

Raman Spectrum of Cyclopropane

THE Raman spectrum of cyclopropane is of great interest in view of the fact that it is the simplest of the cyclic hydrocarbons, and also from the point of view of the structure of the cyclopropane molecule. I have investigated this substance both in the liquid and vapour states and have obtained the following results :

Liquid	{	$\Delta\nu$ (cm. ⁻¹)	736*	863	1185	1434	1503*	2852*	2952*	3010	3028	3080
		Int.	Obd	8b	15	2b	0s	†	1	10	10	6bd
			D	D	P	D	P	P	P	P	P	D
Vapour	{	$\Delta\nu$ (cm. ⁻¹)	863		1185					3010	3028	
		Int.	Ob	2s						1s	2s	
			b = broad ; d = diffuse ; s = sharp ; P = polarised ($\rho \ll 6/7$)		D = depolarised ($\rho \approx 6/7$).							

The frequencies marked with an asterisk in the case of the liquid have not been noticed by the previous investigators^{1,2} and are reported here for the first time. The strongly polarised Raman line at 1185 cm.⁻¹ and the depolarised Raman line at 863 cm.⁻¹ presumably represent the totally symmetric and the deformation vibrations respectively of the triangular carbon ring which forms the nucleus of the cyclopropane molecule. However, for an equilateral

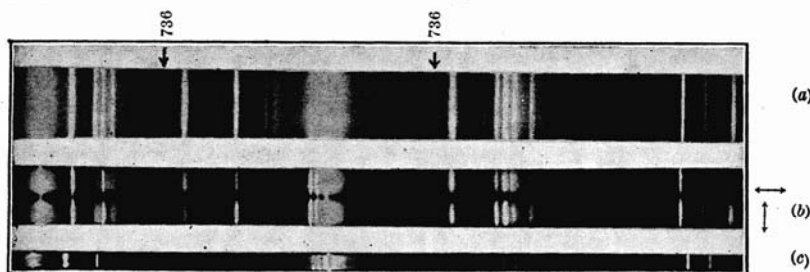


FIG. 1. Raman spectrum of cyclopropane; a, liquid; b, liquid (polarisation); c, vapour.

triangular model, the doubly degenerate deformation frequency is forbidden in the Raman effect according to Placzek's selection rules. The fact that the Raman line at 863 cm.⁻¹ persists even in the vapour state clearly shows that its appearance in the liquid spectrum cannot be due to the influence of the neighbouring molecules. The influence of the hydrogen atoms on the vibrations of the carbon ring might be a possible explanation for the appearance of this line. The matter, however, requires mathematical investigation.

A striking difference between the liquid and the vapour spectra is noticed when we compare the Raman lines at 3010 cm.⁻¹ and 3028 cm.⁻¹. In the liquid picture, these two lines are of equal intensity or perhaps $\Delta\nu=3010$ cm.⁻¹ is slightly more intense than $\Delta\nu=3028$ cm.⁻¹. The intensity of either of

these is less than that of the Raman line at 1185 cm.⁻¹. In the vapour picture $\Delta\nu=3010$ cm.⁻¹ is found to have become considerably weaker, while $\Delta\nu=3028$ cm.⁻¹ has gained in intensity and is almost as strong as Raman line 1185 cm.⁻¹ Such a strong difference between the relative intensities of the Raman lines between vapour and liquid in the case of a non-polar molecule is remarkable, and evidently requires further elucidation.

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¹ R. Lespleau, M. Bourguet and R. Wakeman, *Bull. Soc. Chim. France*, (4), 51, 400 (1932).

² K. W. F. Kohlrausch and F. Koppl, *Z. phys. Chem.*, B, 26, 209 (1934).