VIII. Electronic Spectra and Structure of Organic Molecules

Ultraviolet Absorption Spectra of Substituted Benzenes

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GENERAL INTRODUCTION

AFTER it was possible to give an interpretation[1] of the near ultraviolet absorption spectrum of benzene, it seemed natural to investigate the corresponding spectra of substituted benzenes.

If we make the plausible assumption that the levels, between which the corresponding electronic transitions take place in the substituted benzenes, can be identified with the levels into which the benzene levels go over upon transforming D_{6h} symmetry to the respective other symmetries, then we can predict the nature of these electronic levels and the general appearance of the corresponding spectra.

Symmetrical configuration of nuclei is required for classifying the electronic terms. In the molecules this is realized in general only for equilibrium positions; small displacements usually destroy the symmetry. If the molecule has a certain symmetry, then the various electronic levels can be described by applying different symmetry operations with respect to the different symmetry elements. If we fix a coordinate system in the molecules with the z axis perpendicular to the ring plane and the y and x axes as indicated in Table I, we obtain from such symmetry operations the results given in Tables II–VI. Only the essential symmetry elements are given. C_3^z, C_2^y, etc., are three- and twofold axes in the z and y directions, σ_h and σ_z both mean planes of reflection perpendicular to the z axis, i.e., the molecular plane; i denotes the center of symmetry. All electronic terms, denoted by A and B, are non-degenerate. Their symmetrical and antisymmetrical behavior with respect to the different symmetry elements is indicated by $+$ and $-$ signs. The terms E are twofold degenerate. Their behavior is more complex.[2]

Tables II–VI describe not only the symmetry types of the electronic levels, but also those of the vibrations. In the column headed Vib. is mentioned how many vibrations exist of a certain type and for completeness it is added which ones are Raman or infra-red active.

If the symmetry D_{6h} of benzene is reduced by substitutions then certain symmetry types in D_{6h} correspond to certain types in V_h or C_{2v} and so on. Convenient illustrations of these transformations have been given by Langseth and Lord[3] for the deuterated benzenes. Figure 1 has been prepared from their summary. From it we reach the following conclusions: since the near ultraviolet absorption in benzene represents[4] a transition $A_{1g} \rightarrow B_{2u}$, we find for the substituted benzenes the transitions given in Table I. The ground level stays, of course, totally symmetrical in all of them. Comparing these results with those in Tables II–VI, we find as the next step which of these transitions are allowed and which are forbidden.

Selection rules for the transitions may be found by examining the symmetry of the integrands of the matrix elements of the transition moment $\int \psi_{el}'^* M \psi_{el}'' d\tau_{el}$. Here ψ_{el}' and ψ_{el}'' are the electronic eigenfunctions in the upper and lower states; the asterisk (ψ^*) indicates the conjugate complex value. M is the dipole moment of the system of nuclei and electrons for a definite electronic configuration. $d\tau_{el}$ indicates the integration over all configurations of the electrons. It can be shown that transitions occur only if the direct product[2] of the term symbols belonging to ψ_{el}' and ψ_{el}'' contains a term with the transformation properties of M. Since the latter transforms in the same way as a translation, one may say that in an allowed transition the direct product is required to contain a term which transforms like one of

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

[2] For details see the review on "Electronic spectra of polyatomic molecules," H. Sponer and E. Teller, Rev. Mod. Phys. **13**, 76 (1941).

[3] A. Langseth and R. C. Lord, Kgl. Danske Vid. Sels. Math.-Fys. Medd. **16**, No. 6 (1938).

[4] A. L. Sklar, J. Chem. Phys. **5**, 669 (1937).

TABLE I. Transactions in substituted benzenes.

Symmetry	D_{6h}	D_{3h}	V_h	C_{2v}	C_{2v}^*
Molecule	C_6H_6	1,3,5 $C_6H_3Cl_3$	p-$C_6H_4Cl_2$	C_6H_5Cl $\quad$ m-$C_6H_4Cl_2$	o-$C_6H_4Cl_2$
Transition	$A_{1g}-B_{2u}$ forbidden	$A_1'-A_2'$ forbidden	$A_{1g}-B_{3u}$ allowed parallel x	A_1-B_1 allowed parallel x	A_1-A_1 allowed parallel x
Migrat. moment	zero	zero			
Vibrat. moment produced by	ϵ^+_g vibrations, in molec. plane	ϵ' vibrations, in molec. plane	β_{2g} vibrations, parallel y	β_1 vibrations, parallel y	β_1 vibrations, parallel y

TABLE II. D_{6h}: C_6H_6.

