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## Methods to determine the electrical and geometrical structure of molecules

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Long before we had at our disposal the means offered to us today by the quantum theory to discuss the structure of atoms and molecules, it was clear that in debating this subject we had to deal with electrical structures. Starting from this point of view it seemed appropriate to me in 1912, therefore, to establish what conclusions could be reached with regard to the distribution of electricity in the molecule on the basis of experience with the action of the simplest conceivable electrical disturbance by means of a static field<sup>1</sup>. Since Faraday had introduced the measurement of this disturbance by the aid of the dielectric constant it was usual to consider the reason for the polarization occurring in every insulator on which the dielectric effect is based to be the displacement of the charges produced in the molecule by the field and which disappears again as the field disappears. This concept is still valid today. We know, indeed, that the deformation of the charge structure, which occurs with the normal experiments, is extremely small. For instance, in the helium atom, the displacement of the electron cloud against the nucleus in a field of 300 volts/cm only amounts to about  $2.104 \text{ cm}$ , i.e. a small fraction of the nucleus diameter. Owing to the size of the elementary charge, this tiny displacement is, nevertheless, still large enough to produce easily observable dielectric effects. If, however, a list of the dielectric constants of various bodies is considered, preferably based on measurements for the gaseous state, because there are no complications to be feared here owing to reciprocal influence of the molecules, abnormally large susceptibilities will be found for many molecules, and a particularly great mobility of the charges cannot be regarded as the cause of these. Thus, for example, the molecules of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  show a susceptibility which is some 40 times greater than that of the Ne atom, although the three mentioned particles contain the same number of electrons. The fact that a powerful loosening of the electron bond representing the hydrogen valency is not happening will be seen if the susceptibility of the molecules of  $\text{H}_2$  and  $\text{CH}_4$  is used as a comparison, as they both show only a normal small value. By working on observations

of this nature we can come to the conclusion that often besides the deformation there must also exist another cause of the observed electrical polarization. Now even before 1912 paramagnetic polarization and its diminution, observed by Curie, with an increase in temperature were explained in the theory of Langevin<sup>2</sup> by orientation of permanent elementary magnets. I therefore conjectured that molecules in the state of equilibrium can also be carriers of a permanent electric moment and so the electric polarization in general must be attributed to two simultaneously effective causes, a deformation and an orientation. Molecules with abnormally great electric susceptibility are, then, those with a relatively large permanent moment and its orientation causes the large polarization. This same hypothesis was published a few years later by J. J. Thomson<sup>3</sup>.

As both effects are added in the dielectric constant measured, a method had now to be found of observing them separately. A first process for this purpose results in the transference of Langevin's calculation to the electrical case. The orientation obtainable in a field is the result of an equilibrium between the field effect, which is striving for an orderly arrangement of the dipole directions, and the effect of the heat movement, which is creating disorder. With increasing temperature the mean moment arising from the orientation and produced through a uniform field must therefore decrease, and this is also the result of the theory which for this mean moment gives the value  $\mu^2/3kT$ , where  $\mu$  is the permanent moment in electrostatic units,  $k$  is Boltzmann's constant and  $T$  is the absolute temperature. The assumption here is that the potential energy of a dipole in the field is small against the mean thermal energy of a molecule, otherwise proportionality between the field strength and the polarization produced does not exist. This condition is in fact fulfilled in the great majority of the measurements. From the size of the elementary charge and the dimensions of the molecules it can be deduced that  $\mu$  should have values of the order  $10^{-18}$  (in electrostatic units), and this means that in a field of 300 volts/cm the thermal energy at room temperature is still always about 40,000 times as large as the above-mentioned potential energy. Originally the theory was purely classical. Since the appearance of the quantum theory doubts have arisen regarding the numerical factor of  $\frac{1}{3}$  in the formula for the mean moment; actually other numerical factors were calculated. Since, in the meantime, the methods of calculation of the quantum theory have been definitely formulated in wave mechanics, the factor  $\frac{1}{3}$  has been re-established as correct<sup>4</sup>. A further question which still required an answer was whether the moment produced by the

deformation was not also susceptible to temperature. In agreement with the conceptions which were prevalent 25 years ago, it was at that time shown that the quasi-elastically bound electrons through their displacement produce a moment which is independent of the temperature. Today we would prefer to attribute the actual insusceptibility of displacement against increase of temperature to the fact that the difference in energy between the basic distribution of the electrons and that under excited conditions is in general so great that the latter do not occur in any noticeable frequency.

