

ON THE ULTRAVIOLET ABSORPTION SPECTRA OF METHYL BENZOATE AND ACETOPHENONE IN THE SOLID STATE AT LOW TEMPERATURES*

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(Received for publication, September, 12, 1951)

Plate XV

ABSTRACT: The absorption spectra of methyl benzoate ($C_6H_5COOCH_3$) and acetophenone ($C_6H_5COCH_3$) in the ultraviolet region have been studied in the liquid and solid states. In the case of methyl benzoate three broad bands have been observed in the liquid state in the region 2650 Å to 2900 Å. Continuous absorption begins below 2500 Å. In the solid state these bands are found to be shifted considerably towards the longer wavelength side, while continuous absorption begins below 2440 Å.

The absorption spectrum of acetophenone in the liquid state reveals three broad bands with centres at 35744, 38748, and 40277 cm^{-1} respectively. On solidification, the first band widens considerably on both sides and splits up into three bands, while the second shifts towards the shorter wavelength side and the third disappears. The limit of continuous absorption recedes towards shorter wavelength side. It is pointed out that these changes cannot be due to mere lattice fields and may be due to association of the molecules in the solid state.

INTRODUCTION

Absorption spectra of molecules in the gaseous state exhibit, in general, band systems having large number of bands, both sharp and diffuse. On change of state from vapour to liquid phase, the structure of the band system is expected to show considerable changes, because in the liquid state intermolecular forces are liable to be brought into play. Such changes are actually observed in the absorption spectra of benzene in the region 2700 Å -- 3000 Å (Kronenberger and Pringsheim, 1926).

The experimental data are, however, not sufficient to indicate any general trend of changes suffered by the absorption spectra of molecules with change of state at low temperatures. The results reported earlier, for anisole (Deb, 1951) and toluene (Swamy, 1951) show that changes, much greater than those observed in the case of benzene, take place when these substances are solidified and cooled down to about $-170^{\circ}C$.

* Communicated by Prof. S. C. Sirkar

In order to find out whether any other substituted benzene compound shows such remarkable changes in their absorption spectra with solidification, the ultraviolet absorption spectra of two more organic compounds, *viz.*, methyl benzoate and acetophenone, have been studied and the results have been compared with those for solutions of these substances in ether (Kato and Someno, 1938) and for solution of acetophenone in alcohol (Grammaticakis, 1950).

EXPERIMENTAL

The experimental arrangement was the same as that used in the study of anisole (Deb, 1951). The liquids used were of chemically pure variety and were distilled repeatedly in vacuum before use. A very thin film of the liquid was necessary to produce bands in the absorption spectrum. This was obtained by pressing together the quartz plates of the cell between which the film was formed, and then by carefully sliding one plate over the other.

Spectrograms were taken on Ilford H.P.3 films and Q-plates using a Hilger H1 quartz spectrograph, giving a dispersion of about 3 A.U per mm in the region of 2600 Å. Exposures ranging from 6 minutes to 10 minutes were necessary in the case of the liquid, and about an hour in the case of the solid. The width of the slit was about 0.2 mm.

RESULTS AND DISCUSSION

The spectrograms are reproduced in Plate XV and the positions of the bands are given in Tables I and II. The data for solutions of both liquids in ether reported by Kato and Someno (1938) and those for solution of acetophenone in alcohol, reported by Grammaticakis (1950) are also included for comparison.

TABLE I
Methyl benzoate

Soln. in ether (Kato & Someno, 1938)				Liquid (Present author)				Solid (Present author)			
λ AU	ν cm ⁻¹	Int	Diff	λ AU	ν cm ⁻¹	Int	Diff	λ AU	ν cm ⁻¹	Int	Diff
1	35700	4		1	2811.91	st		1	2841.49	st	
			700				929				934
2	36400	5		2	2740.31	st		2	2768.07	st	
			1180				947				923
3	37580	4		3	2671.0	w		3	2699.0	w	
					?						