	$C_3{}^z$	$C_2{}^z$	$C_2{}^y$	i	Vib.		R	IR
A_{1g}	+	+	+	+	2		+	−
A_{1u}	+	+	+	−	0		−	−
A_{2g}	+	+	−	+	1	R_z	−	−
A_{2u}	+	+	−	−	1	T_z	−	+
B_{1g}	+	−	+	+	0		−	−
B_{1u}	+	−	+	−	2		−	−
B_{2g}	+	−	−	+	2		−	−
B_{2u}	+	−	−	−	2		−	−
$E^+{}_g$	$e^{\pm1}$	+	*	+	4		+	−
$E^+{}_u$	$e^{\pm1}$	+	*	−	2		−	−
$E^-{}_g$	$e^{\pm1}$	−	*	+	1	$R_{x,y}$	+	−
$E^-{}_u$	$e^{\pm1}$	−	*	−	3	$T_{x,y}$	−	+

TABLE III. D_{3h}: $C_6H_3Cl_3$.

	$C_3{}^z$	$C_2{}^y$	σ_h	Vib.		R	IR
A'_1	+	+	+	4		+	−
A''_1	+	+	−	0		−	−
A'_2	+	−	+	3	R_z	−	−
A''_2	+	−	−	3	T_z	−	+
E'	$e^{\pm1}$	*	+	7	$T_{x,y}$	+	+
E''	$e^{\pm1}$	*	−	3	$R_{x,y}$	+	−

TABLE IV. V_h: p-$C_6H_4Cl_2$.

	$C_2{}^y$	$C_2{}^z$	i	Vib.		R	IR
A_{1g}	+	+	+	6		+	−
A_{1u}	+	+	−	2		−	−
B_{1g}	+	−	+	1	R_y	+	−
B_{1u}	+	−	−	5	T_y	−	+
B_{2g}	−	+	+	5	R_z	+	−
B_{2u}	−	+	−	3	T_z	−	+
B_{3g}	−	−	+	3	R_x	+	−
B_{3u}	−	−	−	5	T_x	−	+

TABLE V. C_{2v}: C_6H_5Cl; m-$C_6H_4Cl_2$.

	$C_2{}^y$	σ_z	Vib.		R	IR
A_1	+	+	11	T_y	+	+
A_2	+	−	3	R_y	+	−
B_1	−	+	10	T_xR_z	+	+
B_2	−	−	6	T_zR_x	+	+

TABLE VI. C^*_{2v}: o-$C_6H_4Cl_2$.

	$C_2{}^z$	σ_z	Vib.		R	IR
A_1	+	+	11	T_x	+	+
A_2	+	−	5	R_x	+	−
B_1	−	+	10	T_yR_z	+	+
B_2	−	−	4	T_zR_y	+	+

the translations T_x, T_y, T_z. The direction of this translation gives the direction of the transition moment. Now from Tables II–VI it can be seen that the transitions for D_{6h} and D_{3h} are forbidden because the terms B_{2u} and A'_2 do not

transform like translations,[5] and that the transitions for V_h, C_{2v} and C^*_{2v} are allowed with the transition moment lying parallel to the x axis in all three cases. Hence, in our approximation—

$\mathfrak{M} = \int \psi_{el}'^* M \psi_{el}'' d\tau_{el}$ being considered a constant with the nuclei held fast in their equilibrium position—benzene and sym. trichlorobenzene should not have near ultraviolet absorption spectra, but such spectra appear upon substitution. Sklar[6] has called the transition moment associated with them migration moment because it results from the migration of unsaturation electrons (Mulliken) into or out from the aromatic nucleus.

[5] Forming the direct product, that is multiplying the rows for A_{1g} and B_{2u} in Table II and those for A'_1 and A'_2 in Table III we obtain simply the transformation properties of B_{2u} and A'_2 because A_{1g} and A'_1 are totally symmetrical.

[6] A. L. Sklar, J. Chem. Phys. 7, 984 (1939); 10, 135 (1942); see also Rev. Mod. Phys. 14, 232 (1942).
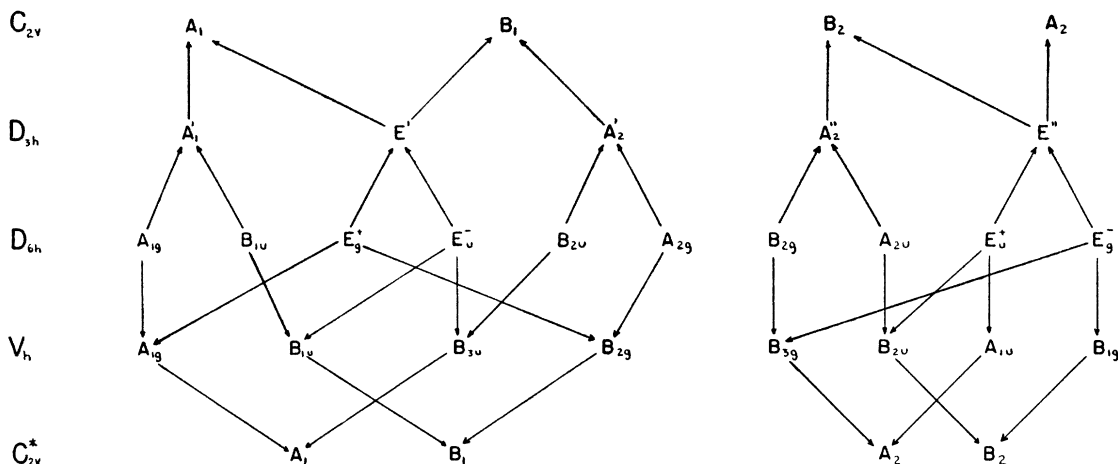
FIG. 1. Corresponding symmetry types obtained by substitutions.

