The Far Ultraviolet Absorption Spectra and Ionization Potentials of C6H6 and C6D6

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The absorption spectra of C_6H_6 and C_6D_6 have been photographed under high dispersion in the region 2000–1000A. The spectra of both substances are very similar. A strong continuous absorption starts fairly sharply around 1840A and gradually weakens out to zero at 1600A. It is followed by a region extending down to about 1360A which contains very strong sharp bands. The strongest of these bands only suffer small shifts to the violet in going from C_6H_6 to C_6D_6. This shift which is due to the change in the difference of zero-point energy between the normal and the excited states reveals the bands to be vibrationless electronic transitions. It was found that these bands could be arranged into two Rydberg series which had approximately the same limit corresponding to an ionization potential of $9.190\pm.005$ volts for C_6H_6. The ionization potential of C_6D_6 is only about 3×10^{-4} volts greater than that for C_6H_6. All the electronic states are split up into patterns which are believed to be caused by true electronic multiplicity. The excitation is apparently from a nonbonding electron more strongly attached to the carbon atom. The vibrations which accompany the bands are comparatively weak. However for C_6H_6 the following vibration frequencies associated with the excited states were observed. $\omega_1=677$ cm^{-1}, $\omega_2=968$ cm^{-1}. These become 630 and 926 cm^{-1} for C_6D_6. Tentative assignments of their modes of vibration are made. The bands below 1360A are considerably more diffuse than those previously mentioned and the isotopic shifts to the violet are much larger for these bands. However they are still believed to be vibrationless electronic transitions though they are due to the excitation of an electron which is considerably more bonding than that corresponding to the first ionization potential. A consideration of them enables the approximate value $11.7\pm.3$ volts to be predicted for the second ionization potential of benzene.

R ECENT investigations[1] have shown that the absorption spectra of many polyatomic molecules in the far ultraviolet are comparatively simple. This is especially so when the excitation is that of a nonbonding electron. In such cases very strong bands are obtained which can usually be ascribed as due to vibrationless electronic transitions. These can frequently be fitted into Rydberg formulas the limit of which gives a very accurate value for the ionization potential of the molecule. The general appear-

ance of such a spectrum, if predissociation does not interfere with it is as follows. At the long wavelength end the bands are strong and well separated. As we go to shorter wavelengths the bands become weaker and closer together, eventually converging to a limit from which a continuous absorption starts. This represents the ionization of the molecule. In the case of a nonbonding electron (cp. the methyl halides H_2S etc.) the vibration transitions accompanying the main electronic transitions are very weak. In cases where the excited electron plays some part in the bond (cp. C_2H_2 and C_2H_4) then the accompanying vibration bands are of the same

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[1] W. C. Price, Phys. Rev. **47**, 444 (1935); J. Chem. Phys. **3**, 256 (1935).
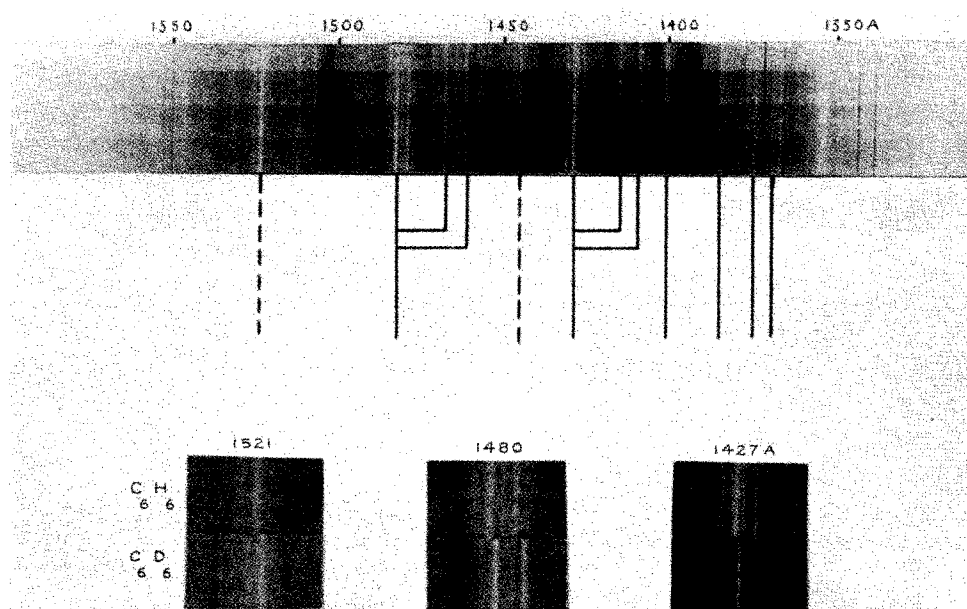
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FIG. 1. The far ultraviolet absorption spectrum of benzene.

order of intensity as the band corresponding to the main electronic transition. The absorption coefficients of bands of the type described above are enormously greater than those for visible or near ultraviolet bands as they correspond to electronic transitions of the highest probability. Most of the bands can usually be obtained with pressures of the order 0.01 to 0.1 mm in an absorbing column of about a meter. It may be remarked here that the first few absorption spectra observed in this region (i.e., the Dieke and Hopfield bands in hydrogen and Hopfield's bands in N_2 and CO) are not of the type described here and furthermore these bands come out at somewhat higher pressures.

