

217. *Structure of Benzene. Part VII. Discussion of Coincidental Frequencies in the Infra-red and Raman Spectra of Benzene and Hexadeuterobenzene.*

By W. R. ANGUS, C. R. BAILEY, J. B. HALE, C. K. INGOLD, A. H. LECKIE,
C. G. RAISIN, J. W. THOMPSON, and C. L. WILSON.

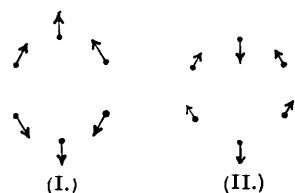
SPECTROSCOPIC evidence has previously been brought to bear on the benzene problem by means of the argument referred to in Part I. This we now propose to consider.

It follows directly from the classical picture of absorption that only those normal vibrations can record their fundamental frequencies in the infra-red spectrum which are associated with an oscillation of dipole moment: the electric vector of the light wave sets up forced vibrations of the distribution of electrons relatively to the distribution of nuclei, *i.e.*, to an oscillation of the dipole moment, and these vibrations become resonance vibrations when there is a natural vibration involving oscillation of dipole moment and agreeing in frequency with the light. Obviously, the molecule has to be considered as a whole in this connexion owing to its smallness compared with the wave-length.

It follows from Placzek's theory of Raman scattering that only those normal vibrations can appear as fundamentals in the Raman spectrum which involve an oscillation of the molecular polarisability. Again, it suffices to set up a classical picture in which an oscil-

lating molecular polarisability gives rise to a periodically varying amplitude in the secondary light radiated by the forced dipole oscillation created by the incident light—this “beat” splitting up in the usual way into two simple harmonic terms whose frequency separation gives the beat frequency, *i.e.*, the vibration frequency of the molecule.

A molecule possessing a centre of symmetry can be divided (except for a possible particle at the centre itself) into pairs of fully equivalent mass-points. Further, the operation of inversion through a centre is one to which all normal vibrations, including degenerate vibrations, are either symmetric or antisymmetric (Part VI). In a symmetric vibration (illustrated by I) each pair of equivalent charged mass-points will move in such a way as to keep its centre of gravity constantly at the centre of symmetry, and hence there can be no variation of dipole moment. It follows that vibrations symmetric to a centre of symmetry cannot record their fundamental frequencies in the infra-red spectrum. In an antisymmetric vibration (II) each member of a pair of equivalent mass-points will at every moment neutralise the other's effect on the molecular polarisability, which will therefore remain invariant. Hence vibrations antisymmetric to a centre of symmetry do not appear as fundamentals in the Raman effect. It follows that in the presence of a centre of symmetry no fundamental vibration can appear both in the infra-red and in the Raman spectrum



—though this does not mean that every fundamental is bound to occur in one spectrum or the other, since elements of symmetry besides the centre may be present which can lead to further exclusions of the frequencies from either spectrum. In order to generalise this principle of mutual exclusion to cover overtones and combination tones, it is necessary to take up a more definitely quantum-mechanical view-point, and consider the symmetry not of the vibrations but of their wave-functions. These are symmetric or antisymmetric to the centre according as the vibration is symmetric or antisymmetric, if the quantum number is odd; and they are symmetric whatever the vibration may be if the quantum number is even (Part VI). In all cases, however, vibrations with symmetric wave-functions are excluded from the infra-red spectrum and those with antisymmetric wave-functions from the Raman effect, so that it holds true quite generally that in the presence of a centre of symmetry the same frequency cannot occur in both spectra.

