CHAPTER 3

CHARGE-TRANSFER COMPLEXES OF SOME POLYENES

3.1 Introduction

Mulliken[1] suggested that charge-transfer (CT) complexes may play an important role in biological systems. Some possible implications have been discussed in a book by Szent-Györgyi[2]. Many workers have produced evidence which, it is claimed, supports this proposition. The idea is that the charge-transfer complexes possess certain properties which could be important in biological systems. The first most obvious property is the transfer of charge from one molecule to another. Electron and charge transfer or transport systems are vitally important in biology.

The balance of electron donors and acceptors of varied biopotential is one of the basic parameters of life and is used in the regulation of activity and the physical state of the cell[3]. Medium range charge-transfer is possibly the most frequent and fundamental in biological reactions. The forces developed due to charge-transfer may bring about the association of two and more entities. It may further influence equilibrium and reactivity. The preferred conformation resulting from CT in turn may confer a biological activity. It has been suggested[2,4] that CT complex formation plays a role in respiratory chain of oxidative phosphorylation, chemical carcinogenesis, drug action and photosynthesis.

The presence of carotenoids (polyenes) in living systems and in plants is well recognised. Some carotenoid pigments are present in cone layers of eyes[5], in olfactory areas[6-8], in skin and in membranes[9,10] of animals. Presence of carotenoids in chloroplasts strongly suggests its involvement in photosynthesis. It was Platt[11] who suggested that donor-carotene-acceptor trimolecular complex could be involved in primary photosynthesis process. Such a complex would shift the carotene absorption band to much longer wavelength below the absorption bands of chlorophylls and the complex would be the energy sink of the whole system. Simple bimolecular CT complex may also work in the same way. Charge-transfer mechanism involving other polyenes may well be responsible for many other biological activities.

Usually CT bands are studied in solutions. Of the polyenes of our interest only vitamin A is well studied[12-16]. Lupinski[17] observed a new absorption band at 10000Å in a mixture of β-carotene and iodine in $ClCH_2Cl$ solution and attributed this to a CT band of β-carotene ....I^+ complex. Ebrey[18], on the other hand, agrued that the band observed by Lupinski, instead of being a charge-transfer band of donor-acceptor type, was a band of β-carotene shifted to longer wavelength due to charge-transfer effect, thus suggesting that β-carotene. I^+ complex has several resonance structures for the β-carotene ground state that would equalise bond length and cause its shifting to longer wavelength. Thus it appears that the usual method of observing the CT bands in solution with suitable acceptors has not been successful with the polyenes except with vitamin A.

The important property of the charge-transfer complex forces is that they are relatively long-range as compared to chemical forces and the typical distances between the molecules in these complexes are 3.2 to 3.4 Å whereas chemical bond lengths are less than about 1.5 Å. Before a charge-transfer interaction can take place, the donor and the acceptor molecule or parts of the molecules must be in sufficient proximity to each other so that the difference in electro-potential can be recognized. In many cases the physical forces (e.g., dipole-dipole force, viscous force etc.) operating between the molecules can prevent such close approach and the formation of the charge-transfer complex is not favoured. In solution, the molecules are not isolated and the interaction between the molecules cannot be divorced from the effects of the immediate surroundings. Generally the polarity and the viscosity of a medium are observed to have a strong effect on the charge-transfer interaction. In the media of low viscosity, Brownian motion which causes the molecules to move about reduces the possibility of their close approach. In a rigid matrix, the molecules do not experience any Brownian motion and are held in such close proximity that charge-transfer are generally facilitated. Thus, the molecules which seem not to interact in solution may do so in the solid state. It was, therefore, thought worthwhile to study the charge-transfer complexes of <u>all-trans</u>-β-carotene, β-apo-8'-carotenal, astacene and methyl bixin in the solid state. For this purpose, we have allowed the vapours of some acceptors to be adsorbed on the transparent solid films of the polyenes in quartz cells and have collected the spectroscopic data to see if CT complexes are really formed in the solid state. In this chapter the results of such studies are presented.

3.2 Experimental and Results

The sample of *all-trans*-β-carotene like other polyenes was obtained from Hoffman-La-Roche Co. Ltd., Switzerland. This was used without further purification. The structure of this polyene is shown in Fig. 3.1.

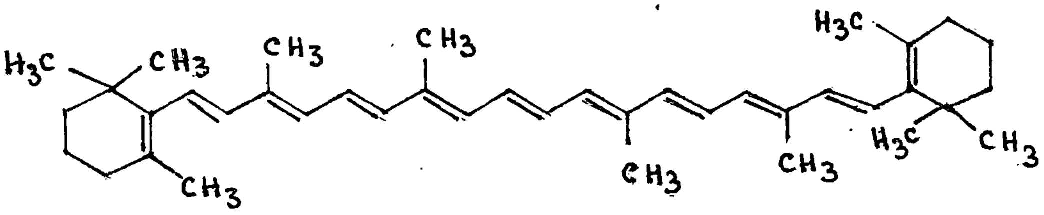


Fig. 3.1 Structure of *all-trans*-β-carotene

Thin films of polycrystals of the polyenes were made on the quartz surface in the same procedure as mentioned in the previous chapter. The solid films thus made were exposed to vapours of nitric acid, iodine, bromine and iodine monochloride. These chemicals were of high quality. The absorption spectra at room temperature (28°C) were recorded immediately after exposing the solid films to vapours by a spectromom - 202 spectrophotometer of Hungarian Optical Works.

The room-temperature (28°C) absorption spectra of *all-trans*-β-carotene, β-apo-8'-carotenal, astacene and methyl bixin in the solid state and the spectra after adsorption of different acceptor vapours are shown in Figs. 3.2 - 3.6. It is seen that on adsorption

FIG. 3.2 : Electronic absorption spectra of all-trans-β-carotene solid film at 28°C after adsorption of different electron acceptor vapours : (1), solid film spectrum without vapour adsorption; (2), nitric acid vapour adsorption; (3), iodine vapour adsorption; (4), bromine vapour adsorption; (5), iodine monochloride vapour adsorption. (The positions, $\bar{\nu}_{max}$, of the new bands are indicated by vertical marks. Spectra on adsorption of different vapours are not normalised).

