

The Raman Spectra of Deuterated Benzenes and the Symmetry of the Benzene Molecule

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The Raman Spectra of Deuterated Benzenes and the Symmetry of the Benzene Molecule

In connection with a study of the structure of the benzene molecule, we have prepared all of the deuterium-substituted benzenes and have obtained their Raman spectra. The preparative and spectroscopic details of this work will be published shortly. We desire, however, to call attention to a striking feature of the Raman spectra of these compounds which offers constructive evidence of the D_{6h} (plane hexagonal) structure of benzene.

It is well known¹ that there are in benzene two fundamental frequencies which have very nearly the same value, viz., the totally symmetric frequency (ν_1) of 992 cm^{-1} and the trigonally symmetric frequency (ν_{12}) at about 1010 cm^{-1} . The latter vibration is, by reason of its symmetry, forbidden in Raman effect. The reduced symmetry of the deuterated benzenes, however, evokes its appearance in the Raman spectra of all these save the *para* di- and the *para* tetra-substituted compounds.

For practical reasons one cannot compute in a rigorous fashion the shifts of these two frequencies caused by the insertion of deuterium atoms in the benzene molecule. On the other hand it is possible to estimate the shifts closely enough for our purposes by making the plausible assumption that a constant frequency decrement results from the substitution of each deuterium atom. The decrements in ν_1 were found simply by dividing the benzene-hexadeutero benzene shift by six. Since ν_{12} is inactive in both compounds, a similar procedure for this frequency is impossible. We have therefore estimated the various ν_{12}

values as follows: The calculated ν_1 values agree quite closely (within $ca. 1\text{ cm}^{-1}$) with observation in the *ortho* and *para* di- and tetra-substituted compounds. Presumably the assumption under which the several ν_1 frequencies were calculated would therefore be equally valid for these same compounds in calculating ν_{12} . This frequency is inactive in the *para* compounds, but from the observable *ortho* frequencies one can compute the shift in ν_{12} for each additional deuterium atom. From this information ν_{12} has been estimated for the various deuterated benzenes.

In Fig. 1 the dotted lines show diagrammatically the calculated shifts in ν_1 and ν_{12} . Our method of calculation of course gives the same value for a given frequency within each group of isomers. The frequencies of ν_1 and ν_{12} observed by us in the Raman spectra of the deuterated benzenes are listed in the table at the foot of Fig. 1, together with the symbols for the symmetry classes of the respective compounds. It is important to remark that in all of the deuterated benzenes with symmetry C_{2v} , except the *ortho* di- and *ortho* tetra-substituted compounds, the vibration ν_{12} is symmetric to the twofold axis. In the *ortho* compounds, however, the twofold axis passes between the two *ortho* carbon atoms, and ν_{12} is thus antisymmetric to the axis. To emphasize this distinction, we have marked the *ortho* compounds C_{2v}^* . ν_1 is of course a totally symmetric vibration in all the compounds. For convenience in comparison with the calculated values, the observed frequencies have been inserted in Fig. 1. The visually estimated intensity ratios of ν_{12} to ν_1 are given in the column I_{12}/I_1 and approximately indicated by the thickness of the plotted levels.

When one examines Fig. 1, one is struck by the fact that in certain of the compounds, the frequency ν_1 is lower than the calculated value by several wave numbers, and that ν_{12} is higher than calculated by about the same amount. This unexpectedly large separation of ν_1 and ν_{12} occurs only in those compounds in which the corresponding normal modes of vibration belong to the same symmetry class. It is further to be remarked that whenever an increased separation is found, the intensity of ν_{12} is enhanced, and the intensity increase is the larger, the larger the separation.

It is difficult to see how these features of frequency and intensity can be explained on the usual mechanical grounds and in accordance with the well-established theoretical principles of the Raman effect unless one assumes the

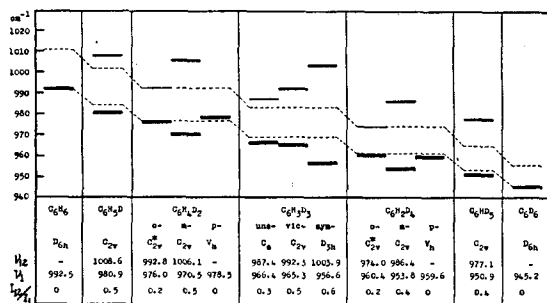


FIG. 1.

D_{6h} structure. Once this assumption has been made, however, the explanation is simple and complete. The discrepancies between calculated and experimental frequencies, and the attendant intensity differences, are due to resonance between ν_1 and ν_{12} . This resonance can occur only in C_s , C_{2v} (but *not* C_{2v}^*), and D_{3h} , and it is *only* in these cases that we find anomalous frequencies and intensities.

We therefore believe that these particular features of

the Raman spectra of the deuterated benzenes strongly support the D_{6h} structure.

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October 1, 1937.

¹ Kohlrausch, *Zeits. f. physik. Chemie* **B30**, 305 (1935); Lord and Andrews, *J. Phys. Chem.* **41**, 149 (1937).