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Raman Spectrum of Benzene Under High Dispersion and the Isotope Effect

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The Raman spectrum of benzene has been photographed using a fine slit and a high dispersion glass Littrow spectrograph. The faint companion at 984 cm^{-1} is found to possess an intensity ratio of 6 : 100 when compared with the principal Raman line at 992 cm^{-1} . The view that this satellite arises from a benzene molecule in which one of the carbon atoms is replaced by the heavier isotope of atomic weight 13 is supported by this result. The distribution of intensity in the 3048 and 3062 Raman lines has been determined and the contours of the lines are drawn separately. The peaks of these two lines are found to be in the ratio of 1 : 1.35. The relatively sharp nature of 3062 and the diffuseness of 3048 are correlated with the facts that the former is a well-polarized Raman line whereas the latter is a fully depolarized line.

INTRODUCTION

THE author is engaged in a systematic study of the fine structure exhibited by the various Raman lines under high dispersion and some of the results obtained with benzene are of special interest as they confirm the recent findings of Cheng, Hsueh and Ta-You Wu.¹ The results given in this paper relate to the 992 and 3060 Raman lines of benzene and are obtained independently by the author during the course of a more extensive investigation. They are now reported here in view of the publication referred to above.

EXPERIMENTAL

A quartz mercury arc is kept close on the top of a Raman tube cooled by circulating water. Polished aluminum reflectors are used to increase the illumination. A Littrow glass spectrograph with a dispersion of about 10Å/mm in the $\lambda 4358$ region has been used to photograph the scattered spectrum. By using a fine slit (0.03 mm) the

¹ Cheng, Hsueh and Ta-You Wu, *J. Chem. Phys.* **6**, 8 (1938).

Raman spectrum of benzene has been photographed in which the component 984 is clearly revealed. In the same picture 3062 and its companion line 3048 are also recorded very strongly. A set of intensity marks are then put on the same plate by the method of varying slit widths. The lines at 984 and 992 and the lines at 3048 and 3062 along with the intensity marks in the corresponding regions are run through a Moll microphotometer and the relative intensities are deduced in the usual manner with the help of density—log intensity curves.

RESULTS AND DISCUSSION

Figures relating to 992 and its component are not reproduced as they have already been given by a number of earlier investigators. The ratio of intensities of 984 and 992 lines, obtained as the average of three measurements comes out in this investigation as 6 : 100. This is in excellent agreement with the recently reported value of Cheng, Hsueh and Ta-You Wu.¹ No other components are recorded alongside this line.



FIG. 1.

Various investigators² have reported results on a study of the components of the 992 cm^{-1} line in benzene. Of these authors Gerlach was the first to suggest that the faint companion at 984 may be due to the principal oscillation of the benzene molecule in which one of the carbon atoms is replaced by its heavier isotope of atomic weight 13. Grassmann and Weiler, Bhagavantam, Specchia and Scandurra and Pattabhiramayya are among those who held that this view was correct. Subsequently Ananthakrishnan expressed the view that the origin of this companion

line may not be isotopic. The fact that the recent quantitative study of Cheng, Hsueh and Ta-You Wu already referred to and the author's work reported here both lead to an intensity ratio of 6 : 100 for the companion line in relation to the main line lends strong support to the view that the origin of 984 is isotopic.

The continuous curve in Fig. 1 is a graph showing the intensity distribution in the 3048–3062 lines. The broken lines represent the separate intensities of 3048 and 3062 which together by partial overlapping go to make up the observed intensity curve. These are drawn on the assumption that the lines are symmetrically broadened and it is easily seen that the line at 3062 is very sharp while that at 3048 is broad and diffuse extending on either side to about 25 cm^{-1} . These intensity characters are in perfect agreement with their observed depolarization factors. Veerabhadra Rao³ and Simons⁴ have respectively given 0.88 and 0.89 for the depolarization factor of 3048 and the line should therefore be expected to exhibit a strong wing on either side. On the other hand they have given 0.30 and 0.34, respectively, for the 3062 line and it is accordingly comparatively much sharper. It may easily be seen from the graph that the ratio of the peak intensities of these lines is 1 : 1.35 which agrees with the figures given by Veerabhadra Rao, namely 1 : 1.28. The figures given in this paper are likely to be slightly in error on account of the fact that illumination from the top is adopted and the intensities of two lines whose states of polarization are different are compared.⁵ Recent work of Angus and others⁶ has shown that both these lines are distinct and they represent two separate fundamental frequencies of the benzene molecule.

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³ Veerabhadra Rao, *Zeits. f. Physik* **97**, 154 (1935).

⁴ Simons, *Comm. Soc. Scien. Fenn.* **6**, 13 (1932).

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⁶ R. Angus and others, *J. Chem. Soc.* 912–987 (1936).