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J. Sharma

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Thermoluminescence of Some Aromatic Hydrocarbons

J. SHARMA*

Department of Physics, Indian Institute of Technology, Kharagpur, India

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The thermoluminescence of diphenyl, solid benzene, toluene, and *p*-xylene has been studied after exciting them with cathode rays at liquid oxygen temperature. Also the decay rates of the afterglow have been measured. The thermoluminescence in each case consists of several peaks emitted at low temperature. The afterglow decay has been found to be exponential.

WHEN some aromatic hydrocarbons are bombarded at liquid oxygen temperature with cathode rays, these substances exhibit strong fluorescence followed by long afterglows. If now the excited specimen is rapidly heated, thermoluminescence is shown. It appears that the afterglow and thermoluminescence are both due to excitation of the molecule to metastable state,¹ whence direct transition to the ground state is forbidden. In terms of the Jablonski² diagram the long period afterglow corresponds with β phosphorescence, owing to transparency of the forbidden state, while the thermoluminescence consists of α phosphorescence involving transition to the higher state owing to thermal stimulation. In the present paper thermoluminescence curves and afterglow decay rates of diphenyl, solid benzene, toluene, and *p*-xylene have been reported. The fluorescence spectra for all these substances, except diphenyl which was measured earlier,³ are presented here.

EXPERIMENTAL TECHNIQUE

In the present paper, the demountable cathode-ray tube with sample holder made of thin silver, described in a previous paper,⁴ has been employed. When working with materials which are solid at room temperature, the substance was smeared as a thin film on the sample holder; for liquids, mounting was done in the following manner. The liquid to be investigated was taken in a 1 cc ampoule with a capillary neck and was placed in the demountable tube very near the bulb of the sample holder. After evacuating the chamber for about fifteen minutes the sample holder was cooled by pouring in liquid oxygen. Immediately some of the liquid vapor, coming out through the capillary, condensed on the sample holder in the form of a thin film. The excitation was made with 2–5 kv cathode rays run from a rectified power unit. The cathode rays were made incident on the sample by bending them with the help of a magnet placed outside the tube. This was intended to protect

the sample from the hazards of ionic bombardment. The fluorescence spectra, during continuous bombardment of the sample, maintained at liquid oxygen temperature, were photographed in 5–6 minutes with a small Fuess quartz spectrograph. The phosphorescence spectrum was recorded for *p*-xylene only. For this an electromagnetic shutter was used and with the help of a rotary switch it was so arranged that during excitation of the sample, the slit of the spectrograph remained covered; it opened immediately after the irradiation stopped. By turning the switch every 30 seconds, intermittent excitation was continued for six hours, the sample being all along maintained at -184°C .

For recording the afterglow, photomultiplier tubes (R.C.A. 931A and 1P28), operated from a conventional electron tube regulated power supply, were used. The output of the photomultiplier tube, amplified with a single stage dc push pull amplifier was fed to a Philips GM 3156 slow sweep (4 sec repetitive) oscillograph. The afterglow decay curves were also obtained directly with a Micro Moll galvanometer (time period 0.3 sec), whose movements were recorded on a photographic rotating drum. For obtaining thermoluminescence curves, the output of the photomultiplier tube and that of a thermocouple attached to the sample holder, were recorded on a photographic drum with two Moll type galvanometers. The rate of heating was kept rather high ($6\text{--}10^{\circ}\text{C}/\text{sec}$) because slow heating flattens the thermoluminescence peaks.

The fluorescence spectra of diphenyl, solid benzene, toluene, and *p*-xylene are given in Fig. 1 (a), (b), (c). The emission spectra can be grouped into two systems of bands: one in the ultraviolet region, the other in the



FIG. 1. Fluorescence spectra of (a) benzene, (b) toluene, (c) *p*-xylene, (d) phosphorescence spectrum of *p*-xylene at -184°C . (Reference lines; copper arc.)

* Formerly at Khaira Laboratory of Physics, University College of Science, Calcutta, where this work was done.

¹ G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.* **66**, 2100 (1944); **67**, 99 (1945).

² A. Jablonski, *Nature* **131**, 839 (1933).

³ Bose, Sharma, and Chatterjee, *Proc. Natl. Inst. Sci. India* **18**, 389 (1952).

⁴ H. N. Bose and J. Sharma, *Proc. Phys. Soc. (London)* **B66**, 371 (1953).

