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The Near Ultraviolet Absorption Spectrum of Monodeuterobenzene

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The analysis of the ultraviolet absorption spectrum of monodeuterobenzene has been given. The spectrum is, as in benzene, a forbidden transition which is made allowed by the 603 vibration corresponding to the 606 ϵ^+_g benzene vibration. The 0,0 band is calculated to be 38,124, and it occurs with extreme weakness.

INTRODUCTION

THE near ultraviolet absorption spectrum of monodeuterobenzene lies in the same region as that of benzene.[1,2] This 2300–2650A region has been measured and the analysis of the bands made with the notation of light benzene.[3]

EXPERIMENTAL

The monodeuterobenzene was a sample prepared by Dr. F. A. Miller and Dr. R. C. Lord, Jr., of The Johns Hopkins University. It was introduced into the absorption cell in air and then the cell was pumped out, with two liquid-air traps arranged so as to avoid impurities from the pump. The spectra showed the presence of some light benzene, the percentage of which was roughly estimated from intensities to be about 15 percent. The light benzene lines can be seen clearly in Fig. 1, which represents the first weak

group of both spectra. Figure 2 shows the gradual appearance of the monodeuterobenzene spectrum with pressure. All spectra were taken with the side arm of the absorption cell in a temperature bath, varying from 25°C to −70°C, while the main part of this quartz absorption cell of 50-cm length was at room temperature. A 5-meter concave aluminized grating, in the first order, with a dispersion of about 3.4A per mm was used. The same all-quartz discharge tube was used under the same conditions as in previous work.[1]

RESULTS

Table I contains the frequencies of the measured band-edges together with the intensities and assignments. The intensities are visual estimates from a plate with vapor pressure varying (in nine equal steps between the above temperatures), the number denoting that exposure at which the band is first visible. Broadness of bands, edge variance with vapor density, and differing microscope magnification contribute to the error in measurement. The main bands, given to tenths of cm^{-1} and measured under high magnification, are probably correct within one or two cm^{-1}. Other bands are somewhat less accurate.

[1] W. F. Radle and C. A. Beck, J. Chem. Phys. 8, 507 (1940) (light benzene).

[2] H. Sponer, J. Chem. Phys. 8, 705 (1940) (heavy benzene).

[3] H. Sponer, G. Nordheim, A. L. Sklar, and E. Teller, J. Chem. Phys. 7, 207 (1939).

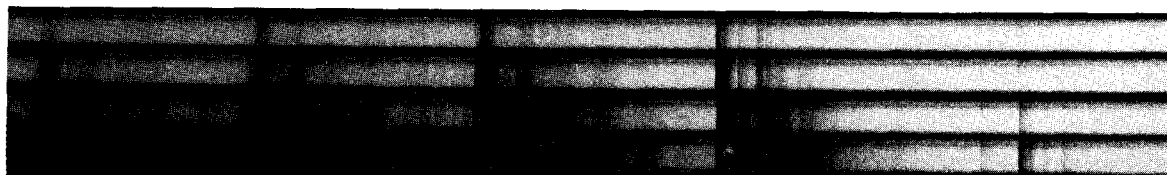Fig. 1. Comparison of first weak group in light and monodeuterobenzene.
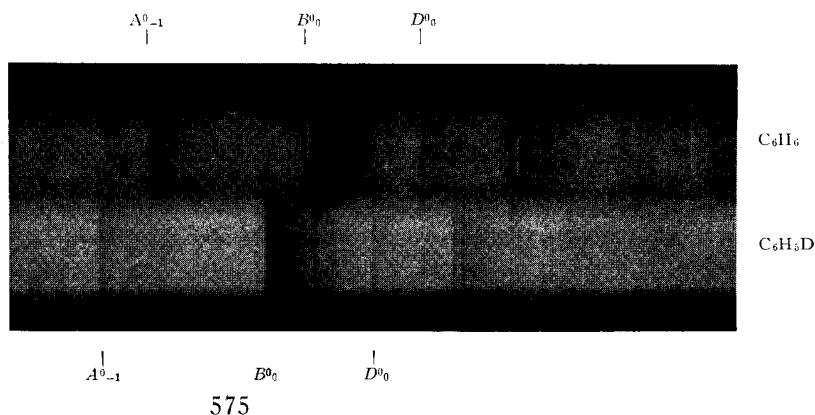
FIG. 2. Absorption spectrum of monodeuterobenzene at different pressures.