The definite character of this principle was first made clear through the work of Placzek (*Leipziger Vorträge*, 1931, p. 71), who specifically referred to benzene and concluded that it could not be in a plane regular hexagon on account of the number of coincident frequencies which had been observed in the Raman and the infra-red spectra. Bhagavantam had already drawn attention to these coincidences (*Indian J. Physics*, 1930, 5, 615) and, later, Krishnamurti revised the evidence and gave a list of twelve (*ibid.*, 1932, 6, 543). Many authors followed Placzek in rejecting the regular hexagonal model, most of them advocating a Kekulé structure, which has not a centre of symmetry (*e.g.*, Cabannes and Rousset, *Ann. Physique*, 1933, 13, 229; Weiler, *Z. Physik*, 1934, 89, 58; Kohlrausch, *Naturwiss.*, 1934, 22, 161, 181, 196). In the meantime Pauling and Wheland's calculations appeared (cf. Part I), and E. B. Wilson (*Physical Rev.*, 1934, 46, 146) suggested that the coincidences were accidental, their large number arising from the considerable error attaching to the older measurements of infra-red frequencies. Furthermore, we stated in our preliminary notes (*Nature*, 1935, 135, 1033; 136, 680) that the Raman and infra-red fundamental frequencies of benzene could be assigned, and the isotope shifts observed in hexadeuterobenzene quantitatively accounted for, on the basis of the regular hexagonal model. These ideas seem to have been accepted, since without further examination of the coincidence question, most of the old arguments have in the past year been reversed (though with no increase in conclusiveness) in favour of the regular model (Kohlrausch, *Naturwiss.*, 1935, 23, 624; *Z. physikal. Chem.*, 1925, 30, B, 305; *Physikal. Z.*, 1936, 37, 58).

The coincidences, supposed or real, are assembled in Table I. The figures on the left are Krishnamurti's. Those on the right are taken from Parts III and IV, and a line is drawn to direct attention to a possible coincidence whenever the frequency difference is anywhere within 2—3 times the estimated total experimental error. The tendency is

therefore to include unreal coincidences rather than to exclude real ones; nevertheless, it must be pointed out that in many cases the agreement of the frequencies is very much closer than the allowed toleration. Evidently the newer work does not much affect the number of possible coincidences: a few of Krishnamurti's become excluded by the narrower limits of precision, but on the other hand, our more complete knowledge of the spectrum reveals several that are additional.

TABLE I.

Suggested Coincidences of Raman and Infra-red Frequencies of Benzene (cm.⁻¹).

No.	Krishnamurti.		Note.	Parts III and IV.			
	I.-red.	Raman.		I.-red (gas).	Raman.	I.-red (liquid).	Note.
1	—	—	—	—	606 <i>m</i> —	610 <i>f</i>	F.I.-red
2	694	687	Beyond error	671 <i>s</i>	685 <i>f</i>	671 <i>s</i>	Beyond error
3	—	—	*	793 <i>ff</i>	{ 781 <i>ff</i> —	773 <i>s</i>	F. Raman, F.I.-red
4	803	806	—	—	{ 802 <i>ff</i>	—	—
5	847	848	No I.-red band	—	849 <i>m</i> —	849 <i>s</i>	F.I.-red
6	971	976	Beyond error	962 <i>ff</i>	977 <i>ff</i>	—	—
7	—	—	—	—	992 <i>s</i> —	985 <i>f</i>	F.I.-red
8	1025	1029	F. Raman	1037 <i>s</i> —	1030 <i>f</i> —	1033 <i>s</i>	F. Raman
9	1183	1178	No I.-red band	—	1178 <i>m</i> —	1170 <i>s</i>	F.I.-red
10	—	—	—	—	1285 <i>ff</i> —	1298 <i>f</i>	F. Raman, F.I.-red
11	1379	1407	Beyond error	1377 <i>f</i>	1404 <i>f</i>	1381 <i>m</i>	Beyond error
12	1481	1477	F. Raman	1485 <i>s</i> —	1478 <i>f</i> —	1480 <i>s</i>	F. Raman
13	1587	1584	No I.-red band	—	1585 <i>m</i> —	1584 <i>s</i>	F.I.-red
14	1613	1603	*	1617 <i>f</i> —	1606 <i>m</i> —	1604 <i>s</i>	F.I.-red
15	—	—	*	2288 <i>f</i> —	2293 <i>f</i>	—	No I.-red band
16	—	—	—	—	2358 <i>ff</i> —	2356 <i>f</i>	F. Raman, F.I.-red
17	3040	3046	No. I.-red band	—	3047 <i>m</i>	—	*
18	3074	3063	*	3080 <i>s</i> —	3061 <i>s</i> —	3070 <i>s</i>	*

Notes.—Band intensities: *s*, strong; *m*, medium; *f*, faint; *ff*, very faint.

