ON THE ABSORPTION SPECTRA OF TOLUENE IN THE LIQUID AND SOLID STATES*

By H. N. SWAMY

(*Received for publication, April 20, 1951*)

Plate X

ABSTRACT. The absorption spectra of toluene in the ultraviolet region have been investigated in the liquid state at 30°C and in the solid state at −180°C. An examination of the photographs reveals that lowering of temperature, contrary to the results reported by some previous workers, causes the bands to become wider ; so that only one band is observed in the solid state, the others merging into one another. It is pointed out that the intermolecular field in the solid state has great influence on the electronic energy levels of the molecule.

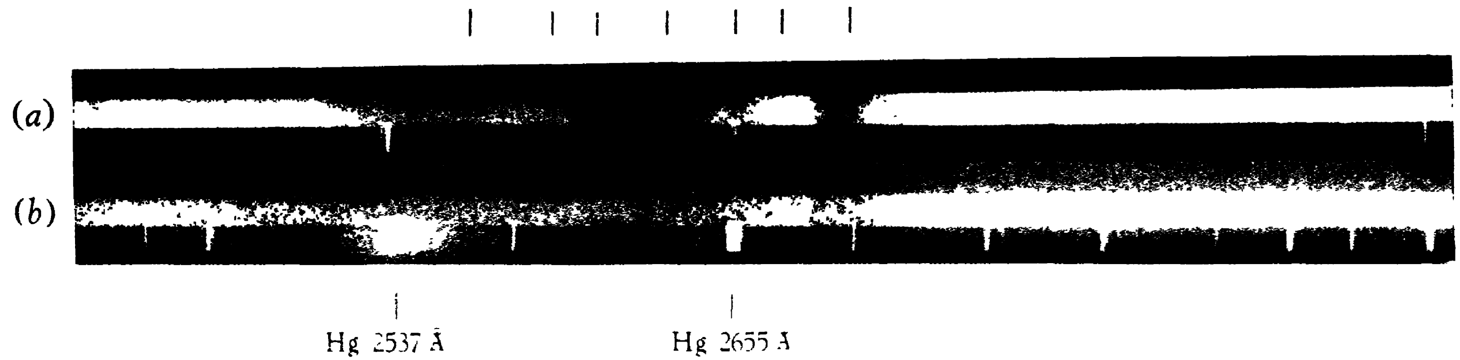
INTRODUCTION

The ultraviolet absorption spectrum of toluene in the vapour state was studied by several previous authors viz., Savard (1929), Sponer (1942), Ginsberg (1946), and others. Recently Padhye (1949) has reported some new bands in the ultraviolet absorption spectrum of toluene in the vapour state. The absorption spectra of toluene in the liquid and solid states, however, were not studied very exhaustively by the previous workers. Very recently, Kanda and Tsu Ji Kawa (1950) have reported some results in the case of toluene in the liquid and solid states at different temperatures and data have been given in the form of microphotometric records. The results observed by them indicate that there is change in intensity and width of bands with the solidification and lowering of temperature of solid. Slight changes also have been observed in the structure and position of the bands. In the programme of work undertaken to study the influence of temperature and change of state on the electronic energy levels of organic molecules in this laboratory, toluene was chosen as one of the substances and it was observed that the results obtained did not agree thoroughly with those reported by Kanda and Tsu Ji Kawa (1950). It was, therefore, thought worth while to report the results obtained in the present investigation.

EXPERIMENTAL

The source of continuous spectrum used is a hydrogen discharge tube fitted with a quartz window. The tube is constantly evacuated and pressure of hydrogen is adjusted by operating stop cocks. About 3 K. V. is applied to run the discharge tube. A Hilger quartz E1 spectrograph with a dispersion

* Communicated by Prof. S C. Sirkar



Absorption spectra of toluene.

(a) Liquid at about 30°C.

(b) Solid ,, ,, −180°C.

of 3 A.U. per mm. in the region of 2600 Å was used for photographing the absorption spectra. Dust free toluene, distilled four times was used for the study.