An effort was made to remove all light benzene lines from the table but some weak lines may have remained unnoticed. The table does not represent a complete list of all the other bands measured in monodeuterobenzene. Some 60 weak and very weak bands which were measured still less accurately are not included in Table I.

The spectrum resembles very much that of light benzene, as should be expected, but the appearance of the spectrograms is somewhat complicated by the simultaneous presence of C_6H_5D and C_6H_6.

ANALYSIS

The analysis of the monodeuterobenzene spectrum should be particularly interesting. Although the substitution of a light by a heavy hydrogen atom reduces formally the symmetry D_{6h} to C_{2v}, the electronic configuration of the benzene molecule remains unchanged. We would, therefore, expect the characteristic features of the benzene spectrum to show up unaltered in the monodeuterated compound. These features include the appearance of bands representing the 0–1 and 1–0 transitions ($A^0{}_0$ and $B^0{}_0$, respectively) of the 606 vibration which made the benzene spectrum allowed, and superimposed progressions of totally symmetrical vibrations and v–v transitions of non-totally symmetrical vibrations. The 0,0 band should not occur in a forbidden transition. However, since we do have the substitution, we actually have a very slight deviation from the benzene case which will result in a very slight perturbation. Although extremely small, it may be just sufficient to bring out the 0,0 band. We should then expect superimposed very faintly on this 0,0 band the features of the allowed C_{2v} transition.

The pure vibrational spectra of benzene and monodeuterobenzene should, contrary to the ultraviolet absorption spectra, be different from each other, one representing the selection rules for D_{6h} symmetry and the other one for C_{2v} symmetry because here the different masses are essential to the symmetry type. This has actually been found from Raman[4] and infra-red[5] investigations. Turning back to the ultraviolet absorption we then have the situation that vibrations resulting from C_{2v} symmetry will occur in the electronic spectrum which is caused by the molecule's electronic behavior almost completely according to D_{6h} symmetry. For example, the totally symmetrical carbon vibration of 981 cm^{-1} (992 in benzene) should represent all strong progressions. Other vibrations which are totally symmetrical only for C_{2v} and not for D_{6h} symmetry may occur, although with much less intensity. We expect especially carbon vibrations.

In analyzing the spectrum we then have a twofold task: to interpret the main part of the spectrum as coming from a forbidden transition $A_{1g} \rightarrow B_{2u}$ as in benzene with a vibrational structure analogous to that in benzene, but with additional probably fainter bands resulting from the vibrational C_{2v} symmetry of the monodeuterobenzene. Secondly, we must search for the possible appearance of a weak 0,0 transition, on which may be superimposed very faint bands with the characteristics of the allowed C_{2v} electronic transition. Finally, a comparison of this spectrum with the spectra of the monohalogenated benzenes should prove very interesting.

Proceeding now with the actual analysis we first note that the monodeuterobenzene has a great number of weak bands, possibly more so than the spectra of light and heavy benzene.

[4] A. Langseth and R. C. Lord, Danske Vidensk. Selskab. Math. Fys. Meddelel. **16**, No. 6 (1938); K. W. F. Kohlrausch, Phys. Zeits. **37**, 58 (1936); C. K. Ingold and collaborators, J. Chem. Soc. (1936), p. 925, p. 971.

[5] C. R. Bailey, J. B. Hale, C. K. Ingold, and J. N. Thompson, J. Chem. Soc. (1936), p. 931, p. 971.

This is in accordance with our theoretical expectations.