The comparisons of intensity are internal to each spectrum: there are no comparisons between different spectra.

F. Raman: Forbidden in Raman effect by selection rules for free molecule.

F.I.-red: Forbidden in infra-red spectrum by selection rules for free molecule.

* Coincidences noted for special consideration.

The most suggestive feature of Table I is that so many more coincidences are obtained by comparing the Raman frequencies with the infra-red frequencies of the liquid than with those of the vapour. We have seen (Part IV) that the infra-red spectrum of the liquid is distinguished from that of the vapour mainly through the circumstance that, although the liquid spectrum contains all the chief vapour bands, it exhibits also a considerable number of new bands. We now see that most of these extra bands correspond to the strong Raman frequencies.

It would therefore appear that the cohesive forces in the liquid substance deform the molecule sufficiently to cause a break-down of those selection rules which depend on the strict preservation of the symmetry of the equilibrium configuration of the molecule. This deformation leads to only slight frequency shifts, accompanied by a certain broadening of the bands, possibly because the distortions are largely random. In the infra-red spectrum, however, it leads notably to the rather strong appearance of bands which the selection rules forbid, and which are in fact absent from the gaseous spectrum. It seems striking that bands forbidden by the symmetry of the undeformed molecule should appear as strongly as most of them do, since the average deformation is expected to be slight. However, this is not more remarkable than the familiar fact that, in the infra-red spectrum, combination frequencies are often comparable in intensity with fundamentals, although the former may depend only on a small anharmonicity in the deformation potential of the molecule.

The Raman spectrum also is measured for the liquid, so that we may expect a reciprocal effect from the break-down of the selection rules, strong infra-red frequencies appearing in the Raman spectrum. Some of the strongest do indeed appear, but only very feebly. This result may be compared to the well-known greater purity of Raman than of infra-red

spectra with respect to fundamental vibrations : overtones and combination tones—in fact, all frequencies depending on the anharmonicity of the deformation potential—are notoriously weak in the Raman effect. It is because of the weakness with which the frequencies we assume to be forbidden appear in the Raman spectrum that we have not studied this spectrum for the vapour. One knows in advance what would happen : a few weak lines would disappear ; but as they were already very weak in the liquid spectrum, it would be hard to establish their disappearance with certainty in view of the difficulty of getting as dense photographs from the vapour as one can from the liquid.

Independent evidence of the lack of molecular symmetry in the liquid results from an inspection of the Raman depolarisation factors. In any vibration which is antisymmetric or degenerate to an element of symmetry, the polarisability, if it varies at all, must increase in some directions and decrease in others in such a way that the average for all directions is constant ; and, as Placzek's theory shows, the result of this condition is that the frequency, if active at all in the Raman spectrum, will be represented by a line with the depolarisation factor $6/7 = 0.86$. Now although our measurements of the depolarisation factors are not as precise as we could wish, they are quite accurate enough to show that most of the depolarised lines of benzene and hexadeuterobenzene have depolarisation factors which fall definitely below $6/7$: the values range from this value to 0.70. This shows that the molecular symmetry necessary for the balancing of the increases of polarisability against the decreases in antisymmetric and degenerate vibrations is not actually realised, and this again may be attributed to deformation by cohesion.

We expect then that, even if the molecule possesses a centre of symmetry in the undeformed state, deformation by cohesive forces in the liquid substance may give rise to the following coincidences : (a) Strong Raman frequencies may appear, perhaps strongly, in the liquid infra-red spectrum, but should be absent completely from the vapour spectrum. (b) Strong infra-red vapour frequencies can appear, though only feebly, in the Raman spectrum. (c) Frequencies which, according to the selection rules, are inactive in both the infra-red and the Raman spectrum may appear, perhaps strongly, in the liquid infra-red spectrum, feebly in the Raman spectrum, and not at all in the infra-red vapour spectrum. With these remarks we return to Table I.