Expectations have been confirmed by experiments on the dependency of the dielectric constant of different gases upon the temperature, conducted by Bádéker<sup>5</sup> even before the theory appeared, and by Jona at my suggestion after its appearance, and then, when electron tubes were available by beautiful and exact measurements by Sängér<sup>7</sup> and C. T. Zahn<sup>8</sup>, *inter alia*. The observable mean moment of a molecule produced through an electric field is in fact a linear function of  $I/T$ ; the experimentally determined factor of  $I/T$  in this presentation yields numerical values of the dipole moment of the order of  $10^{-18}$ . We shall later come back to the connection of the measured moments with the molecular structure. At this point let us make just one remark on the relative significance of deformation and orientation. Very often the latter is the decisive one; a good example is given by the NH, measurements from which it is seen that at room temperature 90% of the susceptibility are due to the orientation of the permanent dipole and only 10% to the deformation.

We come to a second method of determining the dipole moment if the question is considered of the dispersion of the dielectric constant. If we now first confine ourselves to considering the gaseous state again, there exist relatively sharply defined quantum stages of rotation, between which transitions will take place under the influence of the incident radiation. This means that a series of absorption lines exists, of which the first will lie for molecules with larger moments of inertia at a wavelength of the order of 1 cm. If we now pass through the infrared in the direction of increasing frequency, the refractive index in the neighbourhood of each absorption line will show the well-known breaks, and for the determination of its size the influence of the rotation and of the permanent moment will more and more disappear. The orientation can no longer be established, therefore, with high frequencies, and the frequencies of visible light must be considered as such. Only the influence of the deformation is left, for in general the electrons only cause absorption in the ultraviolet part of the spectrum. According to Maxwell's

relation therefore, the square of the optical refractive index (possibly after extrapolation to infinitely long waves, without taking into consideration the above-mentioned ultrared absorption lines) may be regarded as that part of the dielectric constant which is only based on deformation. In this way a separation of the two effects is again achieved and a determination of the dipole moment obtained. The method is clearly very simple, for it requires only the formation of the difference of the dielectric constant and the square of the optical refractive index. It is in fact always usable with good success if the molecule is sufficiently strongly polar. With low polarity the errors of estimation of the static deformation fraction become too important<sup>9</sup>.

A third interesting method is offered by the observation of the deflection of a molecular ray in an inhomogeneous electric field. As a result of the deformation alone there is a deflection of the ray only in the direction of an increasing square value of the deflecting field strength. The existence of a permanent dipole moment, creates a widening of the ray. Experiments of this nature were conducted by Wrede<sup>10</sup>, by Estermann<sup>11</sup> and, recently, by Scheffers<sup>12</sup>. Exact determinations of the dipole moment are so difficult to obtain because its size has to be concluded from the widening of the ray. The method is, however, very valuable for special cases which would otherwise not be accessible by the usual methods. It did good service in the elucidation of the peculiar behaviour of pentaerythritol and substitution products<sup>12</sup> and also in the determination of the large moments of alkali-halogenide molecules ( $\mu = 6.3 \cdot 10^{-18}$  for KCl)<sup>12</sup>.

In discussing the methods so far mentioned I have restricted myself exclusively to measurements on gases, because only thus is it possible in a completely unobjectionable way to denote the field strength actually acting upon the molecule, and because only in gases of low density can the orientation of the molecules be regarded as entirely free. On the other hand, the material accessible in such experiments is very essentially limited. For this reason I decided in 1916 to ignore the objections and to determine moments by measurements on diluted solutions of polar substances in non-polar solvents<sup>9</sup>. It is now first of all necessary to estimate the influence of the neighbouring molecules. This was done by applying the relation of Clausius and Mosotti. It is then shown that the susceptibility of the molecule now no longer follows immediately from the excess of the dielectric constant above 1. Now  $4\pi/3$  times the moment produced in the  $n$  molecules of the unit of volume under the effect of the unit field strength is measured by the fraction  $(\epsilon - 1)/(\epsilon + 2)$ . The excellent constancy established experimentally of the

