CHAPTER 2

ON THE EVIDENCE OF A LOW-LYING FORBIDDEN STATE IN SOME POLYENES

2.1 Introduction

In recent years, spectroscopic investigation of the linear conjugated polyenes[1-7] has been a subject of much interest. Many earlier calculations[8-11] based on approximate theories of molecular electronic structure were carried out to know the electronic behaviour of the polyenes. The basic result obtained from spectroscopic experiments is that there is a strongly allowed electronic transition for all polyenes in the near UV or visible region whose intensity increases and energy decreases as the conjugated chain length increases.[12] The experimental results[13-16] show that the energy of this transition appears to approach an asymptotic value. This apparent convergence is not predicted by the simplest versions of free electron or Hückel (LCAO) molecular orbital theory unless the observed alternation of bond length[8,17] is included into the theory. Then the proper limiting behaviour is observed at the expense of an increased number of parameters. All - trans polyenes possess a center of inversion. In simple Hückel and free electron molecular orbital approaches the energy ordered one-electron molecular orbitals have alternately odd and even symmetry with respect to this inversion. Each of the theories predicts the lowest energy electronic transition to be strongly electric dipole allowed; this is the feature maintained by semi-empirical and a priori methods which include single excitation configuration interaction for the excited states. According to semi-empirical and a priori calculations[18], the excited electronic states of linear conjugated polyenes are ^1A_g, ^1B_u, ^1A_g, ^1A_g, ^1B_u in order of increasing energy. The lowest energy electronic transition is $^1A_g \rightarrow {}^1B_u$, which is said to be the strongly allowed $\pi \rightarrow \pi^*$ transition.

Investigations[3] on the electronic spectra of linear conjugated polyenes have shown that the maxima of absorption and emission bands in the visible region have little or no overlap. This has led to the speculation that the absorption and emission bands in these molecules are severely Franck-Condon forbidden. For 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, such forbiddenness is not easy to rationalise. The energy difference between the lowest energy peak of the absorption spectrum and the highest energy peak of the emission spectrum is not consistent with the theoretical value obtained by semi-empirical and a priori methods.

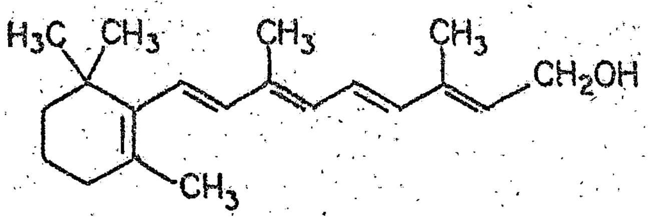
Recently Hudson and Kohler[5,19] have presented some experimental evidence that there exists a low-lying forbidden state below the well-defined lowest π-electronic state in α,ω-diphenylocta-tetraene (DPO). This experimental evidence has also been supported by theoretical treatment of Schulten and Karplus[4]. They have included double-excitation configurations in semi-empirical and a priori calculations of polyenes to improve the π-electron energy level calculations. The inclusion of double-excitation configurations in addition to the singly excited configurations brings about the change in order of excited electronic states. One of the two excited ^1A_g states of <u>all-trans</u> polyenes is significantly lowered in energy and this ^1A_g state is calculated to be at lower energy than the ^1B_u state responsible for the strongly allowed transition in the polyenes.

Thus they have demonstrated that the inclusion of double-excitation configuration for excited states of polyenes leads to the existence of a low-lying weak π-electronic state which has ^1A_g symmetry in the *all-trans* form. The transition from the ground state ^1A_g to this low-lying π-electronic excited ^1A_g state is forbidden. The low-lying state is present in other isomers[4] as well. Recently, Mandal and Misra[6] have reported that adsorption of certain gas molecules on the solid films of some polyenes makes this transition allowed. The present investigation was undertaken to extend such experiment to some more polyenes. In addition to this the solvent behaviour on the absorption and emission spectra of these polyenes has also been studied for collecting information about the absorbing and the emitting states.

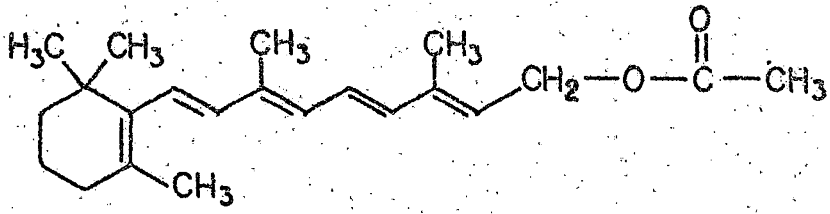
2.2 Experimental and Results

The polyenes employed in the present investigation are *all-trans* vitamin A alcohol, *all-trans* vitamin A acetate, β - apo-8'-carotenal, astacene and methyl bixin. The structure of these chemicals is shown in Fig. 2.1. These compounds of high purity were obtained from Hoffman-La Roche Co., Switzerland. We have used these chemicals without further purification. Organic solvents used in this experiment were either of spectrograde quality of B.D.H. (England) and E. Merck (Germany) or purified by usual procedures. The absorption spectra were recorded by a Perkin-Elmer recording Spectrophotometer-202 and Spectromom-202. The emission spectra were recorded by Aminco Bowman Spectrofluorometer.

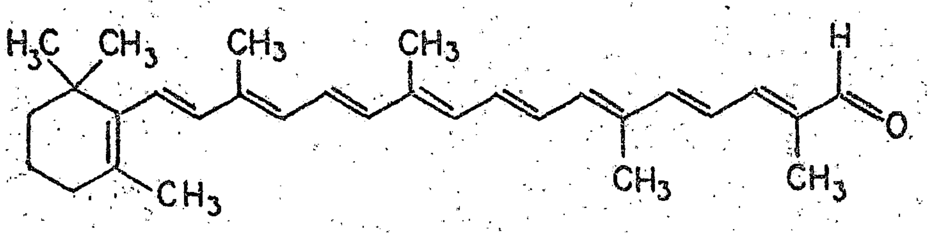
FIG. 2.1 : Structure of some linear conjugated polyenes.



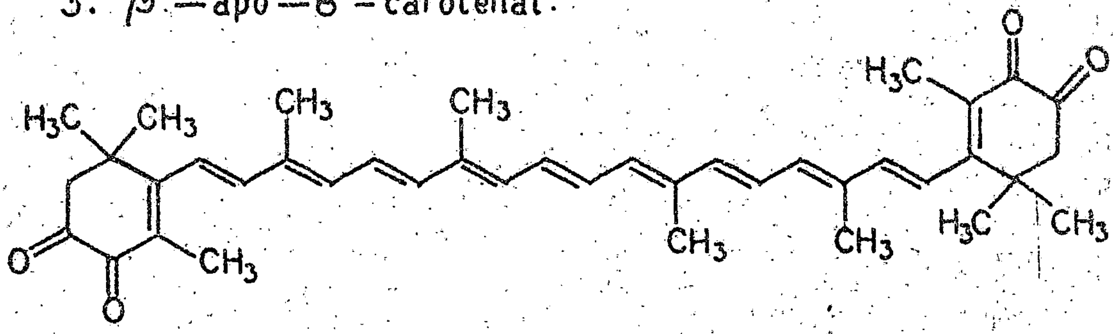
1. Vitamin A alcohol.



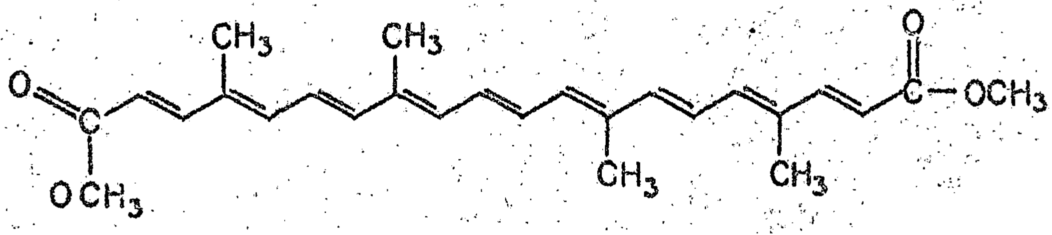
2. Vitamin A acetate.



3. β—apo—8′—carotenal.



4. Astacene



5. Methyl bixin

FIG. 21

Thin films of polycrystals of the polyenes were made on the quartz surface by gently rubbing the material. Solid films thus made were exposed to vapours of some organic solvents like aniline, acetone, benzene, carbontetrachloride, dimethyl aniline, ethanol, methanol, pyridine etc. The exposure was made by holding the films for about 5 minutes over a beaker containing the chemicals at room temperature (26°C) and the absorption spectra were then recorded immediately after the exposure.

The room temperature absorption spectra of the polyenes under investigation are shown in Figs. 2.2 - 2.6. On adsorption of vapours, a new band appears on the longer wavelength side of the spectrum in each case. With all the vapours studied the effect is almost similar except that with certain of these, the effect is more pronounced than with others. Pyridine vapour adsorption on β -apo-8'-carotenal affects absorption spectra intensely whereas aniline vapour shows a strong effect on astacene spectrum. However, no appreciable change in position of the new band is observed with different vapours adsorption. Effect of adsorption of various vapours on the intensity of the weak low energy band system is summarised in tables 2.1 - 2.5 for vitamin A alcohol, acetate, β -apo-8'-carotenal, astacene and methyl bixin respectively.

The absorption spectra of <u>all-trans</u> vitamin A alcohol are shown in Fig. 2.2. When exposed to different vapours, a new weak band appears at about 24000 cm^{-1} along with the bands observed before vapour adsorption. The other bands do not show appreciable shift after vapour adsorption. The absorption spectrum of vitamin A alcohol

Table 2.1

Effect of adsorption of various vapours on the intensity of the weak low energy band system of all-trans vitamin A alcohol

Vapour adsorbed	Relative Intensity
Aniline	1
Acetone	1
Benzene	2
Carbontetrachloride	2
Dimethyl aniline	2
Ethanol	1
Methanol	1
Pyridine	1

Table 2.2

Effect of adsorption of various vapours on the intensity of the weak low energy band system of _all-trans_ vitamin A acetate

Vapour adsorbed	Relative Intensity
Aniline	1
Acetone	2
Benzene	2
Carbontetrachloride	1
Dimethyl aniline	1
Ethanol	1
Methanol	1
Pyridine	1

Table 2.3

Effect of adsorption of various vapours on the intensity of the weak low energy band system of β -apo-8'-carotenal.