The general features of the vibrational structure of an allowed transition can be understood from an application of the Franck-Condon principle to polyatomic molecules.[7,2] Whether we make use of the simple principle of Franck, that the nuclear positions and velocities do not change during the electronic jump, or whether we use the wave-mechanical procedure of obtaining the transition probabilities from an investigation of the matrix elements

$$\int \psi'^{*}_{\mathrm{rel}} M \psi''_{\mathrm{rel}} d\tau_{\mathrm{rel}} = \int \psi'^{*}_{\mathrm{el}} \psi'^{*}_{\mathrm{vib}} M \psi''_{\mathrm{el}} \psi''_{\mathrm{vib}} d\tau_{\mathrm{el}} d\tau_{\mathrm{nucl}},$$

we arrive at the following statements. The strongest bands of the spectrum will be made up of the 0,0 band and excitation of totally symmetric vibrations. Non-totally symmetric vibrations will occur preferably as 0−0, 1−1, $\cdots v−v$ transitions unless they are weakened too much by Boltzmann factors. This corresponds to a change $\Delta v = 0$ in the vibrational quantum number; changes of $\Delta v = 2, 4$, will occur with much less intensity. No transition can occur from a state in which only totally symmetrical vibrations are excited to another state in which in addition one non-totally symmetrical vibration with one quantum is present.

As we shall see shortly, these theoretical considerations describe the major part of the spectra of substituted benzenes. They do not explain the

⁷ G. Herzberg and E. Teller, Zeits. f. physik. Chemie B21, 410 (1933).

occurrence of the benzene spectrum. We know that benzene has an absorption system at 2600A although its intensity is low. We understand its presence at once if we drop the previous assumption that the electronic matrix element of the dipole moment $\mathfrak{M} = \int \psi'^{*}_{\mathrm{el}} M \psi''_{\mathrm{el}} d\tau_{\mathrm{el}}$ does not depend on the nuclear positions. In reality $\mathfrak{M}$ does vary with nuclear displacements. For small displacements $\mathfrak{M}$ can be expanded into a power series in the displacements:

$$\mathfrak{M} = \mathfrak{M}_0 + \sum_i \mathfrak{M}_i \xi_i + \cdots. \tag{1}$$

The ξ_i stand for normal coordinates expressing the displacements of the ith normal vibration. $\mathfrak{M}_0$, $\mathfrak{M}_i$, $\cdots$ are coefficients in the expansion. If $\mathfrak{M}$ consists only of $\mathfrak{M}_0$ then we have the case already considered, namely, the occurrence of an allowed transition caused by the presence of the migration moment. If $\mathfrak{M}_i \neq 0$, then the second term in the expansion gives the contributions $\mathfrak{M}_i \int \psi'^{*}_{\mathrm{vib}} \xi_i \psi''_{\mathrm{vib}} d\tau_{\mathrm{nucl}}$ to the transition matrix element. Closer inspection shows[2] that no new bands appear if the ith vibration is totally symmetrical but that we have then the rules for an allowed transition considered before. However, if ξ_i represents the normal coordinate of a non-totally symmetric vibration, new bands appear in the spectrum the strongest of which have one quantum of the ith vibration excited. This means that through the interaction of unsymmetrical vibrations an additional transition moment is produced, called by Sklar[6] vibrational moment.