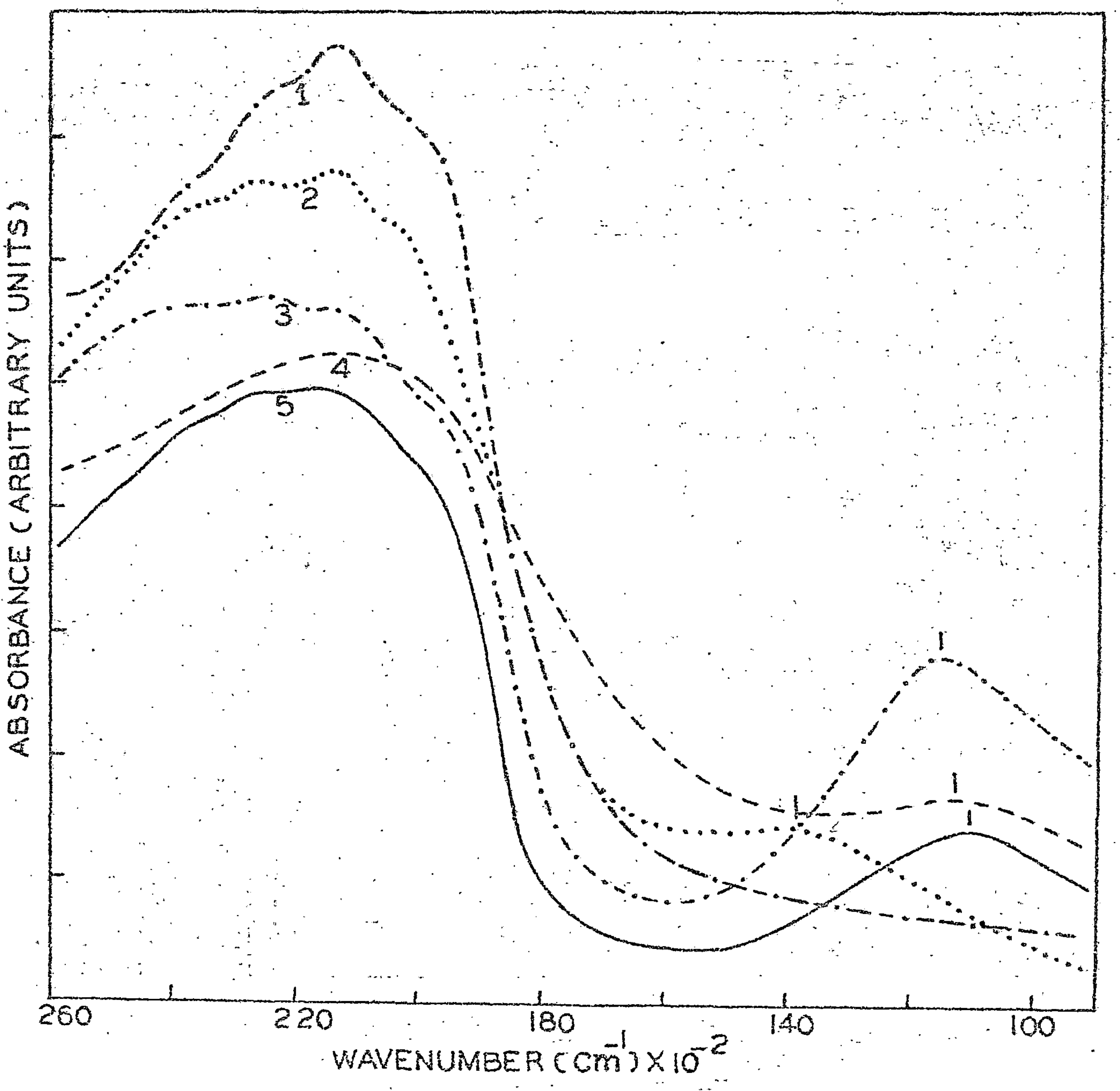

ABSORBANCE (ARBITRARY UNITS)
WAVENUMBER (cm^{-1}) X 10^{-2}
260
220
180
140
100
1
2
3
4
5

FIG: 3·2

FIG. 3.3 : Electronic absorption spectra of β -apo-8'-carotenal solid film at 28°C after adsorption of different electron acceptor vapours : (1), solid film spectrum without vapour adsorption; (2), iodine vapour adsorption; (3), bromine vapour adsorption; (4), iodine monochloride vapour adsorption. (The positions, $\bar{\nu}_{max}$, of the new bands are indicated by vertical marks. The spectra on adsorption of various vapours are not normalised).

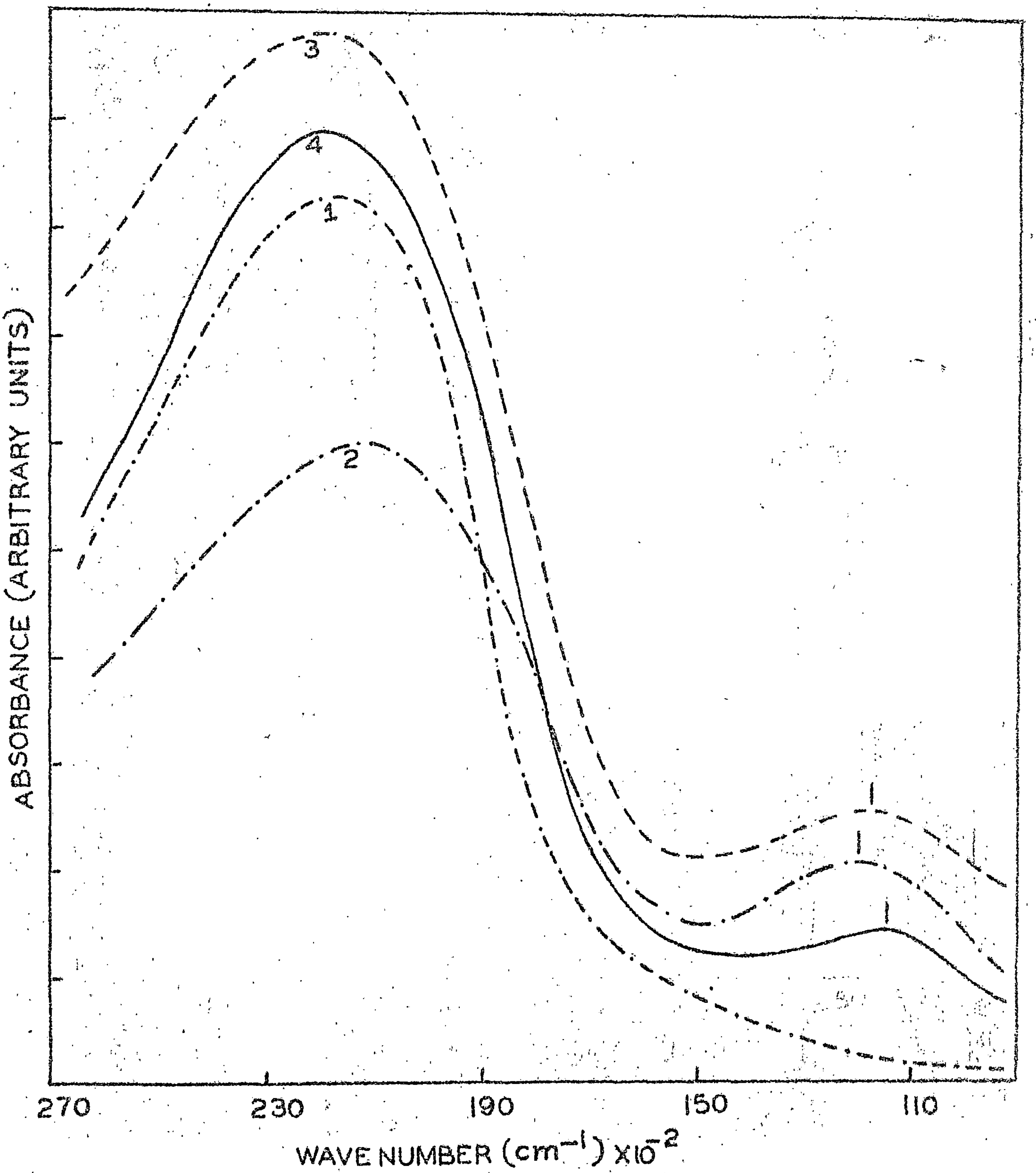

ABSORBANCE (ARBITRARY UNITS)
WAVE NUMBER (cm^{-1}) X10^{-2}
270
230
190
150
110
1
2
3
4

FIG. 3.3

FIG. 3.4 : Electronic absorption spectra of astacene solid film at $22^{\circ}C$ after adsorption of different electron acceptor vapours : (1), solid film spectrum without vapour adsorption; (2), iodine vapour adsorption; (3), bromine vapour adsorption; (4), iodine monochloride vapour adsorption (The positions, $\bar{\nu}_{max}$, of the new bands are indicated by vertical marks. The spectra on adsorption of various vapours are not normalized).

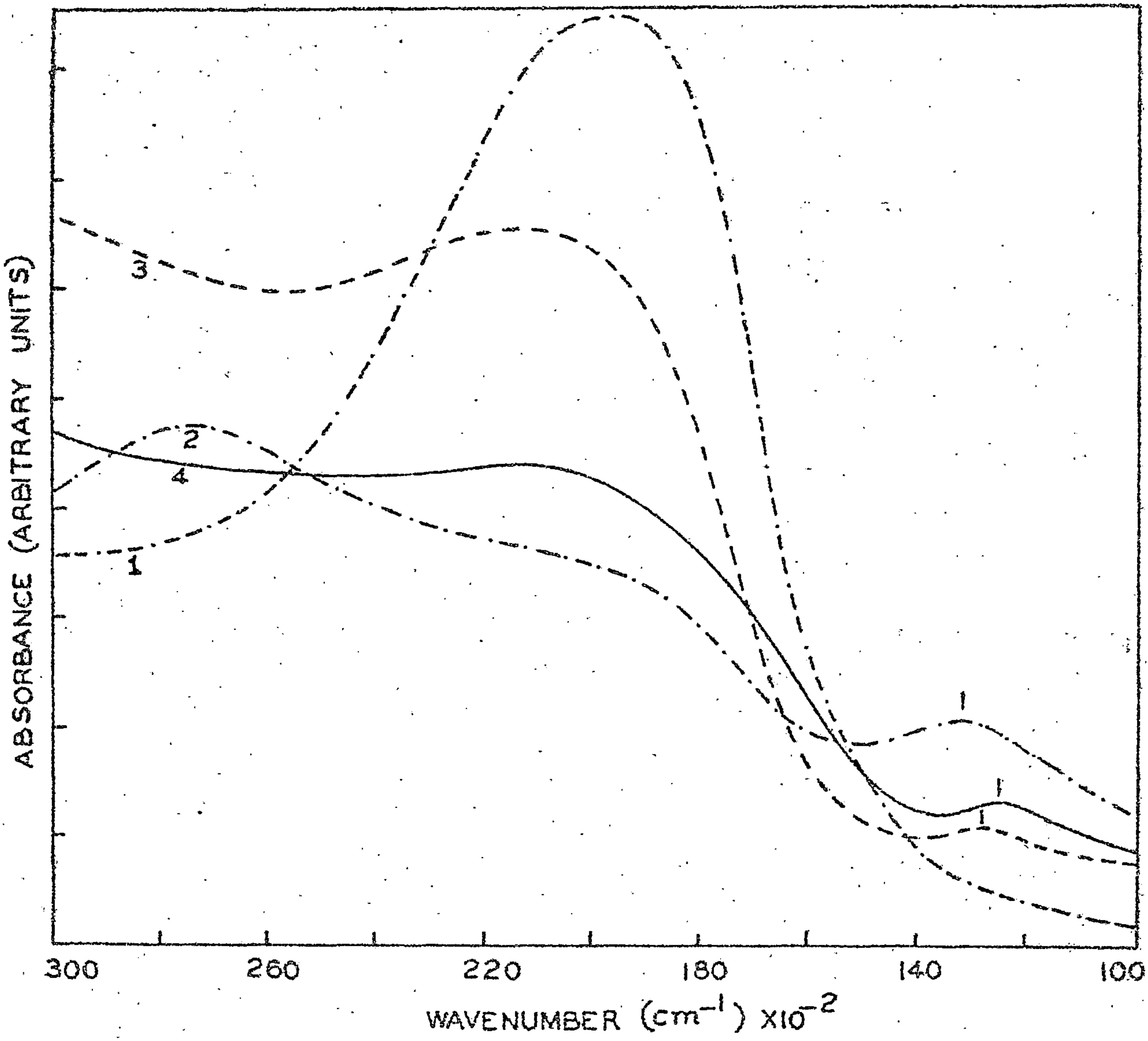

1
2
3
4
300
260
220
180
140
100
WAVENUMBER (cm⁻¹) X10⁻²
ABSORBANCE (ARBITRARY UNITS)

FIG-3·4

FIG. 3.5 : Electronic absorption spectra of methyl bixin solid film at 28°C after adsorption of different electron acceptor vapours : (1), solid film spectrum without vapour adsorption; (2), iodine vapour adsorption; (3), bromine vapour adsorption; (4), iodine monochloride vapour adsorption. (The positions, $\bar{\nu}_{max}$, of the new bands are indicated by vertical marks. The spectra on adsorption of various vapours are not normalized).