Vapour adsorbed	Relative Intensity
Aniline	3
Acetone	1
Benzene	1
Carbontetrachloride	2
Dimethyl aniline	1
Ethanol	3
Methanol	2
Pyridine	3

Table 2.4

Effect of adsorption of various vapours on the intensity of the weak low energy band system of astacene.

Vapour adsorbed	Relative Intensity
Aniline	3
Acetone	2
Benzene	1
Carbontetrachloride	2
Dimethyl aniline	1
Ethanol	2
Methanol	2
Pyridine	2

Table 2.5

Effect of adsorption of various vapours on the intensity of the week low energy band system of methyl bixin

Vapour adsorbed	Relative Intensity
Aniline	1
Acetone	1
Benzene	2
Carbontetrachloride	2
Dimethyl aniline	1
Ethanol	1
Methanol	2
Pyridine	1

FIG. 2.2 : Electronic absorption spectra of all-trans vitamin A alcohol at room temperature (25°C).

1, spectrum in methanol; 2, spectrum for the solid film; 3, spectrum after CCl_4 vapour adsorption.

Qualitative resolution of the total absorption spectrum for the solid film after CCl_4 vapour adsorption : 4, band of the solid film; and 5, new band.

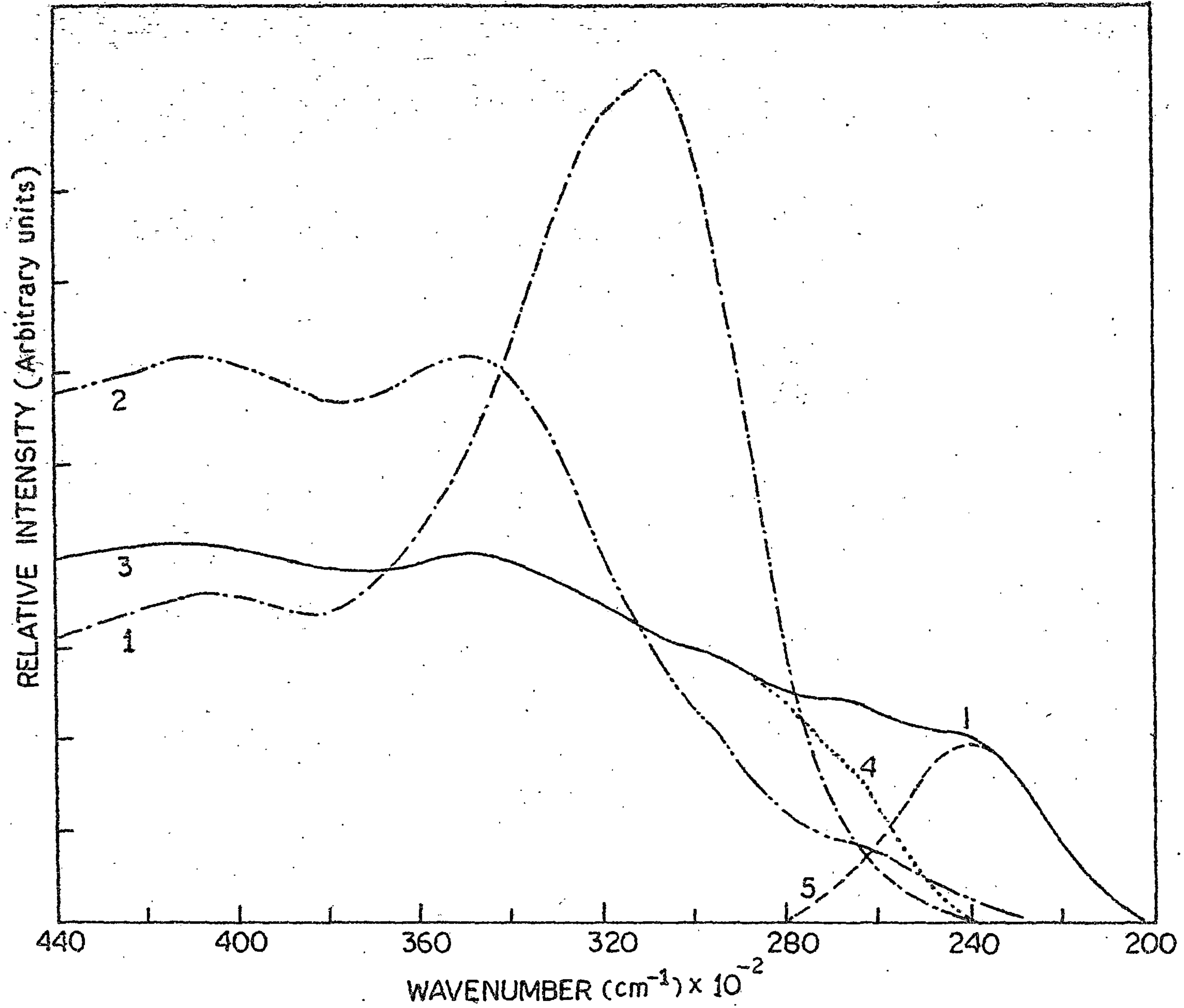

RELATIVE INTENSITY (Arbitrary units)
WAVENUMBER (cm^{-1}) x 10^{-2}
440
400
360
320
280
240
200
1
2
3
4
5
1

FIG. 2.2

in methanol has two strong bands, one at 40600 cm^{-1} and the other at 30264 cm^{-1}. There is a weak hump at about 31900 cm^{-1}. The crystal spectrum shows four main absorption bands at about 41 000, 34300, 29500 and 26666 cm^{-1}. The positions of the absorption bands are given in table 2.6.

In Fig. 2.3, the absorption spectra of all-trans vitamin A acetate in the solid state and in solution are shown. Both in solution and in the solid state, the spectrum of vitamin A acetate is broad. The position of the $\bar{\nu}_{max}$ of the band in solution and in solid state is at about 30534 and 29400 cm^{-1} respectively. After adsorption of acetone vapour, a new band appears at about 26000 cm^{-1} and the original band of vitamin A acetate shifts slightly towards the blue. The position of the bands are summarized in table 2.7.

The absorption spectrum of β-apo-8'-carotenal in n-hexane as shown in Fig. 2.4 appears with bands at 22790, 21790 and 20790 cm^{-1} seperated by about 1000 cm^{-1}. The spectrum in the solid state (Fig. 2.4) loses its vibrational structure. The band is broad and shifts little towards longer wavelength. On being exposed to different vapours a new band appears at 18200 cm^{-1}. The band in the solid state on vapour adsorption is little redshifted. The results are summarized in table 2.8

The absorption spectra of astacene in different states are shown in Fig. 2.5. The spectrum in CCl_4 is broad and structureless with $\bar{\nu}_{max}$ at 20242 cm^{-1}. In the solid state the band is further broadened with $\bar{\nu}_{max}$ at about 19650 cm^{-1}. After exposure to

Table - 2.6

Absorption bands of _all-trans_ vitamin A alcohol

Solution spectrum in methanol at 25°C		Solid state film at 25°C before vapour adsorption		Solid state film at 25°C after adsorption of ccl_4 vapour	
Wavenumber (cm^{-1})	Assignment	Wavenumber (cm^{-1})	Assignment	Wavenumber (cm^{-1})	Assignment
				24000 (w)	Newband system $(^1A_g \rightarrow {}^1A_g)$
30864 (vs)	0(A)	26666(w)	Factor group split component of A	26666(w)	Factor group split component of A
31900(w)	0+1036	29500(vw)	Factor group split component of A	29500(vw)	Factor group split component of A
		34900(vs)	Factor group split component of A	34800(ms)	Factor group split component of A
40600(ms)	0(B)	41000(ms)	Band maxima	41000(ms)	Band maxima

v -- very ; s -- strong; m -- medium; w -- weak.

FIG. 2.3 : Electronic absorption spectra of all-trans vitamin A acetate at room temperature (25°C).
1, spectrum in ethyl acetate; 2, spectrum for the solid film; 3, spectrum after acetone vapour adsorption. Qualitative resolution of the total absorption spectrum for the solid film after acetone vapour adsorption : 4, band of the solid film; and 5, new band.

