get the longest wavelength band contour out of the total spectrum we have resolved qualitatively the whole spectrum into two parts: one part corresponds to the spectral shape of the new band and the other part corresponds to the solid film spectrum before vapour ad-

sorption. The resolved spectra are shown in fig. 2.

The crystal emission spectra of the polyenes studied except vitamin A acetate are not available. However, the emission spectra of vitamin A alcohol, all-*trans* and -*cis* isomers of β -carotene in solution have been reported [1, 6] though emissions from β -carotenes have been questioned [7]. The emission spectra [1] of vitamin A acetate in solution and in the solid state are similar except a slight blue-shift of about $24 \text{ m}\mu$ in the crystalline state. Similar situations may exist in other polyenes as well.

We have, therefore, ventured to compare the emission spectra [1, 6] of the polyenes in solution with the absorption spectra in solid films. The heights of the absorption and emission maxima are normalised. It is evident from the plots that there is a good overlap between emission and the new absorption bands in all the polyenes we have studied. The mirror image relation is also satisfied. We have plotted relative intensity against λ ($\text{m}\mu$) instead of ϵ_ν/ν against ν as suggested by Birks and Dyson [8]. Of all the polyenes studied, overlap between the absorption and emission spectra is greatest in β -carotene and least in vitamin A alcohol. Thus our experimental results suggest that the excited electronic state involved in the new absorption band and the reported emission bands of polyenes is the same and may be the low-lying weak π -electron state suggested by Schulten and Karplus [3]. The transition from the ground state to this low-lying π -electron state is forbidden since this state in all-*trans* polyenes has 1A_g symmetry [3]. Our gas adsorption method thus opens a new avenue in making this low-lying forbidden transition allowed at room temperature.

The adsorbed gas molecules introduce the perturbation required for the enhancement of a low-lying forbidden transition. The exact nature of the perturbation is not yet resolved.

4.2. Factor group splitting

The wavefunctions of translationally non-equivalent interacting molecules in the crystal produce splitting of molecular energy levels [9, 10]. It is of interest to note this factor group splitting in vitamin A alcohol solid film. The weak absorption band of vitamin A alcohol in solution at about $250 \text{ m}\mu$ evidently corresponds to the band at $250 \text{ m}\mu$ in the solid state (fig. 1c). The two bands in solution at about 309 and

325 $m\mu$ have a separation of 16 $m\mu$. In the solid film neither of the bands at 294 and 345 $m\mu$ seems to correspond to the weak solution band at 309 $m\mu$. It is likely that these two bands in the solid state are the factor group split components of the 325 $m\mu$ band in solution. The weak band at 309 $m\mu$ in the solution spectrum is possibly masked by the strong absorption at 294 $m\mu$ in the crystalline state.

Unfortunately the crystal structure of vitamin A alcohol and molecular orientations in the lattice are not known. It was, therefore, not possible to estimate the factor group splitting in the crystal.

In the solid film spectra of other polyenes, no factor group splitting could be detected.

Acknowledgement

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Donor-acceptor Complexes between Vitamin A (Alcohol) & Some Electron Acceptors: Its Biological Implications

KRISHNAGOPAL MANDAL*, K. A. M. PANICKER & T. N. MISRA*

Department of Physics, Birla Institute of Technology & Science, Pilani

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The charge transfer (CT) spectra of all-*trans* vitamin A-alcohol with electron acceptors like chloranil, iodine monochloride, iodine and bromine have been observed. The absorption maximum of the CT band occurs at about 290 m μ in each complex. The CT band of vitamin A-chloranil complex is most intense; the intensity of the CT band of complexes formed by other acceptors is weak. The stability constant of vitamin A-chloranil complex has been determined by Foster-Matheson expression and has a value of $K = 65 \times 10^3$ moles⁻¹. It has been suggested that since vitamin A is present in the living system, CT mechanism may explain the biological processes involved in cell division, growth and its regulation by thyroid hormones, pharmacological reaction of iodine and olfactory transduction.

THERE is much interest in the role of charge transfer (CT) interaction in biology. The balance of electron donors and acceptors of varied biopotential is one of the basic parameters of life and is used in regulation of activity and physical state of the cell¹. Medium range CT is the most frequent and fundamental in biological reactions. The forces developed due to CT may bring about the association of two or more entities. It may further influence equilibrium and reactivity. The preferred conformation resulting from CT in turn may confer a biological activity.

Most of the theoretical works dealing with electron donor acceptor (EDA) complexes have been based on a valence bond type of formalism. Various workers²⁻⁴ have treated EDA complexes in terms of molecular orbital theory. Flurry⁵ has presented a semiempirical linear combination of atomic orbitals description of EDA complexes. The energy of the CT band estimated by this method is given by

$$E_{CT} = I - A + C$$

where I is the ionization potential of the electron donor, A , the electron affinity of the electron acceptor and C , the coulomb contribution to the charge transfer transition.

The presence of vitamin (Vit) A in the living system is well recognized. It is present in the cone layers of eyes⁶, olfactory areas⁷⁻⁹, skin and membranes^{10,11}. Vit A is of value in resistance to infections and it is a growth factor¹². It induces cell division¹³ and is a component in the mechanism of aerobic energy transport¹⁴. No evidence of CT complexes of Vit A seems to have been reported. It was, therefore, thought worth while to carry out the investigation of donor-acceptor complexes of Vit A (alcohol) with various electron acceptor molecules. In this communication, we report the evidence of donor-acceptor complexes between Vit A and some electron acceptors. Biological implications of this observation are discussed.

Materials and Methods

Crystalline all-*trans* Vit A (alcohol) obtained from Roche, Bombay, was used without further purification. Chloranil, bromine, ICl and iodine were used as acceptors. The solutions of donor (Vit A) as well as acceptors were prepared in spectroscopically pure CCl₄ obtained from BDH. The absorption spectra were recorded in a Beckman DU-2 spectrophotometer and also in a Perkin-Elmer 202 recording spectrophotometer.

Results

The electronic absorption spectrum of Vit A in CCl₄ has two broad absorption bands with λ_{max} at 335 and 254 m μ respectively (Fig. 1). The band at 254 m μ is weak, the long wavelength band being fourteen times more intense. When the electron acceptors are added to Vit A solution, the colour of the solution changes and a new absorption band appears. The experiments were carried out at 295°K, and possibly 1:1 complexes were formed. The experimental results have been summarized in Table 1.

The acceptor chloranil has an absorption maximum at 375 m μ . Fig. 2 shows the absorption spectra of Vit A-chloranil complex. The new sharp intense absorption band which exists in neither of the spectra of components of the complex appears at 292 m μ . Change of concentration of the donor does not bring any change in the position of the new CT band, but the intensity of this band increases with the increase of donor concentration. It is of interest to note that the weak band of the donor at 254 m μ gets more intense after the complex formation and the intensity of the first absorption band at 335 m μ decreases.

The absorption maximum of bromine is at 416 m μ in CCl₄. Fig. 1 shows the absorption spectrum of Vit A-bromine complexes. The approximate position of the CT band is given in Table 1. The absorption band of the complex is intense as compared to the complexes with iodine or iodine monochloride.

*Present address: Department of Physics, North Bengal University, P.O. North Bengal University, Dist. Darjeeling, West Bengal.

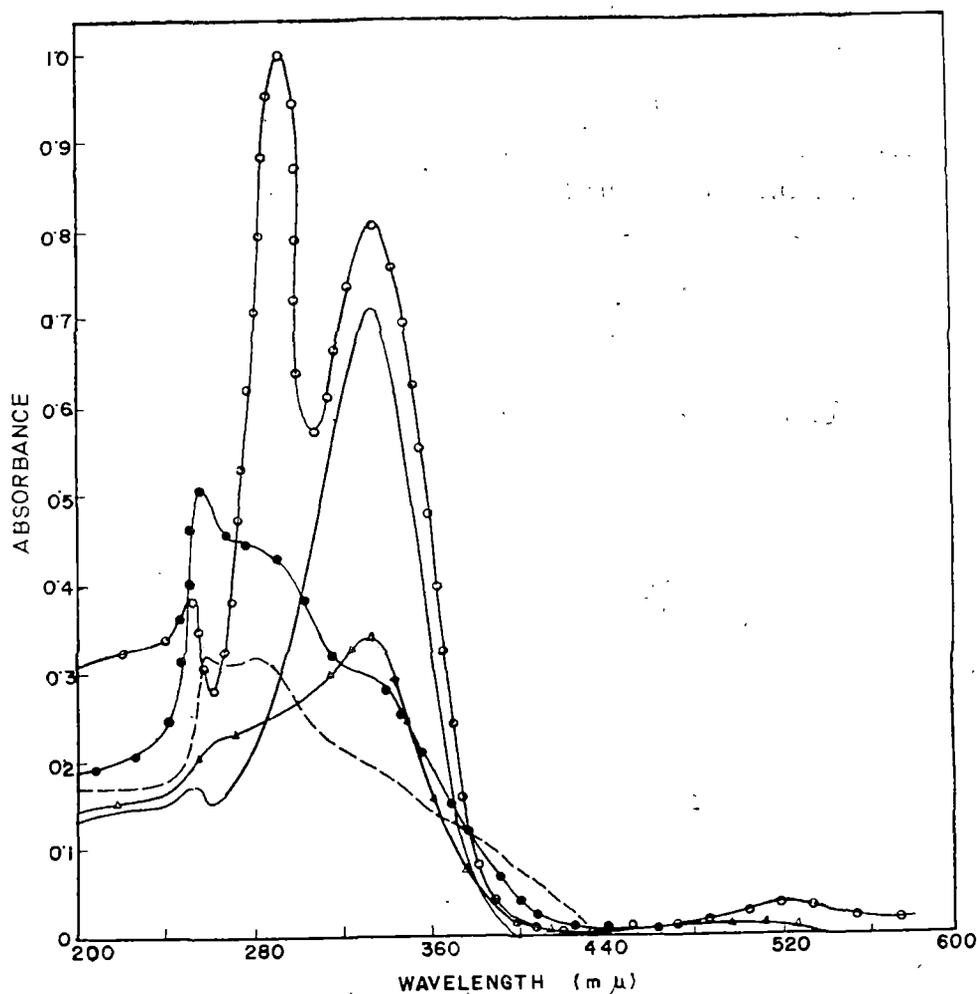


Fig. 1 — Charge transfer spectra of all-*trans* Vit A (alcohol) with various acceptors [O—O, Vit A-chloranil complex; ●—●, Vit A-ICl complex; Δ—Δ, Vit A-iodine complex; ----, Vit A-bromine complex; —, solution spectra of Vit A in CCl₄]