In analogy to benzene we interpret the band at 38,640.8 cm^{-1} as A^0_0. This band appears to consist mainly of one very strong component and the short edge of this was measured for rather low vapor pressure. Here, as in all cases, an effort was made to have a narrow region of light appear between the cross-hair and the short wave-length edge of the bands, which degrade to the red. The B^0_0 band probably consists of two components, and we have chosen the very strong component at 37,520.8 cm^{-1}. The component of longer wavelength which is very weak is not included in the table. A band at 37,529 could possibly belong to B^0_0, although A^0_0 has no corresponding band.

Just as in benzene, the difference between A^0_0 and B^0_0, namely, 1120 cm^{-1}, is the sum of the value of the same vibration in the ground and upper electronic states, which vibration makes the transition allowed. Similarly, the bands at 38,554.7 and 37,433.5 were interpreted as C^0_0 and D^0_0 according to 1-1 transitions of the same vibration superimposed on the A^0_0 and B^0_0 bands. The C^0_0 appears to be single while the D^0_0 appears somewhat like B^0_0. Choosing the strong component of D^0_0 (the very weak one is not included in the table) for the calculation of the drop in the discussed frequency, we obtain 87 cm^{-1}. Comparing this with the A^0_0 to C^0_0 distance, we obtain an average of 86.5. This together with the 1120 as the sum of the frequencies yields 603.2 cm^{-1} for the lower state and 516.7 cm^{-1} for the upper state of this particular vibration. We will use 603 and 517 as values, which gives 86 cm^{-1} for their difference. The 603 cm^{-1} compares well with the Raman[4] effect where 602 cm^{-1} has been observed. A difference of 88 cm^{-1} occurs in light benzene,[6] while it decreases to 82 cm^{-1} in heavy benzene. The 0,0 band can then be computed as 38,124. A pair of very faint bands appears at 38,123/38,124.5, which we are inclined to identify with the 0,0 band. We assume that the occurrence of this band is caused by the very slight deviation from the D_{6h} symmetry, in agreement with the theoretical considerations. No such band was observed in heavy benzene and its occurrence was

very doubtful in light benzene. We estimate very roughly that the 0,0 band is about 10³ times weaker than the A^0_0.

The 603 frequency which makes the transition allowed represents in benzene an ϵ^+_g vibration (value 606 cm^{-1}). In monodeuterobenzene, this splits into a β_1 and α_1 vibration, the first one being non-totally symmetrical, and the second one being totally symmetrical. As follows from the motion during this vibration, the β_1 keeps about the same value as the 606 vibration in benzene, whereas the α_1 is diminished in value. This effect is very pronounced if the substituent is of a heavy mass as in the halogenated benzenes (e.g., in C_6H_5Cl the β_1 is 611 and the α_1 is 416). It seems that in the A^0_0 and B^0_0 we observe mainly the non-totally symmetrical component. The totally symmetrical α_1 component is known from the Raman effect to be 598.5. It could occur according to the vibrational symmetries, also, although very faintly, superimposed on the 0,0 band. Because of the closeness of the values of the α_1 and β_1, the observance of the α_1 might be difficult, but a comparison between the corresponding bands of the three compounds shows that the bands in all three cases are so very much alike, that one may conclude from this that the α_1 component does not show up with appreciable intensity.

The totally symmetrical carbon vibration in the upper state which was 923 in light benzene and 879 in heavy benzene causes in monodeuterobenzene progressions with separations of 920 cm^{-1}. The first member is at 39,561 of which the violet edge was taken for the measurement. Corresponding progressions appear superimposed on B^0_0, C^0_0, and D^0_0 as can be seen from Table I. The vibration appears superimposed on these as well as on bands not yet mentioned. Since we interpreted the occurrence of the very weak 0,0 band as being caused by a very slight perturbation of the D_{6h} symmetry, we might expect bands of about the same very weak intensity resulting from excitations of the 920 vibration superimposed on the 0,0 vibration. There is indeed an indication of such a band at the right position. Of course there is always a possibility of explaining very weak bands by high Boltzmann factors, so that it is safer not to give any definite explanations of such bands.

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[6] A difference of 86 cm^{-1} has been reported in reference 3, but later measurements suggest 88 cm^{-1} as best value; see also the last paragraph of this article.