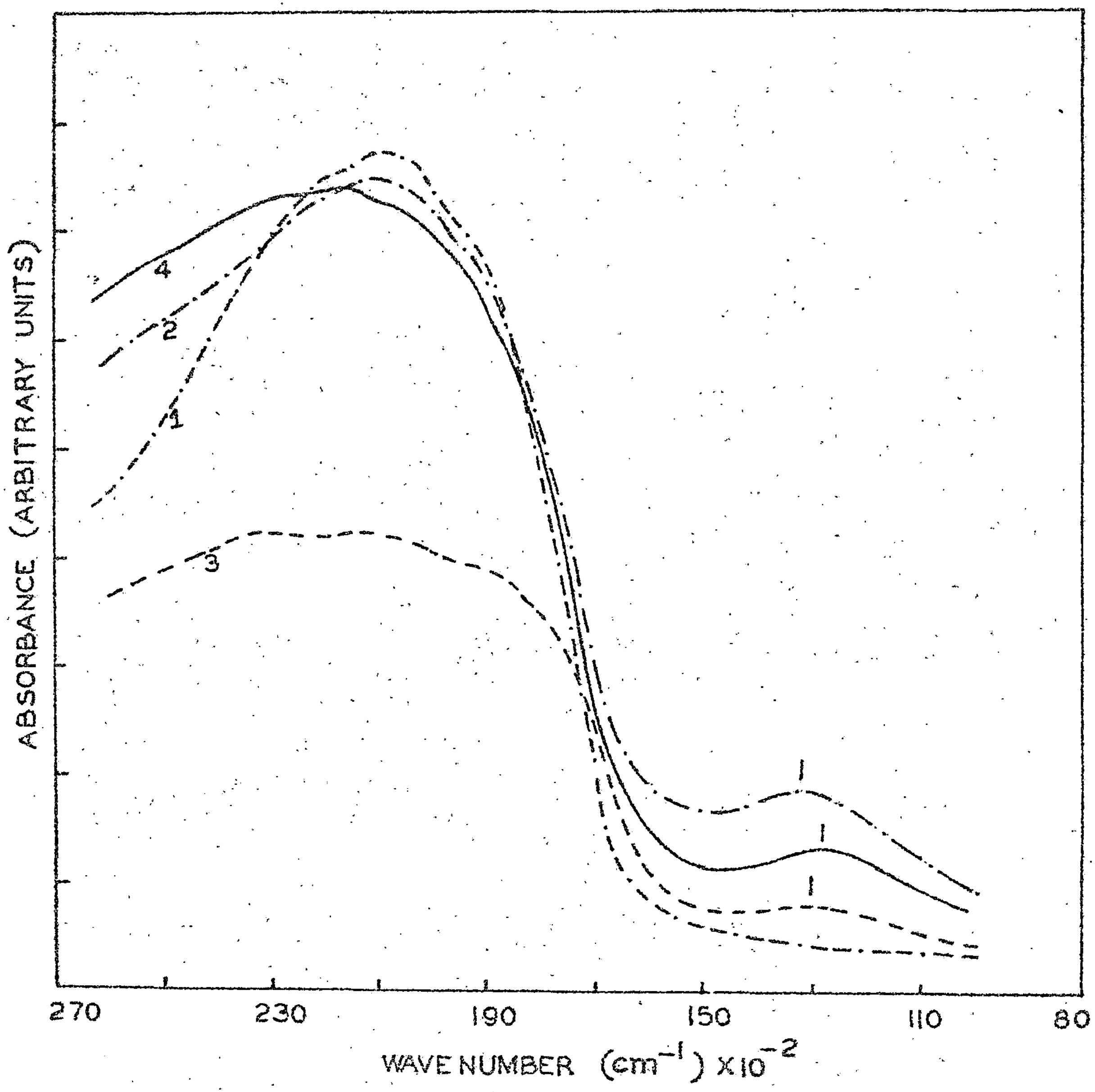

ABSORBANCE (ARBITRARY UNITS)
WAVE NUMBER $(cm^{-1}) \times 10^{-2}$
270
230
190
150
110
80
4
2
1
3

FIG. 3·5

of acceptor vapours, in each polyene a new band appears on the long wavelength side of the spectra in addition to the original bands of the polyene solid films. With the increasing amount of acceptor molecules adsorbed on the film surface, the intensity of this new band increases as is usually observed in case of a charge-transfer band. This observation is shown in Figs. 3.6-3.9 for all-trans- β -carotene, β -apo-8'-carotenal, astacene and methyl bixin, respectively. The position of the new band in each polyene is found to be dependent on the acceptor vapours used and shows appreciable red-shift with the increasing electron affinity of the acceptor molecules. Only acceptors fairly volatile at ordinary temperatures are suitable for such experiment. As the number of such acceptors are very limited, only a few acceptors could be used. The position of the new bands in different polyenes appearing on adsorption of various acceptor vapours are summarized in table 3.1.

3.3 Discussion

In each polyene the new band appears on the lower energy side of the observed emission band of the polyene and its separation is about 5000 - 7000 cm^{-1} from the $\bar{\nu}_{max}$ of the emission band. This excludes the possibility of this band to be the low-lying forbidden band as discussed in the previous chapter. The results presented in the previous section suggest this band to be a charge-transfer band.

FIG. 3.6 : Enhancement of the intensity of the new band with the amount of adsorbed acceptor molecules on the solid film of all-trans β-carotene at 23°C. The solid lines for the neat solid film spectrum. The broken lines represent the spectra after iodine vapour adsorption; (1-4), in order of increasing amount of iodine molecules.

