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IN a forthcoming article[1] on the Raman spectra of the deuterated benzenes, we discuss, *inter alia*, the problem of the origins of the four satellites of the 992 cm^{-1} Raman line in benzene. In view of the recent paper of Cheng, Hsueh and Wu[2] on the origin of one of these satellites, it is perhaps not amiss to give in this place a separate and briefer discussion of the question.

Let us state immediately our interpretation of these lines. Two of the components (denoted I and IV) are due to transitions from the first excited state of the E_g^+ vibration ν_6 to the two levels of the resonance doublet $E_g^+ : A_{1g} + E_g^+$ ($\nu_8 \approx \nu_1 + \nu_6$). The other two (II and V) are two totally symmetrical lines of the molecule $C_5{}^{12}C^{13}H_6$ derived from the frequencies ν_1 and ν_{12} in benzene. Quantitative predictions of the frequency and intensity of the satellites on the basis of this interpretation agree satisfactorily with the experimental data.

The positions of components I and IV can be calculated quite accurately from the differences in the observed frequencies of ν_6 and the resonance doublet. Using the data of Klit and Langseth[3] for the sake of consistency with later comparisons, we find $\bar{\nu}_I = 1585.9 - 606.4 = 979.5$ cm^{-1}; $\bar{\nu}_{IV} = 1604.2 - 606.4 = 997.8$ cm^{-1}. The sum of the intensities of I and IV should be given very closely by the product of the intensity of the main line, due to ν_1 (hereafter denoted by III), and the appropriate Boltzmann factor, namely $2 \times \exp(-hc\bar{\nu}_6/kT)$. The ratio of intensities, I_I/I_{IV}, should be the same as the ratio of the intensity of the *upper* component of the resonance doublet ($\bar{\nu} = 1604.2$) to that of the lower ($\bar{\nu} = 1585.9$), if one makes the assumption that polarizability change due to second order tones is negligible in comparison with that due to allowed fundamentals. The ratio is 0.84.[4]

Therefore the ratios I_I/I_{III} and I_{IV}/I_{III} should be 0.051 and 0.059, respectively, at room temperature.

Satellite II was first ascribed to $C_5{}^{12}C^{13}H_6$ by Gerlach.[5] His interpretation has been accepted by Cheng, Hsueh and Wu,[2] and on its basis they have calculated (by a perturbation method) that the frequency difference between II and III should be 6.3 cm^{-1}. This agrees closely with the shift of 6.2 cm^{-1} which one may compute in a simpler fashion (by calculating ν_1 for the hypothetical molecule $C_6{}^{12.167}H_6$, which should have the same value[6] as ν_1 in $C_5{}^{12}C^{13}H_6$). It does *not* agree, however, with the observed frequency shift, which, according to measurements made by one of us (A. L.), is 8.7 cm^{-1}.[7] The disagreement, which is beyond the limits of experimental error, may be attributed to the circumstance that the approximations which make calculation of the shift possible are not strictly valid because of the presence of a fundamental frequency, ν_{12}, in the immediate vicinity of ν_1. ν_{12} lies at about 1010 cm^{-1} in benzene[8] and should shift to *ca.* 1003 cm^{-1} in $C_5{}^{12}C^{13}H_6$.

If interaction between ν_1 and ν_{12} causes the observed depression of ν_1 by 2.4 cm^{-1} in $C_5{}^{12}C^{13}H_6$, ν_{12} should be raised by a like amount. A more noticeable result of the interaction should be the donation of Raman intensity to ν_{12}, thus enabling it to appear as a satellite (V) of ν_1 in benzene. The amount of intensity transferred from ν_1 to ν_{12} because of resonance interaction may be calculated in the usual fashion.[9] The intensity ratio of V to II will be:

$$I_V/I_{II} = (W - \Delta)/(W + \Delta). \qquad (1)$$

Here W is the actual frequency difference

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[1] Langseth and Lord, Kgl. Danske Vids. Selsk., Math.-fys. Medd. XVI (1938).

[2] Cheng, Hsueh and Wu, J. Chem. Phys. **6**, 8 (1938).

[3] Klit and Langseth, Nature **135**, 956 (1935).

[4] Angus, Ingold and Leckie, J. Chem. Soc. London 929 (1936).

[5] Gerlach, Sitz. Math.-Nat. Bayer. Akad. München, 39 (1932).

[6] Cf. Teller, *Hand und Jahrbuch der chemische Physik*, Vol. 9, pp. 142 ff.

[7] In reference 2 the observed value of the shift appears to be 8.2 cm^{-1} from the accurate frequency values printed at the top of Fig. 1.

[8] Klit and Langseth, J. Chem. Phys. **5**, 925 (1937).

