

Raman Spectrum of Benzened 6

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Citation: [The Journal of Chemical Physics](#) **3**, 444 (1935); doi: 10.1063/1.1749703

View online: <http://dx.doi.org/10.1063/1.1749703>

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Below 1360Å a new set of somewhat diffuse bands starts. The first member, which is partly in the ionization continuum of the above set, is very strong. It is shifted to the violet by quite a large amount ($\sim 285\text{ cm}^{-1}$) by the change from C_6H_6 to C_6D_6 . It is believed that the transition is still a vibrationless electronic transition but that the electron is in this case a more strongly bonding one (i.e., its removal diminishes the vibration frequencies of the molecule considerably). This band is followed by some very weak diffuse bands and a certain amount of general absorption. The next bands which are of sufficient intensity to be linked with it as subsequent members of an electronic series occur around 1180Å. These also suffer isotopic shifts to the violet of the same order of magnitude. Unfortunately general absorption made it difficult to observe higher members of this electronic series, nevertheless it is felt fairly safe to estimate the second ionization potential of benzene to be 11.7 ± 0.3 volts.

The first ionization potential given here must

obviously be that of an electron more strongly attached to a carbon atom. It is interesting to note that its value is considerably lower than the first ionization potentials of C_2H_2 , C_2H_4 , or C_2H_6 (11.36, 10.41 and ~ 12 volts) which are also due to electrons mainly associated with the carbon atoms. In these cases however, the electrons contribute considerably toward the bond. The low ionization potential observed in benzene may be partly caused by a large charge transfer or dipole effect in the phenyl group. It may also be brought about by the resonance which would predict one high and one low ionization potential.

In conclusion the authors wish to express their indebtedness to Professors G. H. Dieke and K. F. Herzfeld for their suggestions with regard to the material of this article and to Professor H. S. Taylor of Princeton for making the heavy benzene available.

Note added in proof: To obtain strong electronic series going to an ionization potential it is necessary that the character of the ion be opposite to that of the normal molecule (i.e., $g \rightarrow u$ or $u \rightarrow g$). It is thus most probable that a "*p*" electron is excited.

AUGUST, 1935

JOURNAL OF CHEMICAL PHYSICS

VOLUME 3

Raman Spectrum of Benzene- d_6

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(Received June 14, 1935)

THE sample of heavy benzene, 1.5 cm^3 , was supplied by Professor H. S. Taylor of Princeton. It was contained in a straight tube 30 cm in length and 6 mm internal diameter closed at one end with a disk of optical Pyrex, and sealed at the other end. The tube was wrapped with insulation tape with the exception of a length of 4 cm near the window, and was mounted in a vertical position, with a right-angle total reflecting prism a short distance below the window.

A 220-volt Hanovia quartz mercury arc in its metal housing, turned into the vertical position, was employed for the excitation. The sliding metal plates were removed from the box, securing perfect ventilation, and the light which emerged from the vertical slot opposite the burner was focused on the benzene tube with a cylindrical lens consisting of a glass tube 4 cm internal

diameter, and 40 cm long, half full of a strong solution of sodium nitrite (for excitation by 4358) or of iodine in carbon tetrachloride for excitation by 4046, as described in a previous paper.¹ This method of operating the illuminating system obviates the necessity of the ventilating fan as described in an earlier paper. The lower portion of the tube, which contains the fluid benzene is backed by a concave cylindrical reflector of thin sheet aluminum and the lamp moved into such a position that the direct and reflected cones of scattered light coincide on the axis of the tube, as viewed in the prism.

The first photograph taken showed a strong continuous background and only one line distinctly, though faint traces of other lines appeared. Having eliminated this troublesome fluorescence in the case of the heavy water,

¹ Wood, *Phys. Rev.* **38**, 2169 (1931).

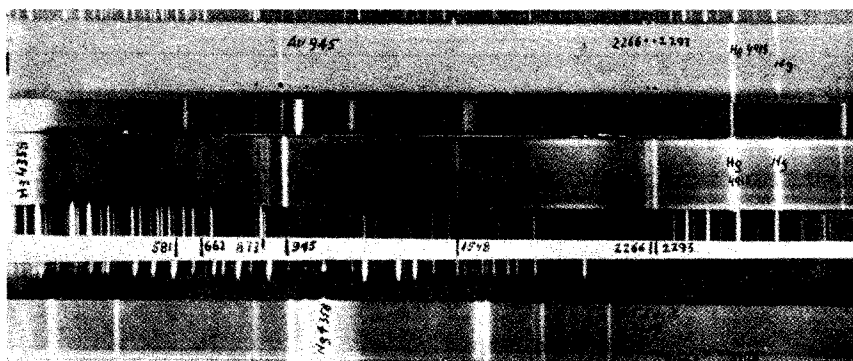


FIG. 1.

The $\Delta\nu$ values of both benzenes are given in Table I.

Corresponding lines of the two benzenes have been placed opposite each other. The shift of the 1178 line to 873 makes it appear out of place in the spectrum with respect to 991 which is shifted only to 945. The doublet 1584-1606 is fused to a single line at 1548. Both of these phenomena were predicted from theory by E. Bright Wilson (communicated by letter). The lines 605 and 849, of very different intensities with ordinary benzene have the same intensity with heavy benzene. Wilson's predictions of the shifts were closely confirmed.

With the heavy benzene a distinct pair of lines was found very near the point at which the strong doublet 3042-3062 is found with ordinary benzene. The $\Delta\nu$ values for these lines were 3052 and 3108, and they were found both by 4046 and 4358 excitation. They are shown on the lowest spectrum obtained by 4046 excitation at the extreme right marked by dots. This made me suspect that a careful search might reveal the corresponding lines for ordinary benzene, with $\Delta\nu$ values of over 3500, though no lines of such large $\Delta\nu$ value have ever been recorded.

A spectrum of a very pure thiophen-free benzene was made with 4358 excitation and an Eastman green sensitive plate, and a pair of lines found at wavelengths 5162 and 5177, giving $\Delta\nu$ values of 3573 and 3627, and as no mercury lines were found at this point, I feel very certain that the lines are real. I was unable to obtain them with 4046 excitation, but the continuous background was stronger in this case. That they have not been observed previously is probably due to the fact that they are in the region of lowest sensitivity of most photographic plates.

The lines 2617 and 2663 (marked doubtful) were obtained with iodine filtered 4046 excitation, the latter coinciding with $\Delta\nu$ 945 excited by 4348 and the former nearly in coincidence with $\Delta\nu$ 945 excited by 4339. The circumstance that $\Delta\nu$ 945 excited by 4358 was rather faint makes it seem possible that the two lines are real. They are marked with interrogation marks on the lowest spectrum. Just to their left is the 2575 line, faint but undoubtedly real.

TABLE 1.

C ₆ H ₆	C ₆ D ₆	C ₆ H ₆	C ₆ D ₆
605	581	2947	
849	662	3042	2266
991	945	3062	2293
	1000 (faint)	3157	2575
1178	873	3176	2617
1584 } 1606 }	1548		2663
	2031 (broad, faint)	3573	3052
		3627	3108