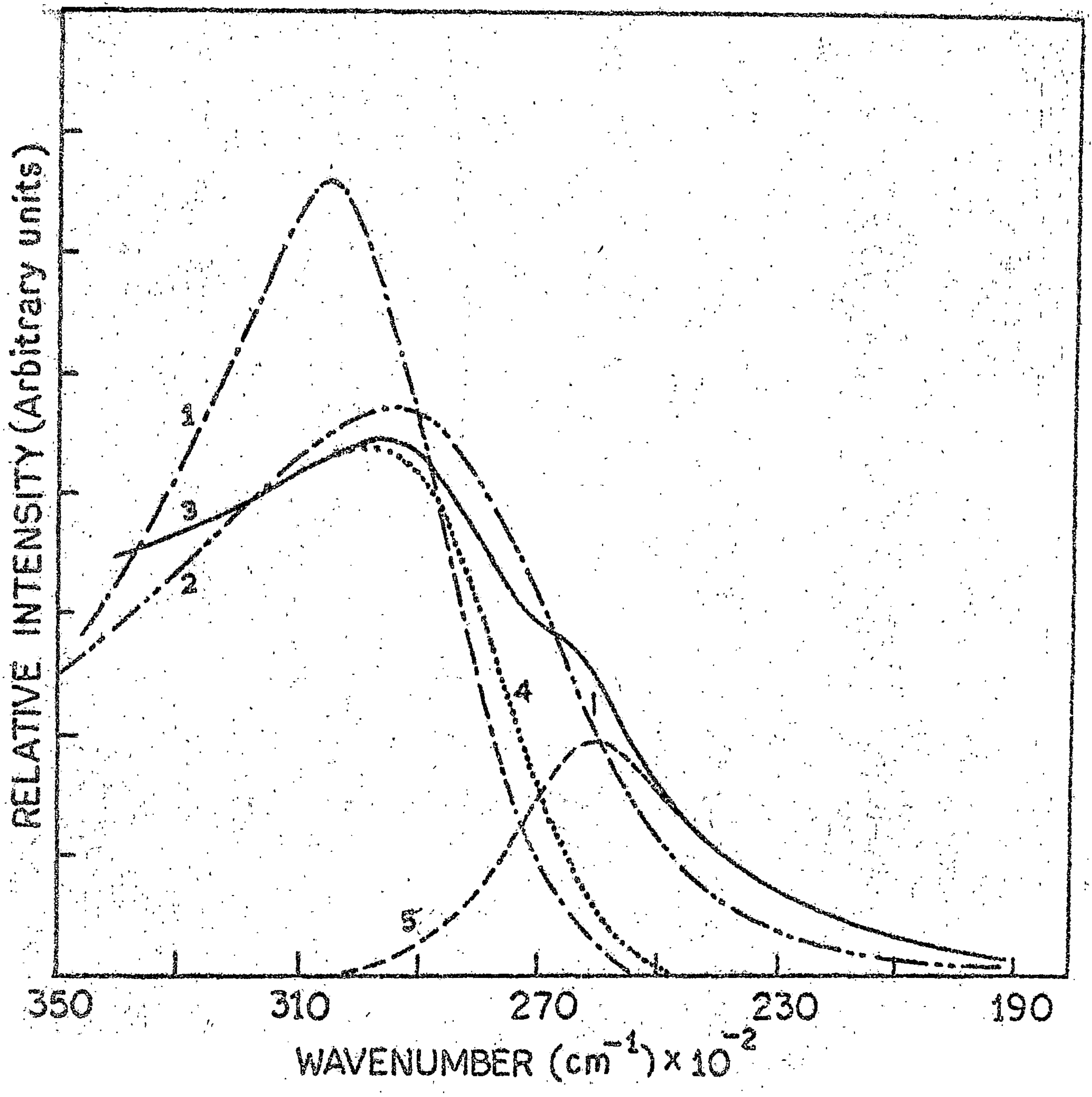

RELATIVE INTENSITY (Arbitrary units)
1
3
2
4
1
5
350
310
270
230
190
WAVENUMBER (cm^{-1}) × 10^{-2}

FIG. 2·3

Table - 2.7

Absorption bands of all-trans vitamin A acetate

Solution spectrum in ethyl acetate solution at 25°C		Solid state film at 25°C before vapour adsorption		Solid state film at 25°C after adsorption of acetone vapour	
Wavenumber (cm^{-1})	Assignment	Wavenumber (cm^{-1})	Assignment	Wavenumber (cm^{-1})	Assignment
				26000(w)	New band system ($1_{A_g} \rightarrow 1_{A_g}$)
Broad structure-less band with $\bar{\nu}_{max}$ at 30534(vs)	Band maxima	Broad structure-less band with $\bar{\nu}_{max}$ at 29400(vs)	Band maxima	Broad structure-less band with $\bar{\nu}_{max}$ at 29500(vs)	Band maxima

v - very
s - strong
w - weak

FIG. 2.4 : Electronic absorption spectra of β-apo-8'-carotenal at room temperature (25°C).

1, spectrum in n-hexane; 2, spectrum for the solid film; 3, spectrum after pyridine vapour adsorption. Qualitative resolution of the total absorption spectrum for the solid film after pyridine vapour adsorption : 4, band of the solid film; and 5, new band.

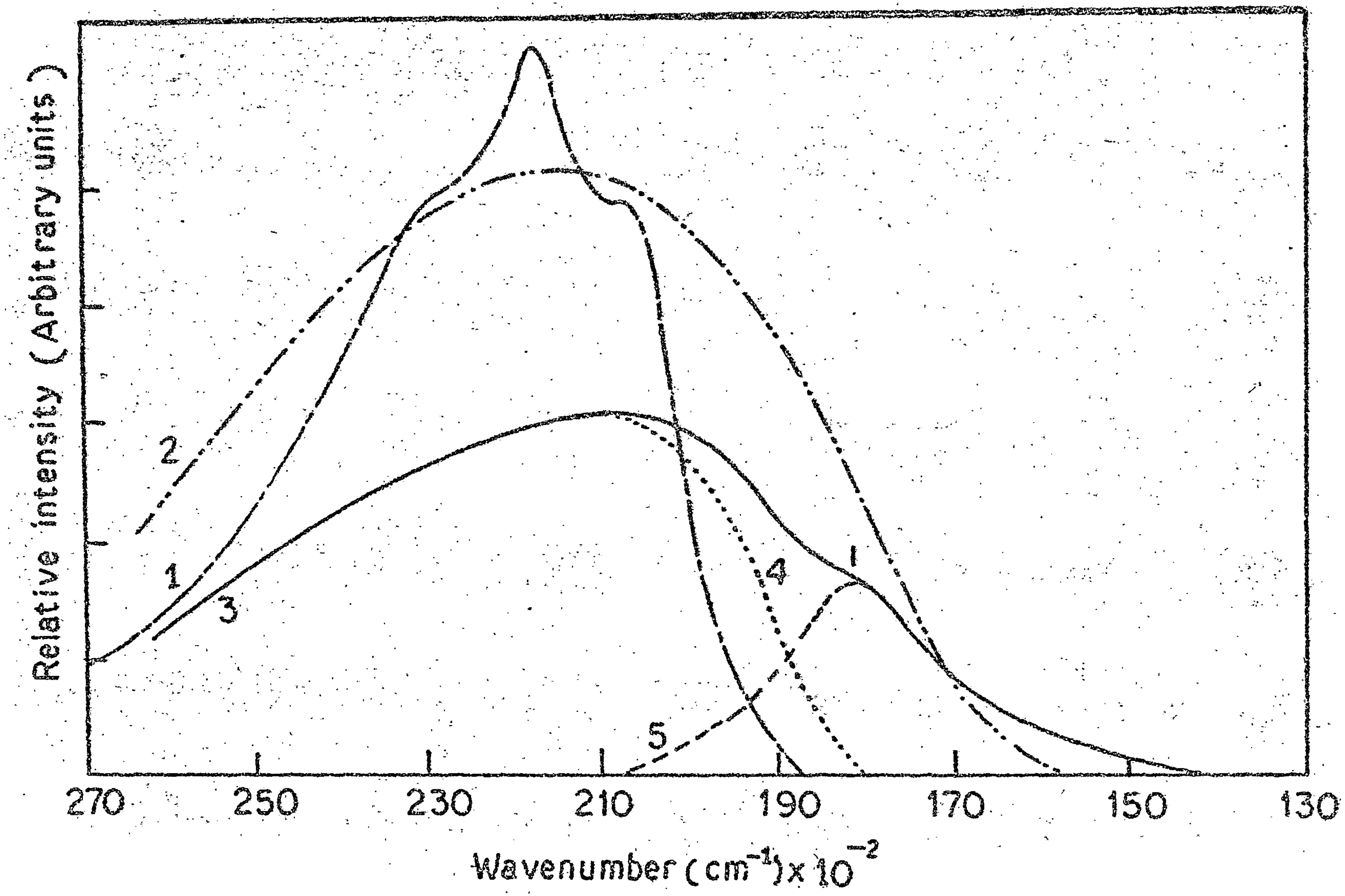

Relative intensity (Arbitrary units)
Wavenumber (cm^{-1}) x 10^{-2}
270
250
230
210
190
170
150
130
1
2
3
4
5

FIG. 2.4

Table-2.8

Absorption bands of β-apo-8'-carotenal visible band system

Solution spectrum in n-Hexane at 25°C		Solid state film at 25°C before vapour adsorption		Solid state film at 25°C after adsorption of pyridine vapour	
Wavenumber (cm^{-1})	Assignment	Wavenumber (cm^{-1})	Assignment	Wavenumber (cm^{-1})	Assignment
				18200(ms)	New band system ($^1A_g \rightarrow {}^1A_g$)
20790(s)	0	Broad structureless band with $\bar{\nu}_{max}$ at 21650(sb)	Band maxima	Broad structureless band with $\bar{\nu}_{max}$ at 21050(sb)	Band maxima
21790(vs)	0+1000				
22790(ms)	0+2x1000				

s - strong
v - very
m - medium
b - broad

FIG. 2.6 : Electronic absorption spectra of astacene at room temperature (25°C).

1, spectrum in CCl_4; 2, spectrum for the solid film; 3, spectrum for the solid film after aniline vapour adsorption. Qualitative resolution of the total absorption spectrum after aniline vapour adsorption : 4, band of the solid film; and 5, new band.

