

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	1	10	10	Obd
	{	e	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 ($e \ll \theta/7$)
 D = depolarised ($e \approx 6/7$).

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

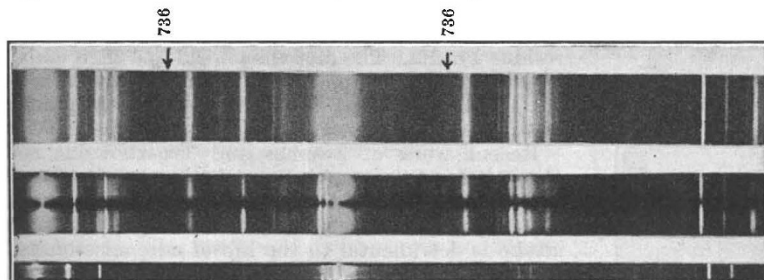


FIG. 1. Raman spectrum of cyclopropane; a, liquid; b, liquid (polarisation); c, vapour.

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.

R. ANANTHAKRISHNAN.

Department of Physics,
 Indian Institute of Science,
 Bangalore. May 6.

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).

Electronic Specific Heat in Palladium

KEESOM and Clark¹ have shown that the atomic heat of nickel at low temperatures contains a linear term $0.0019 T$, which is many times bigger than the contribution from the free electrons to be expected from the Sommerfeld theory. Mott² has suggested that this term is due to the unfilled quantum states (positive holes) in the *d*-shell of nickel, and that a similar term should occur for the other transition metals, whether ferromagnetic or paramagnetic.

In order to test this theory and to make more quantitative data available on the subject, the specific heat of palladium was determined, palladium being chosen on account of its similarity to nickel and its high paramagnetism, which according to Mott should imply a large electronic specific heat. Though the electronic component in these transition metals is larger than usual, it is nevertheless small in absolute magnitude. But since it varies proportionally with the temperature, whereas the specific heat due to the lattice vibrations varies near the absolute zero with the cube of the temperature, the two become comparable in magnitude at sufficiently low temperatures³. Experiments were therefore carried out in the liquid helium region.

The specific heat of a block of metallic palladium (weighing 25 gm.) kindly put at our disposal by Prof. Mott was measured between 2.5° K. and 22° K. in a vacuum calorimeter enclosed in a helium liquefier using the Simon expansion method.

The sample was contained in a small copper calorimeter on which were wound heating and thermometer coils of eureka wire, thermal contact between the calorimeter and the palladium being effected by the use of helium gas at a low pressure.

The results showed that the atomic heat of palladium in the region 2.5°-22° K. could be expressed in the form

$$C = 0.0000224 T^3 + 0.0031 T \text{ cal./degree.}$$

The first term represents the component due to the lattice vibrations and corresponds to a Debye characteristic temperature of $\theta = 275^\circ$, while the second term represents the specific heat of the free electrons or positive holes. At 2.5° K. the linear term is about twenty times as great as the T^3 term, while the two terms become of equal magnitude at about 12° K. The value of the electronic specific heat is, as predicted by Mott, much higher than for normal metals, and is even greater than that of nickel. The above result is considered from the theoretical point of view in a book on metals by N. F. Mott and H. Jones, to appear shortly.

I should like to thank Prof. F. Simon and Dr. N. K rti for their advice and assistance in carrying out this determination.

G. L. PICKARD.

Clarendon Laboratory,
 Oxford.
 June 8.

¹ W. H. Keesom and C. W. Clark, *Physica*, 2, 513 (1935). K. Clusius and J. Goldmann, *Z. phys. Chem.*, B, 31, 256 (1936).
² N. F. Mott, *Proc. Roy. Soc.*, A, 152, 42 (1936).
³ F. Simon, *Z. Elektrochemie*, 34, 530 (1928).