

ELECTRONIC TRANSITIONS IN TRISUBSTITUTED BENZENES IN THE NEAR ULTRAVIOLET¹

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The structure of the near-ultraviolet absorption spectra of the three trichlorobenzenes and of 1,3,5-trimethylbenzene is briefly discussed. The spectra of the two symmetrical trisubstituted benzenes represent forbidden transitions made possible through the distortion of the ring by unsymmetric vibrations. The spectrum of 1,2,4-trichlorobenzene results from an allowed transition, i.e., a transition moment is present at the equilibrium position of the molecule (migrational moment). The spectrum of 1,2,3-trichlorobenzene belongs also to an allowed transition, according to group theoretical rules. However, calculations (Sklar) show that the contributions from the substituents to the migrational transition moment annul one another in the first order, so that the spectrum takes on features characteristic of a forbidden transition. Characteristic differences among the various spectra are pointed out and a comparison is made with the same spectra in solution.

INTRODUCTION

Spectroscopic investigations of benzene derivatives have been made mostly in solutions. This applies to studies in the ground state—infrared, Raman—and in the excited state—electronic spectra—as well. Most electronic spectra were observed in absorption. Here, complicated compounds have been studied to a larger extent than simple derivatives, probably because of their greater biochemical and biological interest and importance.

In order to furnish the maximum information about molecular structure, the spectra have to be obtained in the vapor state. In the condensed phase the close neighborhood of the molecules causes complications (solvation, hydration, broadening of the individual bands) which are absent or at least less pronounced in the vapor phase.

The great difference between a spectrum in the condensed and in the vapor phase may be seen from figures 1 and 2, which show the near-ultraviolet absorption spectrum of benzene. Each maximum in the solution spectrum is resolved into a whole group of narrowly spaced bands in the vapor spectrum. Note in these figures that the wave-length scale goes from smaller to larger values, i.e., decreasing energies. The numbers at the different groups are wave-number values.

The appearance and intensity of a spectrum depend upon the nature of the electronic states between which the electronic transition takes place. Each

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transition is accompanied by a characteristic vibrational structure which is fundamentally different for "allowed" and "forbidden" transitions (8, 14). Symmetry considerations and the application of the Franck-Condon principle lead to a number of predictions and statements about the appearance of the spectrum which are very important for the analysis of electronic polyatomic spectra (8, 14). Although these statements seem simple enough, the interpretation of the spectra is often quite difficult. This is partly so because the knowledge of the vibrations of the molecule in the ground state is usually incomplete, and partly because in many cases bands can be interpreted in several

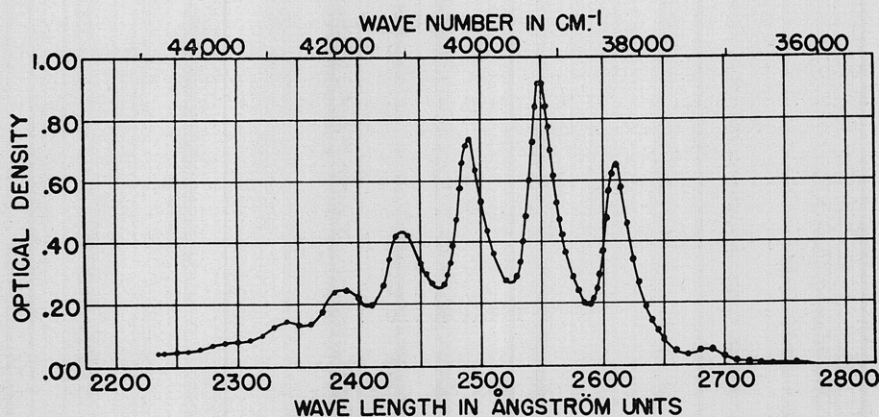


FIG. 1. Absorption spectrum of benzene (liquid solution). Traced from Serial No. 1 of the Catalog of Ultraviolet Absorption Spectrograms (1).



FIG. 2. Absorption spectrum of benzene (vapor)

ways, even to the extent that the ambiguity makes the interpretation meaningless.