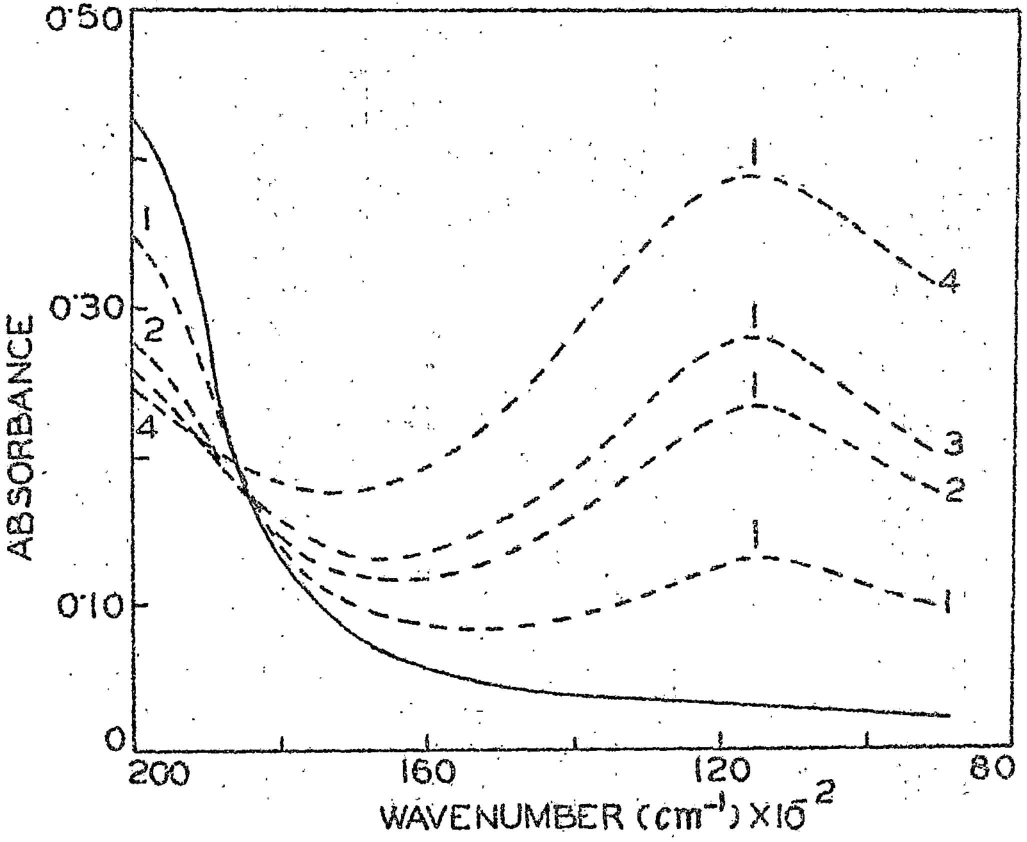
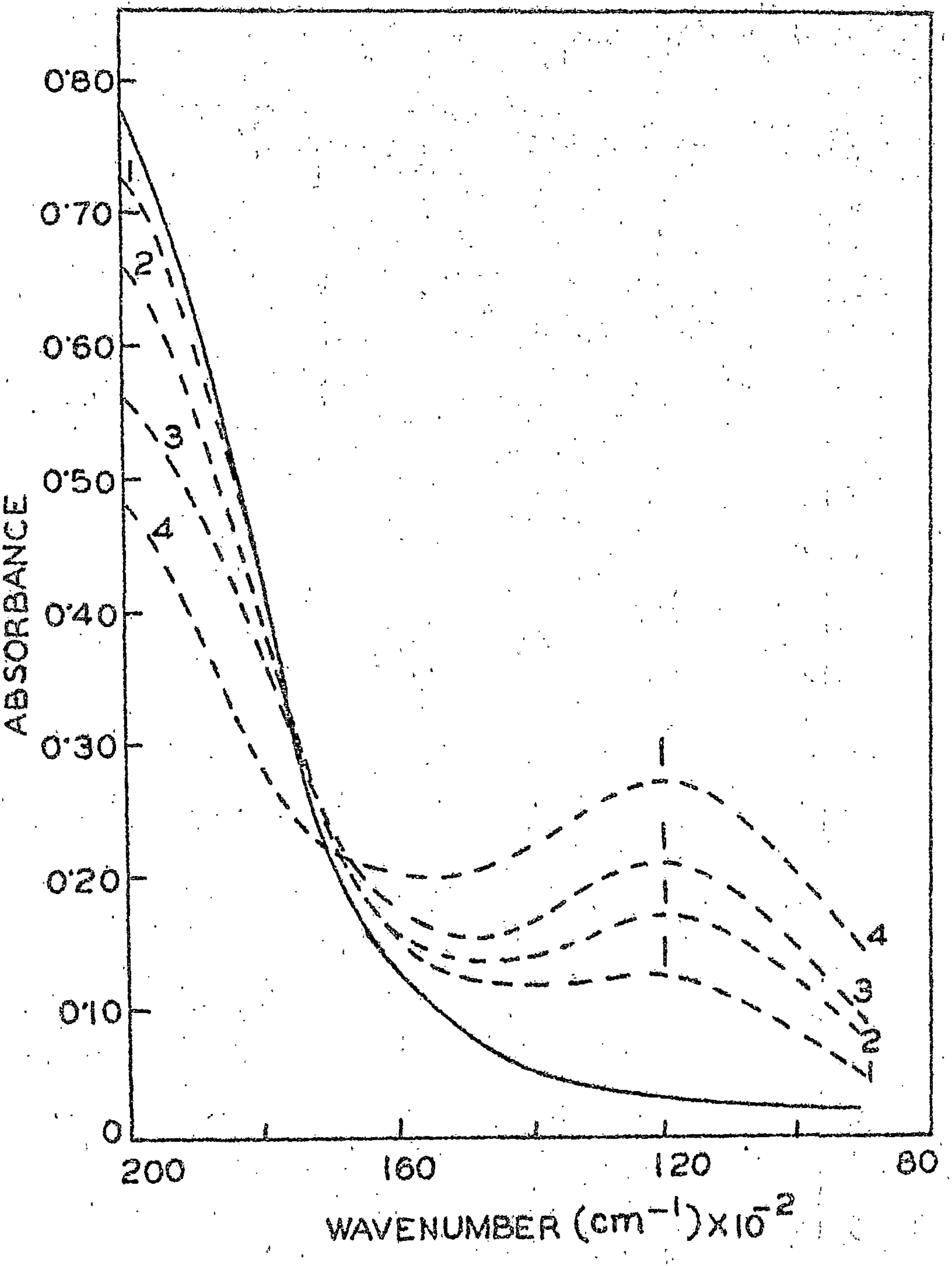

0·50
0·30
0·10
0
ABSORBANCE
200
160
120
80
WAVENUMBER (cm⁻¹) X10⁻²
1
2
4
1
2
3
4

FIG. 3·6

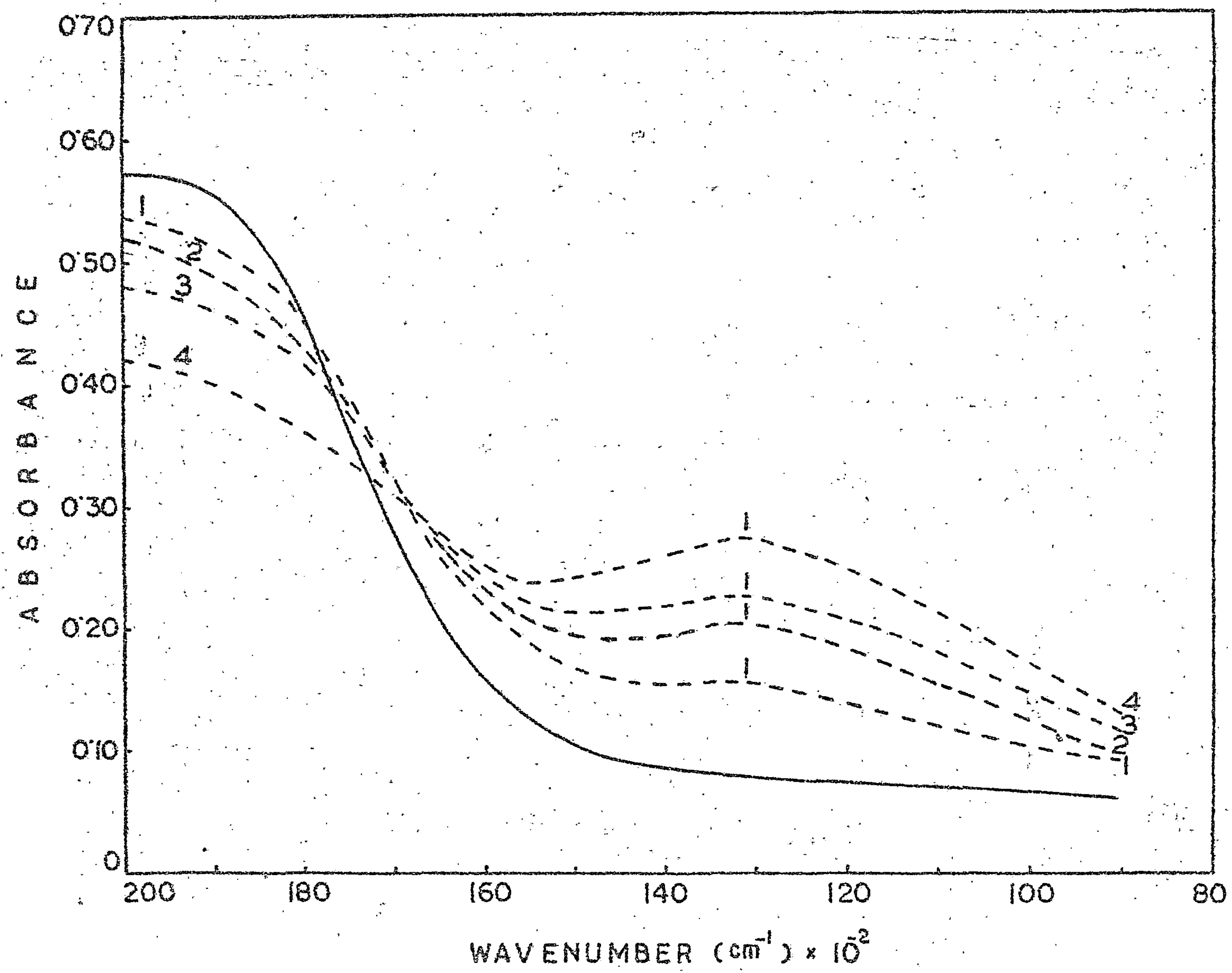
FIG. 3.7 : Enhancement of the intensity of the new band with the amount of adsorbed acceptor molecules on the solid film of β-apo-8'-carotenal at 28°C. The solid line is for the neat solid film spectrum. The broken lines represent the spectra after iodine vapour adsorption; (1-4), in order of increasing amount of iodine molecules.



0'80
0'70
0'60
0'50
0'40
0'30
0'20
0'10
0
ABSORBANCE
200
160
120
80
WAVENUMBER (cm^{-1})X10^{-2}
1
2
3
4
4
3
2
1

FIG.3'7

FIG. 3.8 : Enhancement of the intensity of the new band with the amount of adsorbed acceptor molecules on the solid film of astacene at 28°C. The solid lines for the neat solid film spectrum. The broken lines represent the spectra after iodine vapour adsorption; (1-4), in order of increasing amount of iodine molecules.