[9] See Placzek, *Handbuch der Radiologie*, Vol. 7, Part 2, p. 321.

between V and II, and Δ is the value this difference would have if there were no interaction between ν_1 and ν_{12}. $(W-\Delta)$ is therefore the increased separation of ν_1 from ν_{12} due to interaction, namely 2×2.4, or 4.8 cm^{-1}. From this value of $(W-\Delta)$ and the observed value of W (21.7 cm^{-1}), the ratio (1) is found to be 0.12. The total intensity of II and V should be very nearly that of III save for the rarity of $C_5{}^{12}C^{13}H_6$ molecules. There are about six of the latter in every hundred molecules of benzene. Therefore $I_{II}/I_{III}=0.0536$, and $I_V/I_{III}=0.0064$.

The foregoing frequencies and intensities have been assembled in Table I together with unpublished experimental data obtained by one of us (A. L.) in 1931, and with the frequencies given by Angus, Ingold and Leckie[4] in their summary of the Raman data on benzene. The observed intensities in column 5 are visual estimates (made in 1931) and are not to be considered of more than semi-quantitative significance. The fact remains, however, that component I is decidedly less intense than II, although the calculation assigns them almost equal intensity. This discrepancy is perhaps due to neglect of the effect of second-order polarizability changes in computing I_I/I_{IV}. With this one exception, the interpretation fits the observed facts very well. The methods we have used to compute intensity ratios lead also to the conclusion that all the satellites should have the same depolarization factor as ν_1, namely $\rho=0.09$. This agrees at least qualitatively with reference 2, which sets an upper limit, $\rho=0.4$, for component II.

The fine structure expected for ν_1 in benzene-d_6 is simpler than that in benzene. ν_8 appears in benzene-d_6 as a single line only, and therefore a satellite due to $\nu_8-\nu_6$ should be lacking, since

TABLE I. *Fine structure of ν_1 in benzene.*

	FREQUENCY OF COMPONENTS IN CM^{-1}			INTENSITY OF COMPONENTS		
	OBSERVED			OBSERVED		
No.	LANG-SETH	SUMMARY[4]	CALC.	LANG-SETH	REF. 2	CALC.
I	979.6	979	979.5	5	—	5.1
II	983.8	984	986.2	10	6	5.4
III	992.5	992	(992.5)	100	100	(100)
IV	997.9	999	997.8	10	—	5.9
V	1005.5	1005	ca. 1003	1	—	0.6

TABLE II. *Fine structure of ν_1 in benzene-d_6.*

	FREQUENCY OF COMPONENTS IN CM^{-1}		INTENSITY OF COMPONENTS	
No.	OBSERVED	CALCULATED	OBSERVED	CALCULATED
I	939.5	940.2	10	5.8
II	945.2	(945.2)	(100)	(100)
III	962.1	ca. 960	0.1	0.2

the product of the Boltzmann factor (0.1) and the intensity expected of combination tones (<0.01) is overwhelmingly small. The component $(\nu_1+\nu_6)-\nu_6$ should coincide with ν_1.

The calculated shift of ν_1 in $C_5{}^{12}C^{13}D_6$ is 5.0 cm^{-1}, and the observed one 5.7. Here the difference is more readily ascribable to experimental error than in benzene, but if we attribute all of it to interaction with ν_{12}, we may compute the intensity ratio of ν_{12} to ν_1 in $C_5{}^{12}C^{13}D_6$ as 0.03, i.e. ν_{12} should have only about $\frac{1}{4}$ the relative intensity of satellite V in benzene. ν_{12} should be higher than ν_1 by very nearly the same amount as in benzene, and therefore should lie in the neighborhood of 960 cm^{-1}. Actually there is an extremely faint line at 962 cm^{-1}, but its assignment is not entirely conclusive, because it is known[8] that both ortho- and parabenzene-d_4 have their strongest lines at this point (at 960.0 ± 0.4 cm^{-1}) and it is conceivable that the extended exposures which revealed the line may have been able to record the benzene-d_4 frequencies even though their total concentration was probably less than 0.02 percent. That the line may actually be ν_{12} is given some support by the failure to observe the strongest frequency of metabenzene-d_4 at 954 cm^{-1}. This frequency should appear with not less than half the intensity of the 962 line if the latter is really due to the other benzene-d_4's.

The fine structure data on benzene-d_6, hitherto unpublished, are summarized in Table II. Not included in the table are two very faint lines, observed at 950.7 and 977.3 cm^{-1}, which belong to benzene-d_5,[8] and which are not to be expected in hydrogen-free benzene-d_6. The latter of these lines has also been reported by Angus, Ingold and Leckie.[4] The difference tone $\nu_8-\nu_6$ should lie in this neighborhood (at *ca.* 975 cm^{-1}), but, for reasons just given, should not be expected to make its appearance.