The far ultraviolet absorption spectrum of benzene may now be considered in the light of the previous remarks. It was obtained in the following manner. A vacuum spectrograph of the grazing incidence type having a dispersion of about 2.3A/mm was used. The Lyman continuum which was obtained from a discharge tube of the type designed by Collins and Price[2]

served as a background against which the absorption could be observed. Hydrogen or helium was used as a conducting gas in the discharge tube. The benzene vapor was admitted into the body of the spectrograph and pumped out through the main evacuating pump. Thus the path length in which the absorption took place was that between the slit and the grating, and the grating and the photographic plate. This distance amounted to about 1.5 meters in the particular instrument used here. The partial pressures of benzene present in the spectrograph during an exposure were around 0.1 mm. It was admitted into the spectrograph in small quantities (i.e., volumes of about 15 cc at 10 cm pressure) at frequent intervals of time. The huge volume of the spectrograph which was about 180 liters smoothed out the pressure of the benzene so that it remained sensibly constant throughout the exposure which usually lasted about an hour. Lines in the spectrum of molecular hydrogen were used as standards. Their wavelengths were taken from Hyman.[3]

[2] Collins and Price, Rev. Sci. Inst. 5, 423 (1934).

[3] H. H. Hyman, Phys. Rev. 36, 187 (1930).

Under the conditions described above the absorption spectrum shown in Fig. 1 was obtained. It consists of a strong continuous absorption starting fairly sharply around 1840A. This gradually weakens out and at 1600A its intensity becomes almost zero. Below this a set of very strong discrete bands appears. These are quite narrow and are only slightly degraded towards the red. They get weaker and closer together as we go to shorter wavelengths and eventually merge into a weak continuum around 1360A. Superimposed on this continuum the first members of another set of fairly strong diffuse bands start. Similar bands which are related with these also appear at shorter wavelengths. A great deal could not however be done with them on account of their predissociation and the weakening of the continuum by some general absorption.

The opportunity of studying the absorption spectrum of C_6D_6, a small quantity of which was kindly provided by Professor H. S. Taylor of Princeton University, threw considerable light on the nature of the bands and confirmed an analysis of the spectrum of light benzene which had previously been made by one of us.

Enlargements of a small region of the photographs of both light and heavy benzene are also shown in Fig. 1. The spectra are lined up by the emission lines in the continuum. It can be seen from this photograph that the sets of bands obtained in both light and heavy benzene are essentially similar. However, those of the latter suffer a small shift to the violet relative to those of the former. The magnitude of this shift, which is only about 30 cm^{-1} makes it certain that the bands are mainly due to vibrationless electronic transitions. It can be shown that such a shift is accounted for by the change of the difference in zero-point vibrational energy between the ground state and the excited state as we go from C_6H_6 to C_6D_6. It is given by an expression

$$\tfrac{1}{2}\{\Sigma(\omega'' - \omega^{*''}) - \Sigma(\omega' - \omega^{*'})\}.$$

ω and ω^* refer to C_6H_6 and C_6D_6, respectively. '' refers to the ground state and ' to the excited state. If the vibration frequencies are diminished by the excitation then this shift is positive.

When the frequencies of the strongest bands

of the little pattern which accompanies all the bands were taken, it was found that they could be expressed in two Rydberg series going to approximately the same limit. This limit corresponds to an ionization potential of $9.190 \pm .005$ volts. Unfortunately there appears to be no value of the ionization potential of C_6H_6 determined by the methods of electron impact with which to compare this value. However, the degree of accuracy with which the bands are represented by Rydberg formulas coupled with the facts that they all suffer small shifts to the violet due to zero-point energy changes; that similar patterns accompany each member of a particular series; and the intensities of the bands fall off with increasing quantum number in the manner expected for electronic series make it certain that this is a true ionization potential. Further arguments that could be brought forward are that benzene is expected to have ionization potentials in the range 8–12 volts (cp. C_2H_2, C_2H_4, C_2H_6[1]); that these bands are by far the strongest bands which appear in this region and they come out at such pressures which previous experience has shown to be the usual pressures at which bands going to an ionization potential appear. The Rydberg formulas to which the two sets of bands conform are:

$$\nu_0{}^n = 74,495 - R/(n+.97)^2, \qquad (1)$$
$$\nu_0{}^n = 74,590 - R/(n+.55)^2 \quad n = 3,\ 4,\ 5,\ \text{etc.} \quad (11)$$