TABLE I.

6	42116}	$A'^0_1 = A'^0_0 + 920$	6	39241}	$A^2_1 = A^2_0 + 920$
	42108}		6	39228}	
7 L ?	42087		6	39221	
6	41770		7	39116.7	$G^0_0 = A^0_0 + 2\times240$
	41427		6	39090.6	
6br	41408}	$A^0_3 = A^0_0 + 3\times920$ E^0_2 ?	w	39077	$0,0 + 953$
7br	41393}		5	39068	
6	41205		6	39059	
7	41196	$A'^0_0 = A^0_0 + 2555$	5	39022	
6 L ?	41164		4	38963}	
6br	41111	$C'^0_0 = C^0_0 + 2555$	6	38958}	$G^1_0 = G^0_0 - 160$
6br	41083		6	38938	
6br	41040	$A'^1_0 = A'^0_0 - 160$	4	38913	
6	40998}	$B'^0_1 = B'^0_0 + 920$	4	38891	
6	40986}		4br	38869	
6	40949	$C'^1_0 = C'^0_0 - 160$	4	38799	$G^2_0 = G^0_0 - 2\times160$
6	40918		4	38733	
5	40836	$B'^1_1 = B'^1_0 + 920$	4	38688	
6	40729		10	38640.8	$A^0_0 = 0,0 + 517$
6	40718		7	38598	
6	40597		6	38583	
7	40520.6		8	38554.7	$C^0_0 = A^0_0 - 86$
7	40506.6		7	38504.1	$K^0_0 = A^0_0 - 136$
8	40489.6	$E^0_1 = E^0_0 + 920$	5	38496	
8	40480.7}	$A^0_2 = A^0_0 + 2\times920$	8	38487.8}	$A^1_0 = A^0_0 - 160$
8	40472.5}		8	38480.1}	$B^0_1 = B^0_0 + 920$
br	40390	$C^0_2 = C^0_0 + 2\times920$?	7	38443.0}	
6 L ?	40373		6	38433.7}	
6	40340	$E^1_1 = E^1_0 + 920$? $K^0_2 = K^0_0 + 2\times920$	7	38421.8}	
6	40322}		7	38413.2}	$M^0_0 = A^0_0 - 227$
6br	40311}	$A^1_2 = A^0_2 - 160$	6	38399}	
6	40288		7br	38395}	$C^1_0 = C^0_0 - 160$
6 L ?	40252	sup. $M^0_2 = M^0_0 + 2\times920$	7	38374.5	
5 L ?	40108		5 L ?	38352	$D^0_1 = D^0_0 + 920$
7	40077	$B'^0_0 = B^0_0 + 2555$	6 L ?	38343	$K^1_0 = K^0_0 - 160$
6	40039}	$G^0_1 = G^0_0 + 920$	7	38335	
5	40027}		7	38326.8}	$A^2_0 = A^0_0 + 2\times160$
7	40019		7	38320.8}	
6 L ?	40011		7	38300.8	$L^0_1 = L^0_0 + 912$? $O^0_0 = A^0_0 - 338$
5	39964		6 L ?	38284}	
5br	39917	$B'^1_0 = B'^0_0 - 160$	5	38275}	$B^1_1 = B^1_0 + 920$
5	39894		5	38256	$M^1_0 = M^0_0 - 160$
4	39878}	$G^1_1 = G^0_1 + 920$	5br	38235	$C^2_0 = C^0_0 - 2\times160$
5	39867}		5	38227	
7	39808.0		5	38215	$N^0_1 = N^0_0 + 920$
3	39788		5	38210	
6	39743		5	38196	
5	39675		5	38183	$D^1_1 = D^0_1 - 160$; K^2_0 ?
5br	39650		5	38174	
7	39622		5	38165	
7	39595.7	$A^0_0 + 955$?; $0,0 + 1472$	w	38161	$A^3_0 = A^0_0 - 3\times160$
	39592		4	38156	
8	39581.3}	$E^0_0 = 0,0 + 1458$	4	38142	$O^1_0 = O^0_0 - 160$
8	39571 }	$0,0 + 1448$	4	38130	
9	39561.1}	$A^0_1 = A^0_0 + 920$	v.w.	38125}	$0,0$
9	39552.7}			38123	
7	39473}	$C^0_1 = C^0_0 + 920$		38118}	$B^2_1 = B^2_0 + 920$
7	39466}		5	38114}	
5	39437	$39596 - 160$	3	38108	$P^0_1 = P^0_0 + 920$
8	39419.6	$E^0_1 = E^0_0 - 160$	5br	38059	
7	39401.4}	$A^1_1 = A^0_1 - 160$	4	38036	
7	39392.6}		2	38020	
7	39364	$B^0_2 = B^0_0 + 2\times920$?	3	38013	
6	39343		4	38006}	
L	39331	sup. $M^0_1 = M^0_0 + 920$	4	37997}	$A^4_0 = A^0_0 - 4\times160$
	(39307)	$C^1_1 = C^0_1 - 160$?	4	37982	$O^2_0 = O^0_0 - 2\times160$
6 L ?	39288		2	37975	
6 L ?	39271	$D^0_2 = D^0_0 + 2\times920$	4	37971	
6 L ?	39263	$E^2_0 = E^0_0 - 2\times160$?			
6 L ?	39256				