ABSORBANCE
0·70
0·60
0·50
0·40
0·30
0·20
0·10
0
200
180
160
140
120
100
80
WAVENUMBER (cm^{-1}) x 10^{-2}
1
2
3
4

FIG.3.8

FIG. 3.2 : Enhancement of the intensity of the new band with the amount of adsorbed acceptor molecules on the solid film of methyl bixin at 28°C. The solid line is for the neat solid film spectrum. The broken lines represent the spectra after iodine vapour adsorption; (1-4), in order of increasing amount of iodine molecules.

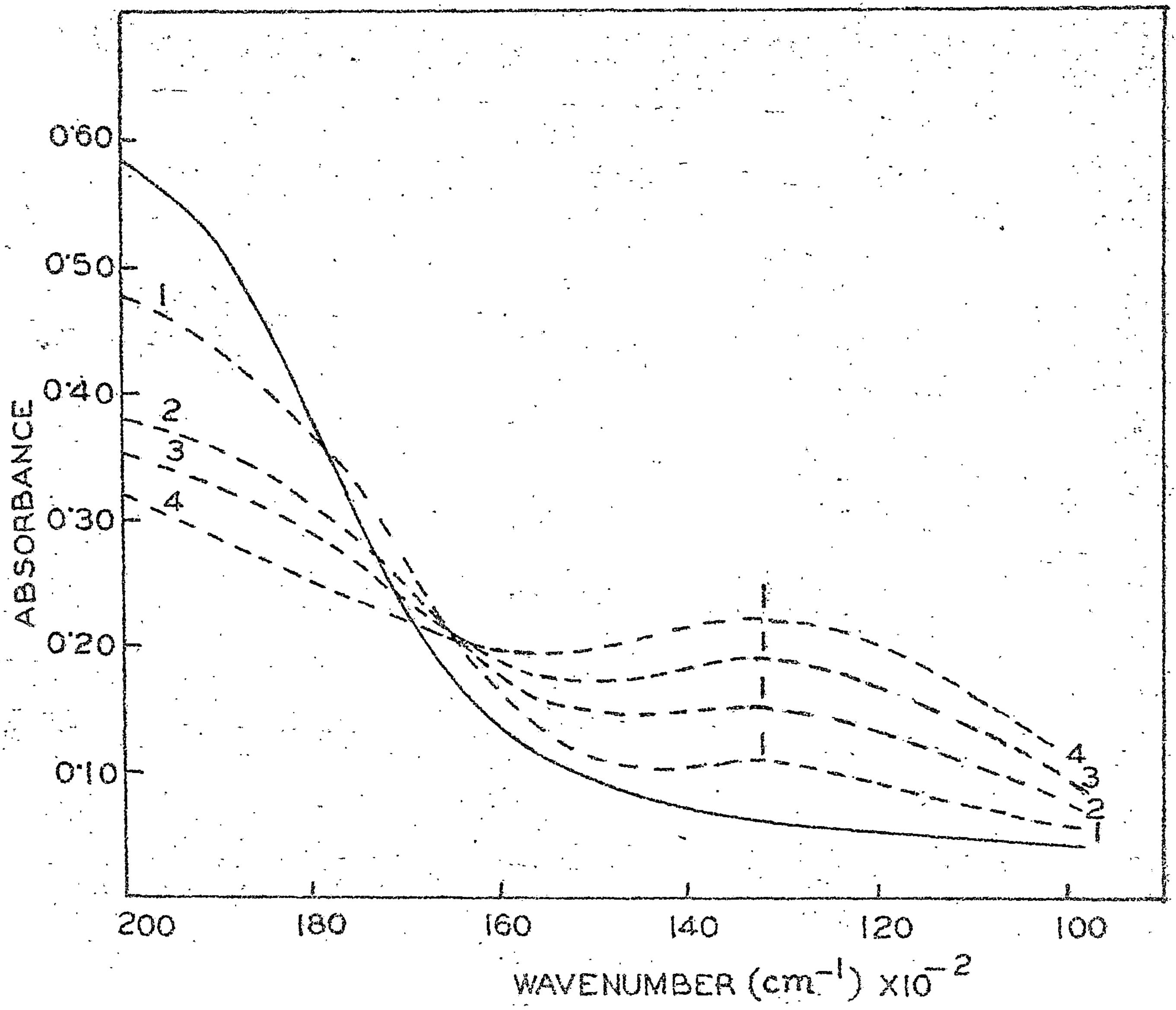

0·60
0·50
0·40
0·30
0·20
0·10
ABSORBANCE
200
180
160
140
120
100
WAVENUMBER (cm^{-1}) X10^{-2}
1
2
3
4
4
3
2
1

FIG. 3·9

Table - 3.1

Position ($\bar{\nu}_{max}$) of the new band appearing on adsorption of different acceptor vapours on the solid films of some polyenes

Acceptor used	E_A(eV)	$\bar{\nu}_{max}$ (Cm^{-1}) for			
		all-trans-β-Carotene	β-apo-8'-Carotenal	Astacene	Methyl bixin
Nitric acid	1.83	13900	-	-	-
Iodine	2.40	11560	12000	13150	13200
Bromine	2.60	11300	11800	12800	13000
Iodine monochloride	2.70	11100	11500	12500	12700

It has already been discussed in chapter 1 that Mulliken's theory for charge-transfer complex formation leads to the equation (from eqn. (1.41))

$$h\nu_{CT} = I_D^v - E_A^v + C_1 \qquad (3.1)$$

Thus for a particular donor, a plot of ν_{CT} against E_A^v should be linear. Unfortunately, reliable values of vertical electron affinities are very scarce. Apart from the necessary distinction between the vertical and adiabatic values, different experimental methods yield different results and also sometimes the substance of interest has not been studied at all. The value of E_A^v for nitric acid is not available in the literature. Recently, Chen and Wentworth[19] have emphasized that the correlation of $h\nu_{CT}$ with the absolute electron affinities (E_A) of acceptors is consistent with the usual linear equations and their associated assumptions. The adiabatic electron affinities of I_2, Br_2 and ICl estimated theoretically by Person[20] were 2.4 ± 0.3, 2.6 ± 0.3 and 2.7 ± 0.3 eV respectively agreeing satisfactorily with the experimental absolute values measured by Hughes et al.[21] We have, therefore, used these adiabatic electron affinity values as the absolute values. The value of E_A for nitric acid has been taken from Chen and Wentworth's table[19].

A plot of ν_{max} (cm^{-1}) of the new band of <u>all-trans</u>- β - carotene against E_A is shown in Fig. 3.10. A satisfactory straight line is obtained. The ionization potential of β-carotene can be

FIG. 3.10 : Plot of $\bar{\nu}_{max}$ (cm^{-1}) against E_A for <u>all-trans</u>-β-carotene.