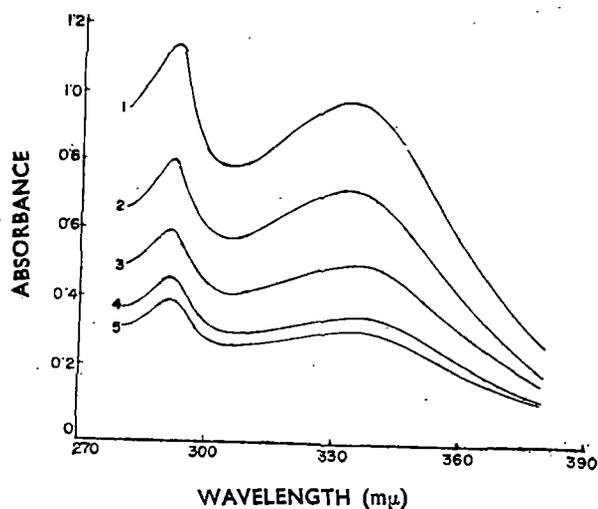


Fig. 2 — Charge transfer spectra of Vit A-chloranil complex with different concentrations of the donor and acceptor $\{[D]_0$ and $[A]_0$ for curves 1-5 are given in Table 2}

TABLE 1 — CHARGE TRANSFER SPECTRA OF VIT A (ALCOHOL) WITH VARIOUS ACCEPTORS

Complex	Conc. of donor $\times 10^{-4}$ mole/litre	Donor band, $m\mu$		CT band $m\mu$
		1st	2nd	
Vit A-chloranil	0.594	330	248	292*
	1.188	331	250	292*
	1.782	335	252	292*
Vit A-bromine	0.386	335 ± 5	260	280†
	1.748	335 ± 5	260	280†
	2.622	335 ± 5	260	280†
Vit A-ICl	0.4371	Blurred	258	$285 \pm 5\ddagger$
	0.8742	335 ± 5	259	$285 \pm 5\ddagger$
	1.311	335 ± 5	260	$285 \pm 5\ddagger$
Vit A-iodine	0.105	335	254	$290 \pm 5\S$
	0.117	335	256	$290 \pm 5\S$
	0.175	335	260	$290 \pm 5\S$

Intensity of band: *Very strong; †strong; ‡weak; §blurred.

TABLE 2—ABSORBANCE OF CT BAND AT 292 m μ OF VIT A-CHLORANIL COMPLEX AT VARIOUS DONOR AND ACCEPTOR CONCENTRATIONS

Serial No. of curves as shown in Fig. 2	$[D]_0$ $\times 10^{-5}$ mole/litre	$[A]_0$ $\times 10^{-5}$ mole/litre	A	$1/[A]_0$ $\times 10^4$ litre/mole	$[A]_0/A$ $\times 10^{-5}$ mole/litre
1	5.984	1.022	0.54	9.79	18.9
2	4.488	0.766	0.38	13.05	20.0
3	2.992	0.511	0.24	19.56	22.1
4	2.169	0.371	0.14	26.99	24.6
5	1.87	0.319	0.12	31.30	26.6

Iodine monochloride gives an absorption maximum at 465 m μ in CCl₄. The absorption spectrum of Vit A-ICl complex is reproduced in Fig. 1. The absorption band of the donor at 254 m μ is very prominent in Vit A-ICl complex. The CT complex band is broad in the complex.

Iodine bands have two absorption maxima at 258 m μ and 522 m μ in CCl₄. Fig. 1 shows the absorption spectrum of Vit A-I₂ complex. Here the CT band is again broad and measurement of the band maxima is impaired. The absorption band of the acceptor also has been observed. There seems to be a slight blue shift of this band in complex as compared to that of the free acceptor.

A linear relationship proposed by Foster and Matheson¹⁵ has been used to estimate the stability constant of Vit A-chloranil complex. In this method, a constant ratio of donor and acceptor concentrations is maintained so that

$$[D]_0 = n[A]_0$$

Here $[D]_0$ and $[A]_0$ are donor and acceptor concentrations respectively. Foster and Matheson's expression is

$$\frac{[A]_0}{A} = \frac{1}{nK\epsilon} \cdot \frac{1}{[A]_0} + \frac{n+1}{n} \cdot \frac{1}{\epsilon}$$

where A = the absorbance of the CT band for 1 cm path length at λ , the wavelength of measurement, ϵ = molar extinction coefficient K = stability constant of the complex.

Unlike that in Benesi-Hildebrand¹⁶ method, here the condition $[D]_0 \gg [A]_0$ need not be satisfied.

Since our donor absorption band has its tail extended in the region of λ_{\max} for CT band (where the measurement has been made) we made an estimate of the absorbance of the CT band by subtracting the donor absorbance from the total absorbance at the wavelength λ_{\max} . Absorbance of the CT band at λ_{\max} obtained in this way for various concentrations of donor and acceptor are given in Table 2.

A plot of $[A]_0/A$ against $1/[A]_0$ should be a straight line, from the intercept and gradient of which K and ϵ may be evaluated. Fig. 3 shows such a plot for Vit A-chloranil complex. Values obtained for K and ϵ are 65×10^3 and 75×10^3 respectively. The observations that our plot gives a straight line and that reasonable values for K and ϵ have been obtained suggest that this procedure is satisfactory.

Discussion

The spectra—The electronic spectral study of Vit A has provided some interesting information about the donor acceptor complexes of this mole-

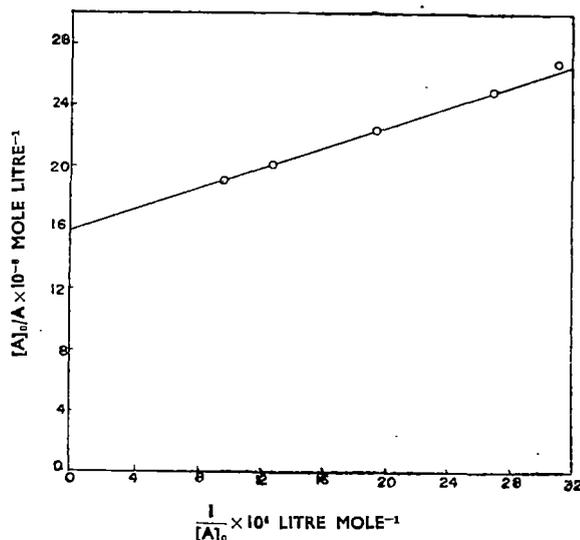
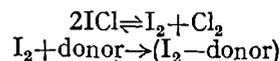


Fig. 3—Determination of stability constant of Vit A-chloranil complex using Foster-Matheson expression

cule with different acceptors. While discussing with Vit A-ICl complex, I₂ band at 520 m μ has been observed. The spectrum of Vit A-I₂ is distinctly different from what has been observed in Vit A-ICl complex. It is possible that in this case, in addition to ICl molecule forming Vit A-ICl complex, I₂ also acts as an acceptor. The Vit A-I₂ complexes may be formed through the following mechanism:



The CT absorption band of Vit A-iodine complex is very weak. This may be due to the fact that the Vit A-I₂ charge transfer interactions proceed through the path



Finally I⁻ combining with free iodine molecule I₂ gives rise to I₃⁻. The absorption band of I₃⁻ in CCl₄ is around 300 m μ and it may be superimposed on the band of Vit A with an absorption maxima at 335 m μ . As a result, the broad band around 335 m μ becomes more intense and the intensity of the CT band appears weak.

The present study shows that of all the complexes studied Vit A-chloranil complex is the most intense, complexes with Br₂, ICl and I₂ are comparatively weak. Vit A-chloranil is a π - π complex, there is more orbital overlap resulting in high value of stabilization constant. The other acceptors are

σ -acceptors and for π - σ complexes the orbital overlap is less and the CT band is weak.

Biological Implications

Cell division — Vit A is mitogenic¹⁷ and influences cell differentiation. It enhances malignant growth and increases the incidence of sarcoma producing more tumours¹⁸. During cell division there is an accumulation of —SH— radicals in the cell. The radical is electron donor in nature. This indicates cell division, possibly through charge transfer mechanism.

Now it has been confirmed that Vit A (alcohol) forms CT complexes with various acceptors. It may reasonably be argued that by virtue of its electron donating properties Vit A may initiate cell division by similar CT mechanism. The pre-cancerous exudate cells showed somewhat more Vit A than the normals¹⁹.

Growth and its regulation by thyroid hormones — Growth takes place ultimately by cell division. Vit A is a growth factor. The thyroid hormones act as regulators of growth. From the structural formula of thyroid hormones it can be seen that the thyroid hormones contain one or more iodine atoms. It has also been observed that the biological activities of trichloro, tribromo and triiodo thyronine are in the same order as the electron affinities of chlorine, bromine and iodine atoms²⁰. The electron affinity conferred by halogen substitution is independent of the nature of the molecule in which it is substituted provided no other electrophores are present²¹.

As the Vit A is an electron donor and is capable of forming CT complexes with electron acceptors, it seems reasonable to propose that the controlling effect of thyroid hormones on growth may be due to its ability to form CT complexes with Vit A.

Pharmacological reaction of iodine — In the intact skin the cells are strongly attached to one another. When the skin or the membrane is injured, a free semiliquid condition is created. The pharmacological application of iodine on wounds are prima facie on the basis that they are bacteriostatic. Now it comes to that the acceptors promote CT by accepting the electron from Vit A in the dermis and accelerate the bringing together of molecules by the merging of their orbitals.