If the only aim of the absorption study is the determination of the absorption coefficient and a knowledge of the gross features of the spectrum, then a spectroscopic investigation in solution is entirely satisfactory. It may also reveal whether the transition in question is allowed or forbidden. Small absorption coefficients of the order of that in benzene usually indicate forbidden transitions; larger absorption coefficients belong to allowed transitions.

The gross features of the spectrum may be used to recognize it in other cases, maybe as impurity, but a correct interpretation of the individual maxima will,

in most cases, be difficult to achieve. These statements will be amplified from our results on the near-ultraviolet absorption spectra of some trisubstituted benzenes.

EXPERIMENTAL METHOD

The near-ultraviolet absorption spectra of the trichlorobenzenes and of *sym*-trimethylbenzene (mesitylene) were investigated in the vapor phase. Quartz absorption tubes 16, 25, and 75 cm. long and provided with side arms containing the body substances were used. Two separate furnaces regulated the temperature of the main tube and of the appendix, the latter always being kept at a slightly lower temperature than any other part of the tube. In all cases the absorption was studied in dependence on the vapor pressure of the substance.

The 1,3,5- and 1,2,4-trichlorobenzenes were obtained from the Eastman Kodak Company. After the 1,3,5-trichlorobenzene had been recrystallized in methyl alcohol, it melted sharply at 65–65.5°C. The 1,2,3-trichlorobenzene was obtained through the courtesy of the Dow Chemical Company, and the

TABLE 1
Melting and boiling points of the compounds investigated

SUBSTANCE	MELTING POINT*	BOILING POINT*
	°C.	°C.
1,3,5-Trichlorobenzene.....	65.5	208.5
1,2,4-Trichlorobenzene.....	17	213
1,2,3-Trichlorobenzene.....	52	219
1,3,5-Trimethylbenzene†.....	–52.7	164.54–164.66

* Reference 9.

† Reference 15.

1,3,5-trimethylbenzene through the courtesy of the Chemistry Department of Duke University. Both substances were very pure samples. All compounds were filled into the absorption tubes by vacuum distillation. Table 1 gives the melting and boiling points of the compounds investigated.

Spectrograms were obtained with the Hilger medium quartz spectrograph E₂. It has a dispersion of 14.2 Å/mm. at 2950 Å., 11.5 Å/mm. at 2750 Å., and 9.8 Å/mm. at 2600 Å. An iron arc of the Pfund type was used as source of the comparison spectrum.

RESULTS AND DISCUSSION

The general region of the spectra of the trichlorobenzenes is 2600–2950 Å.; that of mesitylene is 2400–2800 Å. Previously, the absorption of all four substances was studied in hexane solution (3, 4, 17), but no interpretation was given. Figures 3 and 5 show the solution spectra of the trichlorobenzenes and of mesitylene. The solution spectra show several distinct maxima. A comparison of the absorption coefficients with that of benzene, also taken in hexane solution, shows that, except for 1,2,4-trichlorobenzene, they have very similar

small values. This may be understood from the theoretical result that the spectrum of 1,2,4-trichlorobenzene represents an allowed transition, while the other two chloro derivatives have forbidden spectra. Of these, the spectrum of 1,3,5-trichlorobenzene is, like that of benzene (6, 11, 13), forbidden for symmetry reasons. The same is true for 1,3,5-trimethylbenzene because of its trigonal symmetry (12). These spectra appear weakly only through the distortion of the ring by unsymmetrical vibrations. The spectrum of 1,2,3-trichlorobenzene, although allowed from symmetry considerations, happens to