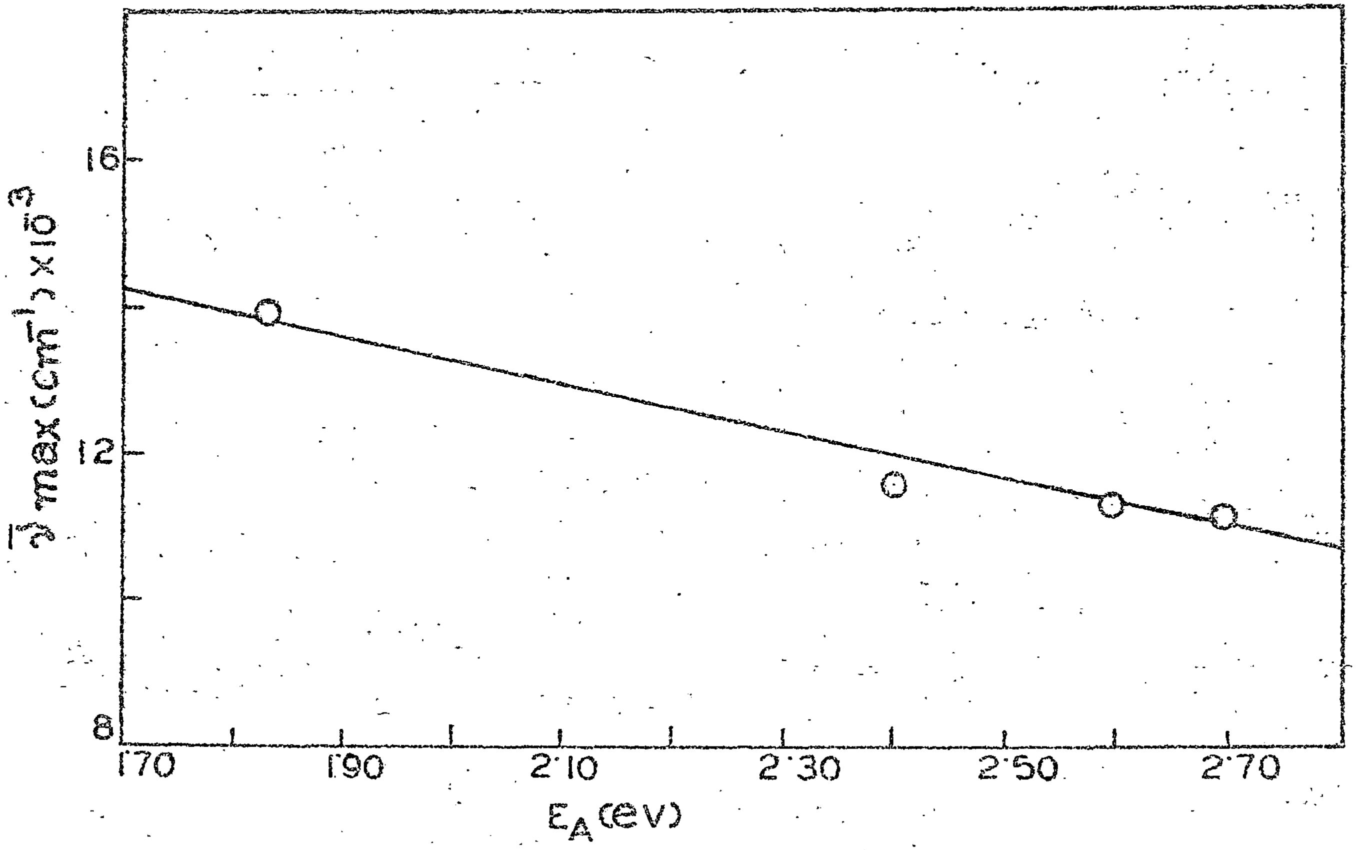


FIG.3·10

estimated from this $\bar{\nu}_{max}$ vs. E_A plot. The intercept of this curve gives $I_D + C_1 = 2.44$ eV. In typical donor-acceptor CT complexes, $-C_1$ is usually around 3 eV[19,22]. This gives a value of the ionization potential of β-carotene as 5.44 eV. The experimental value[23,24] of ionization potential (measured from photo-emission thresholds) of β-carotene is 5.5 eV. This agreement leads credence to the above linear plot and also to the CT concept[25] for this complex. From equation (3.1), one expects a slope of unity for $\bar{\nu}_{CT}$ vs. E_A^V plot. Fig. 3.10 gives a slope of 0.44. This low value of slope could be due to that the electron affinity values used for the plot being absolute rather than vertical. Further, equation (3.1) is only approximate and there is no reason to expect that the last term in equation (1.40) is negligible for all the pairs of donors and acceptors. Indeed, such deviation of slope from unity is a general observation in these types of experiments[26,27].

The relationship between the ionization potentials of two donors and the values of ν_{max} corresponding to their CT complexes with a common acceptor can be written (assuming that the C_1 values do not differ much in the two complexes) as

$$I_D \text{ (donor-2)} = I_D \text{ (donor-1)} + h\nu_{CT}(2) - h\nu_{CT}(1) \qquad (3.2)$$

From this equation (3.2), one can estimate the value of ionization potential of donor-2 if the ionization potential of the donor-1 and the associated values of the ν_{CT} are known. We have estimated the value of ionization potential of β-apo-8'-carotenal, astacene and methyl bixin from this equation (3.2) considering I_D (donor - 1) as 5.50 eV for β -carotene and taking $\bar{\nu}_{max}$ of the new band for iodine vapour adsorption in all these polyenes. The estimated values are 5.56, 5.69 and 5.70 eV for β -apo-8'-carotenal, astacene and methyl bixin respectively. For charge-transfer bands, the estimated values of ionization potential should show a good agreement with the values obtained by other methods. As the values of ionization potential of these polyenes are not reported, we have alternatively evaluated these values from the I_D vs. $\bar{\nu}_{CT}$ plot for a large number of other donors[22] with iodine acceptor as shown in Fig. 3.11. These values are shown in table 3.2 for comparison with our estimated values. The excellent agreement between these two sets of values confirms that the new bands are charge-transfer bands of the polyenes.

The weak low-lying $^1A_g \rightarrow {}^1A_g$ band is not observed on adsorption of these acceptor vapours possibly due to the broadening of the intense $^1A_g \rightarrow {}^1B_u$ band.

The room-temperature absorption spectra of all-trans- β -carotene, β -apo-8'-carotenal, astacene and methyl bixin after adsorption of I_2 vapour are shown in Figs. 3.12 - 3.15. From these spectra, it is observed that in addition to the new band in the longer wavelength side another new absorption band is also observed at about 27800 cm^{-1} in each case. This is the well-known absorption band of I_3^- ion[29]. The other absorption band of this molecular ion expected at about 33900 cm^{-1} has possibly been merged with the

FIG.3.11 : Plot of $\bar{\nu}_{CT}$ against I_D for CT complexes of a number of donors with iodine acceptor. The donors are : (1), benzene; (2), toluene; (3), m-xylene; (4), mesitylene; (5), naphthalene; (6), durene; (7), pentamethylbenzene; (8), triphenylene; (9),hexamethylbenzene; (10), chrysene; (11), anthracene; (12), pyrene. (Values of $\bar{\nu}_{CT}$ and I_D have been taken from Refs. 23 and 19 respectively).

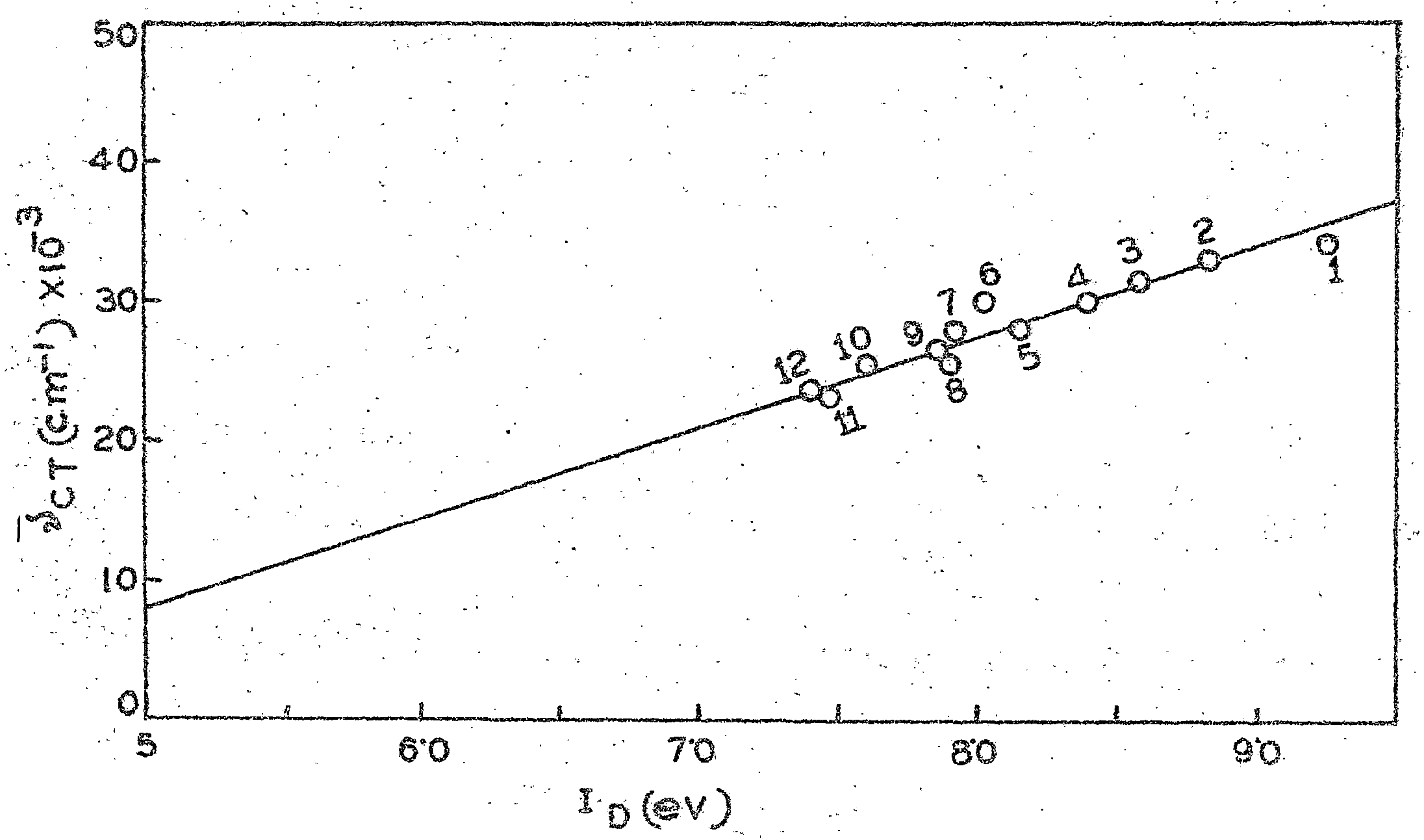

50
40
30
20
10
0
5
6.0
7.0
8.0
9.0
$\bar{\nu}_{CT}$ (cm^{-1}) x10^{-3}
I_D (eV)
1
2
3
4
5
6
7
8
9
10
11
12

FIG. 3.11

Table - 3.2

Comparison of the values of ionization potential of some polyenes estimated from this experiment and obtained from Fig. 3.11

Polyenes	Estimated I_D(eV)	Value of I_D(eV) obtained from Fig.3.11
all-trans- β -Carotene	5.44	5.56
β-apo-8'-Carotenal	5.58	5.62
Astacene	5.69	5.67
Methyl bixin	5.70	5.70

FIG. 3.12 : Electronic absorption spectra of *all-trans*- β -carotene solid film (28°C) : (1), spectrum without adsorption of vapour; (2), spectrum after adsorption of iodine vapour. (The positions of the new bands are indicated by vertical marks).