Coincidences 1, 5, 7, 9, 13, and 14 (liquid) belong to class (a). As will be shown later, they are Raman fundamentals, and they appear in the liquid infra-red spectrum but not in the vapour spectrum. Attention may be directed to the Raman doublet (13, 14) which appears as a doublet with the same pair of frequencies in the liquid infra-red spectrum—whereas in hexadeuterobenzene the corresponding Raman frequency is single, and also single in the liquid infra-red spectrum. (The infra-red vapour band, 1617 cm.^{-1} , is distinct from the double band, $1584\text{—}1604 \text{ cm.}^{-1}$, which obscures it in the liquid spectrum.) Coincidences Nos. 8 and 12 are of type (b) : they represent infra-red fundamentals appearing weakly in the Raman spectrum of the liquid substance. Coincidences No. 3 (liquid), 10, and 16 belong to type (c), and represent frequencies which by the selection rules are inactive in both spectra. Krishnamurti's coincidences Nos. 2, 6, and 11 are rejected as involving too large an assumed error, and this leaves six coincidences (marked *) for special consideration. The two which involve frequencies of the infra-red liquid spectrum may be dealt with now.

No. 17. A coincidence here was suggested by Krishnamurti, and, although our work shows that there is no infra-red band of the right frequency in benzene vapour, we cannot make a corresponding assertion about the liquid. The fact is that the liquid band at 3070 cm.^{-1} is broad enough to cover 3047 cm.^{-1} , although a distinct frequency could not be measured in this neighbourhood. A coincidence is therefore possible, but it would only be one of type (a).

No. 18. The occurrence of the strong Raman frequency 3061 cm.^{-1} in the liquid infra-red spectrum would produce a coincidence of type (a). This may happen, without prejudice to the question as to whether the infra-red gas frequency 3080 cm.^{-1} is distinct—in which case it would still form the main constituent of the broad band at 3070 cm.^{-1} in the liquid.

We postpone the last stages of the discussion of Table I, and next set forth the corresponding observations on hexadeuterobenzene in Table II. There are only four co-

incidences with infra-red vapour frequencies, two fewer than in the case of benzene, and eleven with infra-red liquid frequencies, one fewer than with benzene.

TABLE II.

Suggested Coincidences of Raman and Infra-red Frequencies in Hexadeuterobenzene (cm.⁻¹).
(Data from Parts III and IV.)

No.	Note.	I.-red (gas).	Raman.	I.-red (liquid).	Note.
1	—	—	577 <i>m</i> —	581 <i>f</i>	F.I.-red
2	—	—	661 <i>m</i> —	662 <i>m</i>	F.I.-red
3	—	—	750 <i>ff</i> —	754 <i>m</i>	F. Raman, F.I.-red
4	—	—	867 <i>m</i> —	864 <i>m</i>	F.I.-red
5	—	—	945 <i>s</i> —	943 <i>m</i>	F.I.-red
6	—	—	976 <i>ff</i> —	979 <i>m</i>	F. Raman, F.I.-red
7	*	1009 <i>ff</i> —	1000 <i>f</i> —	1012 <i>f</i>	*
8	F. Raman	1333 <i>m</i> —	1327 <i>f</i> —	1332 <i>s</i>	F. Raman
9	F. Raman	1450 <i>m</i> —	1457 <i>f</i> —	1454 <i>s</i>	F. Raman
10	—	—	1559 <i>m</i> —	1552 <i>m</i>	F.I.-red
11	—	—	2264 <i>m</i>	—	*
12	*	2294 <i>s</i> —	2292 <i>s</i> —	2283 <i>s</i>	*

(Notes.—See Table I.)

Coincidences Nos. 1, 2, 4, 5, and 10 are of type (*a*); they are Raman fundamentals appearing in the infra-red liquid spectrum but not in the gaseous spectrum. Coincidences Nos. 8 and 9 belong to type (*b*); they represent prominent infra-red frequencies appearing weakly in the Raman spectrum of the liquid. Coincidences Nos. 3 and 6 are of type (*c*), and represent frequencies which the selection rules would exclude from both the Raman and the infra-red spectrum, but which the cohesive forces of the liquid allow to appear. The remaining coincidences, those marked with an asterisk, require special consideration, and we may deal immediately with the three which relate to the liquid infra-red frequencies.