Olfactory transduction — High concentration of free and protein bound carotenoids, Vit A, etc., is present in the olfactory organ of animals. The importance of carotenoids and Vit A in olfaction has been proved²². It has been proposed by Rosenberg *et al.*²³ that molecules like Vit A, present in the olfactory organ, can form weakly-bound reversible complexes with adsorbed gas molecules which increase the conductivity of the membrane incorporated with carotenoids and lead to the electrical

event of olfaction. The complexes were thought to be donor-acceptor type but no experimental evidence was presented. The present experiments prove that Vit A (alcohol) does indeed form donor-acceptor complexes with various acceptor molecules. The weakly-bound reversible complexes involved in the mechanism of olfactory transduction may very well be of charge transfer nature.

The fact that all-*trans* Vit A (alcohol) is a semiconductor with low conductivity does not explain the various functions attributed to it in the living system. The conjugated π -electron system in Vit A gives a vague clue. The electron donating property leading to the formation of charge transfer complexes is a novel outcome and can successfully elucidate and elaborate the mechanism underlying the processes associated with life in which Vit A is involved.

Acknowledgement

Thanks are due to the Head of the Department of Biological Sciences for providing the authors with the laboratory facilities. Thanks are also due to Dr A. S. N. Murthy for helpful discussions. A generous gift of high quality all-*trans* Vit A (alcohol) from Roche, Bombay, made this work possible.

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IN an earlier communication,¹ the evidence of formation of charge transfer complexes between vitamin A alcohol and some electron acceptors and implications of this charge transfer mechanism in biological systems have been stressed. We have recently extended the investigation to vitamin A acetate. In this communication, the results of their study are reported.

High quality vitamin A (Roche, Bombay) has been used without purification. Br₂ and ICl have been used as electron acceptors. Spectrograde quality solvent CCl₄ has been used. The solutions of CT complexes have been prepared by mixing the respective components in suitable concentrations. The spectra have been recorded in a Spektrinom-202 spectrophotometer.

The absorption spectra of vitamin A alcohol-Br₂ complex is presented in Fig. 1. The new sharp intense absorption band which is absent from the spectra of either of the components of the complex, appears at 280 mμ. Change of concentration of the donor does not bring any change in the position of the new CT band, but the intensity of this band increases with the increase of donor concentration. In vitamin A acetate-Br₂ complex, the lowest singlet absorption band in CCl₄ is at 335 mμ. The CT band appears broad at about 295 mμ. It is seen that in both vitamin A alcohol and vitamin A acetate there is some overlap between the donor and the CT band.

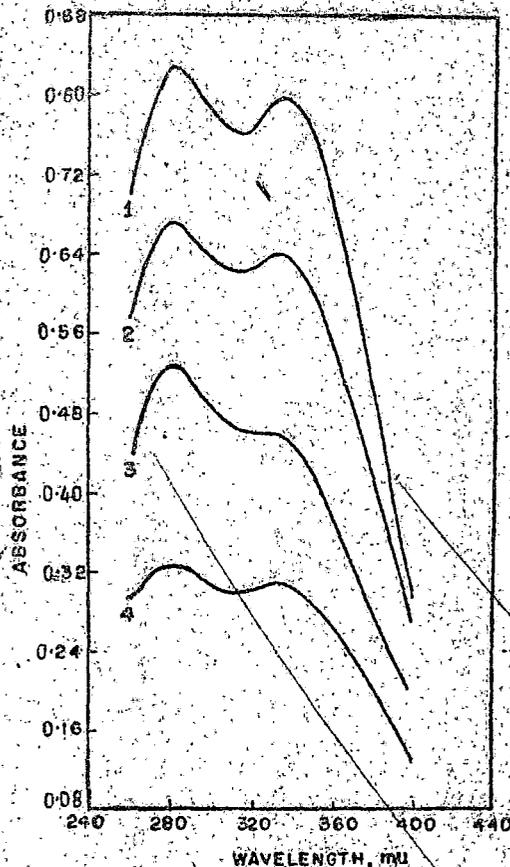


Fig. 1 — Charge transfer spectra of vitamin A alcohol-Br₂ complex with different concentrations of the donor and acceptor [1, $[D]_0 = 0.7972 \times 10^{-4}$ mole/litre, $[A]_0 = 0.7829 \times 10^{-4}$ mole/litre; 2, $[D]_0 = 0.6377 \times 10^{-4}$ mole/litre, $[A]_0 = 0.6263 \times 10^{-4}$ mole/litre; 3, $[D]_0 = 0.4783 \times 10^{-4}$ mole/litre, $[A]_0 = 0.4697 \times 10^{-4}$ mole/litre; 4, $[D]_0 = 0.3188 \times 10^{-4}$ mole/litre, $[A]_0 = 0.3131 \times 10^{-4}$ mole/litre]

Stability Constants of Donor-acceptor Complexes between Vitamin A & Some Electron Acceptors

KRISHNAGOPAL MANDAL & T. N. MISRA

Department of Physics, North Bengal University, Darjeeling

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Stability constants of the charge transfer complexes of vitamin A with some electron acceptors, determined at 25°C using Foster-Matheson's method, are 9×10^3 , 12×10^3 and 6.7×10^3 moles⁻¹ for vitamin A alcohol-bromine, vitamin A alcohol-iodine monochloride and vitamin A acetate-bromine complex respectively.

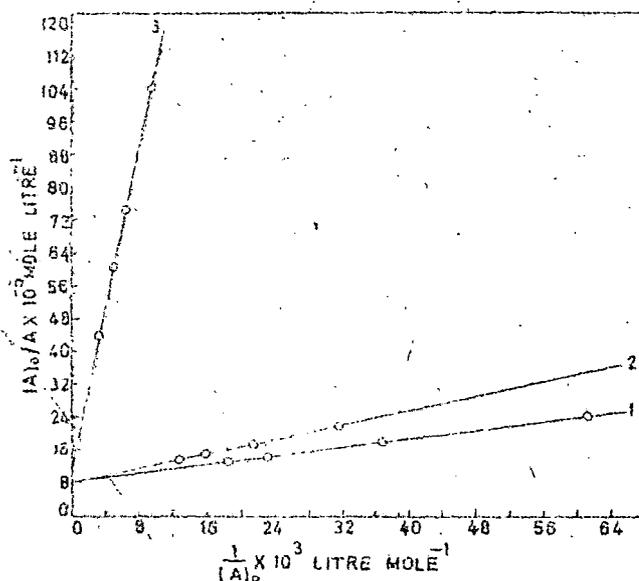


Fig. 2 — Determination of stability constant of CT complexes using Foster-Matheson expression [1, vitamin A alcohol-ICl complex; 2, vitamin A alcohol-Br₂ complex; 3, vitamin A acetate-Br₂ complex]

The stability constants of the complexes have been estimated by means of Foster-Matheson method² at room temperature (26°C). This method is valid for 1:1 complexes. The advantage of this method is that the total concentration of one component of the complex can be expressed in terms of the other, i.e. $[D]_0 = n[A]_0$ where $[D]_0$ and $[A]_0$ are the donor and acceptor concentrations respectively and n is a number being the constant ratio of concentrations of the donor and acceptor. The expression used is

$$\frac{[A]_0}{A} = \frac{1}{nK\epsilon} \cdot \frac{1}{[A]_0} + \frac{n+1}{n} \cdot \frac{1}{\epsilon}$$

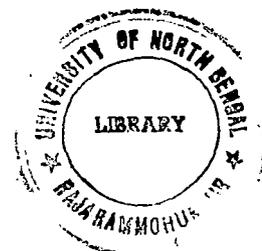
A being the absorbance of the CT band for 1 cm path length at the wavelength of CT band maxima; ϵ , the extinction coefficient and K , the stability constant.

Due to overlap between the donor and the CT band, in determining stability constants, the donor absorbance has been subtracted from the total absorbance of the CT band. The plots of $\frac{[A]_0}{A}$ against $[A]_0^{-1}$ for different complexes are linear (Fig. 2). From the plots thus obtained, the values of ϵ for vitamin A alcohol-Br₂, vitamin A alcohol-ICl and vitamin A acetate-Br₂ complexes have been evaluated as 24.77×10^3 , 19×10^3 and 22×10^3 litres mole⁻¹ cm⁻¹ respectively. The stability constants (K) determined, using these values of ϵ , are 9×10^3 , 12×10^3 and 6.7×10^2 moles⁻¹ for vitamin A alcohol-Br₂, vitamin A alcohol-ICl and vitamin A acetate-Br₂ respectively.

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Delayed emission from organic mixed crystals: Phosphorescence spectrum of biphenyl guest-carbazole host mixed crystal

T. N. Misra and Krishnagopal Mandal

Department of Physics, North Bengal University, Darjeeling, India

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The phosphorescence spectrum of a biphenyl guest-carbazole host mixed crystal with guest concentration 10^{-2} mole/mole has been investigated in the temperature range 15–90°K. At 15°K the spectrum consists of three superimposed spectra, the most intense one being that of biphenyl guest with the origin at 22 986 cm^{-1} . The two other spectra have been attributed to emission from traps T_1 and T_2 . Emission from shallow trap T_1 has its origin at 24 572 cm^{-1} and that from deep trap T_2 at 23 552 cm^{-1} . A tentative vibrational analysis of the spectra has been made. It has been observed that at very low temperature the guest and the two traps are all populated. As the temperature is raised, the shallow trap T_1 is depopulated and emissions from the deep trap T_2 and the guest are observed. On further increase of temperature T_2 is also depopulated and the emission is wholly of biphenyl.

I. INTRODUCTION

In earlier communications¹⁻⁶ we have discussed delayed emission of organic mixed crystals with biphenyl as the host and a number of polyacenes as guests. In all these systems the host and the guests were chosen in such a way that the lowest excited singlet S_1 and the lowest excited triplet T_1 of the guests are energetically lower than S_1 and T_1 of the host. In all these systems, delayed fluorescence has been observed. Temperature and guest concentration dependence of delayed fluorescence and phosphorescence and their decay characteristics have been studied and mechanistic models for guest-guest, guest-trap, and trap-trap annihilation have been proposed and substantiated.

We have recently extended our investigation to the carbazole host-biphenyl guest mixed crystal system where the singlet and triplet exciton bands of the host are energetically sandwiched between S_1 and T_1 of the guest. In the present paper we report our results.