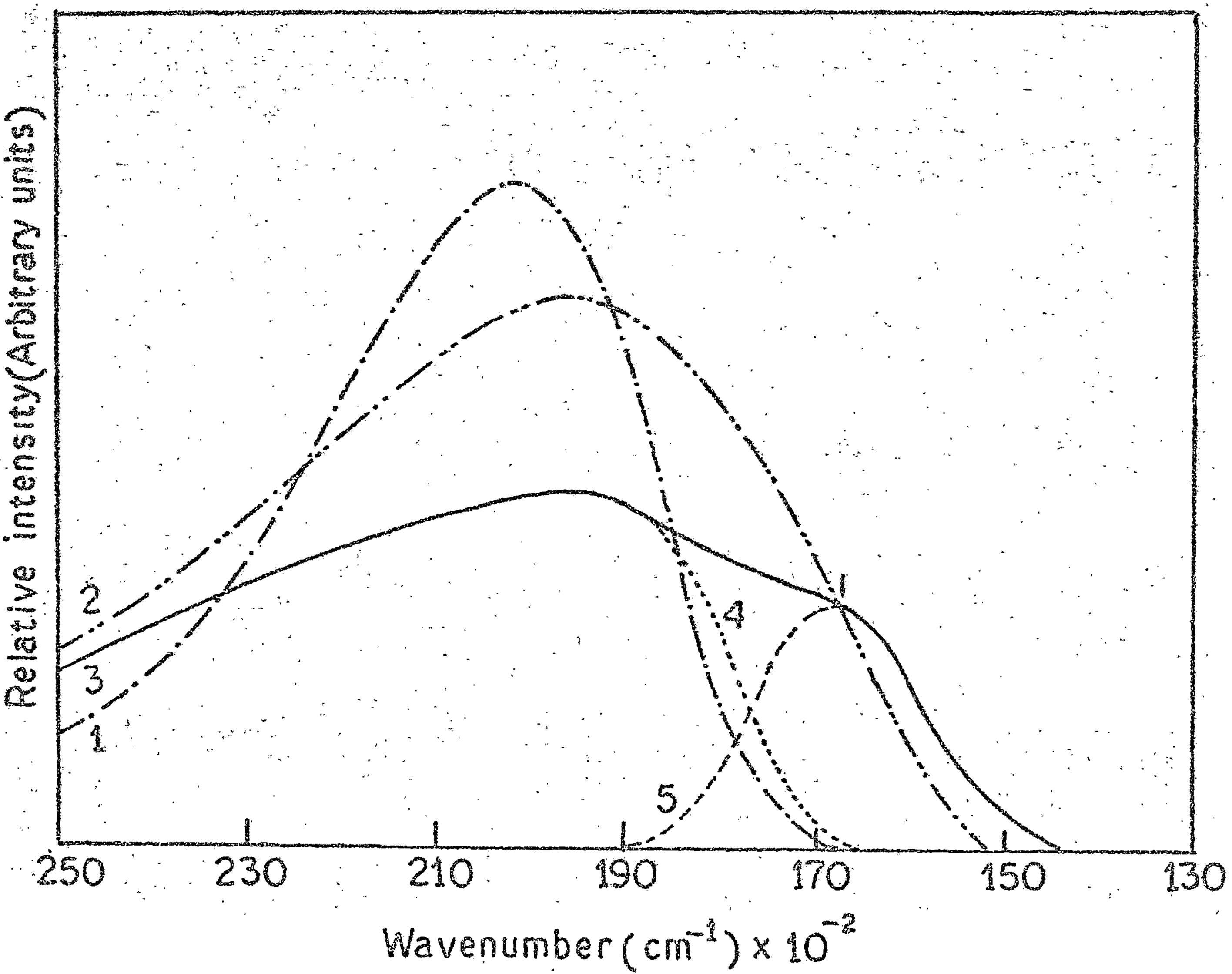

Relative intensity(Arbitrary units)
Wavenumber (cm^{-1}) x 10^{-2}
250
230
210
190
170
150
130
1
2
3
4
5

FIG. 2·5

various vapours the solid state spectrum appears with a new band at about 16660 cm^{-1} with a small change in position of the band in the crystalline state as shown in table 2.9.

The absorption spectrum of methyl bixin in acetone consists of three bands at 20650, 21650 and 23160 cm^{-1} (Fig. 2.6). In the solid state film as shown in Fig. 2.6, the spectrum is broad and redshifted. When various vapours are adsorbed on the surfaces of the crystallites in the films, a marked change in the solid film spectrum is observed. On being exposed in methanol vapour as shown in Fig. 2.6 a new band appears at about 17500 cm^{-1} in addition to the original bands of methyl bixin in the solid state. The results are summarized in table 2.10.

Table-2.9

Absorption bands of astacene visible band system

Solution spectrum in CCl_4 at 25°C		Solid state film at 25°C before vapour adsorption		Solid state film at 25°C after adsorption of aniline vapour	
Wavenumber (cm^{-1})	Assignment	Wavenumber (cm^{-1})	Assignment	Wavenumber (cm^{-1})	Assignment
				16660(ms)	New band system ($^1A_g \rightarrow {}^1A_g$)
Broad structureless band with $\bar{\nu}_{max}$ at 20242(s)	Band maxima	Broad structureless band with $\bar{\nu}_{max}$ at 19660(s)	Band maxima	Broad structureless band with $\bar{\nu}_{max}$ at 19450(sb)	Band maxima

s - strong
m - medium
b - broad

FIG. 2.6 : Electronic absorption spectra of methyl bixin at room temperature (25°C).
1, spectrum in acetone; 2, spectrum for the solid film; 3, spectrum for the solid film after methanol vapour adsorption. Qualitative resolution of the total absorption spectrum after methanol vapour adsorption : 4, band of the solid film; and 5, new band.

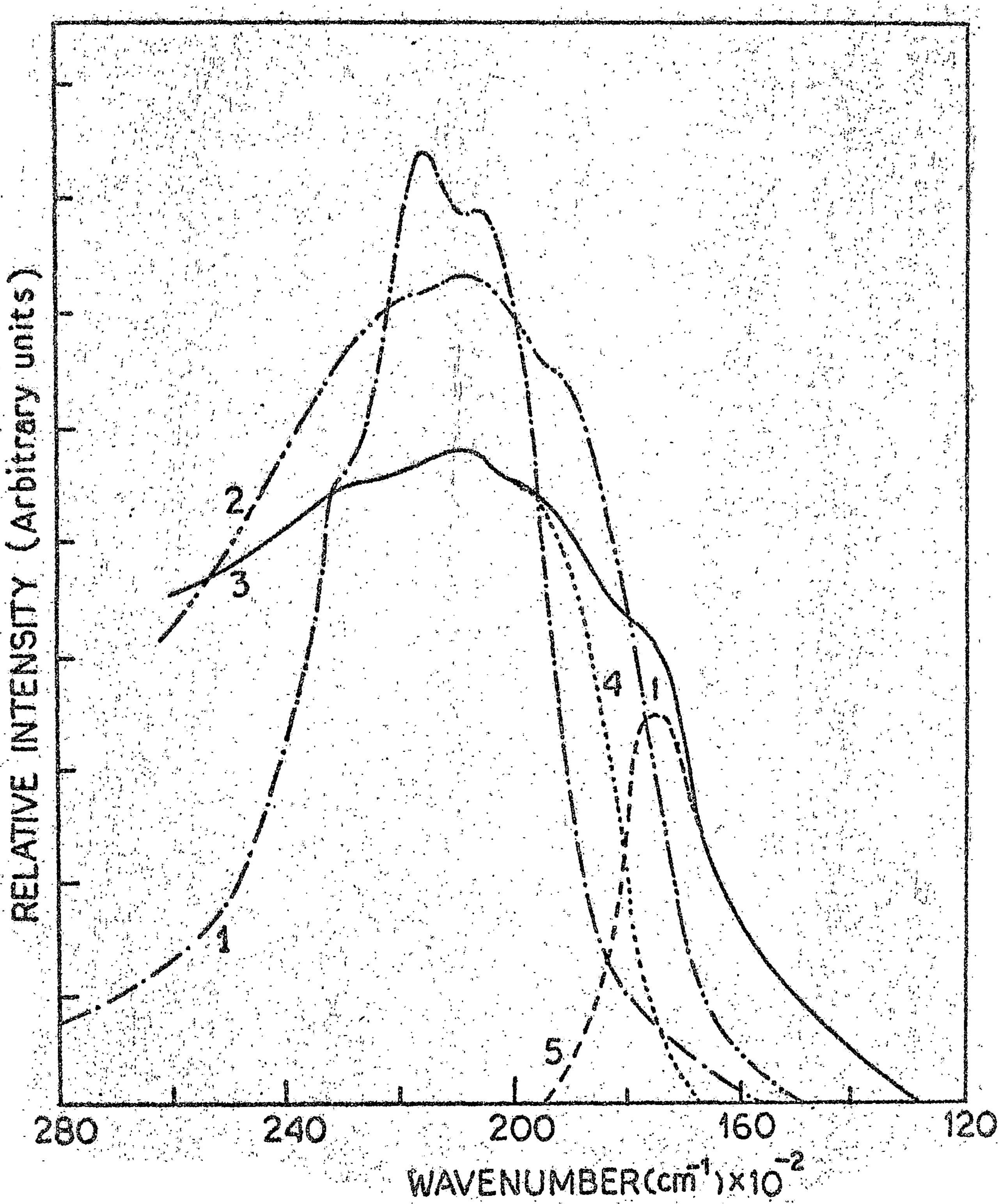

RELATIVE INTENSITY (Arbitrary units)
1
2
3
4
1
5
280
240
200
160
120
WAVENUMBER(cm^{-1})$\times 10^{-2}$

FIG. 2.6

Table - 2.10

Absorption bands of methyl bixin visible band system

Solution spectrum in acetone at 25°C		Solid state film at 25°C before vapour adsorption		Solid state film at 25°C after adsorption of methanol vapour	
Wavenumber (cm^{-1})	Assignment	Wavenumber (cm^{-1})	Assignment	Wavenumber (cm^{-1})	Assignment
				17500(w)	New band system ($^1A_g \rightarrow {}^1A_g$)
20550(ms)	0	19500(wb)	0	19700(wb)	0
21550(vs)	0 + 1000	20800(sb)	0 + 1300	21000(ms)	0 + 1300
23150(w)	0 + 2 x 1000	22100(vw)	0 + 2x1300	23000(w)	0 + 2x1300

m - medium
s - strong
v - very
w - weak
b - broad

2.3 Discussion

2.3.1 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 the polyene crystals. The intensity of this new band depends on the polyenes used and also on the vapour adsorbed. But the position of this new band in a particular polyene remains almost unchanged with different vapours adsorption. This excludes this band to be a charge-transfer absorption band. There is a large overlap between the well-studied long wavelength band system and the new band. So it is difficult to locate exactly the position of this new band. In order to get the longer 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 adsorption. Reasonably good resolved spectra are achieved in most of the polyenes. In vitamin A alcohol, to resolve the total absorption spectrum in two components becomes complicated as the intensity of the factor group split components are affected by vapour adsorption.

Of the polyenes studied, vitamin A is known to fluoresce strongly. In ethylacetate solution, the absorption and the emission spectra of vitamin A (alcohol and acetate) are shown in Fig. 2.7. Here, practically no overlap between the absorption and the emission spectra is observed which indicates that possibly the absorbing and the emitting states are different.

FIG. 2.7 : Electronic absorption and emission spectra of vitamin A in ethyl acetate at room temperature (25°C).
Vitamin A alcohol : 1, absorption; 2, emission.
Vitamin A acetate : 3, absorption; 4, emission.