TABLE I.—*Continued.*

3	37969⎱			5	37529	
4	37961⎰	$H^0 = 0,0 - 160$?		7	37520	$B^0_0 = 0,0 - 603$
4	37948			2	37454	
2br	37914			2	37442	
4	37896	$0,0 - 227$		6	37433.5	$D^0_0 = B^0_0 - 87$
2	37884			4	37387	$L^0_0 = B^0_0 - 134$
2	37860			1	37381	
2	37851			1	37375	
2	37844			6	37367.8⎱	
3	37828			6	37360.7⎰	$B^1_0 = B^0_0 - 160$
3br	37820			4	37346	$D' = D^0_0 - 87$
3	37801	$H^1 = H^0 - 160$		4	37328	
3	37796			4	37295	$N^0_0 = B^0_0 - 226$
3	37788			4	37280⎱	
3	37767			4	37275⎰	$D^1_0 = D^0_0 - 160$
3	37739			3	37270	
3	37700			4	37256	
2	37677			w	37226	$L^1_0 = L^0_0 - 160$
2br	37668			4	37207⎱	
6	37659	$A^0_{-1} = A^0_0 - 981$		4	37201⎰	$B^2_0 = B^0_0 - 2 \times 160$
3	37636			4	37185	$P^0_0 = B^0_0 - 338$
4	37630			3	37134	$N^1_0 = N^0_0 - 160$
2	37604			2	37119	
4	37578			w	37046⎱	
2br	37564			w	37041⎰	$B^3_0 = B^0_0 - 3 \times 160$
				1w	37026	$P^1_0 = P^0_0 - 160$

L means light benzene.

The 1008 vibration which is a β_{1u} in benzene and becomes totally symmetrical in monodeuterobenzene may be found to occur extremely weakly, if at all, superimposed on the A^0_0 and B^0_0 bands. It also, just as the 920 vibration, may occur in connection with the 0,0 band. From a careful search of the spectrum and a rough estimate of the percentual drop of this vibration we conclude that bands in the region of 39,590 may be associated with the superposition of this vibration on A^0_0, particularly the one at 39,595. This would give a frequency value of 955 cm^{-1} in the upper state. The band might, however, have another explanation or might represent the superposition of two different transitions. A faint band may be ascribed to a twofold excitation of 955 cm^{-1}. However, no definite evidence could be found for the occurrence of 955 superimposed on the B^0_0, which may be expected from the foregoing. A very weak band at 39,077 fits the assignment of 0,0+953.