II. EXPERIMENTAL

Excitation was provided by the light from a PEK model 401 mercury lamp operated at an output of 100 W. A liquid helium cryostat of the standard Duerig and Mador⁷ design somewhat modified by following the suggestion of Roberts⁸ was used. The sample was cooled by helium heat exchange gas in contact with the liquid helium container and experiment could be conducted over a range of temperatures. The temperature of the samples was estimated to within about a degree during the cooling and warming up process by monitoring the pressure of the helium heat exchange gas in the sample chamber. The sample

chamber was filled with helium to about one atmosphere at room temperature and the tap closed. On cooling, two calibration points were obtained: one at liquid nitrogen temperature (77°K) and the other at liquid helium temperature (4.2°K). Other temperatures in the range 4.2–77°K were then found approximately from measured pressure by linear interpolation. A rotating disc phosphoroscope was used to cut off the fast emission. The emission was passed through a Spex model 1700-II (Czerny-Turner, 3/4 meter, $f/6$ spectrometer/spectrograph) with a grating blazed at 7500 Å and a dispersion of 10 Å/mm. The slit width was 100–200 μ depending on the intensity of the emissions but was kept constant for each complete experiment. The emission was detected by an RCA 1P28 photomultiplier mounted at the exit slit. The photocurrent was amplified by a Keithley 414 micro-microammeter, and displayed on a Bristol chart recorder.

Biphenyl was purified by treating the commercial material with maleic anhydride. The resulting material was further purified by repeated zone refining. Carbazole supplied by Eastman Kodak was freed from anthracene by treatment with maleic anhydride. The sample was then chromatographed following a technique developed by Sangster⁹ on silica gel using petroleum ether as an eluent.

Single crystals were grown under vacuum from the melt with guest concentrations about 10^{-2} mole/mole by slowly lowering the sample through Bridgeman furnace.

Strain free, single crystal portions of an ingot were selected by examining the sample for complete uniform extinction under a polarizing microscope.

TABLE I. Phosphorescence bands of biphenyl guest-carbazole host mixed crystal.

15 °K			25 °K			90 °K			Assignment
Wavenumber (cm ⁻¹)	Intensity	Separation from the first band (cm ⁻¹)	Wavenumber (cm ⁻¹)	Intensity	Separation from the first band (cm ⁻¹)	Wavenumber (cm ⁻¹)	Intensity	Separation from the first band (cm ⁻¹)	
24 572	w	00							T ₁ (origin)
24 498	s	74							T ₁ -74
24 352	w	220							T ₁ -220
24 290	w	282							T ₁ -282
24 152	vw	420							T ₁ -420
23 886	vw	686							T ₁ -686
									T ₁ -(612+74)
23 828	vw	744							T ₁ -744
23 754	ms	818							T ₁ -(744+74)
23 617	w	955							T ₁ -955
23 552	s	1020	23 549	m	00				T ₂ (origin)
23 393	w	1179							T ₁ -(1105+74)
23 349	vw	1223							T ₁ -1223
23 270	vw	1302							T ₁ -1302
23 215	vw	1357							T ₁ -1357
23 156	w	1416	23 130	w	419				T ₂ -420
23 091	w	1481							T ₁ -1481
22 986	vvs	1586	22 998	vvs	551	23 003	vvs	00	(0, 0) _B
22 952	w	1620							T ₁ -1620
22 857	s	1715	22 863	vw	686				T ₁ -(1620+74)
									T ₂ -686
									T ₂ -(612+74)
22 815	w	1757	22 805	vw	744				T ₂ -744
22 655	s	1917	22 663	ms	886	22 670	s	333	0 _B -333
22 520	vw	2052	22 594	vw	955				T ₂ -955
22 416	vw	2156	22 413	vw	1136				T ₁ -(744+1302+74)
22 306	vw	2266	22 326	vw	1223				T ₂ -1223
22 226	ms	2346	22 248	ms	1301	22 252	s	751	0 _B -751
22 145	vw	2427	22 159	vw	1390				T ₁ -(744+1620+74)
22 121	vw	2451	22 119	vw	1430				T ₂ -(744+612+74)
22 065	vw	2507	22 068	vw	1481				T ₂ -1481
21 981	vs	2591	21 988	vs	1561	21 994	vs	1009	0 _B -1008
21 932	w	2640	21 929	w	1620				T ₂ -1620
21 902	w	2670	21 914	w	1635	21 919	w	1084	0 _B -(333+751)
21 759	ms	2813	21 770	w	1779	21 776	w	1227	?
21 716	vs	2856	21 618	s	1931	21 720	vs	1283	0 _B -1283
21 640	w	2932	21 648	w	1901	21 662	w	1341	0 _B -(333+1008)
21 595	w	2977							T ₁ -(1357+1620)
21 471	vw	3101							T ₁ -(1481+1620)

TABLE I. (Continued)

15 °K			25 °K			90 °K			Assignment
Wavenumber (cm ⁻¹)	Intensity	Separation from the first band (cm ⁻¹)	Wavenumber (cm ⁻¹)	Intensity	Separation from the first band (cm ⁻¹)	Wavenumber (cm ⁻¹)	Intensity	Separation from the first band (cm ⁻¹)	
21 484	w	3088	21 496	vw	2053	21 501	vw	1502	0 _B -2 × 751
21 380	vw	3192	21 388	vs	2161	21 396	vvs	1607	0 _B -1607
									0 _B -(333 + 1283)
21 227	w	3345	21 238	w	2311	21 244	w	1759	0 _B -(751 + 1008)
21 043	m	3529	21 050	w	2499	21 063	mw	1940	0 _B -(333 + 1607)
20 979	m	3593	20 966	vw	2583	20 970	w	2033	0 _B -(751 + 1283)
									0 _B -2 × 1008
20 708	ms	3864	20 698	w	2851	20 702	w	2301	0 _B -(1008 + 1283)
20 636	ms	3936	20 638	w	2911	20 645	w	2358	0 _B -(751 + 1607)
									0 _B -(2 × 1008 + 333)
20 468	w	4104	20 478	w	3071	20 482	w	2521	0 _B -(2 × 751 + 1008)
20 428	w	4144	20 434	yw	3115	20 441	w	2562	0 _B -2 × 1283
20 380	ms	4192	20 378	m	3171	20 385	ms	2618	0 _B -(1008 + 1607)
20 197	w	4375	20 200	vw	3349	20 202	vw	2801	0 _B -(2 × 751 + 1283)
									0 _B -(2 × 1008 + 751)
20 112	ms	4460	20 108	m	3441	20 115	ms	2888	0 _B -(1283 + 1607)
19 954	vw	4618	19 964	vw	3585	19 966	vw	3037	0 _B -3 × 1008
19 905	vw	4667	19 930	vw	3619	19 941	vw	3062	0 _B -(751 + 1008 + 1283)
19 856	vw	4716	19 863	vw	3686	19 868	vw	3135	0 _B -(2 × 751 + 1607)
19 790	ms	4782	19 780	m	3769	19 785	m	3218	0 _B -2 × 1607
19 690	vw	4882	19 695	vw	3854	19 700	vw	3303	0 _B -(2 × 1283 + 751)
19 438	w	5134	19 450	w	4099	19 455	w	3548	0 _B -(2 × 1607 + 333)
19 352	w	5220	19 357	w	4192	19 362	w	3641	0 _B -(751 + 1283 + 1607)
19 152	vw	5420	19 154	vw	4395	19 159	vw	3844	0 _B -3 × 1283
19 087	w	5480	19 090	w	4459	19 095	w	3908	0 _B -(1008 + 1283 + 1607)
19 015	vw	5557	19 022	vw	4527	19 027	vw	3976	0 _B -(2 × 1607 + 751)
18 901	vw	5671	18 913	vw	4636	18 918	vw	4085	0 _B -(2 × 1283 + 2 × 751)
18 846	vw	5726	18 850	vw	4699	18 854	vw	4149	0 _B -(3 × 1283 + 333)
									0 _B -(2 × 1283 + 1607)
18 762	w	5810	18 766	w	4783	18 772	w	4231	0 _B -(2 × 1607 + 1008)
18 505	w	6067	18 514	w	5035	18 520	w	4483	0 _B -(2 × 1607 + 1283)
18 177	w	6395	18 180	w	5369	18 185	w	4818	0 _B -3 × 1607