It was found that a layer of liquid having a thickness of about 0.1 mm. produced absorption bands in the spectrum. Such a layer was obtained by introducing a drop of liquid between two quartz plates held together. in a brass frame by screws. An exposure of about 20 minutes was necessary in the case of the liquid.

For studying the absorption at low temperatures, the frame containing the cell with the liquid was suspended in a Dewar vessel of fused silica containing some liquid oxygen. The annular region between the walls of the vessel was constantly evacuated. The lower portion of the brass frame was dipped in the liquid oxygen to solidify the substance. Liquid oxygen was replenished from time to time to keep it at a proper level in the vessel. The upward drift of cold air prevented the condensation of water vapour on the surfaces of the quartz plates. The beam of light coming from the hydrogen tube was made parallel with a quartz lens and the cell was placed in the path of the parallel beam. An exposure of about one and a half hours was necessary to record the absorption spectrum of the solid.

RESULTS

Two spectrograms, one for the liquid state and another for the solid state are reproduced in Plate X. The wave numbers of the bands observed are given in Table I in which the data reported by Kanda and Tsu Ji Kawa (1950) are also included for comparison. The absorption spectrum of the liquid was investigated at 30°C.

TABLE I

Absorption bands of toluene

ν in cm^{-1}

Kanda and Tsu Ji Kawa (1950)				Present Author				
Band No	Liquid at −88°C	Band No	Solid at −173°C	Band No	Liquid at 30°C	Remarks	Solid at −180°C	Remarks
1	37372	1	37330	1	37122	Broad, extends from 2704 to 2638 A.U.		
2	37792	2	37768	2	37428		37161	Broad, extends from 2705 to 2684 A.U.
3	38180	3	38152	3	37649			
4	39112	4	38392	4	38039			
5	39400	5	39069	5	38142			
		6	39310	6	38376			
		7	40312	7	39066			

DISCUSSION

The results given in Table I show that while in the liquid state toluene gives seven bands, in the solid state, it shows only one broad band and in the place of the other bands there is continuous feeble absorption. Probably the latter bands become broader and merge into one another in the solid state. These results are contradictory to those reported by Kanda and Tsu Ji Kawa (1950) who reported that there are only five bands in the liquid state and that the bands become sharper and more intense in the solide state. As regards the position of the band which persists in the solid state it is observed in the present iuvestigation that there is a small shift towards shorter wavelength side with the solidification. The previous authors also mentioned in the abstract of their paper that the bands shift towards the shorter wavelength side, but the microphotometric records reproduced by them show that the shift is towards the longer wavelength side. It is difficult to understand these discrepancies. The fact that the general absorption in the region between 2537 and 2654 A.U. increases at $-180°C$ indicates that the bands in this region become broader and produce continuous absorption.

The results show that solidification and lowering of temperature has considerable influence on the electronic energy levels of the molecule. It has been observed by Ray (1950) that in the Raman spectrum of toluene in the solid state, a few sharp lines appear in the low-frequency region. These lines were attributed by him to the oscillations in groups of associated molecules. Probably the change in absorption spectra, which is observed to take place with the change of state of the substance and lowering of temperature, indicates that such association has influence on the electronic state of molecules in the solid state at low temperatures. The investigations are being continued with other substances.

ACKNOWLEDGMENTS

The auther is indebted to Prof. S. C. Sirkar for his kind interest and guidance throughout the progress of the work and to the Government of India, Ministry of Scientific Research for the award of a scholarship.

Optics Department,
Indian Association for The
Cultivation of Science,
Calcutta—32.

REFERENCES

Ginsberg, Matsen and Robertson. 1946, *J. Chem. Phys.*, **14**, 511.
Kanda and Tsu Ji Kawa. 1950, *Science Reports Tohoku University*, 5.
Padhye, M. R. 1949, *Ind. J. Phys.*, **23**, 339
Ray, A. K. 1950, *Ind. J. Phys.*, **24**, 111.
Savard, 1929, *Ann. de. Chimie.*, **11**, 287.
Sponer, 1942, *J. Chem. Phys.*, **10**. 672.