It is in general much smaller than the migration moment, but it becomes important in cases where $\mathfrak{M}_0 = 0$. In these cases, which according to electronic selection rules alone are forbidden, the electronic transition matrix element differs from zero when certain vibrations are excited. Thus the benzene absorption is produced through the distortion of the ring by unsymmetrical vibrations. Application of group theoretical rules permits one to determine which transitions can be made allowed by a single vibration or which particular vibration must be excited to make a forbidden transition allowed. We may give the result[2] by saying that a transition is made allowed by a vibration with the displacement ξ_i when

$\psi'_{el} M \psi''_{el}$ contains the transformation properties of ξ_i. Applying this to our examples, we find in Table II that by forming the direct product $A_{1g} \times T_{x,y} \times B_{2u} = A_{1g} \times E^-_u \times B_{2u}$, that is, by simply multiplying the two rows for B_{2u} and E^-_u we obtain the row for E^+_g. We conclude that excitation of vibrations[8] of type ϵ^+_g causes the appearance of the benzene spectrum and this is precisely what has been found. Similarly, ϵ' vibrations will produce the forbidden spectrum of sym. trichlorobenzene. Hence, instead of the 0,0 band of an allowed transition there will occur $0 \rightarrow 1$ and $1 \rightarrow 0$ transitions of these particular vibrations. Of course, on top of these "forbidden transitions" appears the whole vibrational structure of an allowed system.

As mentioned before, bands resulting from the presence of a vibrational moment will be weaker than bands resulting from the migration moment. Thus, the spectrum of an allowed transition consists in general of two parts: the "allowed" bands which we discussed before, and the "forbidden" bands which appear on account of additional weak moments caused by excitation of vibrations of proper symmetry. The transition moments of these forbidden bands lie in a direction perpendicular to that of the main moment. Now in the substituted benzenes, where the substitution does not produce a great change of the charge distribution of the ring, the migration and vibration moments do not differ much in magnitude. This is particularly the case in

monochlorobenzene[9] as we shall see presently. Sklar[6] has calculated the intensity ratio of the allowed parts of the spectra of C_6H_5P : o-$C_6H_4P_2$: m-$C_6H_4P_2$: p-$C_6H_4P_2 = 1$: 1 : 1 : 4. Here P denotes the substituent. He has also roughly estimated for a number of substituted benzenes how much of the total intensity is due to the migrational and to the vibrational effects separately.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 exhibits the near ultraviolet absorption spectra of benzene and two monoderivatives, C_6H_5Cl and C_6H_5F. The analysis of the benzene spectrum[1] and that of monochlorobenzene[9] have been published in detail so that a few remarks about these spectra should suffice here. The benzene spectrum appears in absorption and fluorescence as well. The band at 38,160 represents the $0 \rightarrow 1$ transition of the ϵ^+_g vibration whose excitation makes the forbidden $A_{1g} \rightarrow B_{2u}$ transition allowed. The vibration is well known from the Raman effect as being 606 and its value in the upper state is 518. The $1 \rightarrow 0$ transition is not shown in the spectrogram. Upon the $0 \rightarrow 1$ and $1 \rightarrow 0$ transitions are superimposed progressions of the totally symmetrical carbon vibration of 923 cm^{-1}. The bands lying to the red from the main bands are caused by $v - v$ transitions of unsymmetric vibrations. Thus, the just mentioned ϵ^+_g vibration occurs superimposed in $1 - 1$ and $2 - 2$ transitions on the $0 \rightarrow 1$ and $1 \rightarrow 0$ transitions of that same vibration. A spacing of 160 cm^{-1}, which occurs in long progressions in absorption and fluorescence, is a difference between a frequency of 404 in the ground state and 244 cm^{-1} in the excited level, both belonging to the degenerate carbon vibration ϵ^+_u. The analysis has offered an understanding of the general features of the absorption spectrum not only of gaseous but also of solid benzene and of the fluorescence spectrum of gaseous benzene.

The spectrum of monochlorobenzene looks more complicated for two main reasons: in agreement with the foregoing theoretical discussion it consists really of two spectra, an allowed and a forbidden one, and secondly, because of the much lower symmetry of the molecule

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[8] Symmetry types of vibrations will be denoted by small Greek letters.

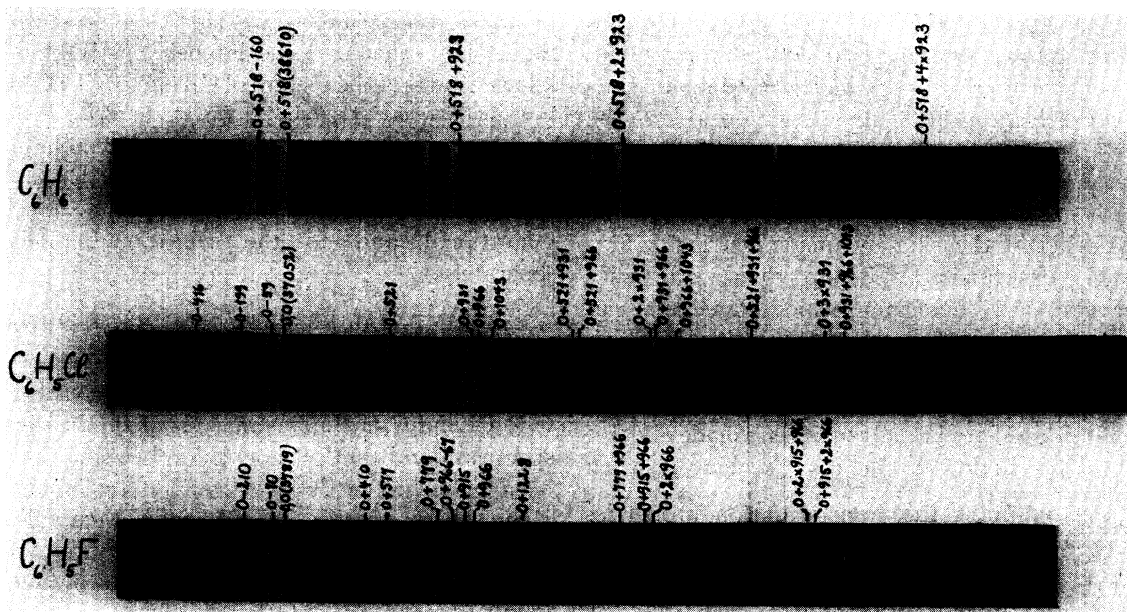[9] H. Sponer and S. H. Wollman, J. Chem. Phys. 9, 816 (1941).