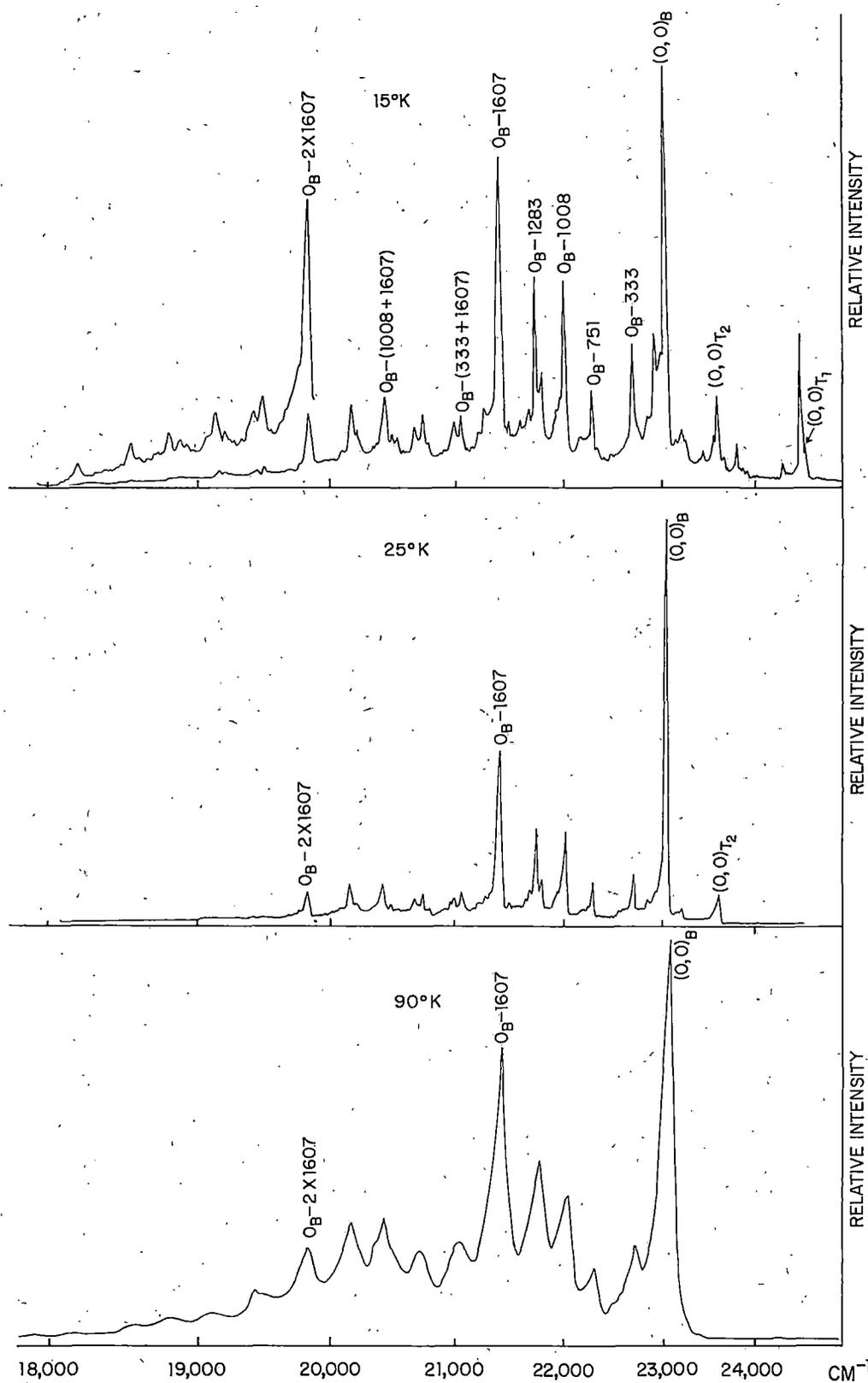


FIG. 1. Phosphorescence spectra of a biphenyl guest-carbazole host mixed crystal at different temperatures.

III. RESULTS

The phosphorescence spectrum of a biphenyl guest-carbazole host mixed crystal has been studied at 15 °K, 25 °K, and at 90 °K. In Fig. 1 we reproduce the spectra at different temperatures. At 15 °K the spectrum is very sharp. The shortest wavelength band is weak and is at 24 572 cm^{-1} . This band is associated with a strong band at 24 498 cm^{-1} . At 25 °K the spectrum also retains its very sharp structure but the first band now appears at 23 552 cm^{-1} with moderate intensity. No band is observed at higher energy. At 90 °K, the bands are broad and the first band now is very strong and is at 22 986 cm^{-1} . All the bands on the higher energy side no longer appear at 90 °K. This band is approximately at the same energy where 0, 0 band of the biphenyl phosphorescence has been observed by other workers in rigid glassy solution.¹⁰⁻¹² A comparison of the spectrum we have observed at 90 °K with the reported phosphorescence spectrum of biphenyl dispersed in glassy solution indicates that our spectrum in this case is indeed the biphenyl phosphorescence spectrum. With this as the 0, 0 band, the spectrum has been analysed in terms of five ground state fundamentals 333, 751, 1008, 1283, and 1607 cm^{-1} .

The bands at 23 552 cm^{-1} and 24 572 cm^{-1} in our phosphorescence spectrum at 15 °K are taken as the 0, 0 bands of two other traps or impurity emissions. A tentative vibrational analysis of the bands in the spectra at different temperatures is presented in Table I.

IV. DISCUSSION

A. Energy Levels

The host and the guest energy level arrangement of the mixed crystal system studied in the present investigation is shown in Fig. 2; only the lowest excited singlet states and triplet states are shown. In this system the lowest singlet exciton and the lowest triplet exciton bands of the host S_{1H} and T_{1H} are energetically sandwiched between the lowest excited singlet and triplet energy levels S_{1G} and T_{1G} of the guest. In a mixed crystal system it is easy to locate S_{1H} , S_{1G} , and T_{1G} , since emissions from these states are observed. In our case the biphenyl fluorescence and phosphorescence spectra are well known.¹³ Crystal fluorescence of carbazole has also been reported.¹⁴ Difficulty is mainly encountered in locating T_{1H} . Phosphorescence is normally not observed from the host triplet; also singlet-triplet absorption of the host is obscured by singlet-singlet absorption of both the host and the guest species.

We have tentatively placed T_{1H} in our case at 24 600 cm^{-1} . Teplyakov *et al.*¹⁵ have reported the

phosphorescence spectrum of carbazole in *n*-heptane at 20 °K. They have observed the band at 24 591 cm^{-1} . Zwarich *et al.*¹⁶ have observed that carbazole triplet state is about 1700 cm^{-1} higher than that of biphenyl. Our present result also supports a similar value for T_{1H} .

B. The Spectra

A comparison of the spectra at three different temperatures; 15 °K, 25 °K, and 90 °K clearly shows that the spectrum at 15 °K consists of about sixty sharp bands and is in fact a superposition of three different spectra. We have accordingly made an analysis of the spectra. One of the emissions has its origin at 24 572 cm^{-1} in the mixed crystal at 15 °K, we call this emission T_1 arising from a shallow trap below the host triplet exciton band. This emission disappears when the crystal temperature is raised to 25 °K. At this temperature the first band of the spectrum is at 23 549 cm^{-1} which again disappears at higher temperature. We have attributed this emission to trap emission T_2 with the origin at 23 549 cm^{-1} . The guest biphenyl emission has its origin at 22 986 cm^{-1} at 15 °K which shifts slightly to the blue as the temperature is raised; it is at 22 998 cm^{-1} at 25 °K and at 23 003 cm^{-1} at 90 °K. At 90 °K, only biphenyl emission is observed.

We have made a tentative analysis of the spectra in Table I. The biphenyl phosphorescence spectrum has an intense 0, 0 band; this being a ${}^3B_{1u} - {}^1A_g$ transition (assuming the molecule to be planar) which is symmetry allowed. The biphenyl spectrum has been analyzed in terms of ground state vibrational frequencies 333, 751, 1008, 1283, and 1607 cm^{-1} . The frequency of 1607 cm^{-1} forms the main progression. Fruhling¹⁷ has

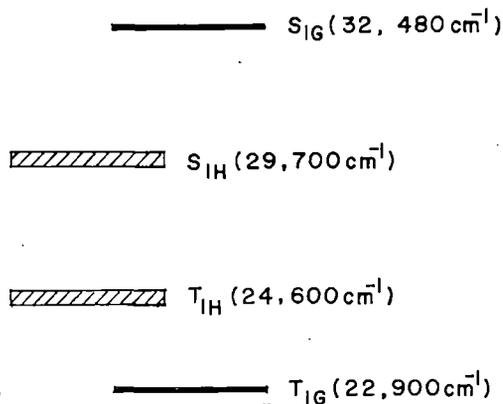


FIG. 2. Energy levels of the biphenyl guest-carbazole host mixed crystal (only the lowest singlets and triplets are shown).

reported the Raman frequencies of biphenyl as 309, 736, 997, 1277, and 1606 cm^{-1} . Kovner¹⁸ has reported Raman frequencies 315, 742, 1003, 1280, and 1611 cm^{-1} . These Raman frequencies agree very well with the ground state vibrational frequencies we have observed in our biphenyl phosphorescence spectrum. Fruhling¹⁷ has assigned the Raman frequencies 309, 736, 957, 1297, and 1606 cm^{-1} as totally symmetrical vibrations. Our biphenyl phosphorescence spectrum also supports his interpretation.

The analysis of the other spectra due to emissions from T_1 and T_2 is less straightforward. T_1 emission has its origin at 24 572 cm^{-1} which is a weak band, but the band at 24 498 cm^{-1} on the long wavelength side of this band is very intense. The separation between these two bands is 74 cm^{-1} . This indeed is a carbazole lattice vibration as observed by Zwarich *et al.*¹⁴ Thus this emission seems to be phonon induced. We have attempted an analysis of this T_1 spectrum at 15 °K and a tentative assignment of the bands has been possible in terms of the ground state fundamentals 220, 282, 420, 612, 686, 744, 955, 1105, 1223, 1302, 1357, 1481, and 1620 cm^{-1} . These frequencies agree with the reported ground state fundamentals of carbazole.^{14,15} The third emission arising from trap T_2 has been analyzed in terms of carbazole frequencies 420, 612, 686, 744, 955, 1223, 1481, and 1620 cm^{-1} . Other carbazole frequencies observed in T_1 spectrum are absent in this weak T_2 emission. A band with a particular vibrational frequency is usually more intense in T_1 emission than that in T_2 emission. However, the vibronic band with the frequency 420 cm^{-1} is of medium weak intensity in T_2 emission, the band with this frequency in T_1 spectrum is extremely weak (in fact it appears very weak only at high sensitivity of the recording system).

These observations are in agreement with that reported recently by Zwarich¹⁶ from his investigation of the phosphorescence emission spectrum of a biphenyl crystal doped with carbazole, that the emission from traps below the triplet exciton band gives host ground state fundamentals. When carbazole was doped with biphenyl, the phosphorescence discussed above was observed. Evidently, substitution of biphenyl in the carbazole lattice perturbs the biphenyl molecules of the lattice adjacent to the impurity site so as to create corresponding energy minima in the local triplet band structure. That our T_1 emission is not from the host triplet exciton band but from some shallow trap is evident from the high temperature study.

We have observed two traps emissions, one from shallow and the other from deep traps. Minute

concentration of impurity could create the traps. However, in view of the extensive purification that was carried out, we believe that these two traps are due to at least two different ways that biphenyl may substitute in the carbazole lattice causing two distinct energy minima. It is not, however, clear at this point why the two emissions are different in that the one from T_2 behaves as an allowed transition, while the other from T_1 seems to be phonon induced. The interaction of trapped excitons with phonons and their consequent de-trapping is indeed a plausible process. There may be more than one inequivalent site available for the guest in the host lattice.¹⁹ The guest and the host, in such a case, usually show multiplet structure in each of the vibronic bands. We, however, have not observed any multiplet structure in our biphenyl phosphorescence spectrum.

The absence of delayed fluorescence in this mixed crystal system is to be noted. As has been pointed out before, the relative energy position of host-guest lowest excited singlet and triplet states in the present system is distinctly different from that in mixed crystal systems from which delayed fluorescence has been observed so far.