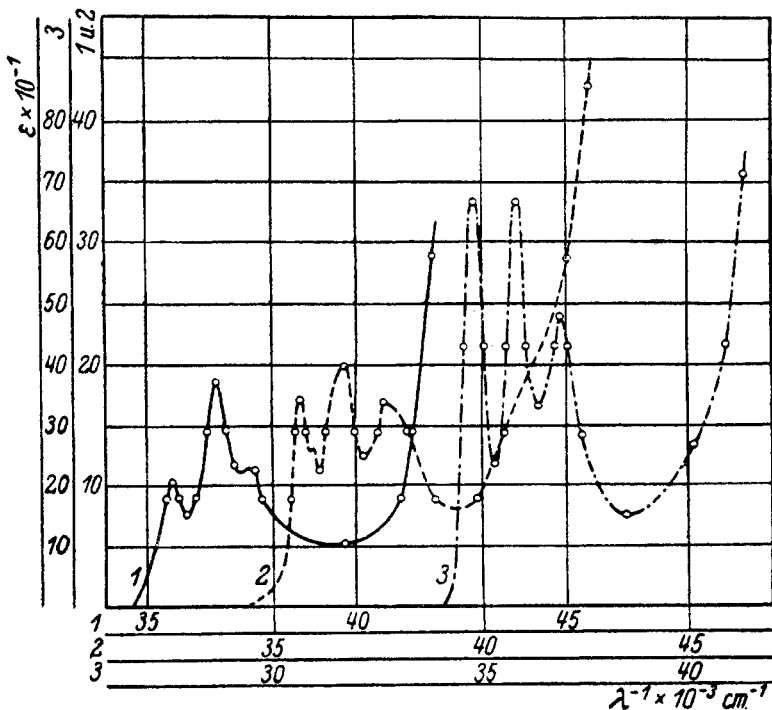


FIG. 3. Absorption spectra of trichlorobenzenes in hexane solution (concentration $7 \times 10^{-4}M$). Curve 1, 1,2,3-trichlorobenzene; curve 2, 1,3,5-trichlorobenzene; curve 3, 1,2,4-trichlorobenzene. (Taken from Conrad-Billroth: *Z. physik. Chem.* **B19**, 83 (1932))

be forbidden by a cancellation of the contributions of the substituents in the ortho and meta positions to the migrational transition moment (12).

A proof of these theoretical predictions can be obtained only from the spectra in the vapor phase where structure may be expected. In connection with these predictions and with chemical considerations, it is of interest to observe what particular vibrations will show up in the different spectra.

Figure 4 is a reproduction of the vapor spectra of the trichlorobenzenes. It can be seen that the three maxima or groups of the solution spectra break up into a number of individual bands in the vapor phase. The bands develop

with pressure and broaden and overlap each other at higher pressures. A brief discussion will be given for each spectrum separately.

1,3,5-Trichlorobenzene²

The bands are not sharp but their degradation towards the red can be recognized clearly. Those bands which appear with sufficient clarity are seen to be doubled with a spacing of about 4.5 wave numbers. Although figure 4 shows only three groups of bands there appears, at higher pressures, a fourth group on the long-wave-length side of the spectrum.

The sixfold symmetry of benzene, D_{6h} , drops to the trigonal group D_{3h} for 1,3,5-trichlorobenzene, and the near-ultraviolet electronic transition $A_{1g}-B_{2u}$