FIG. 2. Absorption spectra of benzene, monochlorobenzene, and monofluorobenzene.

C_6H_5Cl, there will be present several totally symmetrical vibrations which will cause progressions of bands and so will obliterate the distinct group appearance characteristic of the benzene spectrum. The band at 37,052 represents the 0,0 band. This band and all bands which can be built up upon it constitute the "allowed" part of the spectrum. These are, for instance, bands caused by the totally symmetric carbon vibrations in the 1000 cm^{-1} region and their multiples. Weaker bands on the red side of the main bands with distances of 59, 2×59 cm^{-1}, and 199 cm^{-1} belong also to the allowed part of the spectrum and must be ascribed to $v-v$ transitions. A very interesting situation prevails for the totally symmetrical $C-Cl$ vibration. It appears in a $1\rightarrow0$ transition 705 cm^{-1} apart from the 0,0 band with normal intensity while its $0\rightarrow1$ transition represents only a weak band. This peculiar behavior may be understood by assuming that excitation of this vibration influences the transition moment. Using then Eq. (1) for the normal coordinate ξ of the $C-Cl$ vibration, we obtain

$$\int \psi_{el}'^* \psi_{C-Cl}'^* M \psi_{el}'' \psi_{C-Cl}'' d\tau_{el} d\xi = \mathfrak{M} \int \psi_{C-Cl}'^* \psi_{C-Cl}'' d\xi$$

$$= \mathfrak{M}_0 \int \psi_{C-Cl}'^* \psi_{C-Cl}'' d\xi + \mathfrak{M}_1 \int \psi_{C-Cl}'^* \xi \psi_{C-Cl}'' d\xi.$$

The magnitude of the first integral of the last two expressions is given by the shift in equilibrium position during the transition (Franck-Condon principle) while the second integral represents the change $\mathfrak{M}_1\xi$ of the transition moment during the vibration. If one writes down these last two integrals for the $1\rightarrow0$ and $0\rightarrow1$ transitions of the $C-Cl$ vibration, one can show from a discussion[2,9] of the magnitude of these integrals that it is conceivable that there is an adding effect of the matrix elements for the $1\rightarrow0$ transition and a cancelling effect for the $0\rightarrow1$ transition.

The second group in the spectrum of C_6H_5Cl is due to the vibrational moment. It is caused by a β_1 vibration, more specifically by the β_1 vibration which results from the splitting of the degenerate $606\epsilon^+{}_g$ vibration in benzene. It is also numerically close to the benzene vibration; namely, 608 in the lower and 521 cm^{-1} in the upper state. The second group and all bands superposed on it constitute the forbidden part of the monochlorobenzene spectrum. As can be seen from Fig. 2 and as was mentioned before, the intensities of the allowed and the forbidden part do not differ much from each other. Hence, the total absorption strength of the chloroben-
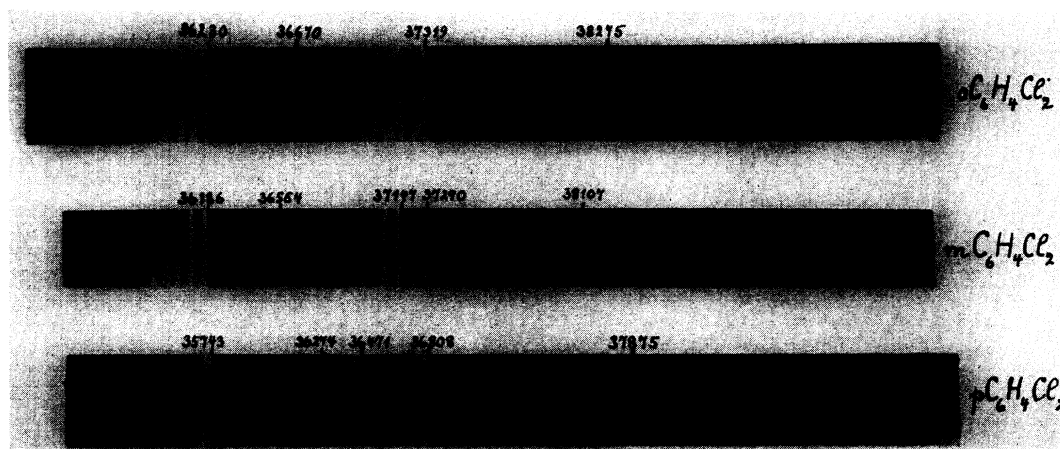
FIG. 3. Absorption spectra of dichlorobenzenes.