The 160 progression of light benzene seems to occur unaltered in value in monodeuterobenzene. The appearance of the bands, however, is different. While in light benzene the B^1_0 has the same appearance as the B^0_0 (namely, a strong red component and a faint violet companion not quite 6 cm^{-1} apart) and the A^1_0 has two components of about equal intensity 4 cm^{-1} apart, in monodeuterobenzene there appear always two bands of about the same intensity, about 8 cm^{-1} apart from each other. It is quite possible that this doublet character of the 160 series comes from a splitting of the corresponding degenerate ϵ^+_u vibration in benzene, although one might expect that such a splitting would probably produce more diffuse bands on account of the overlapping of the components.

The H series, which in light benzene owes its existence to an excitation of an ϵ^+_u vibration in both the ground and excited states, occurs also in the spectrum of monodeuterobenzene, as can be seen in Table I. So does the G series which is an example of a 0–2 transition of this ϵ^+_u vibration superimposed on A^0_0.

The bands at 39,571 and 39,581 resemble bands in light benzene at 39,561 and 39,569 which have been called the first member of an E series arising from the excitation of the other ϵ^+_g vibration of 1596 cm^{-1} in the ground state. There appear in heavy benzene two bands at 39,693 and 39,706 which were taken as the first member of a similar E series, but it was pointed out that the larger distance of 13 cm^{-1} and particularly the larger drop of the ϵ^+_g vibration in heavy benzene made the explanation somewhat doubtful. In

TABLE II. The positions of the 0,0, $A^0{}_0$, and $B^0{}_0$ transitions for C_6H_6, C_6H_5D, and C_6D_6.

	C_6H_6	C_6H_5D	C_6D_6
0,0	38,090(calc.)	38,123.8	38,292(calc.)
$A^0{}_0$	38,610	38,641	38,790
$B^0{}_0$	37,482	37,521	37,712

monodeuterobenzene the bands are 10 cm^{-1} apart and the drop would be between those in the other two benzenes, but nearer to light benzene. The comparison of the E bands in all three benzenes makes the proposed explanation still seem to be the best, although it is not certain. We have bracketed the bands in the table but it is quite possible that only one of them qualifies for the proposed explanation. If we accept it for one or both bands we should expect, just as for the 606 vibration, a splitting of the 1596 into a totally symmetrical α_1 and a non-totally symmetrical β_1 component which give rise to a more complicated appearance of the E bands in the mono-compound. It is not probable that such a splitting occurs; there are two bands at 39,539 and 39,553 which fall in the $A^0{}_1$ region and might be taken as the pair belonging to the second component, but since we could not detect any indication of a splitting in the A and B bands, we hesitate to assume it for the E bands. We have not found any conclusive evidence for the occurrence of the totally symmetrical component of 1594 in the ground state and that of the non-totally symmetrical component of 1576 is very uncertain because it would coincide with $B^0{}_{-1}$.

Bands at 38,413/422 and 37,295 can be considered analogous to the bands $M^0{}_0$ and $N^0{}_0$ in heavy benzene. The separation of the $M^0{}_0$ and $N^0{}_0$ from the $A^0{}_0$ and $B^0{}_0$ was 202 cm^{-1} in heavy, 263 cm^{-1} in light benzene, and is 227 in mono-deuterobenzene. The origin of these bands has been discussed previously[2] and it was pointed out that the occurrence of bands displaced by 207 and 263, respectively, from the 0,0 bands may indicate a square combination of symmetry $\epsilon^+{}_g$ for these bands. In monodeuterobenzene there occurs correspondingly a band displaced from the 0,0 band by 227 cm^{-1} toward longer waves, namely at 37,896 cm^{-1}. If we take this fact as support of the above-mentioned proposition and

if, from intensity considerations and in analogy to the benzenes, we estimate the Boltmann factor of $M^0{}_0$ as being of the same magnitude as that of $D^1{}_0$, we may conclude that H vibrations of about 700–800 cm^{-1} are involved in these bands. The $\epsilon^-{}_g$ and $\epsilon^+{}_u$ vibrations were proposed previously as possibilities. No further decision, even with our additional data, can be given, however. The 920 progression and the difference of 160 appear superimposed on both the $M^0{}_0$ and $N^0{}_0$ bands.