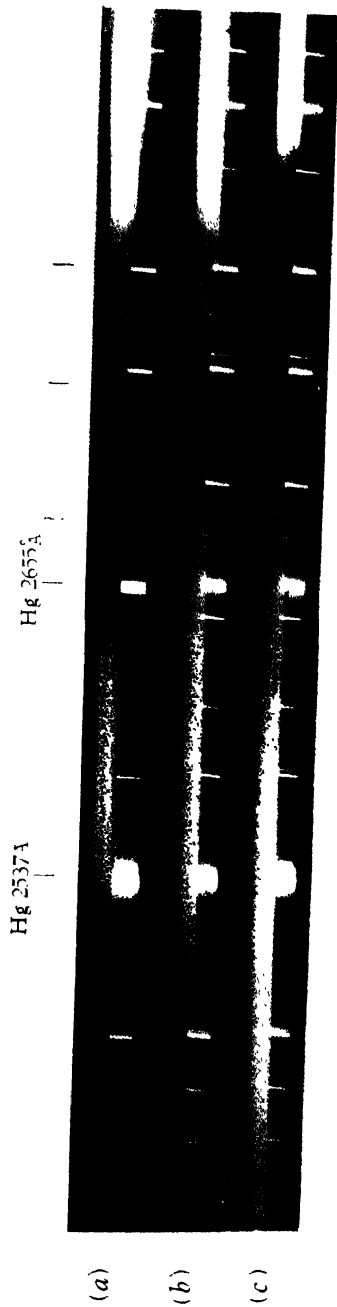


Fig 1

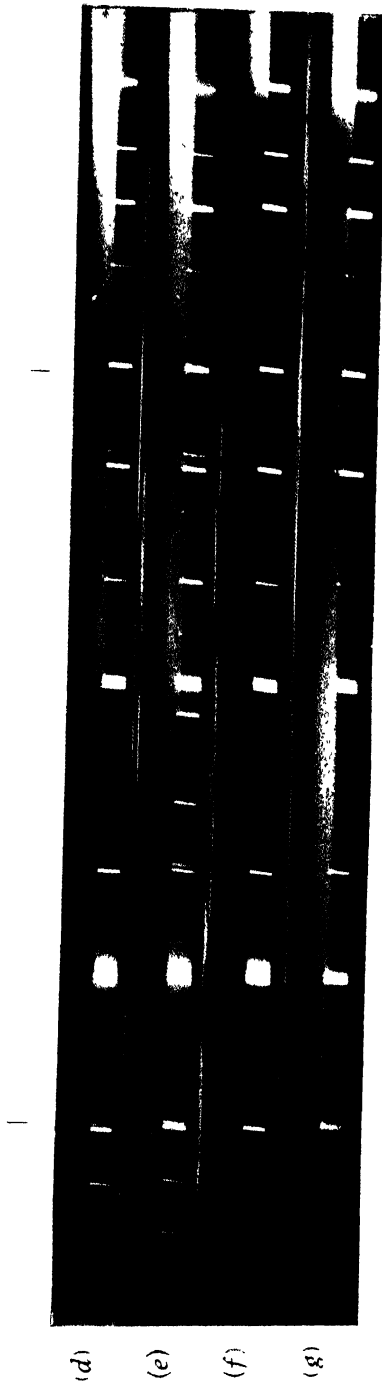


Fig 2

Ultraviolet absorption spectra

Fig. 1.—Methyl benzoate

- (a) Liquid at about 30 C
- (b) Do (Thinner film than (a))
- (c) Solid at about -170 C

Fig 2—Acetophenone

- (d) Liquid at about 30°C
- (e) Do (Thinner film than (a))
- (f) Solid at about -170°C
- (g) Do (Thinner film than (c))

TABLE II
Acetophenone

Soln. in ether (Kato & Someno, 1938)				Liquid (present author)				Solid (present author)							
	λ AU	ν cm ⁻¹	Int	Diff		λ AU	ν cm ⁻¹	Int	Diff		λ AU	ν cm ⁻¹	Int	Diff	
1		34900	8	1000						1	2925.76	34170			
2		35900	9	1100	1	2706.89	35744	st	3004	2	2836.3	35249		1079	
3		37000	6							3	2752.9	36315		1066	
Soln in alcohol (Grammaticakis, 1950)*					2	2580.0	38748	w	1529		4	2566.16	38957		
	2800	35700													
	2440	40900			3	2482	40277	w							

"St" means strong and "w" means weak.

* These results have been obtained from the frequency-log E₁ plot.

(a) Methyl benzoate

It is seen that the absorption spectrum of methyl benzoate [figure (1) Plate XV] consists of three bands at 35552, 36481 and 37428 cm⁻¹, the third band being weak and flat with the maximum hardly recognizable. The approximate difference between the frequencies of the successive bands are 929 and 947 cm⁻¹ respectively in the case of the liquid. The bands shift towards longer wavelength when the substance is solidified and cooled to about -170°C. The difference between the successive bands in the case of the solid are 934 and 923 cm⁻¹ respectively. This frequency seems to be that of the symmetric vibration of the benzene ring in the excited electronic state. Kato and Someno (1938), however, reported the frequencies 700 and 1180 cm⁻¹ as the difference of the successive bands in the case of the solution of methyl benzoate in ether. Neither of these frequencies have been observed in the present investigation.

(b) Acetophenone.

In this case the liquid gives three bands with their centres at 35744, 38748 and 40277 cm⁻¹ respectively (figure 2, Plate XV). On comparing these with the data published by Kato and Someno (1938) for solution in ether, it was found that the second band observed by these authors corresponds to the first band of the present work. A band was also observed

in this position by Grammaticakis (1950) in solution of acetophenone in alcohol. But the other two bands observed by Kato and Someno were not observed in the present work. Corresponding to the second band at 33748 cm^{-1} no band was observed by those authors in solution; but the third band roughly corresponds to the second band observed by Grammaticakis in alcohol solution. The frequency-differences observed in the liquid state are 3000 and 1500 cm^{-1} .

In the solid state at about -170°C , in the place of the first band of liquid state, three bands are observed, two of which are on the longer wavelength side of the original one and the third band is on the shorter wavelength side. The second band observed in the liquid state shifts by about 14 \AA to the shorter wavelength side in the solid state, and the third band of the liquid is not at all observed in the solid state.

These changes are too large to be explained on the assumption that the lattice field splits up the electronic levels of the molecule. Evidently these changes are due to a stronger intermolecular association in the solid state.

The investigations are being continued with other organic compounds.

ACKNOWLEDGMENT

The author is indebted to Prof. S. C. Sirkar, D.Sc., F.N.I., for his kind permission to carry out the investigation in the Optics Laboratory of the Indian Association for the Cultivation of Science, and for his guidance during the progress of the work.

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