An idea of the accuracy with which these formulas represent the bands may be obtained from an inspection of Table I. The accuracy of

TABLE I. *Table showing the observed and calculated frequencies of the C_6H_6 bands of series (1) and (11) along with the bands of C_6D_6 and the isotopic shifts.*

		Series (1)				Isotopic shift
n	I	ν obs. C_6H_6	calc.	I	ν obs. C_6D_6	
3	10	67529	67535	10	67562	33
4	10	70047	70052	10	70075	28
5	9	71415	71416	9	71447	32
6	8	72242	72236	8	72275	33
7	5	72777	72767	3	72807	30
8	3	73124	73136			

		Series (11)				Isotopic shift
n	I	ν obs. C_6H_6	calc.	I	ν obs. C_6D_6	
3	10	65716	66882	10	65746	30
4	8	69273	69289	7	69312	39
5	blend	71025	71027	3	71061	36
6	2D	72035	72032	2	72075	40
7	1D	72668	72665			

D = diffuse.

the measurements is such that the frequencies given are probably correct to within ten wave numbers.

The first member of series (11) is somewhat off the series but this is to be expected as large dipole effects are present and the bands should only approximate to Rydberg series for the higher quantum numbers. Another difficulty with series (11) is that the bands fall off rapidly in intensity and also that some of them are obscured by overlapping. The bands used in the series are the strongest bands in the little pattern which accompanies each main electronic transition. In fact, the spectrum might best be described by saying that the bands occur in patterns. This appears to be a more or less unique feature of the spectrum of C_6H_6 and has not been observed to the same extent in any of the other molecules investigated in this laboratory. We will postpone further discussion of this pattern until we have dealt with two vibration frequencies which were found to accompany all the strong electronic transitions.

THE ω_1 AND ω_2 VIBRATIONS

To the short wavelength side of all the strong patterns, two very much weaker patterns were observed at distances of ~ 677 cm^{-1} and 968 cm^{-1} from the corresponding strong pattern (*vide* Table III). As is indicated in Fig. 2 these patterns are identical with the particular pattern they accompany. This is so within the error of measurement. These frequencies become about 630 cm^{-1} and 926 cm^{-1} for C_6D_6. They will be here designated as the vibrations ω_1 and ω_2. ω_2 undoubtedly corresponds to the Raman frequency of 991 cm^{-1}. The small difference between the value in the excited state and that in the normal state is in harmony with the fact that the isotopic shifts due to changes in zero-point energy are small. Combined with the fact that these vibrational transitions are much weaker than the main electronic transition, this becomes strong evidence that the electron is of a non-bonding type. It seems very probable that ω_2 corresponds to the type of vibration given as 1 by Wilson[4] or type II by Teets and Andrews.[5]
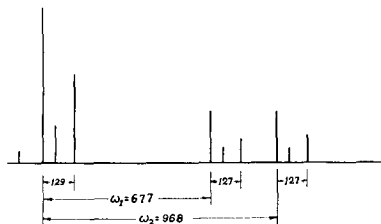
[4] E. B. Wilson, Jr., Phys. Rev. **45**, 707 (1934).
[5] D. E. Teets and D. H. Andrews, J. Chem. Phys. **3**, 175 (1935).

FIG. 2. Diagram of band at λ1427.6 showing the weak vibrations ω_1 and ω_2 accompanying it.

At least this is the assignment given to the 991 frequency of the ground state by the latter authors. It is supported by the isotope factor which is only a little less than $(13/14)^{\frac{1}{2}}$ and is just what would be expected if the carbon and hydrogen atoms move together along the radii. A more detailed calculation[6] involving plausible assumptions with regard to the force constants between the atoms enables the isotope shift to be predicted fairly exactly if this mode of vibration is assumed. The symmetry of the vibration is such that its appearance would not be forbidden in the spectra obtained here. It is interesting to note that it also appears in the near ultraviolet bands[7] though as is usual in these bands its frequency is somewhat more greatly modified becoming about 928 cm^{-1}.

