Letters to the Editor

The Board of Editors does not hold itself responsible for opinions expressed in the letter published in this section. The notes containing short reports of original investigations communicated to this section should not contain many figures and should not exceed 500 words in length. The contributions reaching the Secretary by the 15th of any month may be expected to appear in the issue for the next month. No proof will be sent to the author.

15

THE PROBLEM OF FORBIDDEN FUNDAMENTALS IN THE RAMAN AND INFERA-RED SPECTRA OF LIQUID BENZENE

N. RAJESWARA RAO AND MISS S. SAKKU

DEPT. OF PHYSICS, OSMANIA UNIVERSITY, HYDERABAD

(*Received June* 30, 1967; *Resubmitted February* 28, 1968)

The molecule of benzene is highly symmetrical, belonging to the point group D_{6h}. One expects 7 lines in the Raman spectrum and 4 in the infra-red. But, the large amount of literature shows that the spectrum of the liquid gives to a maximum of 47 lines. Although, many of them are accounted for as combination lines, the appearance of almost all the following forbidden lines remains a problem. 1326(a_{2g}), 703(b_{2g}), 999(b_{2g}), 671(a_{2u}), 1005(b_{1u}), 405(e_{2u}), 1485(e_{1u}), 1037(e_{1u}) in the Raman spectrum and 985(b_{2g}), 605(e_{2g}), 1585(e_{2g}), 1606(e_{2g}), 1178(e_{2g}), 849(e_{1g}) in the infra-red. It is proposed to explain their existence assuming that the short range order is more or less crystalline.

Evidence for quasi-crystalline state of benzene

Specific heat of benzene is much nearer to that of the crystal than of vapour, the values being 15.68, 21.15 and 21.4 for vapour, liquid and solid in order (Bhagavantam, 1942). This shows that the intermolecular forces in the liquid state are quite strong, as is indeed evidenced by the strong wing accompanying its Rayleigh line. One, of course, need not expect separated lattice lines, as even in crystals at high temperatures they are observed to be diffuse (O'Shea *et al*, 1967). If this contention is accepted, one can expect the degenerate lines to be resolved, but the problem of forbidden lines still remains unsolved.

Raman and infra-red spectra of liquid benzene

Recently, a faint, but, sharp line at $d\nu = 1012\ cm^{-1}$ (perhaps, B_{1u}) was observed in the Raman spectrum taken by Mitsueo Ito (1965) and in the infra-red spectrum taken by Mair and Hornig (1949), Swenson and Pearson (1960) and

Hollenberg and Downs (1962), who have not been able to account for it as a combination line. Mitsuo Ito concludes' selection rules for the vibrational spectrum of the crystal are not strictly applicable to polycrystalline aggregates'. In the liquid, a line at $d\nu = 999$ appears fairly sharp in the microphotometric records of the fine structure of $d\nu = 992.5\ \text{cm}^{-1}$ published by Grassmann and Weiler (1933).

A possible explanation

A possible explanation can be in terms of induced effects by the neighbours. The fact that some of the lines (e.g. 3046) show large changes from liquid to gaseous states (Sirkar, 1936), shows that the induced effects are strong. In a liquid, since the density is fairly large, induced effects are strong enough to produce asymmetry in the molecules temporarily. But, the forbidden lines produced that way, can only be weak and diffuse. The lines observed, however, are not all quite feeble and diffuse, especially $d\nu = 999\text{cm}^{-1}$ referred to above.

Rajeswara Rao and Ramanaiah (1966) quoted evidence to show that in sulphuric acid, the short range order is crystalline, the molecules in the interior of the crystals having T_d symmetry and those on the periphery C_{2v} symmetry, due to asymmetrical distribution of hydrogen bonds in the latter case. Similar asymmetrical induced effects in the molecules on the surface of small crystals in benzene can give rise to the appearance of sharp forbidden lines tempting one to think that the short range order in liquid benzene is crystalline. Perhaps, the appearance of $d\nu = 1912\ \text{cm}^{-1}$ in the spectrum of the polycrystalline mass studied by Mitsuo Ito (1965) and others is also due to similar reasons.

REFERENCES

Bhagavantam, S, 1930, *Indian J. Phys.*, **5**, 615,.

———— ,1940, *Light Scattering and Raman Effect*, Andhra University Press.

Grassmann, P. and Weiler, J., 1933, *Z. Physik*, **86**, 321.

Hollenberg, D. A. and Dows, J., 1962, *J. Chem. Phys.* **37**, 1300.

Mair, R. D. and Hornig, D. F., 1949, *J. Chem. Phys.* **17**, 1236.

Mitsuo Ito, 1965, *J. Chem. Phys.*, **42**, 284.

O'Shea, D. C., Kolluri, R. V. and Cummins, H. Z., 1967, *Johns Hopkins University* (preprint).

Rajeswara Rao, N. and Ramanaiah, K. V., 1966, *Indian J. Pure and Appl. Phys.*, **4**, 385, 206.

Sirkar, S. C., 1936, *Indian J. Phys.*, **10**, 189.

Swensen, C. A. and Pearson, W. B., 1960, *J. Chem. Phys.*, **33**, 56.