zene spectrum is only a few times that of the benzene spectrum.

It may be interesting to mention in this connection that the spectrum of monodeutero-benzene[10] looks of course like that of benzene and not like that of chlorobenzene. Here the substitution does not cause any charge migration. The perturbation of the sixfold symmetry from this effect is so slight that the 0,0 band appears about 10^3 times weaker than the forbidden transition.

The spectrum of fluorobenzene[11] is in its main features similar to that of chlorobenzene but shows two interesting deviations: in contrast to C_6H_5Cl the carbon-halogen frequency appears strongly in C_6H_5F; furthermore, bands resulting from a vibrational moment appear rather weakly while they are quite strong in C_6H_5Cl. The first discrepancy is probably connected with the fact that the $C-F$ frequency is numerically rather close to the carbon vibrations so that it will have contributions from the motion of the other carbon atoms and hence will be intensified. The second result may be explained, at least partly, from the stronger intensity of the allowed bands in C_6H_5F than in C_6H_5Cl, so that the forbidden bands appear relatively weaker in C_6H_5F than in C_6H_5Cl.

Figure 3 contains the spectra of the dichloro-benzenes.[12] The simplest of the three is the para-spectrum. It is also the strongest of the three spectra in agreement with Sklar's calculations. The spectrum represents an $A_{1g} \rightarrow B_{3u}$ transition with the dipole moment in the molecular plane penpendicular to the paracarbons. The 0,0 band lies at 35,743 cm^{-1}. The main progression appears to be double with the first members at 36,797 and 36,808 cm^{-1}. Although the bands look as if they were components of one band it is quite possible that they belong to separate vibrations. The carbon-chlorine vibration appears strongly in the lower and upper states in the bands $34,992 = 0 - 751$ and $36,471 = 0 + 728$. The bands on the red side of the main bands are, as usual, caused by $v - v$ transitions. Frequent separations are 25 and 84 cm^{-1}.

The faint group at 36,274 results from the vibrational moment caused by the β_{2g} vibration the value of which is 625 cm^{-1} in the ground and 531 cm^{-1} in the excited state. From a very rough estimate of intensities it may be concluded that the forbidden part [13] of the spec-

[10] C. A. Beck and H. Sponer, J. Chem. Phys. 10, 575 (1942).
[11] S. H. Wollman, Ph.D. Thesis, Duke University (1941); H. Sponer and S. H. Wollman, Phys. Rev. 59, 924A (1941).

[12] These spectra have been photographed and measured by Dr. S. H. Wollman and detailed results will be published elsewhere.
[13] The forbidden part consists in reality not only of the bands appearing through the interaction of β_{2g} but also of the bands made allowed by α_{1u} vibrations. The latter bands are caused by a moment in the z direction, that is, perpendicular to the molecular plane. No bands could be assigned unambiguously to this transition. Similar remarks apply to the derivatives of symmetry C_{2v} and C^*_{2v} discussed here.
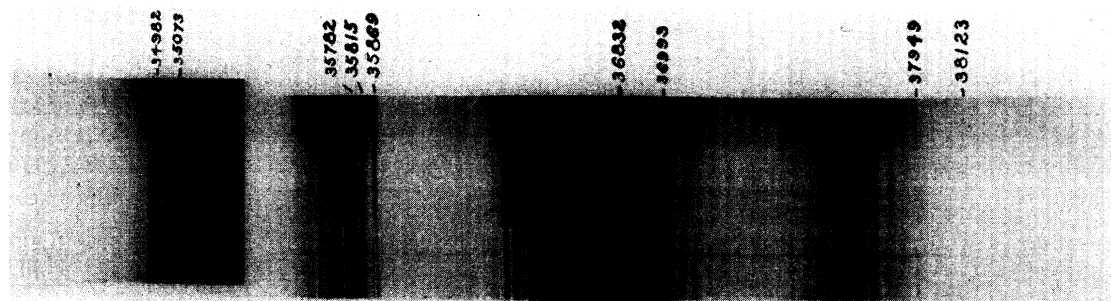
FIG. 4. Absorption spectrum of sym. trichlorobenzene.

trum is about ten times weaker than the allowed part.