The value of ω_1 in the ground state is also probably not a great deal different from its value of 680 cm^{-1} in the excited state. It cannot be associated with the nearest Raman lines at 849 and 605 cm^{-1} (662 and 581 for C_6D_6)[8] on account of the difference in the isotope factors. Thus it is most likely a vibration whose appearance in Raman spectra and the infrared is in some way forbidden. This is also true of the 162 frequency associated with the ground state by Henri from an analysis of the near ultraviolet bands. In fact, these two vibrations may be the two that are necessary to complete the vibration scheme for benzene. Twenty independent modes of vibration are predicted by Wilson and eighteen have so far been found in Raman spectra and the infrared. ω_1 may well correspond to the type of

[6] Murray, Squire and Andrews, J. Chem. Phys. **2**, 714 (1934).
[7] V. Henri, J. de phys. et rad. **9**, 249 (1928).
[8] R. W. Wood, article in this issue.

vibration designated as D by Teets and Andrews. At least this satisfies the requirement of the isotopic shift which is that the vibration should be mainly among the carbon atoms, the hydrogens merely following the carbons with which they are associated. This mode of vibration should also correspond to a fairly low frequency in agreement with what is found (i.e., it is a vibration in a carbon-carbon bond which is modified by the additional mass of the rest of the ring).

We have now to discuss the patterns which accompany all the bands. The pattern for series (1) is composed of two strong bands and two weak bands. That for series (11) is mainly one strong band which is accompanied by one or two weak bands to the long wavelength side of it. The patterns for subsequent electronic states of the same series resemble one another in a general way (i.e., the corresponding bands in the pattern can be easily picked out). However, there does

not seem to be any simple relation between the members of the patterns except that they get closer together with increasing quantum number. An idea of the frequency differences which are associated with the patterns may be obtained from Table II. It does not seem probable that any of the small differences associated with a particular pattern correspond to vibration frequencies. Some of them are of such intensities as virtually to demand more than two members of a vibrational progression which were certainly not found in our case. No exact regularity could be found in them in passing from one state to another. The accuracy of measurement was far greater than that necessary to establish such a regularity. Nothing could be gained from the isotope shifts in the patterns as these were sometimes such that the differences were increased not diminished by the substitution of the heavy isotope. It remains therefore for us to suggest rather cautiously that the pattern is caused by some multiplicity of the electronic states. This would at least take care of the increase in the dimensions of some of the patterns by the substitution of the heavy isotope. The apparent anomaly can be then accounted for by the difference in change of zero-point energy of the two different excited electronic states. The force constants would not be the same and thus the vibrations involved in the zero-point energy would be affected to a different extent.

Most of the bands observed above 1360A are given in Tables I, II and III. All the bands of appreciable intensity are accounted for in this analysis.

TABLE II. *Table of frequencies for the various band patterns.*

			Series (1)			
n	I	ν obs.	$\Delta\nu$	I	ν^* obs.	$\Delta\nu$
3	2	67429		4	67466	
			100			96
	10	529		10	562	
			74			115
	3	603		3D	677	
			81			97
	6	684		9	744	
4	3	69947		2D	69988	
			100			87
	10	70047		10	70075	
			49			52
	4	096		5	127	
			80			73
	6	176		6	200	
5	2D	71334		2D	71367	
			81			80
	9	71415		9	447	
			42			37
	7	457		6	485	
			56			53
	6	513		5	538	
6	1	72186				
			56			
	8	242		8	72280	
			37			35
	7	279		6	315	
			45			49
	3	324		4	364	

			Series (11)			
n	I	ν obs.		I	ν^* obs.	
3	2D	65540		3	65582	
			84			87
	4D	626		5	669	
			90			77
	10	716		10	746	
4		—			—	
	2D	69183		1	69224	
			90			88
	8	273		7	312	

— refers to bands too weak to be observed.

TABLE III. *Table showing derivation of* ω_1, ω_2, *and* ω^*_1, ω^*_2.

n	I	ν	I	$\nu+\omega$	ω	I	ν^*	I	$\nu^*+\omega^*$	ω^*
3	10	67529	4	68208	679	10	67562	3	68205	643
			4	495	966			3	483	921
	6	684	2	348	664	9	774		—	—
			2	646	962				—	—
4	10	70047	4	70725	678	10	70075	3	70711	636
			4	71017	970			2	71003	928
	4	096	2	70774	678	5	127	2	70762	635
			2	71066	970			2	71061	934
	6	176	2	70852	676	6	200	2	70826	626
			2	71144	968			2	71124	924
5	9	71415	3	72092	677	9	71447	2	068	621
			3D	383	968			1D	367	920
	7	457	2	134	677	6	485	1	120	635
			2	423	966					
	6	513	1	188	675	5	538			
			2D	477	964			b	447	911
6	8	72242	2	911	669					
			2	73211	969					
	7	279	2	72946	667					

* refers to C₆D₆. D =diffuse. b =blend.

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

Raman Spectrum of Benzene-d_6

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THE sample of heavy benzene, 1.5 cm³, 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).