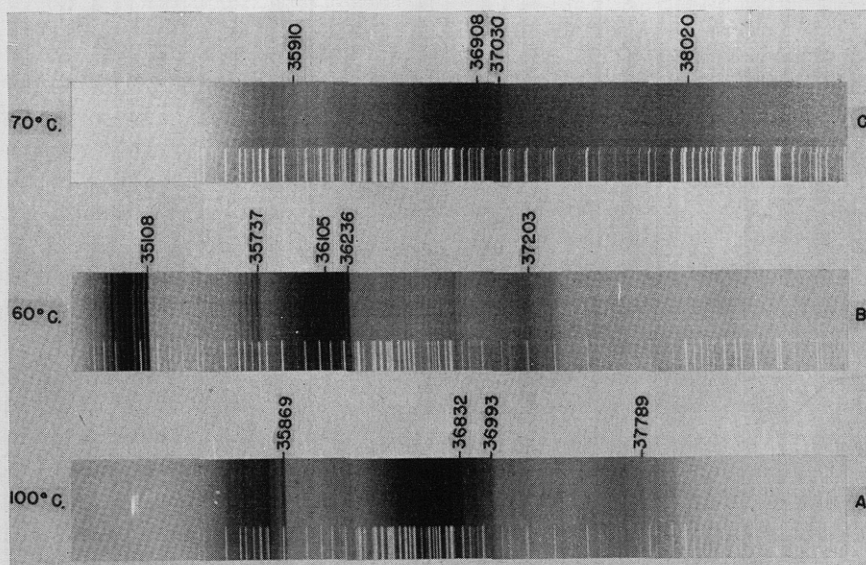


FIG. 4. Absorption spectra of trichlorobenzenes at different temperatures of the reservoir. A = 1,3,5-trichlorobenzene (16-cm. absorption tube); B = 1,2,4-trichlorobenzene (25-cm. absorption tube); C = 1,2,3-trichlorobenzene (75-cm. absorption tube).

of benzene becomes an $A'_1-A'_2$ in 1,3,5-trichlorobenzene. The transition is forbidden as in benzene because, as may be seen from group theory, there is no moment connected with it. However, a suitable distortion of the molecule's symmetry will make the production of a moment possible. It can be shown that when an unsymmetric vibration of type ϵ' is singly excited with the electronic transition, a small transition moment is produced and the spectrum will appear with weak intensity. That is, instead of a 0-0 band (electronic transition without vibration) as in allowed transitions there will be a 0-1 band which corresponds

² The detailed analysis will be published jointly with Dr. Maurice B. Hall in a contribution to a monograph, *Contributions à l'étude de la structure moléculaire*, which is to be dedicated to the memory of Victor Henri and printed in Belgium.

to a transition from the vibrationless ground state to the upper state in which that particular vibration is excited with one quantum. Superimposed on the 0-1 band should occur the pattern of an allowed band system, i.e., particularly progressions of totally symmetric vibrations. A 1-0 band in which the ϵ' vibration will now be singly excited in the ground state should appear with smaller intensity because of the Boltzmann factor involved.

It was found that the main features of the spectrum conform to theoretical expectations. A difficulty may be expected to arise from the fact that there are seven ϵ' vibrations in 1,3,5-trichlorobenzene as compared to four in benzene, and further that the vibrational frequencies in the ground state of 1,3,5-trichlorobenzene and their assignments to modes of vibration are far less well known than those in benzene. A discussion of the possibilities leads to the reasonably safe conclusion to assign the band $35,869\text{ cm}^{-1}$ of the first strong group and the very weak band $35,073\text{ cm}^{-1}$ of the new high-pressure group to 0 \rightarrow 1 and 1 \rightarrow 0 transitions of an ϵ' carbon vibration of wave number 425 in the ground state and 371 cm^{-1} in the excited level. 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 non-appearing 0-0 band may be calculated as $35,869 - 371 = 35,073 + 425 = 35,498\text{ cm}^{-1}$. The strongest bands in each of the four groups appear in pairs with a separation of 87 cm^{-1} . It probably corresponds to a 1-1 transition of a low non-symmetric vibration. Displacements by 2×87 and even 3×87 have been found in several places and also superpositions of the 54 difference on the 87 displacements.

The whole pattern of the first strong group is repeated in two subsequent groups. Bands at 36,832 and 36,993 are the first members and the bands 37,789 and 38,123 cm^{-1} the second members of progressions of the symmetric carbon vibrations 963 and 1122 cm^{-1} . The values in the ground state (5) are 995 cm^{-1} and probably 1146 cm^{-1} .

The bands appearing between the groups are more difficult to explain. There is a possibility that the pair between the first and second groups might result from the excitation of the carbon-chlorine valence vibration, but this is not definite.

There is a weak continuous absorption underlying the spectrum. This indicates a dissociation process as a result of the illumination.

1,2,4-Trichlorobenzene

The spectrum of this compound looks entirely different from that of the 1,3,5-isomer. The three maxima of the solution spectrum appear resolved into a large number of almost equally spaced bands of varying intensities. With increasing pressure the bands begin to merge into each other, while new bands appear between the groups and on both wave-length sides of the spectrum. The bands are degraded to the red but, in contrast to those of 1,3,5-trichlorobenzene, most of them are very sharp.