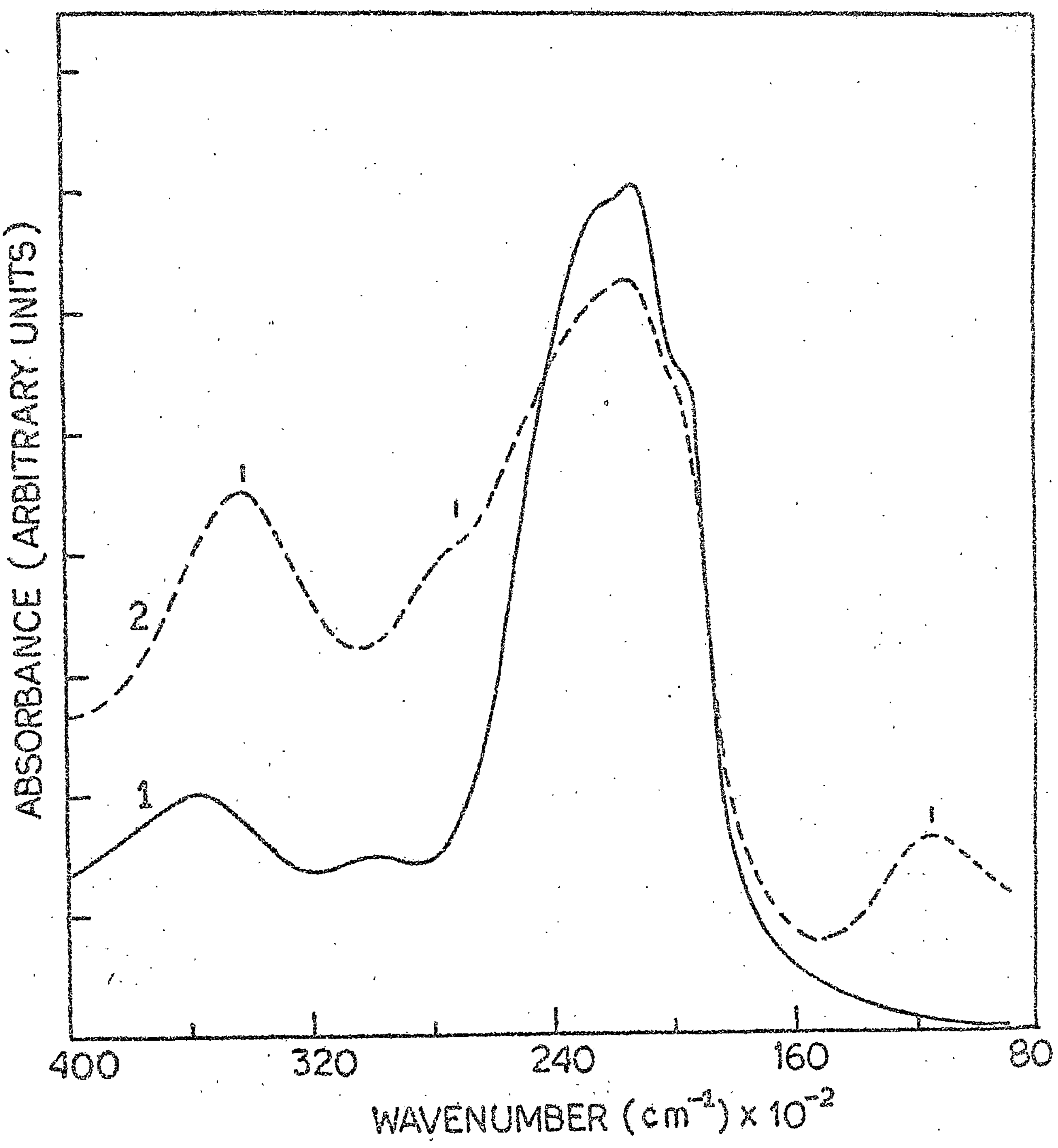

ABSORBANCE (ARBITRARY UNITS)
WAVENUMBER (cm^{-1}) x 10^{-2}
400
320
240
160
80
1
2

FIG. 3·12

FIG. 3.13 : Electronic absorption spectra of β-apo-8'-carotenal solid film (23°C) : (1), spectrum without adsorption of vapour; (2), spectrum after adsorption of iodine vapour. (The positions of the new bands are indicated by vertical marks).

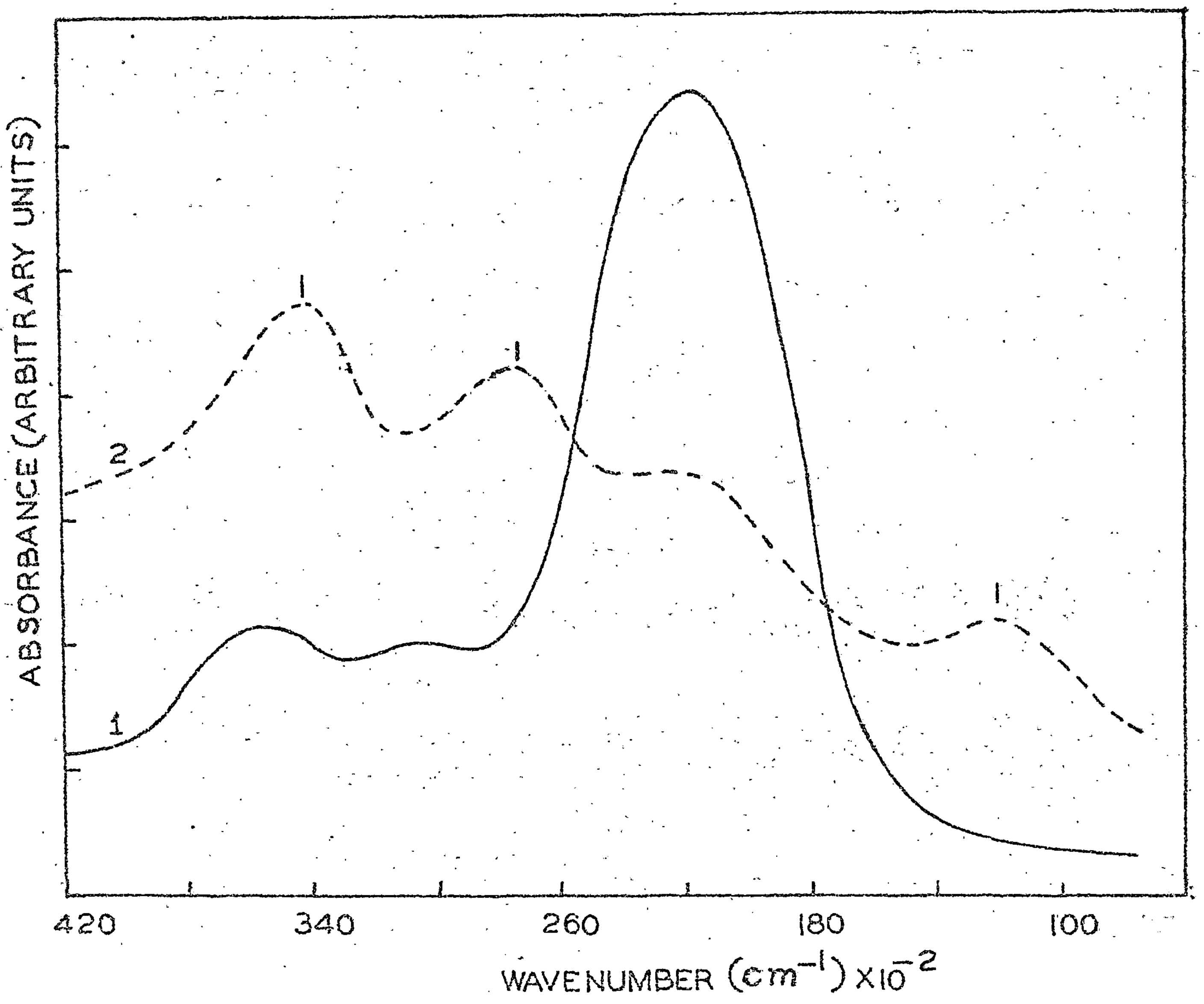

ABSORBANCE (ARBITRARY UNITS)
1
2
420
340
260
180
100
WAVENUMBER (cm^{-1}) $\times 10^{-2}$

FIG.3'13

FIG. 3.14 : Electronic absorption spectra of astacene solid film (22°C) : (1), spectrum without adsorption of vapour; (2), spectrum after iodine vapour adsorption. (The positions of the new bands are indicated by vertical marks.)