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Delayed emission from an organic mixed crystal: Decay and rise characteristics of phosphorescence from a biphenyl guest-carbazole host mixed crystal

T. N. Misra and Krishnagopal Mandal

Department of Physics, North Bengal University, Darjeeling, India
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The decay and buildup characteristics of phosphorescence of biphenyl guest-carbazole host mixed crystal have been investigated in the temperature range 15–110°K. The phosphorescence decay and rise are nearly exponential in the temperature range investigated. It has been found that the phosphorescence rise time of biphenyl guest is less than its decay time. This difference between rise and decay time in the "real" mixed crystal arises from heterogeneous triplet-triplet annihilation involving a guest triplet and a defect triplet. The delayed fluorescence of annihilative origin has not, however, been observed owing to a very small fraction of the triplets involved in annihilation. The temperature dependence of the guest phosphorescence lifetime is an intermolecular process and is controlled by the thermally excited process $T_{1D} \rightarrow T_{1D}^* \rightarrow T_{1H} \rightarrow T_{1G}$. A kinetic scheme for guest-impurity heterogeneous triplet-triplet annihilation is discussed. The thermal energy gap obtained from various Arrhenius plots relevant to the kinetic scheme is in good agreement with the spectroscopic energy difference $T_{1H} - T_{1D}$.

INTRODUCTION

The temperature dependence of the guest phosphorescence lifetime in a mixed crystal has been of much interest in recent years. Hadley, Rast, and Keller¹ put forward the hypothesis that such temperature dependence is an intramolecular process and the nonradiative decay route $T_{1G} \rightarrow T_{1G}^* \rightarrow S_{0G}^* \rightarrow S_{0G}$ is completed in which the first step is a thermally excited process within the molecular energy levels. T_{1G}^* and S_{0G}^* , the higher vibronic levels in the lowest triplet state and the ground state, respectively, are quasidegenerate. Kinoshita *et al.*,² on the other hand, suggest that the intermolecular event $T_{1G} \rightarrow T_{1H}$ controls the guest phosphorescence lifetime in an "ideal" two-component mixed crystal. In a real mixed crystal, in addition to the host and the guest, some defects of chemical or physical nature are always present. Our earlier investigations³⁻⁷ of the delayed emissions of organic mixed crystals with the lowest guest singlet (S_{1G}) and triplet (T_{1G}) having energy lower than the lowest host singlet (S_{1H}) and triplet (T_{1H}), respectively, have led us to suggest that the temperature dependence of guest phosphorescence lifetime in a "real" mixed crystal is governed by the thermally excited process $T_{1D} \rightarrow T_{1H}$ followed by annihilation of T_{1G} ; here T_{1D} is the lowest triplet energy of the "defect." In order to test the validity of the thesis further we have extended the investigation to other mixed crystals for which $S_{1G} > S_{1H} > T_{1H} > T_{1G}$.

In an earlier communication⁸ we have reported the phosphorescence spectrum of a biphenyl guest-carbazole host mixed crystal at different temperatures in the range 15–90°K. At 15°K, the spectrum consists of three superimposed spectra, the most intense one being that of biphenyl guest phosphorescence. The other two spectra have been attributed to emissions from two traps T_1 and T_2 . As the temperature is raised to 25°K, the shallow trap T_1 is depopulated and emissions from the deep trap T_2 and the guest are observed. At a still higher temperature of 90°K, the emission is wholly of the biphenyl guest. In the present paper we discuss the tem-

perature dependence of decay and buildup characteristics of delayed emissions from this real mixed crystal.

EXPERIMENTAL

The experimental setup was the same as reported earlier.⁸ The emission spectra were recorded on a Spex Czerny-Turner spectrophotometer model 1700 II equipped with a 1P28 photomultiplier and Keithley 414 micro-micro ammeter. The sample was cooled by helium heat exchange gas in contact with the liquid helium container. The decay and buildup characteristics of the delayed emissions were obtained from the decay and buildup of the photomultiplier signals and were followed on a chart recorder running at a constant speed of 40 in/min.

Biphenyl was purified by treating the commercial material with maleic anhydride. The resulting material was further purified by repeated zone refining. Carbazole supplied by Eastman Kodak was freed from anthracene by treatment with maleic anhydride. The sample was then chromatographed on silica gel using petroleum ether as eluent.

Results

The phosphorescence spectrum of the biphenyl guest-carbazole host mixed crystal at 15°K consists of three superimposed spectra, the most intense one being that of the biphenyl guest with an origin at 22 986 cm^{-1} . The two other spectra have been attributed to emissions from traps T_1 and T_2 . Emission from shallow trap T_1 has its origin at 24 572 cm^{-1} and that from deep trap T_2 has its origin at 23 552 cm^{-1} . It has been observed that at very low temperature the guest and the two traps are all populated. As the temperature is raised to 25°K the shallow trap T_1 is depopulated and emissions from the deep trap T_2 and the guest are observed. On further increase of temperature to 90°K T_2 is also depopulated and the emission wholly from biphenyl guest is observed.

The decay and buildup characteristics of phosphores-

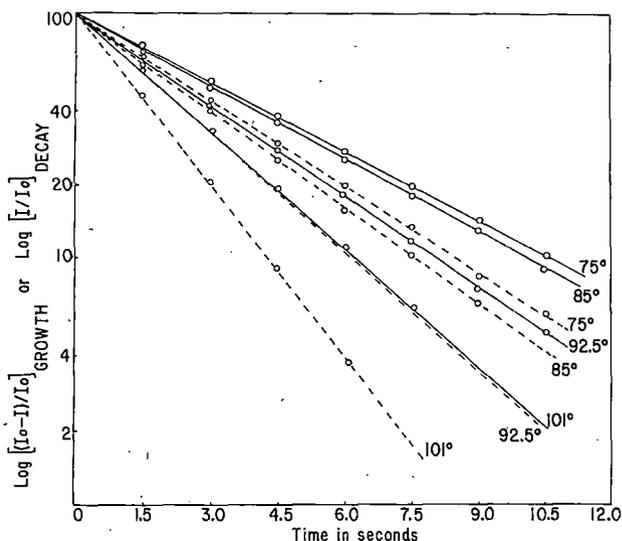


FIG. 1. Decays and growths of phosphorescence of biphenyl in carbazole at different temperatures. Temperature is in $^{\circ}\text{K}$. The initial intensities of the decays and growths are normalized to 100 (arbitrary units): —, decays; - - - - growths.

cence of the carbazole host-biphenyl guest mixed crystal have been investigated in the temperature range 15–110 $^{\circ}\text{K}$. The general features of phosphorescence decays at various temperatures are similar to those observed earlier in other mixed crystals. The phosphorescence decays are nearly exponential at low temperatures. A slight deviation from exponentiality in the short time region was observed at high temperatures. In Fig. 1 we show the temperature dependence of decays and growths of phosphorescence of biphenyl guest in carbazole host by usual semilog plots. Decay and growth of phosphorescence of trap T_1 at 15 $^{\circ}\text{K}$ are shown in Fig. 2. The mean lifetimes of growth and decay of trap T_1 are 2.16 and 4.97 sec respectively. It is generally found that $\tau_p^R < \tau_p^D$ with τ_p^R and τ_p^D denoting the lifetimes of phosphorescence rise and decay, respectively. Both τ_p^R and τ_p^D for the guest are temperature dependent.

DISCUSSIONS

Energy levels

The energy level diagram of the biphenyl guest-carbazole host mixed crystal containing all available informations on the lowest triplet levels is shown in Fig. 3. Placement of T_{1H} is rather tentative based on the fact that Teplyakov *et al.*⁹ have reported the origin of phosphorescence of carbazole in *n*-heptane at 20 $^{\circ}\text{K}$ to be at 24591 cm^{-1} . Zwarich¹⁰ has also observed that carbazole triplet state is about 1700 cm^{-1} higher than that of biphenyl.

Kinetics

In an earlier paper⁷ we have discussed the kinetics of guest triplet-triplet heterogeneous annihilation in a mixed crystal system. The relevant rate constants are identified in Table I. At temperature $T > 15$ $^{\circ}\text{K}$, trap T_1 is completely depopulated and the mixed crystal system becomes a three-component system consisting of

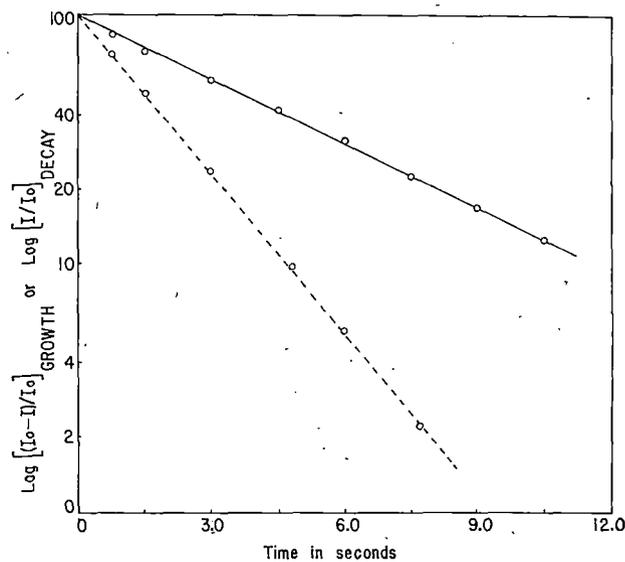


FIG. 2. Decay and growth of phosphorescence of trap T_1 at 15 $^{\circ}\text{K}$: —, decay; - - - - growth.

the host, and guest and one trap T_2 . In such a case the kinetic scheme presented in Table I should be applied, T_{1D} standing for the deep trap T_2 and the rate equations obtained are

$$\begin{aligned} \frac{d}{dt} [S_{1G}] &= R_0 - (K'_1 + k'_2) [S_{1G}] + k_4 K_0 \exp(-\Delta E/kT) [T_{1D}] [T_{1G}], \\ \frac{d}{dt} [T_{1G}] &= k'_2 [S_{1G}] - K'_3 [T_{1G}] + K_0 \exp(-\Delta E/kT) [T_{1D}] \\ &\quad - (k_4 + k_5) K_0 \exp(-\Delta E/kT) [T_{1D}] [T_{1G}]. \end{aligned} \quad (1)$$