The 1,2,4-trichlorobenzene has the lowest symmetry of the halogenated benzenes, namely C_s . The group provides two kinds of levels only. The only symmetry element is the molecular plane. Hence there are only two types of

electronic and vibrational levels which are symmetric or antisymmetric to the molecular plane. The transition is allowed. It is an $A'-A'$, because both the A_{1g} and the B_{2u} states of benzene are symmetric to the molecular plane. From the simplicity of the group theoretical rules, we shall expect a complicated spectrum, because the variety of possible transitions is very large. We should have a strong 0-0 band. Superimposed on it should be progressions of numerous symmetric vibrations and combinations between them. The great number of symmetric vibrations in the unsymmetric compound as compared to the few in the symmetric substance—twenty-one against four—increases greatly the possibility of excitation of strong bands in 1,2,4-trichlorobenzene. On the long-wave-length side of the principal bands we expect a number of ν - ν transitions and the occurrence of low-lying symmetric vibrations. Indeed, the spectrum of 1,2,4-trichlorobenzene has not only many more bands than the spectrum of 1,3,5-trichlorobenzene but it is also of astonishing regularity. This regularity adds to the difficulty of interpretation.

The band 35,108 on the short-wave-length side of the first group is taken as 0-0 band of the spectrum. Closer inspection of the first and third groups reveals that the pattern of the first group is repeated twice in the third group, involving two symmetric vibrations of wave numbers 997 and 1128 cm^{-1} . Both are quite likely carbon-ring vibrations. The 997 occurs doubly and trebly excited, as well as in combination with the 1128 difference.

The carbon-chlorine valence vibration was found excited in the lower and upper electronic states, forming a progression in the latter state. The appearance of the second group is ascribed to its single excitation in the upper electronic state, giving a wave number of $35,737 - 35,108 = 629$ (676 ground-state value (5, 10)).

Many Raman frequencies occur at higher pressures in bands on the long-wave-length side of the 0-0 band. The individual bands in a group which are all about 30 cm^{-1} apart can be explained only when several independent small vibrations are assumed to be involved in these bands.

The bands become diffuse towards shorter wave lengths and there is some continuous absorption in that region. On the whole, there is much less continuous background in the spectrum of 1,2,4-trichlorobenzene than in the spectrum of 1,3,5-trichlorobenzene.

1,2,3-Trichlorobenzene

The solution spectrum resembles that of 1,3,5-trichlorobenzene more than that of 1,2,4-trichlorobenzene. This applies to strength of absorption and appearance of the maxima as well. The vapor spectrum, on the other hand, does not show much resemblance to either spectrum of the two isomers. It has the weak intensity of the spectrum of 1,3,5-trichlorobenzene but a different structure, and it is much more diffuse than this spectrum. The structure, which consists of three groups of rather regularly spaced bands, resembles somewhat that of the spectrum of 1,2,4-trichlorobenzene, but the two spectra differ markedly in intensity and sharpness of the bands.

The spectrum of 1,2,3-trichlorobenzene is particularly interesting. Accord-

ing to its symmetry the molecule belongs to the group C_{2v} and its near-ultraviolet absorption spectrum should represent an A_1-B_1 transition. This transition is allowed. However, Sklar (12) has calculated that the contributions from the substituents to the migrational transition moment annul one another in the first order. This means that, theoretically, a spectrum will appear only through a vibrational moment, that is, by distorting the symmetry of the molecule through excitation of vibrations. This distortion may be brought about by many vibrations. In reality, the appearance of the spectrum is more that of an allowed transition, since the existence of a 1-0 transition could not be traced, but the intensity is that of a forbidden transition. The groups are apart from each other by about 995 cm^{-1} , which very likely corresponds to a symmetric carbon ring vibration. More work is needed in order to obtain an understanding of the structure of this spectrum.

1,3,5-Trimethylbenzene³

The vapor spectrum consists of a number of rather diffuse groups of bands which correspond to the six maxima found in solution. It appears at a pressure of a few tenths of a millimeter and looks almost completely continuous at about 45 mm. , while a new group makes a faint appearance on the long-wave-length side. Since motions within the methyl groups of the molecule will hardly influence the characteristic features of the electronic absorption system, these groups are considered as big "atoms" in first approximation and the molecule then belongs to symmetry group D_{3h} . Hence, the transition may be treated as an $A'_1-A'_2$, as in 1,3,5-trichlorobenzene. Figure 6 shows the development of the spectrum at vapor pressures of about 3.5 and 70 mm. of mercury.