REVIEWS

(2)

Fundamental of Optics—By F. A. Jenkins and H. E. White Pp. 647. McGraw-Hill Book Company, Inc. New York, Toronto, London, 1950. Price $ 7.00.

The present volume is the second edition of a similar volume published in 1937. The first ten chapters dealing with geometrical optics and the last chapter on photons are new additions in this edition. As mentioned in the preface to the first edition, the book was intended for use in an advanced undergraduate course in optics. The discourses on geometrical optics are also of the same standard, excepting those on lens aberrations given in Chapter 9. Quantitative expressions for various types of aberrations used in this chapter has raised the standard a little.

Chapters 11 and 12 dealing with wave motion includes detailed discussions on Doppler effect, superposition of waves and group velocity. Chapters 13 and 14 deal with interference of two beams of light and interference involving multiple reflection respectively. As usual, principles of different types of refractometers, *e.g.*, Michelson's, Jamin's and Rayleigh's refractometers have been explained in the former chapter and discussions on interferometers have been included in the latter chapter. Numerous illustrations have been included to explain the use of the interferometers. The phenomenon of diffraction of light has been discussed elaborately in chapters 15-18. These chapters will be useful even to the students preparing for the B.Sc. Honours course of any Indian University. The principle of phase contrast microscope has been explained briefly at the end of Chapter 15. The treatment of diffraction by a grating is quite exhaustive. Also, Fresnel's diffraction has been discussed in great detail and a table of Fresnel's integrals has been included in Chapter 18.

Chapter 19 deals with velocity of light. Principle of Relativity has also been briefly mentioned at the end of this chapter. In the next chapter a brief exposition of electromagnetic theory of light has been included. Different sources of light and their spectra have been described in Chapter 21 and the next chapter deals with absorption, scattering and dispersion of light. Polarization of light, optical properties of transparent crystals and double refraction have been discussed exhaustively with the help of illustrations in chapters 24-26. The phenomenon of optical activity of liquids and crystals has been explained in the next chapter. Chapter 28 dealing with reflection is of a little higher standard as the phenomenon of reflection including metallic reflection has been explained on the electro-magnetic theory of light. The treatment of the problems on magneto-optics and electro-optics given in the next chapter does not include such theoretical deductions. The last chapter on photons deals briefly with the dual character of light.

The book is beautifully got up, and is printed on real art paper. The quality of illustrations leaves nothing to be desired and the number of such beautiful illustrations is quite large. Chapters on interference and diffraction deserve special mention in this respect. The book will certainly prove useful not only to undergraduate students who are preparing for the B.Sc. Pass course but also to those who have taken up B.Sc. Honours course in any Indian University.

S. C. S

(3)

Heat and Temperature Measurement.—By Robert L. Weber, Pp. 422 + x. Prentice Hall Inc., New York, 1950. Price $ 6.65.

The book is divided into two parts. The first part deals with well known principles of heat, but the order in which these topics have been arranged is a little different from that found in conventional text books. After chapters on temperature scales and different forms of thermometers, theory of conduction of heat has been discussed. This has been followed by two chapters dealing with thermo-electricity and thermo-electric measurements Laws of radiation and theory of optical and radiation pyrometers have been given in the next two chapters. This has been followed by two chapters dealing with resistance thermometers and temperature recording. Chapter 10 deals with calorimetry in a rather elementry way and phase diagram and phase rule have been discussed in the next chapter. This has been followed by chapters on laws of thermodynamics, production and measurement of extreme temperatures and some special methods of temperature measurement. In the last chapter of part I international temperature scale has been discussed.

Part II of the book deals with 29 laboratory experiments on heat. These experiments include, besides those on different methods of measuring temperatures, a few on calorimetry, relative humidity and viscosity of fluids. The theory of the experiment has been given in each case and in some cases photographs of the actual apparatus have been included.

The book is copiously illustrated and printed on art paper. The book may be useful to under-graduate science students of Indian Universities preparing for their practical course and also to those who are engaged in any work in which accurate temperature measurement is involved.

S. C. S.