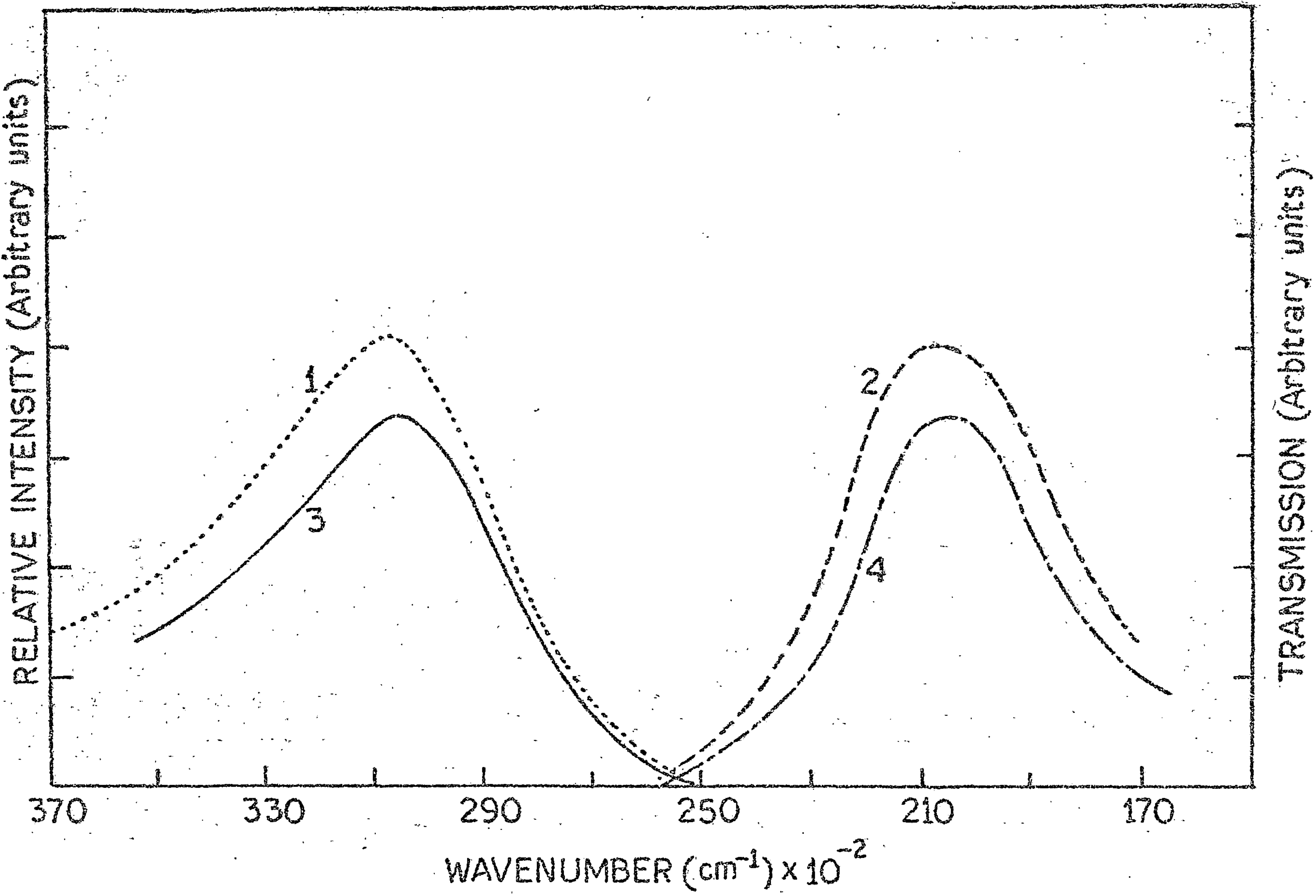

RELATIVE INTENSITY (Arbitrary units)
TRANSMISSION (Arbitrary units)
1
2
3
4
370
330
290
250
210
170
WAVENUMBER (cm^{-1}) x 10^{-2}

FIG. 2·7

The crystal emission spectra of the polyenes studied except vitamin A acetate[3] are not available. However, we have recorded the crystal emission spectra of vitamin A alcohol and have compared the emission band of vitamin A (alcohol and acetate) with the new band in the solid film (Figs. 2.8 and 2.9). The heights of the absorption and emission maxima are normalized. It is evident from the Figs. 2.8 and 2.9 that there is a good overlap between the emission and the new absorption band in vitamin A alcohol and acetate. The mirror image relationship is also satisfied. We have plotted transmission against the wavenumber (cm^{-1}) instead of ϵ_ν/ν against ν for the emission spectra as suggested by Birks and Dyson[20]. Unfortunately, the emission from the crystalline films of β-apo-8'-carotenal, astacene and methyl bixin could not be recorded. In these polyenes, the emission in solution is slightly on the high energy side of the new band in the crystal films. In view of the fact that free molecular electronic energy states are generally lowered in the state of aggregation, the emission of these polyene crystal films is expected to be on the lower energy side of that in solution. One can then reasonably expect to get good overlap between the new absorption band and the emission band of these polyenes in the crystalline state. Thus, our experimental results[21] suggest that the excited electronic state involved in the new absorption band and the reported emission band of the polyenes studied is the same and may be the low-lying weak π-electronic state suggested by Schulten and Karplus[4]. The transition from the ground state to this low-lying π-electronic state is forbidden since this state in <u>all-trans</u> polyenes has ^1A_g symmetry[4]. Our vapour adsorption method thus opens a new avenue in

FIG. 2.8 : Electronic absorption and emission spectra of *all-trans* vitamin A alcohol.
1, total spectrum after CCl_4 vapour adsorption;
2, resolved part for solid film; 3, new band; and
4, emission spectrum in the solid state.

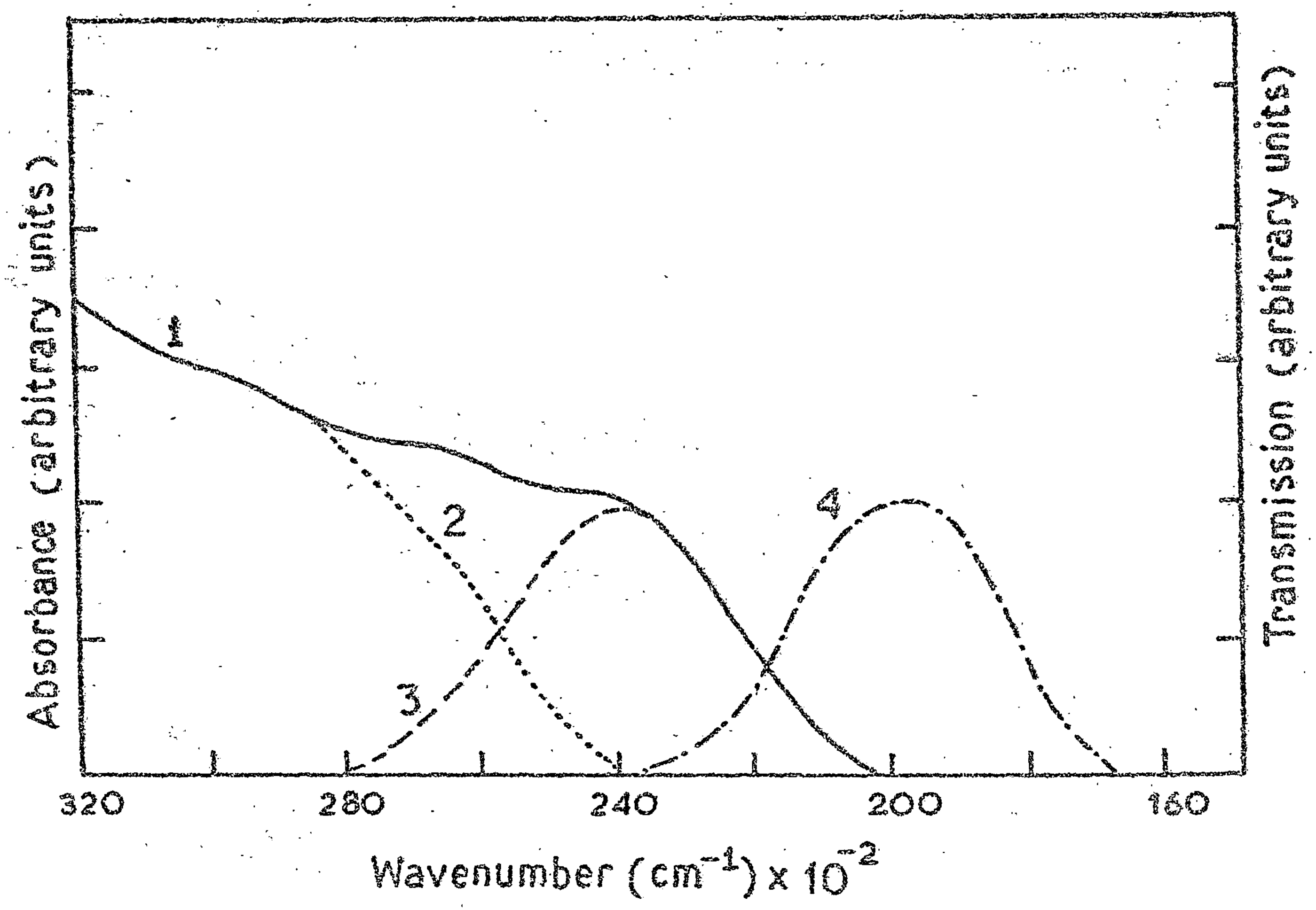

Absorbance (arbitrary units)
Transmission (arbitrary units)
1
2
3
4
320
280
240
200
160
Wavenumber (cm^{-1}) x 10^{-2}

FIG. 2·8

FIG. 2.9 : Electronic absorption and emission spectra of *all-trans* vitamin A acetate.
1, total spectrum after acetone vapour adsorption; 2, resolved part for the solid film; 3, new band; and 4, emission spectrum in the solid state.