The spectrum has a simple appearance. It looks as if a single ϵ' vibration is responsible for its production. This was the conclusion in the case of 1,3,5-trichlorobenzene, and the same interpretation offers an understanding of the mesitylene spectrum. Fortunately, the Raman spectrum of mesitylene is known, together with polarization measurements (7, 16). From a comparison with benzene and 1,3,5-trichlorobenzene we may conclude that the depolarized line at 516 cm^{-1} corresponds to the 606 cm^{-1} in benzene and to the 425 cm^{-1} in 1,3,5-trichlorobenzene. With this assumption the band 37,000 is taken as the 0-1 band of the ϵ' 516 vibration and the extremely weak band at 36,041 as the corresponding 1-0 transition. The separation between the two bands is 959 cm^{-1} , and it cannot be identified with a Raman line. This is in confirmation of the proposed interpretation. The location of the forbidden 0-0 band may be calculated as $37,000 - 443 = 36,557\text{ cm}^{-1}$. All strong bands appear in pairs, with separations of about 68 cm^{-1} between them. These are attributed to 1-1 transitions of a low-lying non-symmetric vibration.

The pattern of the first group is repeated more or less distinctly in subsequent

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groups. They can be explained by means of three different vibrations: 968, 1300, and 555. The first two are very probably symmetric carbon ring vibrations, and the 555 is the C—CH₃ valence vibration. It is believed that the

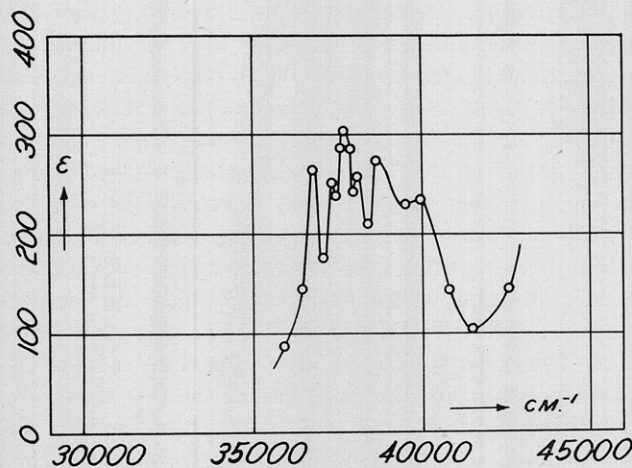


FIG. 5. Absorption spectrum of 1,3,5-trimethylbenzene in hexane solution (concentration $7 \times 10^{-4} M$). (Taken from Conrad-Billroth: *Z. physik. Chem.* **B29**, 177 (1935))

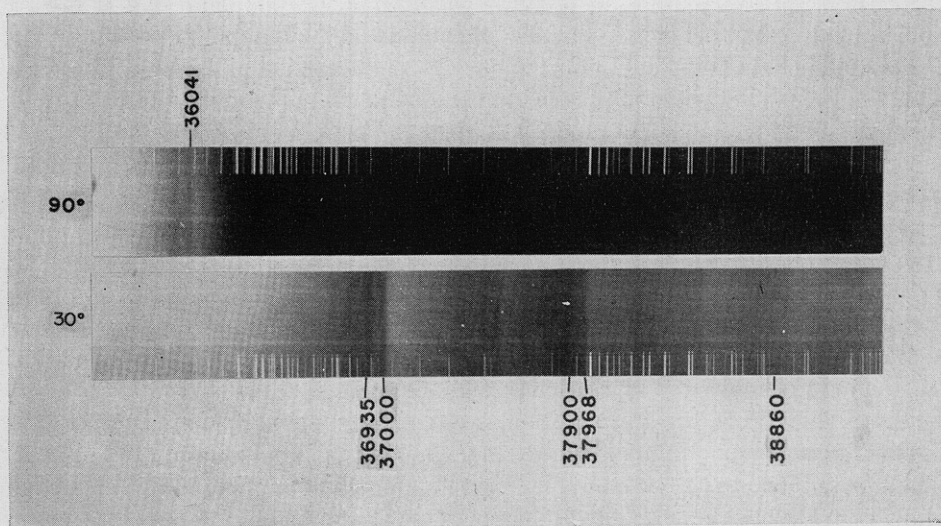


FIG. 6. Absorption spectrum of 1,3,5-trimethylbenzene at different temperatures of the reservoir.