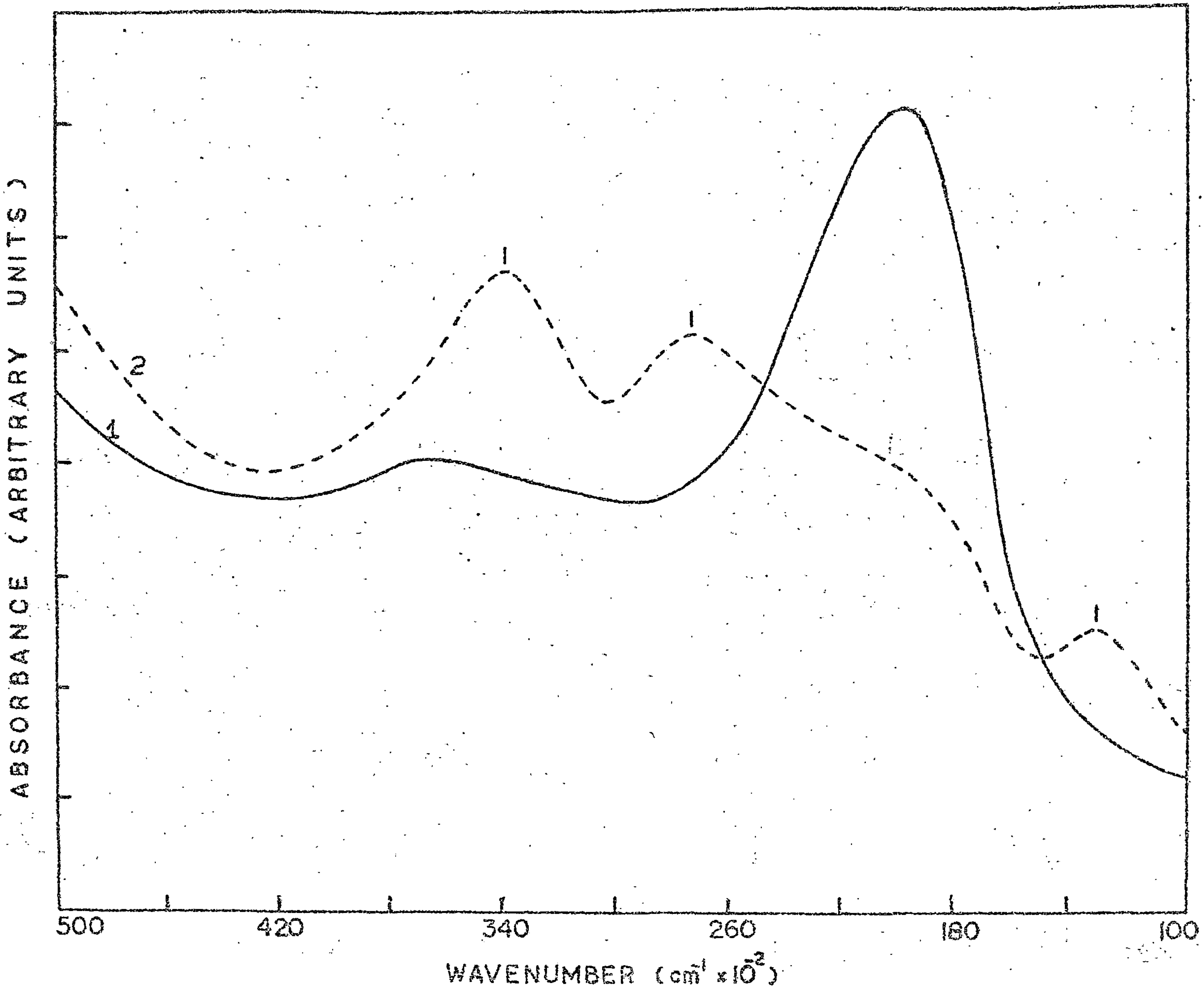

ABSORBANCE (ARBITRARY UNITS)
1
2
500
420
340
260
180
100
WAVENUMBER (cm^{-1} x 10^{-2})

FIG.3·14

FIG. 3.15 : Electronic absorption spectra of methyl bixin solid film (28°C) : (1), spectrum without adsorption of vapour; (2), spectrum after iodine vapour adsorption. (The positions of the new bands are indicated by vertical marks).

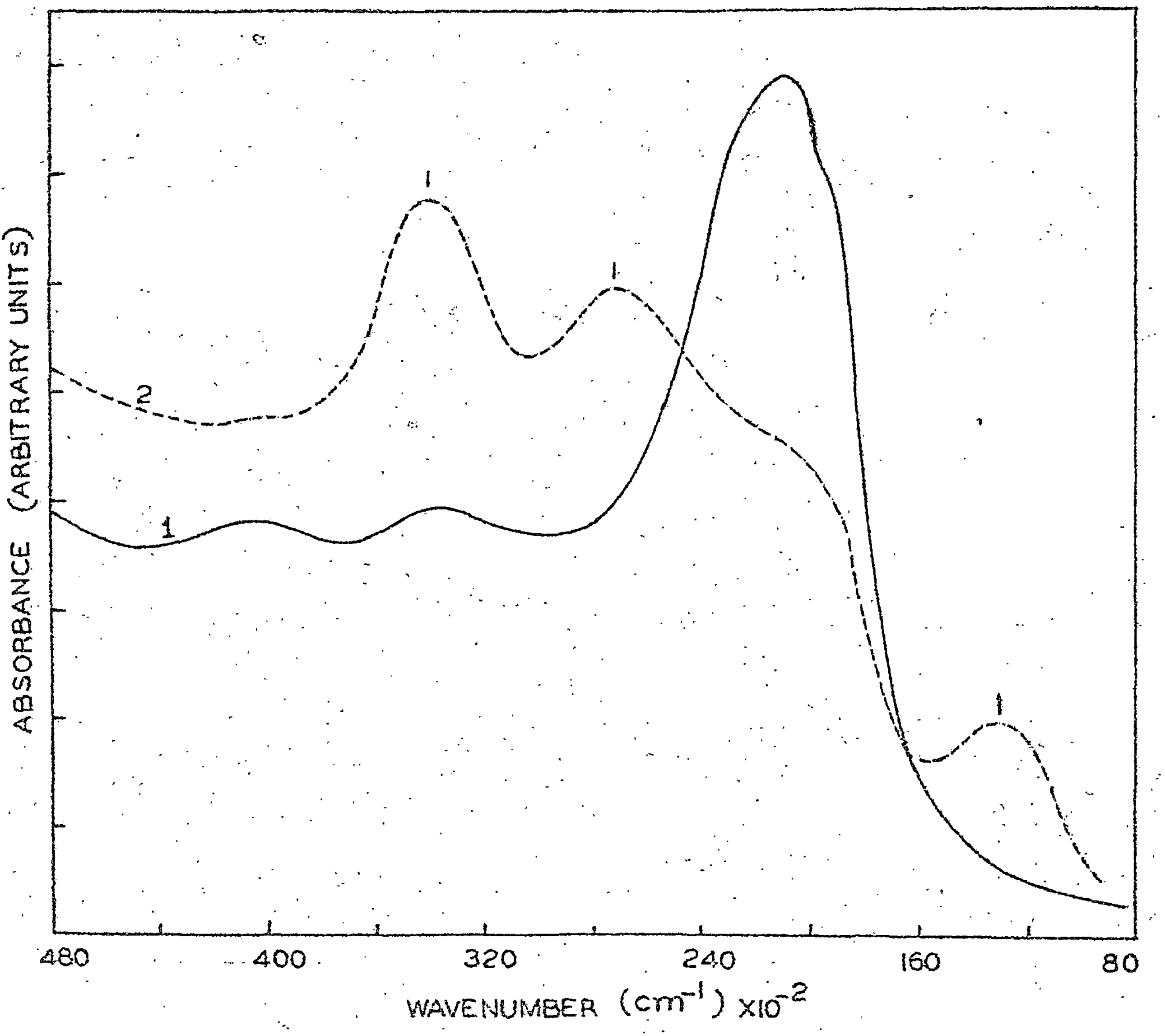

ABSORBANCE (ARBITRARY UNITS)
WAVENUMBER (cm^{-1}) x10^{-2}
480
400
320
240
160
80
1
2

FIG 3·15

original bands of these polyenes in this region. In case of iodine, possibly through the reaction

$$\text{Polyene} + 2I_2 \rightleftharpoons (\text{Polyene} \;.....I)^{+} + I_3^{-}$$

the polyenes form CT complexes with iodine. The new band arises due to transition from the ground state (Polyene .....I^{+}) to the excited state (Polyene^{+} .....I) of the complex.

Contrary to that suggested by Ebrey[18] our results for the polyenes studied indicate that at least in the solid state single resonance structure

$$C = C - (C = C)_n - C = C \cdots\cdots I^{+}$$

is quite stable and usual donor acceptor complexes are formed.

3.4 Conclusion

The polyenes under investigation can form charge-transfer complexes with suitable acceptors in the solid state.

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