

The Raman Spectrum of DeuterioBenzene (C₆D₆)

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The experiments discussed originated from H. N. Russell's⁷ discussion of the absorption spectra of stellar atmospheres in which he mentioned the fact that the astronomer, restricted to the glass and part of the quartz region, is observing absorption spectra mainly of *unstable* molecules, whereas most *stable* molecules have their absorption spectra in the extreme ultraviolet. This property of unstable molecules suggested the application of the spectrograph to such reactions in gases.

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September 12, 1934.

¹ K. F. Bonhoeffer and H. Reichardt, *Zeits. f. physik. Chemie* **139**, 75 (1928).

² K. F. Bonhoeffer and T. G. Pearson, *Zeits. f. physik. Chemie* **14**, 1 (1931).

³ P. Harteck, *Trans. Faraday Soc.* **30**, 139 (1934). Cf. W. Frankenburg and H. Klinkhardt, *Zeits. f. physik. Chemie* **15**, 440 (1931).

⁴ O. Oldenberg, *Phys. Rev.* **46**, 210 (1934).

⁵ This has been pointed out by Bonhoeffer and Pearson² discussing the afterglow of water vapor discovered by G. I. Lavin and F. B. Stewart (*Proc. Nat. Acad. Sci.* **15**, 829 (1929)).

⁶ W. H. Rodebush and M. H. Wahl (*J. Chem. Phys.* **1**, 696 (1933)) obtained H_2O_2 as the principal product of the electric discharge through water vapor. Their hypothesis of a bimolecular association $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2$ is based on the assumption of a very short life of OH.

⁷ Russell, Lecture at the Harvard Observatory, 1931; *Astrophys. J.* **79**, 317 (1934).

The Raman Spectrum of Deuterio-Benzene (C_6D_6)

In order to facilitate the interpretation of the Raman spectrum of benzene, we have investigated the Raman spectrum of deuterio-benzene. Efforts were made to synthesize this material in our laboratory. An experiment with an exchange reaction between heavy water and benzene showed that no exchange took place in the vapor state at 450° in the presence of platinum black or between the two liquid phases which were in contact for ten days. An attempt to prepare deuterio-benzene by the polymerization of acetylene made from heavy water and calcium carbide yielded only about one cubic millimeter of liquid hydrocarbon from 3 cc of heavy water although the by-products were recovered and reprocessed several times. This indicates that the reaction with deuterio-acetylene gives a very small yield of benzene compared to the reaction with ordinary acetylene as judged by preliminary trial experiments and by the work of Zelinsky¹ on this reaction.

The material used in this investigation was loaned to us by Professor Zanetti of Columbia University who prepared it from heavy water of better than 99 percent purity by the polymerization of acetylene, working on a much larger scale. Due to the very small yield, the product could not be purified very thoroughly but a small amount of a liquid which smelled like benzene was obtained. The preparation of this material will be described elsewhere by Professor Zanetti. The liquid was distilled once in air over a water bath and then distilled into the Raman tube in vacuum, passing the vapors over P_2O_5 to remove traces of water.

The technique used for obtaining the Raman spectrum was that described by Murray and Andrews.² The Raman tube was made of Pyrex capillary of 1.2 mm bore fused to a Pyrex window. The length of the illuminated portion of the tube was 15 mm. Two spectra were obtained using the 4358 mercury line as the exciting light and one using the 4046 mercury line.

The two plates taken with the 4358 excitation showed a Raman line of 943 cm^{-1} displacement. Due to the very small size of the tube required, satisfactory elimination of parasitic light was impossible and the spectra were superimposed upon a rather strong continuous background which masked the other lines. Two other lines appeared to be present but are so weak as to be doubtful. These lines were at about 2290 excited by the 4046 line and 1600 excited by the 4358 line.

The selection rules for Raman spectra indicate that the 992 cm^{-1} line in benzene originates in a very symmetrical type of vibration. This suggests that it is due to the motion in which the six carbon atoms and the six carbon atoms attached to them move in and out along the lines drawn through the atoms to the center of the ring, all of the atoms vibrating in phase with each other. Other assignments have been suggested by various authors. The correctness of this assumption has been confirmed by studies with vibrating mechanical models of the two series of compounds: C_6H_6 , $\text{C}_6\text{H}_5\text{CH}_3$, $\text{C}_6\text{H}_5\text{Cl}$, $\text{C}_6\text{H}_5\text{Br}$, $\text{C}_6\text{H}_5\text{I}$; and C_6H_6 , $\text{C}_6\text{H}_5\text{Cl}$, *o*, *m*, and *p* $\text{C}_6\text{H}_4\text{Cl}_2$, (1, 2, 3), (1, 2, 4), and (1, 3, 5) $\text{C}_6\text{H}_3\text{Cl}_3$, and C_6Cl_6 . The first of these series was studied by D. Teets, and the second by J. W. Murray and V. Deitz, the results being in process of publication in *The Journal of Chemical Physics*. In passing from compound to compound, the shifts of the mechanical frequency associated with the symmetrical expansion correspond exactly in sign and magnitude with the shifts observed in this strong line in the Raman spectra. Similar evidence indicates that the 3065 cm^{-1} line in benzene compounds corresponds to symmetrical expansion with the hydrogen atoms in a phase opposite to that of the carbon atoms.

On the basis of these correlations, a calculation may be made of the shift to be expected from the substitution of six deuterium atoms for the six hydrogen atoms in benzene. Let us assume that in this type of motion, the effect of the C—C bonds attached to one carbon atom is the same as if that carbon were attached by a bond to a fixed point in the center of the ring. Let S_I be the stretching force constant for this fictitious bond and S_{II} for the C—H bond. We may then define the motions of the atoms by the equations:

$$m_1 4\pi^2 \nu \alpha^2 x_{\alpha 1} = S_I x_{\alpha 1} + S_{II} (x_{\alpha 1} - x_{\alpha 2}),$$

$$m_2 4\pi^2 \nu \alpha^2 x_{\alpha 2} = S_{II} (x_{\alpha 2} - x_{\alpha 1}),$$

where $\alpha = 1$ or 2 , $\nu_1 = 992.5\text{ cm}^{-1}$, $\nu_2 = 3065\text{ cm}^{-1}$, $m_1 = 12$ and $m_2 = 1.008$. Since the amplitude of the vibration is arbitrary, we may let $x_{\alpha 1} = 1$. Solving these equations simultaneously, we obtain $S_I = 7.55\text{ dynes cm}^{-1}$, and $S_{II} = 6.12\text{ dynes cm}^{-1}$. Using these values, we may let $m_2 = 2.016$ and solve for ν_1 , obtaining a value of 945 cm^{-1} . The close agreement of this with the observed value indicates several things. First, it supports the assumed identity of the

material studied as deuterio-benzene. This was previously indicated by the method of preparation, the smell, and the general appearance of the Raman spectrum in which the only line which showed up distinctly bore the expected relation to the very strong 992 line of benzene. Secondly, assuming the spectrum to be that of C_6D_6 , it supports the correlation of the two Raman lines with the assumed types of motion. Thirdly, it indicates that there is no appreciable change in the force constants of the bonds in benzene on account of the substitution of deuterium for hydrogen.

The authors acknowledge the invaluable cooperation of Professor Zanetti in furnishing the deuterio-benzene.

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¹ Zelinsky, Ber. **57**, 264 (1924).

² J. W. Murray and D. H. Andrews, J. Chem. Phys. **1**, 406 (1933).