corresponding ground-state frequency is represented by the strong polarized Raman line 575 cm^{-1} . The three frequency differences occur in progressions and combinations.

The spectrum is much more diffuse than that of 1,3,5-trichlorobenzene.

Comparison of the spectra

A comparison of the spectra may be made with different aspects in mind: as to the spectral position of the groups, as to intensity, and as to appearance (structure and diffuseness). As far as the three trichlorobenzenes are concerned, the general region of the spectra is the same and the different groups in the individual spectra are only slightly shifted with respect to each other (see figures 3 and 4). However, these shifts cannot be compared directly with each other, because the different groups in the spectra do not correspond directly to each other. The first group of the 1,2,4-trichlorobenzene spectrum, which is an allowed transition, contains the 0-0 band (vibrationless electronic transition) in the band $35,108\text{ cm}^{-1}$ on the short-wave-length side. The first group of the 1,3,5-trichlorobenzene spectrum, however, owes its presence to the 0-1 transition of the particular vibration whose excitation makes the otherwise forbidden electronic jump possible. The band $35,869$ on the short-wave-length side represents this 0-1 transition with no other vibrations excited. Consequently, what should be compared are the positions of the 0-0 bands of the different spectra, i.e., the observed 0-0 band of 1,2,4-trichlorobenzene should be compared to the calculated 0-0 band of 1,3,5-trichlorobenzene, or $35,108\text{ cm}^{-1}$ against $35,498\text{ cm}^{-1}$. In the case of 1,2,3-trichlorobenzene the first weak group contains probably the 0-0 band. Characteristic for forbidden transitions is the absence of a 0-0 band and instead the occurrence of a 0-1 band and at higher pressures a 1-0 band of a particular vibration. In solution spectra the group representing this latter transition is usually too weak for observation, because it is masked by the much stronger absorption of the 0-1 group which is broadened into the region of the 1-0 group. It may be seen, however, in the benzene spectrum of figure 1 in the first small maximum on the long-wave-length side. The 1-0 group is included in the vapor spectrum of mesitylene (figure 6) and cannot be found in the solution spectrum of that substance for the reasons just mentioned (see figure 5). The distance of the weak 1-0 group from the first strong maximum should be different from the separations between successive strong maxima. It is clear from these remarks that comparisons of solution spectra with respect to spectral positions of the maxima should be made with caution in the case of molecules of relatively high symmetry.

As mentioned in the introduction, weak absorption intensities suggest forbidden transitions. From this criterion, they may often be recognized even in solution spectra, as can be seen from figure 3, where the extinction coefficients for 1,2,4-trichlorobenzene are about twice the values of those of the two other isomers. The interesting behavior of 1,2,3-trichlorobenzene has already been noted. The cancellation of the contributions to the migrational transition moment in first approximation works even for substances like 1,3-dimethyl-2-ethylbenzene or 1,2-dimethyl-3-ethylbenzene. Their absorption strength is of the same order as that of mesitylene or benzene, whereas 1,2-dimethyl-4-ethylbenzene and 1,4-dimethyl-2-ethylbenzene are much stronger absorbers. This may be seen from the corresponding series of spectrograms (2). That

the attached groups in the mentioned alkylbenzenes are not the same is not as important as the position in which they are substituted. The structure of the alkyl groups will cause only second-order effects in the appearance of the spectra.

The vapor spectra discussed were studied in collaboration with Dr. Maurice B. Hall, Dr. Hedwig Kohn, Miss Mary Jane Stallcup, and Mr. Casimir Z. Nawrocki.

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