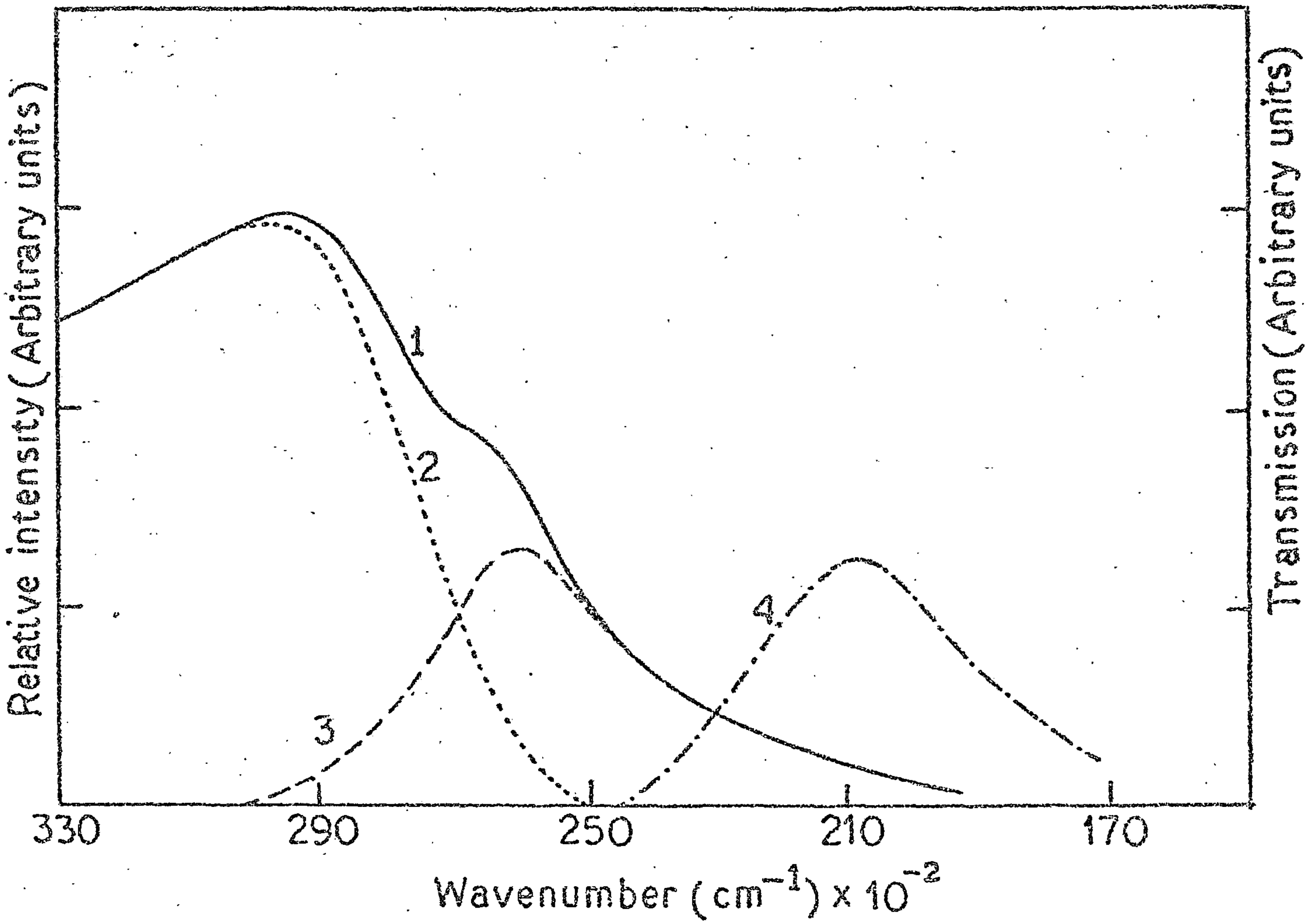

Relative intensity (Arbitrary units)
Transmission (Arbitrary units)
1
2
3
4
330
290
250
210
170
Wavenumber (cm^{-1}) x 10^{-2}

FIG. 2.9

making this low-lying forbidden transition allowed at room temperature.

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

2.3.2 Solvent Behaviour

The study of the solvent shift of the absorption and the emission bands helps in understanding the nature of the corresponding states. The major contribution to the solvent shift of the strong transition has the form[22]

$$hc(\bar{\nu}-\bar{\nu}_{gas}) = -\frac{2}{a^3}\cdot\frac{n^2-1}{n^2+2}\cdot\frac{E}{E'+E}\left[|P_{eg}|^2 - E(\alpha_g-\alpha_e)\right] \qquad (2.1)$$

where $hc\bar{\nu}$ is the transition energy, a is a characteristic molecular size parameter, n is the solvent refractive index, E is an average excitation energy of the solvent, E' is an average excitation energy for the solute, P_{eg} is the transition dipole for the transition from the state g to e and α's are the ground and excited state polarisabilities. Equation (2.1) can be written as

$$\Delta\bar{\nu} = k\cdot f\cdot\frac{n^2-1}{n^2+2} \qquad (2.2)$$

where k is a parameter which is constant for a given molecule, f is the oscillator strength for a particular transition. Solvents of different refractive indices were chosen to study the solvent effect on the absorption and emission bands of the polyenes. The effect of different solvents on the absorption and emission bands of the polyenes under investigation are presented in tables 2.11 - 2.15. From the tables it is seen that the absorption bands of the polyenes show a large red-shift with the increase of the refractive index of the solvents. But in case of emission, this shift is very small compared to that for absorption. Our experimental results[21,23] show that in all the polyenes studied, the plot of $\bar{\nu}_{max}$ for both absorption and emission against $(n^2-1)/(n^2+2)$ is a straight line. The plots of $\bar{\nu}_{max}$ (the frequency of the first intense absorption band usually observed in solution and the highest energy emission band) vs. $(n^2-1)/(n^2+2)$ are shown in Figs. 2.10 - 2.14 for vitamin A alcohol, vitamin A acetate, β -apo-8'-carotenal, astacene and methyl bixin respectively. The slope for the first absorption band of all the polyenes is about six to eight times greater than that for the emission band. This estimate of the relative strengths of the absorption and emission oscillator strengths indicates that the absorption and the emission under discussion involve two different excited states of the molecules. The fluorescence originates from a state other than that involved in the intense absorption band observed in solution. Thus it seems that there is a weakly absorbing singlet state with an energy lower than the strongly allowed excited state ^1B_u reached by absorption. The forbidden electronic state which has been allowed by our vapour absorption method is the low-lying singlet excited state.

Table - 2.11

Solvent effect on the absorption and emission bands of vitamin A alcohol at room temperature (25°C)

Solvent	$\frac{n^2-1}{n^2+2}$	$\bar{\nu}_{max}$ (cm^{-1}) for emission	$\bar{\nu}_{max}$ (cm^{-1}) for absorption
Methanol	0.203	21008	30864
Ethanol	0.221	20964	30769
Ethyl acetate	0.227	20942	30722
1,4-Dioxane	0.254	20942	30534
Carbon tetrachloride	0.275	20964	30303
Benzene	0.294	20920	30303

FIG. 2.10 : Plots of $\bar{\nu}_{max}$ against $(n^2-1)/(n^2+2)$ for the lowest energy absorption band and the highest energy emission band of *all-trans* vitamin A alcohol.

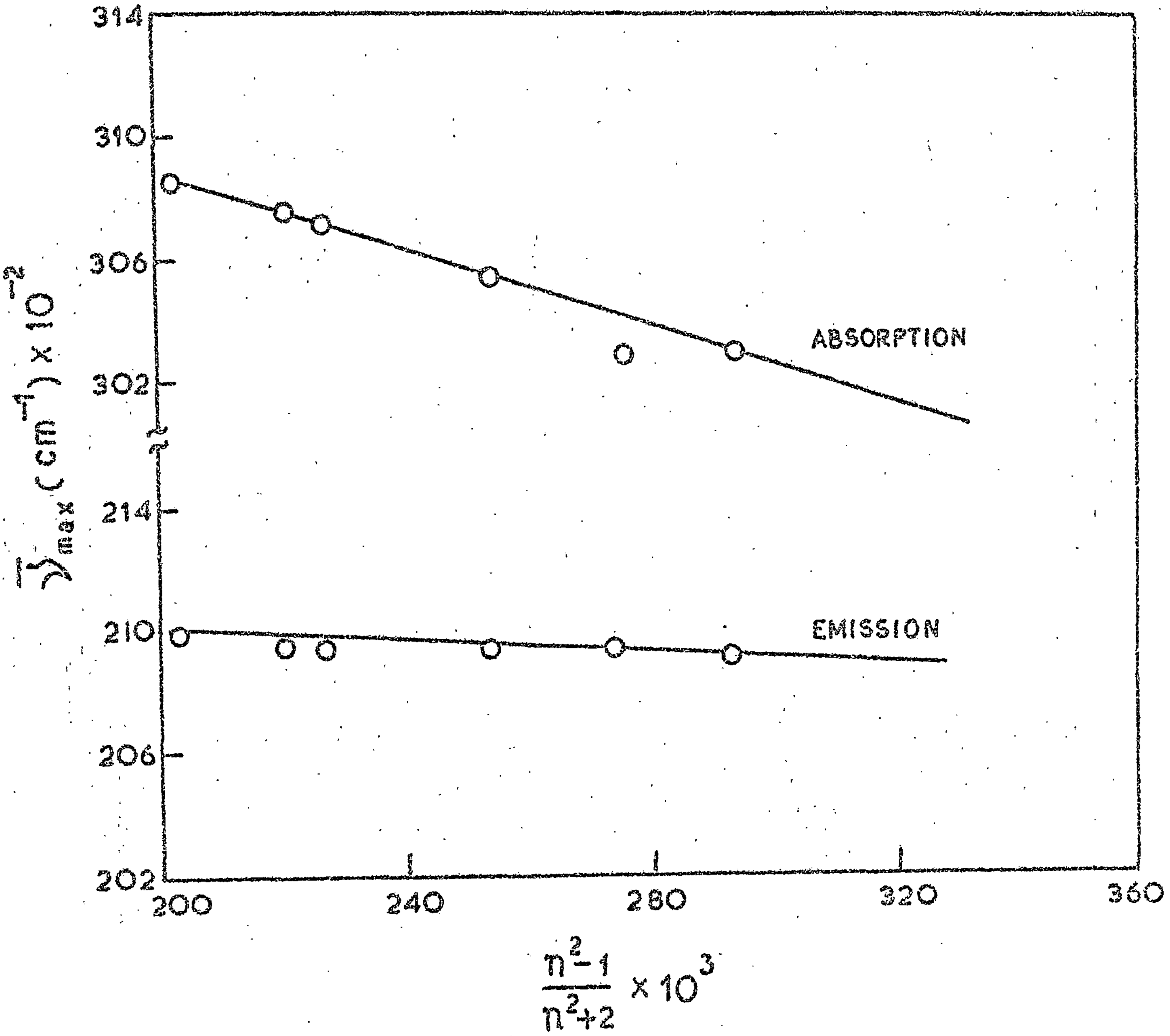

314
310
306
302
214
210
206
202
200
240
280
320
360
ABSORPTION
EMISSION
$\bar{\nu}_{max}\,(cm^{-1}) \times 10^{-2}$
$\frac{n^2-1}{n^2+2} \times 10^3$

FIG. 2·10

Table - 2.12

Solvent effect on the absorption and emission bands of vitamin A acetate at room temperature (25°C)

Solvent	$\frac{n^2-1}{n^2+2}$	$\bar{\nu}_{max}(cm^{-1})$ for emission	$\bar{\nu}_{max}(cm^{-1})$ for absorption
Methanol	0.203	20833	30614
Ethanol	0.221	20833	30581
Ethyl acetate	0.227	20730	30534
1,4-Dioxane	0.254	20730	30487
Carbon tetrachloride	0.275	20876	30030
Benzene	0.294	20730	30030

FIG. 2.11 : Plots of $\bar{\nu}_{max}$ against $(n^2-1)/(n^2+2)$ for the lowest energy absorption band and the highest energy emission band of <u>all-trans</u> vitamin A acetate.