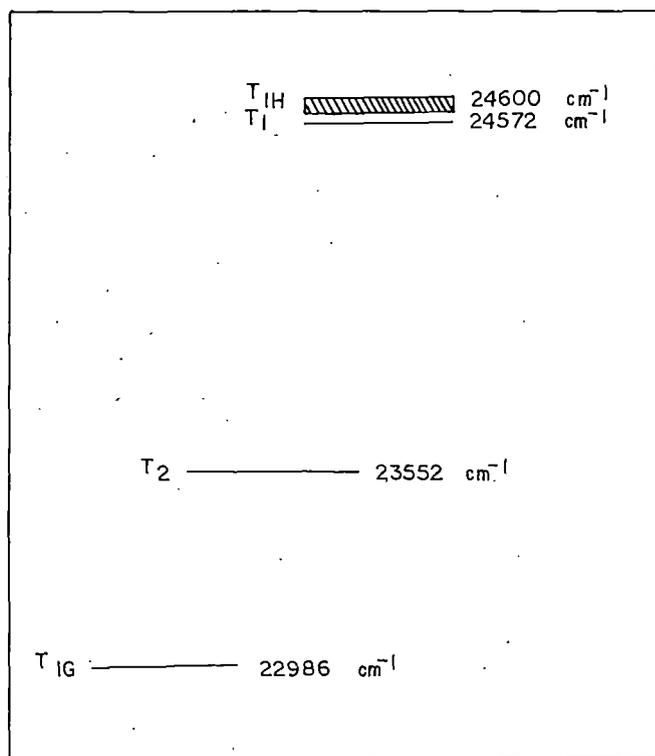


FIG. 3. Schematic diagram of the observed emitting levels of the biphenyl guest-carbazole host mixed crystal (triplet excitation band of the host is also shown).

TABLE I. Mechanistic steps and parametrization.

	Rate processes	Rate constant	Remarks
1.	$S_{0H} + h\nu \rightarrow S_{1G}$	R_0	Overall rate constant for guest lowest singlet population
2.	$S_{1G} \rightarrow S_{0G} + h\nu_{F(guest)}$	k_1^{*}	Guest fluorescence (radiative)
	$S_{1G} \rightarrow S_{0G}$	k_1'	Guest fluorescence quenching (nonradiative) $K_1' = k_1^{*} + k_1'$
3.	$S_{1G} \rightarrow S_{1D}$	k	Singlet-singlet energy transfer
4.	$S_{1D} \rightarrow S_{0D} + h\nu_{F(defect)}$	k_1^{*}	Defect (impurity) fluorescence (radiative)
	$S_{1D} \rightarrow S_{0D}$	k_1	Defect (impurity) fluorescence quenching (nonradiative) $K_1 = k_1^{*} + k_1$
5.	$S_{1G} \rightarrow T_{1G}$	k_2'	Intersystem crossing in the guest species
6.	$S_{1D} \rightarrow T_{1D}$	k_2	Intersystem crossing to the defect (impurity)
7.	$T_{1G} \rightarrow S_{0G} + h\nu_p(guest)$	k_3^{*}	Guest phosphorescence (radiative)
	$T_{1G} \rightarrow S_{0G}$	k_3'	Guest phosphorescence quenching (nonradiative) $K_3' = k_3^{*} + k_3'$
8.	$T_{1D} \rightarrow S_{0D} + h\nu_p(defect)$	k_3^{*}	Defect phosphorescence (radiative)
	$T_{1D} \rightarrow S_{0D}$	k_3	Defect phosphorescence quenching $K_3 = k_3^{*} + k_3$
9.	$T_{1D} \rightarrow T_{1D}^* \rightarrow T_{1H} \rightarrow T_{1G}$	$K_0 \exp(-\Delta E/kT)$	Thermal activation and energy transfer $\Delta E =$ Energy difference between T_{1H} and T_{1D}
10.	$T_{1H} + T_{1G} \rightarrow S_{1G} + S_{0G}$	k_4	Annihilation leading to delayed fluorescence
	$T_{1H} + T_{1G} \rightarrow T_{1G} + S_{0G}$	k_5	Bimolecular triplet quenching

Reaction 3 in Table I though efficient, has not been considered. This does not affect our conclusion in any way. Assuming that the concentrations of the defect triplets and the guest triplets are in dynamic equilibrium, this equilibrium constant being Λ ,

$$\frac{d}{dt} [T_{1G}] = k_2' [S_{1G}] - [K_3' - K_0 \Lambda e^{-\Delta E/kT}] [T_{1G}] - (k_4 + k_5) K_0 \Lambda e^{-\Delta E/kT} [T_{1G}]^2 \quad (3)$$

Under the steady state approximation, integration of the above expression leads to

$$(I/I_0)_p(guest) = (1-A) / [\exp(K_3' - \bar{K}_0)t - A] \quad (4)$$

This describes the guest phosphorescence decays.

$$\bar{K}_0 = K_0 \Lambda \exp(-\Delta E/kT) \quad (5)$$

$$A = k_6' [T_{1G}]_0 / (K_p' + k_6' [T_{1G}]_0) \quad (6)$$

$$K_p' = K_3' - \bar{K}_0 \quad (7)$$

and

$$k_6' = \frac{K_1' k_4 \Lambda K_0 \exp(-\Delta E/kT)}{(K_1' + k_2')} + k_5 \Lambda K_0 \exp(-\Delta E/kT) \quad (8)$$

$K_3' - \bar{K}_0 = K_p'$ is the first order triplet decay constant and

A is a parameter which gauges the relative contribution of first and second order decay routes to the total guest phosphorescence decay. The phosphorescence growth in such case is¹¹

$$[(I_0 - I)/I_0]_p(guest) = (1+A) / \{\exp[K_p'(1+4K')^{1/2}t] + A\} \quad (9)$$

Here,

$$K' = k_2' k_6' R_0 / (K_1' + k_2') K_p'^2 \quad (10)$$

If A is small, $A \ll 1$, both phosphorescence decay and growth become exponential

$$(I/I_0)_p(guest) \approx \exp(-K_p' t) \quad (11)$$

and¹¹

$$[(I_0 - I)/I_0]_p(guest) \approx \exp[-K_p'(1+4K')^{1/2}t] \quad (12)$$

This gives us

$$\tau_p^D(guest) = 1/K_p' \quad (13)$$

and

$$\tau_p^R(guest) = 1/K_p'(1+4K')^{1/2} \quad (14)$$

TABLE II. Summary of values of K' , K_p' , and $K'K_p'^2$ at different temperatures.

$T(^{\circ}K)$	$\tau_p^D(\text{sec})$	$\tau_p^R(\text{sec})$	$1/\tau_p^D(T) - 1/\tau_p^D(0)$	K'	$K_p'(\text{sec}^{-1})$	$K'K_p'^2(\text{sec}^{-2})$
65	4.30	3.70	0.0000	0.0876	0.2325	0.0047
70	4.30	3.65	0.0000	0.0969	0.2325	0.0052
75	4.30	3.65	0.0000	0.0969	0.2325	0.0052
80	4.20	3.50	0.0055	0.1100	0.2380	0.0062
85	4.15	3.35	0.0084	0.1336	0.2409	0.0077
90	3.75	3.05	0.0341	0.1279	0.2666	0.0090
95	3.35	2.70	0.0664	0.1348	0.2989	0.0120
100	2.80	2.25	0.1246	0.1371	0.3571	0.0175
105	2.25	1.75	0.2119	0.1632	0.4444	0.0322
110	1.60	1.30	0.3925	0.1286	0.6250	0.0502

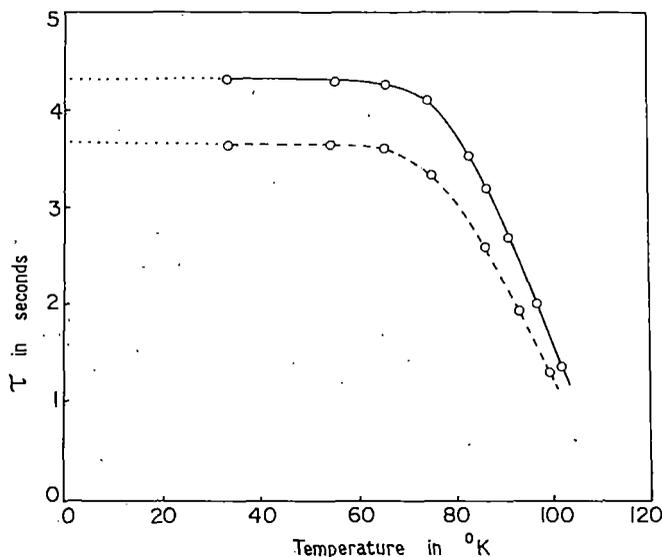


FIG. 4. Temperature dependence of lifetimes of biphenyl guest in carbazole host: —○—, phosphorescence decay; ---○--- phosphorescence rise.

Evaluation of activation energy

The numerical value of K' can, hence, be obtained from the experimentally observed mean lifetime of phosphorescence decay and buildup. In our present system the condition $A \ll 1$ is satisfied, as is evident from the fact that the guest phosphorescence decays and buildups are exponential (Fig. 1). Also, delayed fluorescence intensity is so weak that it could not be recorded. That a small fraction of triplets did, indeed, annihilate is based on the fact that the above kinetic scheme satisfactorily explains the difference between τ_p^D and τ_p^R . The temperature dependences of τ_p^D and τ_p^R are shown in Fig. 4. In Table II, the numerical values of K' obtained from the mean lifetime of phosphorescence decays and buildups at different temperatures are summarized. K' is obtained from the expression

$$K' = \frac{1}{4} \left[\left(\frac{\tau_p^D}{\tau_p^R} \right)^2 - 1 \right] \quad (15)$$

In the last column of the Table II, temperature dependences of $K'K_p'^2$ are also shown. From expressions (8) and (10) it is evident,

$$K'K_p'^2 \propto \exp(-\Delta E/kT),$$

provided the rate constants k_2' , R_0 and K_1' are temperature independent. In Fig. 5 we make a plot of $K'K_p'^2$ vs $1/T$. In the high temperature region a reasonably good straight line is obtained. The activation energy evaluated from the slope is $900 \pm 100 \text{ cm}^{-1}$. Table II shows that K' lies between 0.08 and 0.16.