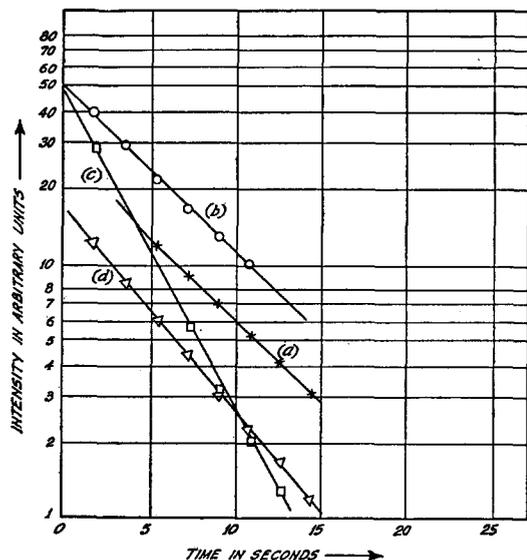


FIG. 2. Afterglow decay graphs at -184°C . (a) benzene, (b) toluene, (c) *p*-xylene, (d) diphenyl.

visible part. The phosphorescence spectrum has been recorded in the case of *p*-xylene only and in it the ultraviolet band system is completely absent, so that the bands terminate at $453\text{ m}\mu$. This indicates that during phosphorescence only the longer wavelength group of bands is emitted.

The afterglow measurements have revealed that the decay is exponential (Fig. 2) in all cases. The value of the exponential decay constants have been given in Table I. It has been found that the decay constants are not dependent on the initial intensity of excitation. By measuring the decay constants at different temperatures for benzene, between 90°K to 150°K , it has been found that it does not vary with temperature; however, the phosphorescence intensity becomes small at high temperature. This definitely indicates that the phosphorescence is due to transitions direct from the metastable state without intermediary excitation to the allowed

TABLE I.

	Exponential constant of the afterglow in sec^{-1}	Temperatures of maximum glow in absolute scale	Trap depths in ev assuming $s=10^{13}\text{ sec}^{-1}$
Benzene	0.37	131	0.34
		166	0.43
Toluene	0.35	101	0.26
		109	0.29
<i>p</i> -Xylene	0.29	116	0.30
		128	0.33
		156	0.40
Diphenyl	0.18	121	0.31
		150	0.39
		195	0.51
		224	0.57

upper state, since the latter process would be temperature dependent.

The thermoluminescence curves in all cases consist of a number of distinct peaks as shown in Fig. 3. The trap depths corresponding to these peaks have been estimated from the approximate formula suggested by Randall and Wilkins⁵

$$E=30KT_g$$

assuming s the frequency factor equal to 10^{13} sec^{-1} , corresponding to the vibration frequency of the lattice.

The depth of the metastable state from thermoluminescence experiments is $0.3\text{--}0.4\text{ ev}$ for *p*-xylene, but from the difference between the shorter wavelength edges of the fluorescence and phosphorescence spectra ($325, 453\text{ m}\mu$), it is about 1 ev . Taking into consideration that thermal excitation always requires less energy

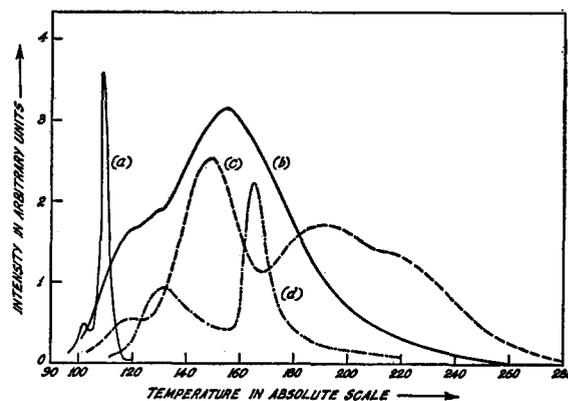


FIG. 3. Thermoluminescence curves of (a) toluene, (b) *p*-xylene, (c) diphenyl, (d) benzene.

than optical excitation, the result is quite reasonable. The structure in the thermoluminescence curves indicates the presence of similar structure in the metastable states of the molecules. Further investigation is necessary for understanding the nature and individual cases of the metastable states.

It was further observed that at the end of thermoluminescence experiment, if heating was continued till the sample evaporated, the vapor gave spontaneous irregular flashes without any external excitation. These flashes lasted for a few minutes. It is obvious that some of the evaporating molecules still remain in some metastable state, and they come to normal state by emitting extra energy as light. Similar results in the case of other organic compounds have been reported earlier.

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⁵ J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) A184, 365 (1945).