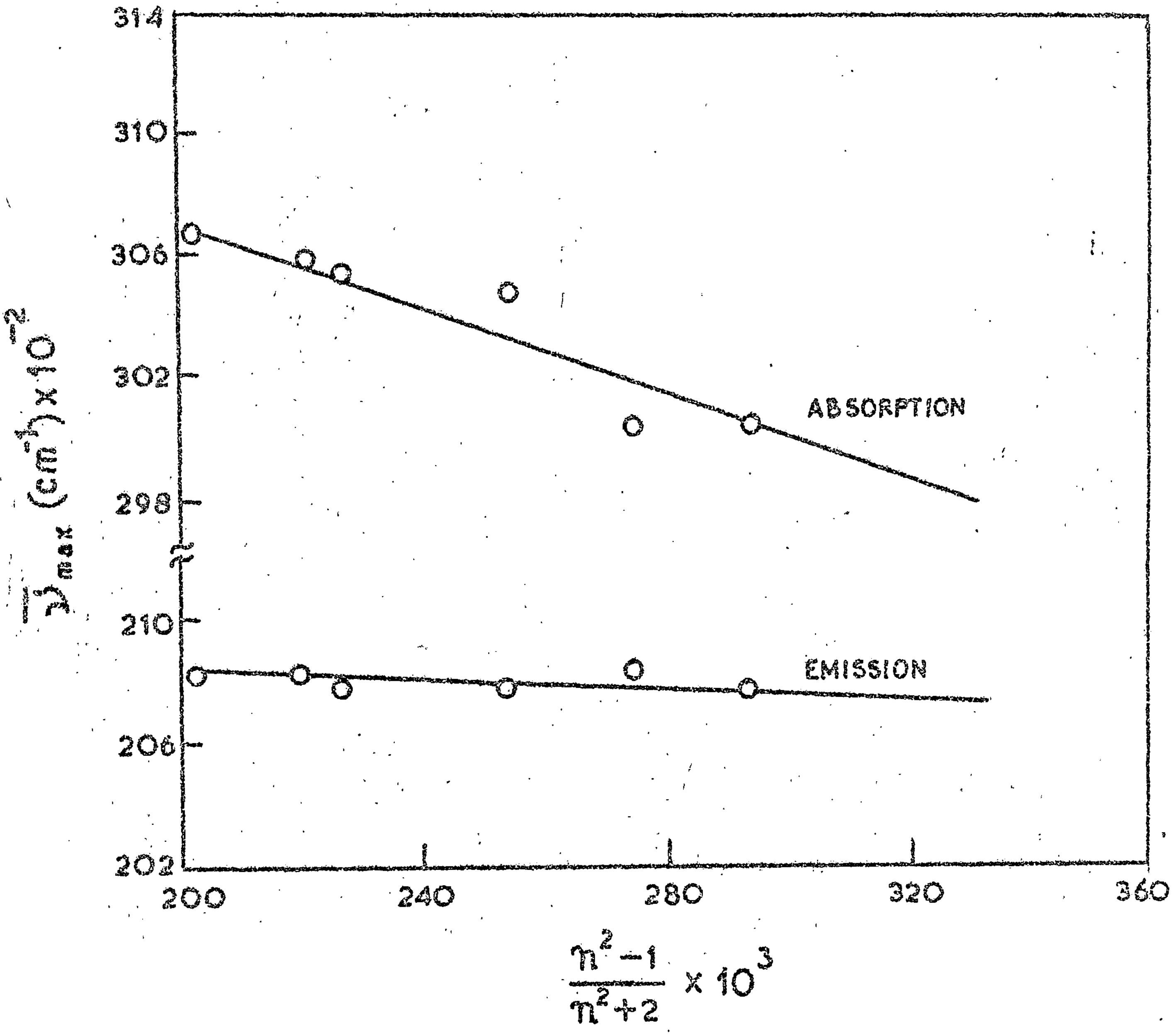

314
310
306
302
298
210
206
202
200
240
280
320
360
$\bar{\nu}_{max}$ (cm^{-1}) x 10^{-2}
$\frac{n^2-1}{n^2+2}$ x 10^3
ABSORPTION
EMISSION

FIG. 2·11

Table - 2.13

Solvent effect on the absorption and emission bands of β -apo-8'-carotenal at room temperature (25°C)

Solvent	$\frac{n^2-1}{n^2+2}$	$\bar{\nu}_{max}(cm^{-1})$ for emission	$\bar{\nu}_{max}(cm^{-1})$ for absorption
Acetone	0.219	19167	21880
Ethyl acetate	0.227	19157	21739
n-Hexane	0.228	19011	21790
1,4-Dioxane	0.254	19083	21459
Cyclohexane	0.257	19120	21600
Carbon tetrachloride	0.275	19047	21270
Benzene	0.294	19083	21229

FIG. 2.12 : Plots of $\overline{\nu}_{max}$ against $(n^2-1)/(n^2+2)$ for the lowest energy absorption band and the highest energy emission band of β-apo-8'-carotenal.

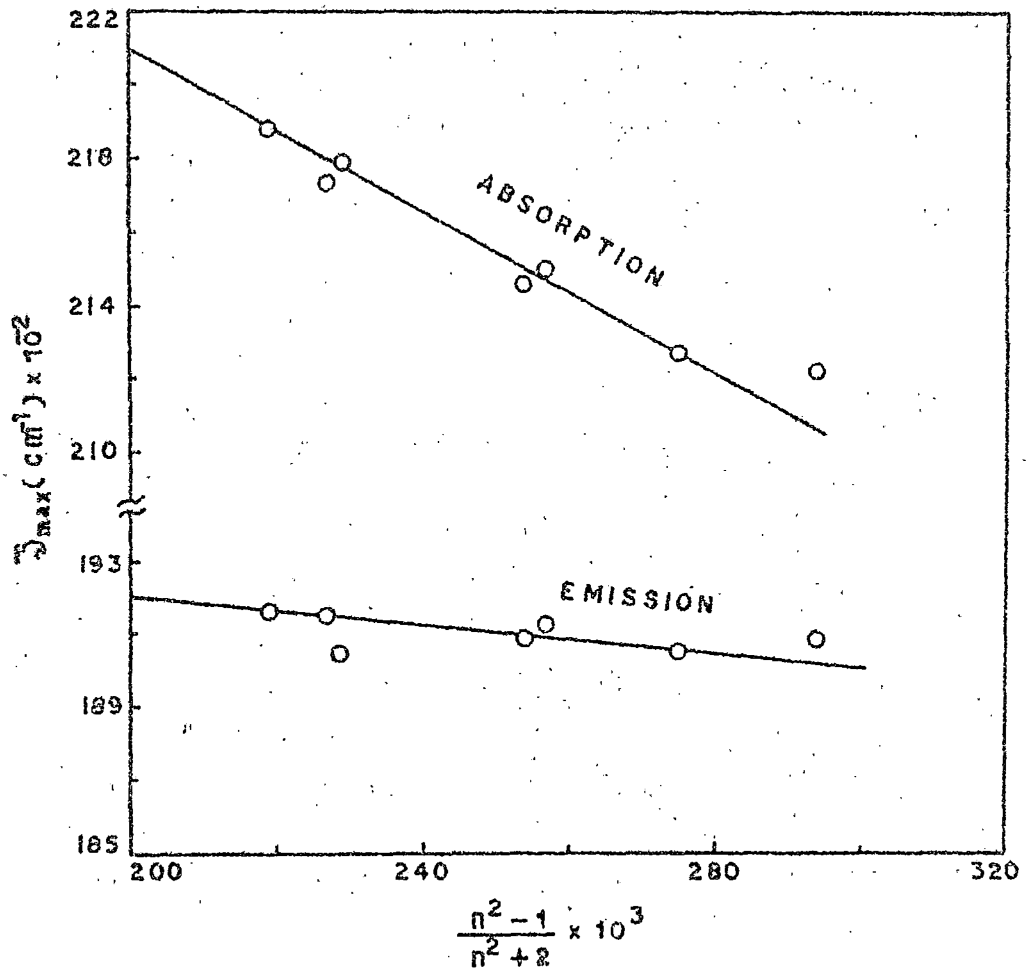

222
218
214
210
193
189
185
200
240
280
320
$\bar{\nu}_{max}(cm^{-1}) \times 10^{-2}$
$\frac{n^2-1}{n^2+2} \times 10^3$
ABSORPTION
EMISSION

FIG. 2.12

Table - 2.14

Solvent effect on the absorption and emission bands of astacene at room temperature (25°C)

Solvent	$\frac{n^2-1}{n^2+2}$	$\bar{\nu}_{max}(cm^{-1})$ for emission	$\bar{\nu}_{max}(cm^{-1})$ for absorption
Acetone	0.219	18018	20746
Ethyl acetate	0.227	17857	20661
1,4-Dioxane	0.254	17921	20408
Carbon tetrachloride	0.275	17889	20242
Benzene	0.294	17889	20202

FIG. 2.13 : Plots of $\bar{\nu}_{max}$ against $(n^2-1)/(n^2+2)$ for the lowest energy absorption band and the highest energy emission band of estacene.