The spectra of meta-$C_6H_4Cl_2$ and ortho-$C_6H_4Cl_2$ resemble each other more closely than the paraspectrum does either of the two. Both molecules have the same symmetry, the only difference lies in the different orientation of the twofold axis. Both spectra are $A_1\rightarrow B_1$ transitions with moments in the molecular plane. (See Table I). The 0,0 bands lie at 36,186 in the meta-compound and at 36,230 in the orthocompound. In both cases appear two main progressions. The first members in m-$C_6H_4Cl_2$ are the bands at 37,147 and at 37,276/90 giving vibrational frequencies of 960 and 1089/1103. The 960 corresponds to the Raman line 1000 cm^{-1} in the ground state. The 1089 and 1103 may correspond to the Raman lines 1070 and 1126. In o-$C_6H_4Cl_2$ the first members of the two outstanding progressions are represented by the bands 37,174/187 and 37,319 cm^{-1}. From this, vibrational frequencies of 944/57 and 1089 are obtained which may be connected with the Raman frequencies of 1041 and 1129 cm^{-1} and possibly with that of 1020 cm^{-1}. Of course, the discussed progressions involve totally symmetrical carbon vibrations. The characteristic appearance of the individual groups—i.e., the companions on the red side of all main bands—can again be explained by $v-v$ transitions. Important separations of these bands from the main bands are 63/70 and 147 cm^{-1} in the metacompound and 25 and 60 cm^{-1} in the orthocompound. Plausible interpretations of these small separations are possible for all dichlorobenzenes. They will be discussed, together with other interesting particulars, in the detailed publication.

Here will be pointed out two more features only. One concerns the carbon-chlorine vibration which in both spectra appears in the ground state with expected intensity but which cannot be traced unambiguously in the upper state. It is present at best in a very faint band. This is the same situation as we encountered in the spectrum of monochlorobenzene. The other remark refers to the bands which result from the vibrational moment. The groups at 36,565 in m-$C_6H_4Cl_2$ and at 36,670 in o-$C_6H_4Cl_2$ owe their existence very probably to a transition moment in the molecular plane perpendicular to the main moment. The vibrations responsible for this moment are a β_1 vibration for both molecules. The two groups are much weaker here than in monochlorobenzene. This is not so because the main moment is so much stronger in these dichlorobenzenes than in monochlorobenzene, but it seems that the bands are absolutely of smaller intensity. It would be interesting to find an experimental method for determining the relative intensities of the allowed and forbidden part in these various spectra separately.

Remembering that paradichlorobenzene has in its ground state the dipole moment zero, that orthodichlorobenzene has the highest moment (about 2.4–2.5)[14] and that the moment of metadichlorobenzene lies between the two others (1.57), we see that by far the greatest percental change in moment occurs in the paraderivative and the smallest in the orthoderivative.

The spectrum of a trisubstituted benzene is reproduced in Fig. 4. It belongs to sym. tri-chlorobenzene whose near ultraviolet absorption

[14] Private communication from Dr. P. Gross.

is another example of a forbidden transition.[15] It is an $A'_1 \rightarrow A'_2$ system made allowed through the interaction of an ϵ' vibration. The bands at 35,869 and 35,073 are tentatively assigned to the 0→1 and 1→0 transitions of this vibration whose value is taken as 425 in the ground level and 371 in the excited level. In Fig. 4 the first group representing the 1→0 transition has been reproduced from a plate taken at considerably higher pressure than the rest of the spectrum. The interpretation is supported by the frequent occurrence

of a displacement toward the red of 54 cm⁻¹ which is considered as 1−1 transition of this vibration. The calculated position of the forbidden 0,0 band is then at 35,498 cm⁻¹. Bands at 36,832 and 36,993 are the first members of progressions of the totally symmetric carbon vibrations of 963 and 1122 cm⁻¹.

Spectrograms of unsym. trichlorobenzene taken by Dr. Hedwig Kohn[16] have revealed an allowed spectrum as is expected from theory. Its comparison with the spectrum of sym. trichlorobenzene should prove interesting.