Expression (11) describes the phosphorescence decay. Since

$$K_p' = K_3' - \bar{K}_0,$$

$$1/\tau_p^D(0) - 1/\tau_p^D(T) = \bar{K}_0$$

$$\propto \exp(-\Delta E/kT).$$

$\tau_p^D(0)$ is the phosphorescence lifetime measured at 0°K and $\tau_p^D(T)$ that at any other temperature. We have made

a plot of $1/\tau_p^D(T) - 1/\tau_p^D(0)$ against $1/T$ in Fig. 6. A good straight line is obtained. The activation energy evaluated is $950 \pm 100 \text{ cm}^{-1}$. The spectroscopic energy gap $T_{1H} - T_{1D}$ between the host triplet exciton band and the deep trap T_2 is 1020 cm^{-1} (Fig. 3). The activation energies obtained from various Arrhenius plots are in good agreement with this value.

Expression (7) relates the guest phosphorescence lifetime at different temperatures with Reaction 9 in the kinetic scheme in Table I. Thus the present result supports our thesis put forward earlier⁷ that in a real mixed crystal, the temperature dependence of guest phosphorescence lifetime is controlled by the thermally excited process $T_{1D} \rightarrow T_{1D}^* \rightarrow T_{1H} \rightarrow T_{1G}$.

Evaluation of A

Approximate values of A can be obtained from expression (4). This nonlinear expression can be rearranged

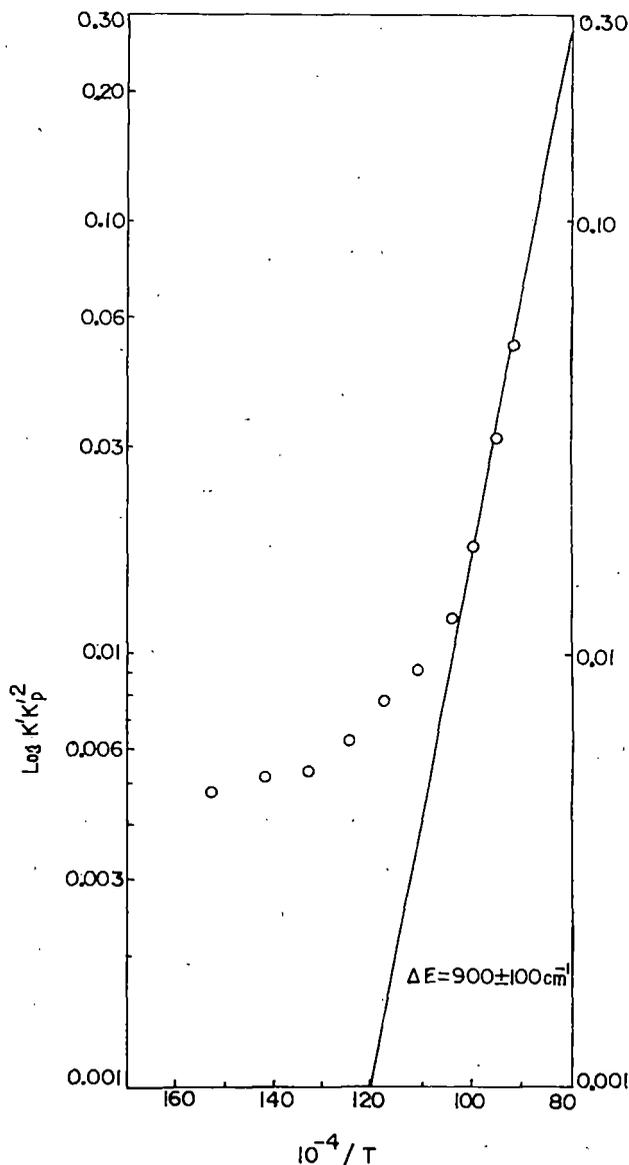


FIG. 5. Arrhenius plot of $\log(K'K_p'^2)$ vs $1/T$ for biphenyl in carbazole. The slope yields an activation energy $\Delta E \approx T_{1H} - T_{1D}$ (see text).

to the linear equation,

$$\exp(K'_p t) = A + (1 - A) (I_0/I) \quad (16)$$

Thus a plot of $\exp(K'_p t)$ vs the reciprocal of the intensity will yield a straight line with the slope $(1 - A)$ and intercept A . As Hatch and Nieman¹² have pointed out, only the correct

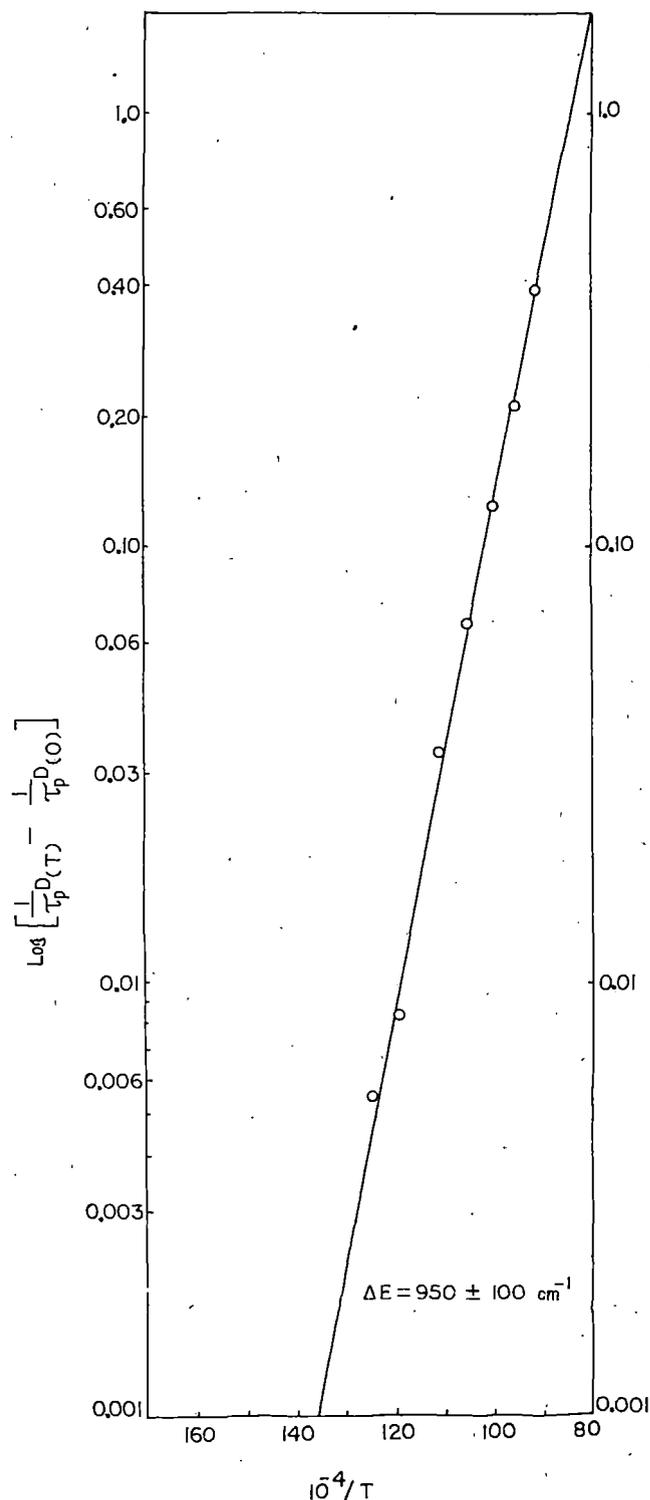


FIG. 6. Arrhenius plot of $\log[1/\tau_p^D(T) - 1/\tau_p^D(0)]$ vs $1/T$ for biphenyl in carbazole. The slope yields an activation energy of $\Delta E \approx T_{1H} - T_{1D}$ (see text).

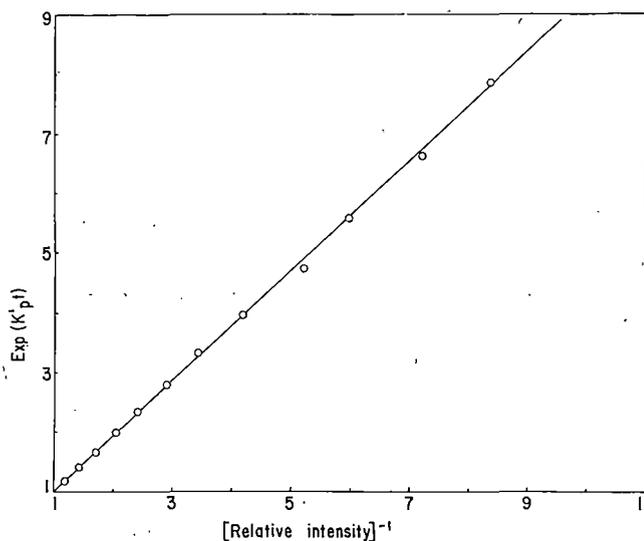


FIG. 7. Second order analysis (Eq. 16) of the experimental decay curve of biphenyl phosphorescence in carbazole host at 75 °K. $K'_p = 0.23 \text{ sec}^{-1}$ as observed experimentally.

value of K'_p could give a straight line. An incorrect K'_p would give a curved plot. Since K'_p is strongly temperature dependent, to evaluate A at different temperatures, one has to assume different values for K'_p .

We have made an attempt to evaluate A at 75 °K from the experimentally observed decay curves. Around this temperature, K'_p is rather temperature independent. Assuming $K'_p = 0.23 \text{ sec}^{-1}$, our measured value, we have made a plot of $\exp(K'_p t)$ vs (I_0/I) shown in Fig. 7. A reasonably good straight line has been obtained, and the value of A obtained from this plot is 0.07.

The parameter A can also be obtained from the expression

$$A = [(4K' + 1)^{1/2} - 1] / [(4K' + 1)^{1/2} + 1]$$

The numerical values of K in Table II show that A lies between 0.07 and 0.12 which is rather small compared to value 0.9 when intense delayed fluorescence is observed.¹³ Thus, this method of evaluation also gives a small value for A .

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