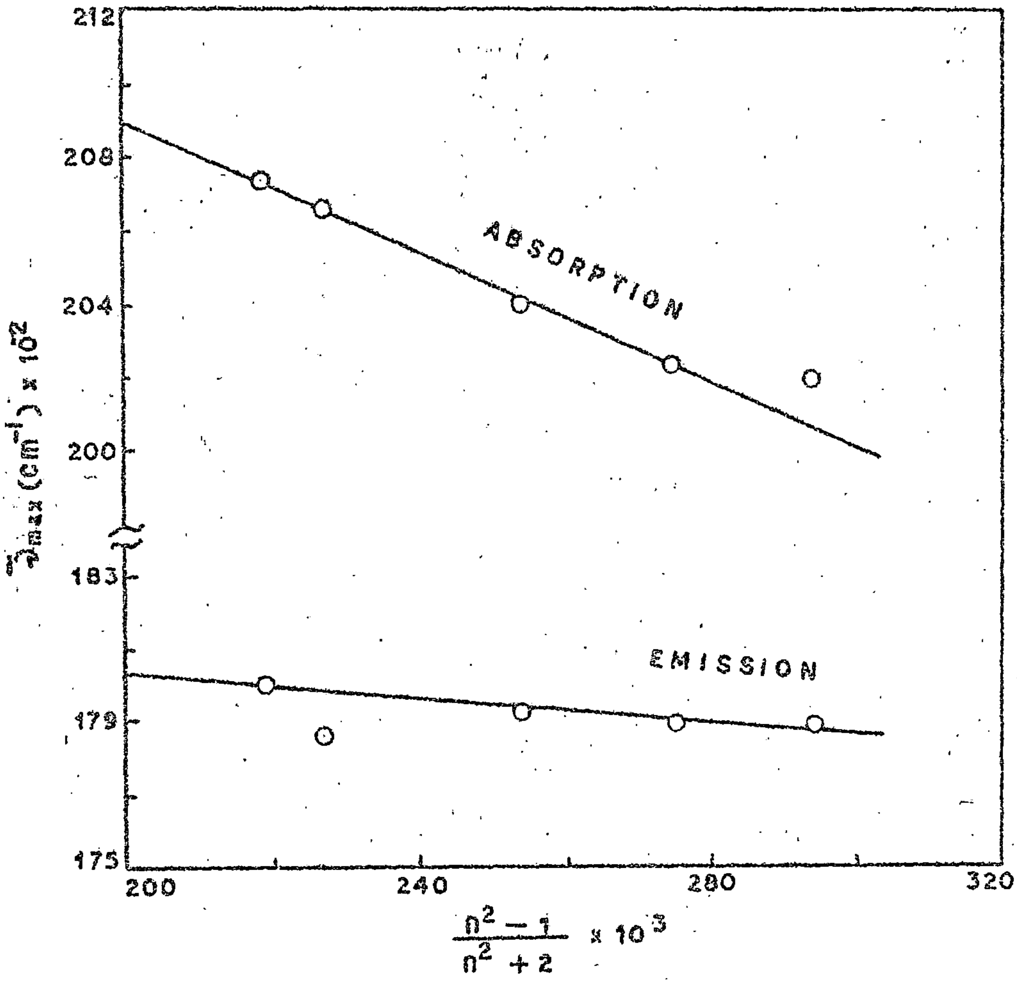

212
208
204
200
183
179
175
200
240
280
320
$\bar{\nu}_{max}$ (cm^{-1}) x 10^{2}
$\frac{n^2-1}{n^2+2}$ x 10^{3}
ABSORPTION
EMISSION

FIG. 2.13

Table - 2.15

Solvent effect on the absorption and emission bands of methyl bixin at room temperature (25°C)

Solvent	$\frac{n^2-1}{n^2+2}$	$\bar{\nu}_{max}(cm^{-1})$ for emission	$\bar{\nu}_{max}(cm^{-1})$ for absorption
Acetone	0.219	18796	21645
Ethanol	0.221	18761	21598
Ethyl acetate	0.227	18726	21505
1,4-Dioxane	0.254	18691	21220
Cyclohexane	0.257	18796	21186
Carbon tetrachloride	0.275	18726	20920
Benzene	0.294	18691	20920

FIG. 2.14 : Plots of $\bar{\nu}_{max}$ against $(n^2-1)/(n^2+2)$ for the lowest energy absorption band and the highest energy emission band of methyl bixin.

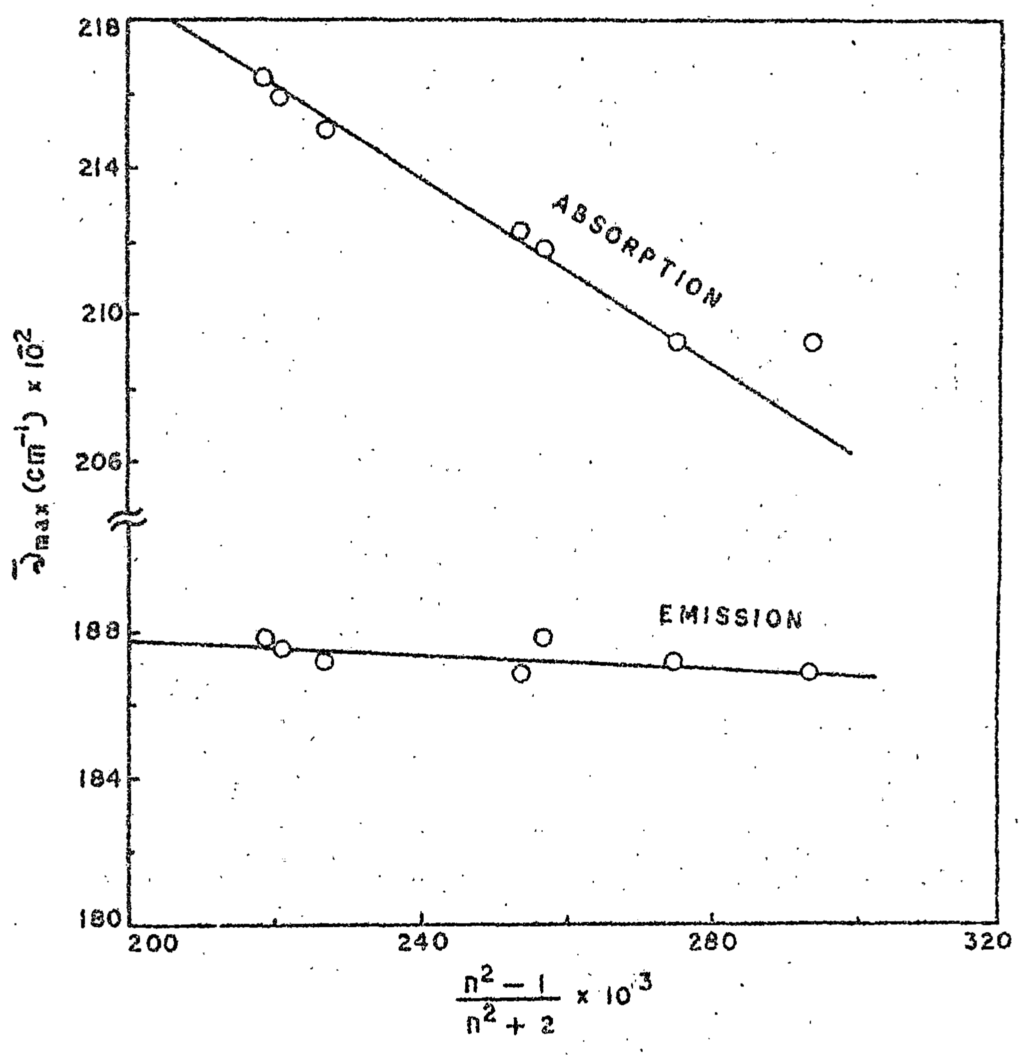

218
214
210
206
188
184
180
200
240
280
320
$\bar{\nu}_{max}$ (cm^{-1}) x 10^{-2}
$\frac{n^2-1}{n^2+2}$ x 10^{-3}
ABSORPTION
EMISSION

FIG. 2·14

This lowest excited electronic state in polyenes is ^1A_g state which is symmetry forbidden. The life-time of this state is long because of its forbidden nature. Therefore, this lowest state seems to be involved in the photochemical processes.

2.3.3 Factor Group Splitting

The wavefunctions of the translationally non-equivalent interacting molecules in the crystal produce splitting of the molecular energy levels[24,25]. 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 40600 cm^{-1} evidently corresponds to the band at 41000 cm^{-1} in the solid state (Fig. 2.2). The two bands in solution at about 31900 and 30864 cm^{-1} have a separation of 1036 cm^{-1}. In the solid film none of the bands at 34900, 29500 and 26666 cm^{-1} seems to correspond to the weak solution band at 31900 cm^{-1}. It is likely that these three bands in the solid state are the factor group split components of the band at 30864 cm^{-1} in solution. The weak band at 31900 cm^{-1} in the solution spectrum is possibly masked by the strong absorption at 34900 cm^{-1} in the crystalline state.

Unfortunately the crystal structure of vitamin A alcohol and molecular orientations in the lattice are not known. It is, 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.

2.4 Conclusion

The new absorption band appearing on the long wavelength side of the $^1A_g \longrightarrow {}^1B_u$ transition due to adsorption of various vapours on the solid films of polyenes studied shows a good overlap and mirror image relationship with the emission band of these polyene solid films. The solvent effect on the $^1A_g \longrightarrow {}^1B_u$ absorption band and on the observed emission band suggests that two different electronic states are involved in the absorption and in the emission. It is suggested that the low energy band appearing on vapour adsorption is due to the transition from the ground ^1A_g state to the next excited ^1A_g state wherefrom the emission in these polyenes also originates. Thus, we conclude that a low energy ^1A_g state lies below the ^1B_u state in these polyenes.

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