[15] M. B. Hall, Ph.D. Thesis, Duke University (1942); H. Sponer and Maurice B. Hall, Phys. Rev. **61**, 107A (1942), to be published in detail soon.
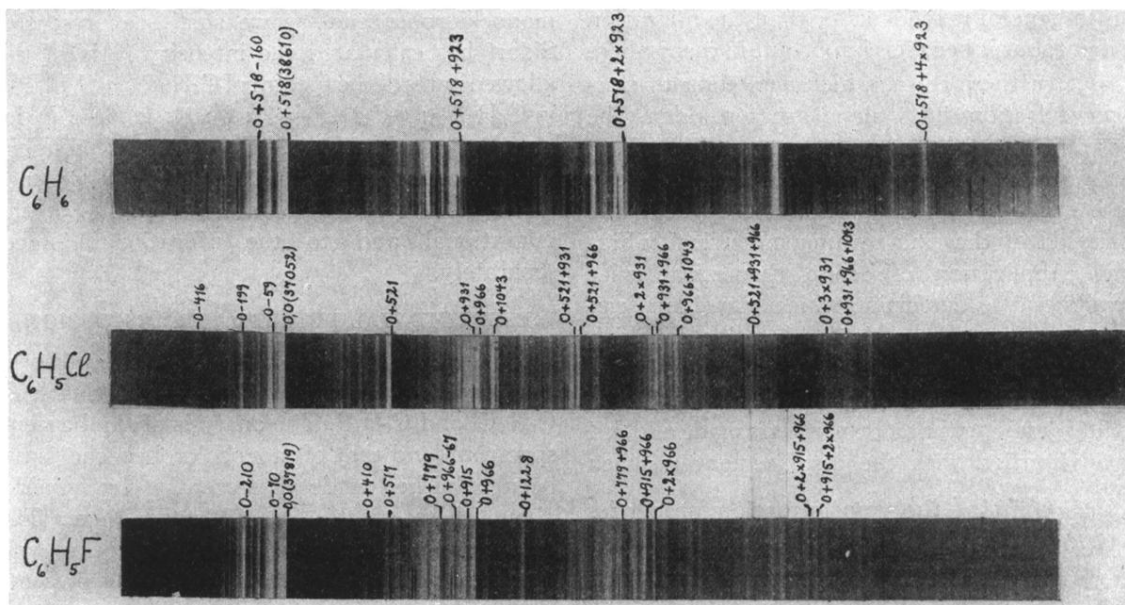
[16] To be published elsewhere.

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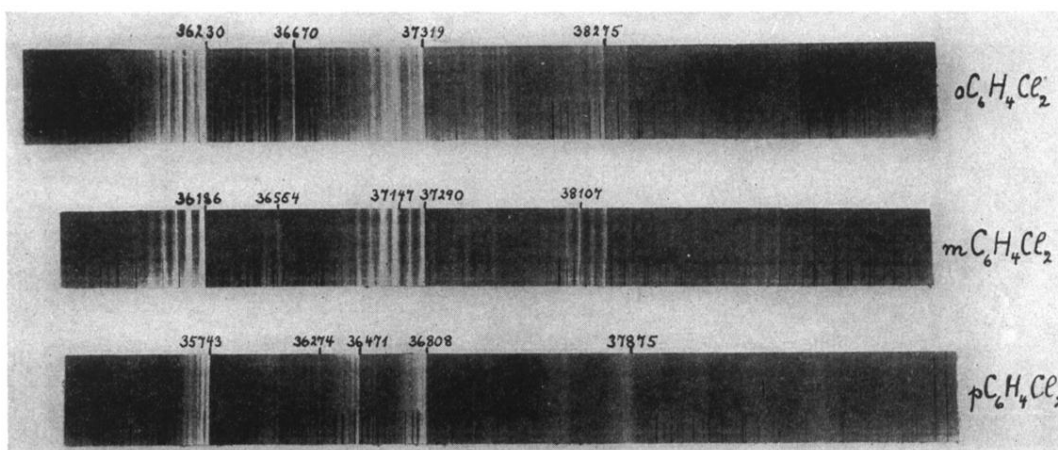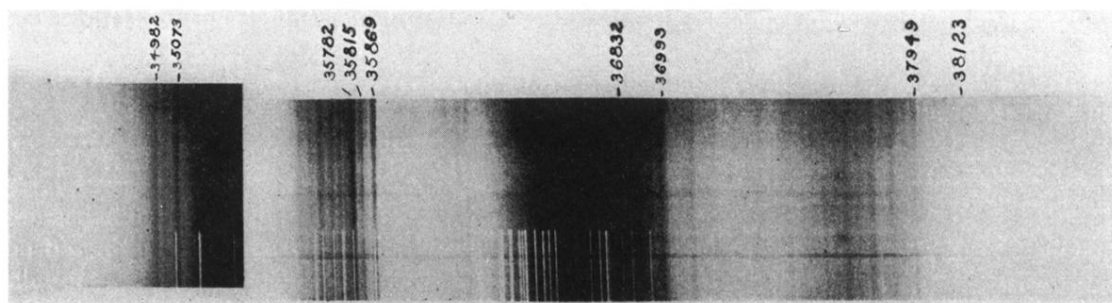
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FIG. 4. Absorption spectrum of sym. trichlorobenzene.