In heavy benzene the letters $K^0{}_0$ and $L^0{}_0$ were assigned to bands which appear midway between $C^0{}_0$ and $A^1{}_0$, and $D^0{}_0$ and $B^1{}_0$, respectively. Their distances from $C^0{}_0$ and $D^0{}_0$ were 113 cm^{-1}. Light benzene showed no analogous bands of comparable intensity. In monodeuterobenzene we have found bands displaced from $C^0{}_0$ and $D^0{}_0$ by 135 cm^{-1} to the red. Their intensity is definitely smaller than that of the corresponding heavy benzene bands. It seems obvious that the bands represent 1–1 transitions but we are not able to assign them to a definite vibration. The superimposed 920 and 160 progressions do not stand out clearly because of some overlapping.

The totally symmetrical H vibration which was found to be 2565 cm^{-1} in the upper state of C_6H_6 obviously occurs also in monodeuterobenzene in the band at 41,196 with a value of 2555 cm^{-1}. It also occurs superimposed on $B^0{}_0$ and $C^0{}_0$. It is not possible to identify the totally symmetrical D vibration. The band in which it could occur in the ground state must be too weak for detection and as for the upper state there are too many bands which could be explained with the help of this vibration.

Finally, a few words may be said about the fine structure of the bands. As in the benzenes many bands appear to be double-headed. (The doublet character of the 160 series has probably a different cause and has been mentioned before.) We have taken here for the calculations the strong head. For the $A^0{}_0$ and $C^0{}_0$ bands this is the only measured edge, as also for $B^0{}_0$ and $D^0{}_0$. In the 920 progression of the A bands it is always the violet head if the two adjacent bands (for example, $A^0{}_1$, 39,553 and 39,561) constitute one band. The 920 progression of the B bands looks single. In this way our scheme of differences and frequency values was obtained. It is very

doubtful whether the faint companions on the violet side of the B^0_0 and D^0_0, 37,529 and 37,442, respectively, really are parts of these bands. We are inclined to believe that they are not, and we would like in this connection to take this question up again for the light benzene.

For C_6H_6 it had been tentatively suggested[3] to consider the corresponding strong red and weak violet bands of B^0_0, D^0_0, C^0_0 as R and Q branches of one band. The single nature of A^0_0 was explained by assuming that the strong absorption masked the structure and that the separation of 6 cm^{-1} found in the other bands between the R and Q bands, must be subtracted from the measured A^0_0 edge to obtain consistent numerical relations. The calculations were based on the measured value of 38,614.7 cm^{-1} of A^0_0. Since then it has been found in heavy benzene that a consistent scheme of relations and frequency values could be obtained by using always the strong edges and the present investigation yields the same result for monodeuterobenzene. Moreover, a remeasuring of the benzene bands changed the value of 38,614.7 for A^0_0 to 38,610.7 cm^{-1} so that the formerly obtained numerical relations do not come out consistently any more. This means that the difference between the values of the 606 ϵ^+_g vibration in the ground and excited states as calculated from the distance $A^0_0 - B^0_0$ and from the known Raman value of 606 does not agree any more so closely with the distances $A^0_0 - C^0_0$ or $B^0_0 - D^0_0$. In fact, this close agreement is gone whether we subtract 6 cm^{-1} or not. Measurements of the bands with high dispersion* seem also to furnish doubt that the previous procedure of subtracting 6 cm^{-1} from the A^0_0 edge when making calculations is valid.

From the remeasured bands the 86 cm^{-1} difference becomes rather 88 cm^{-1}. The present small discrepancies would disappear if the value of the ϵ^+_g vibration in question were 608 instead of 606 cm^{-1}. The Raman frequency of 606 seems, however, well established. Another possibility is that the A^0_0 is still 2 cm^{-1} too high, although we feel this is a remote possibility only. It is, of course, always difficult to make sure that the edges of the bands are measured at a comparable "appearance pressure." With increasing pressure the bands broaden and the edges move a little toward the violet. Finally it is also possible that a slightly different structure of A^0_0 and B^0_0 could account for the deviations. Only from measurements with high dispersion may further information be expected.