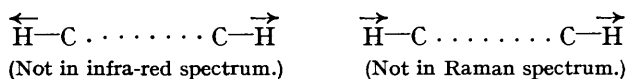
Coincidence No. 7 with the liquid infra-red frequency is in the same case as the corresponding coincidence with the gaseous frequency, and this is to be considered later. No. 11 is marked in the table because the liquid band at 2283 cm.⁻¹ overlaps the region 2264 cm.⁻¹: there may be a coincidence here, but if so, it will be of type (*a*). In No. 12 a coincidence of type (*a*) may occur between the Raman frequency, 2292 cm.⁻¹, and the liquid infra-red band, 2283 cm.⁻¹. This possibility does not prejudice the question, considered below, as to whether the gaseous infra-red frequency, 2294 cm.⁻¹, is distinct; if it is, it must still be the principal source of the liquid infra-red band 2283 cm.⁻¹.

It is now necessary to return to the four remaining benzene coincidences, all involving infra-red vapour frequencies, Nos. 4, 14, 15, and 18 of Table I. No. 4 relates to the weakest frequencies in both spectra, and has little importance. No. 15 is also weak in both spectra. No. 14 can be seen to be accidental on the internal evidence: the Raman frequency 1606 cm.⁻¹ is one peak of the doublet 1585–1606 cm.⁻¹, and this corresponds to the infra-red doublet 1584–1604 cm.⁻¹, which can have nothing to do with the single band at 1617 cm.⁻¹. Confirmation of the accidental character of all three coincidences Nos. 4, 14, and 15 follows from the circumstance that there are no coincidences in the hexadeuterobenzene spectra which could possibly correspond to them.

Two hexadeuterobenzene coincidences were reserved for further discussion, Nos. 7 and 12 of Table II. The approximate coincidence No. 7 need hardly have been counted, since each of the frequencies should be accurate to within ± 2 cm.⁻¹. However, the accidental character of the agreement is confirmed by the absence of any coincidence in the benzene spectra which could possibly correspond.

Thus we are left with the high-frequency coincidences for—benzene No. 18 of Table I, and for hexadeuterobenzene No. 12 of Table II—as the only coincidences which are not demonstrably accidental or due to the use of liquids. These coincidences certainly correspond, but they furnish no evidence on the question of the presence or absence of a centre of symmetry, because the high-frequency extreme of the spectral range of the fundamentals is the one position in this range where, whatever may be the symmetry of the molecule,

“accidental” coincidences are “bound” to occur. Thus although, in the presence of a centre of symmetry, the infra-red and Raman frequencies would have to represent different vibrations, they could never be separated by more than a few wave numbers for the following reason. These high-frequency vibrations depend substantially on the motion of hydrogen (protium or deuterium) atoms along the lines of their linkings. The different normal modes of vibration for which this is true differ essentially in the phase relations of the individual hydrogen motions. We may illustrate by means of the symmetric and antisymmetric vibrations of a pair of *p*-hydrogen atoms: if there is a centre of symmetry one phase relation renders the vibration inactive in the infra-red spectrum and hence possibly active in the Raman spectrum only, whilst the other makes the vibration inactive in the Raman spectrum and therefore possibly active in the infra-red spectrum only:



The phase relations are, of course, established by the interaction of the individual hydrogen motions through the connecting carbon ring. However, the coupling of such rapid vibrations through a structure whose natural deformation frequencies are all much smaller must obviously be weak. It follows that the phase relations cannot much affect the frequencies, so that in either of the cases illustrated the frequency of the normal mode will closely approximate to the hydrogen frequencies which would obtain in each separate C—H link in the absence of any coupling. Yet, in spite of the nearly equal frequencies, the vibration forms are radically different, and the selection rules exclude their frequencies from different spectra.

This completes our discussion of the Raman and infra-red coincidences of benzene and hexadeuterobenzene. The conclusion is that there is none which need convey any suggestion of the absence of a centre of symmetry from these molecules.

We have been much assisted in the development of these arguments by personal discussion with Dr. Placzek, and wish to thank him for his valued help.

UNIVERSITY COLLEGE, LONDON.

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