molecular refraction calculated according to the Lorentz-Lorenz formula in the transition from the gaseous to the liquid state guarantees that, at least for non-polar molecules, the Clausius-Mosotti method of calculation may also still be applied for the frequency  $\nu$ . Nevertheless it is always essential throughout the experiment to see that the reciprocal influence of the polar molecules is infinitesimally small. This will be achieved if, to determine the moment, only sufficiently diluted solutions are used, or by extrapolation to infinite dilution of the measured values, limiting values are obtained for the dielectric effect of the dissolved molecules. A second condition is that the polar molecule should not be influenced either in its moment or in the freedom of its adjustment by the surrounding non-polar molecules of the solvent.

The method consists, then, in the determination, by measurements of the dielectric constant of diluted solutions, of the mean moment of the polar molecule in a unit field, and next in the separation, by measuring the refraction, of the orientation fraction from the deformation fraction. As a variant it was later proposed by Errera<sup>13</sup> to infer the last-named fraction from measurements on solids.

After the first measurements of this kind had been made at my suggestion by Miss Lange (Göttingen thesis, 1911)<sup>14</sup> and later measurements had been very much simplified by the introduction of electron tubes and the beat-method, in the course of time a very large number of molecules had been investigated regarding their polarity by many observers, amongst whom I would like to mention in particular Ch. P. Smyth<sup>15</sup> and J. W. Williams<sup>16</sup>. In an article in the *Handbuch und Jahrbuch der Chemischen Physik* for 1935, O. Fuchs and K. L. Wolf<sup>17</sup> published a list of the dipole moments of 1,100 substances; 12% of these proved to be non-polar. A very valuable summary of dipole moments has also been published by the Faraday Society, edited by Sidgwick<sup>18</sup>.

We can also consider investigating the diluted solutions at different temperatures and then, as with gases, from conclusions on their polarity from the temperature coefficients of the susceptibility of the dissolved molecules. This is indeed the most exact method of moment determination when applied to gases. In the case of solutions, however, solvent influences appear which are not taken care of in the simple theory and although they do not make the method unusable, its accuracy is affected and it cannot be given preference over the dispersion method. As the latter is also far simpler to operate, the temperature method has only occasionally been used for solutions.

With this remark we now touch upon a section of the development to which increased attention has been paid of late. As an assumption for the completely faultless functioning of the dispersion method, a second condition was mentioned above as required, viz. that there should be no influences of any kind of the solvent upon the dissolved molecules. The validity of this assumption was of course tested at the outset of the development of the method by J. W. Williams, *inter alia*<sup>19</sup>. The question was whether for a definite molecule the same moment was found in different solvents. At that time the validity of this assumption was found within the experimental limits of error. When, more recently, H. Müller<sup>20</sup> at my suggestion carried out more exact measurements with improved experimental methods, it was shown that there does exist an unmistakable though small influence of the solvent, which means that for the same molecule in different solvents not exactly the same moment is found. The results of the experiments were also confirmed from another source, and different authors tried to substantiate and to evaluate theoretically the influence of the solvent. I do not have the impression that in this point we succeeded in obtaining full clarity, and I therefore tried last year to obtain an insight into the dielectric behaviour of pure and undiluted polar fluids, in which the reciprocal influence of the molecules is particularly strong, and in which we are compelled to expect large effects. It is in fact impossible to predict the dielectric behaviour of liquids, such as water, alcohols, nitrobenzene, etc. on the basis of the theory valid for gases. The molecules behave in these cases throughout as if their moment is smaller than that observed for free particles. Exactly similar conditions are present with the Kerr effect. Here too, experiment showed that even non-polar molecules, when near each other in the liquid, behave as if the differences of their polarizability are smaller in different directions (upon which the Kerr effect is based) in the liquid than in the gas. Obviously we can think just as little in this case of a real change of the electron structure of the molecule as of a real change of moment in the case of the polar molecules, for the refraction which depends on the sum of the polarizabilities in the three main directions is scarcely influenced by the liquefaction. Now from the clear interferences, which monatomic liquids themselves produce, when they scatter X-ray light, and also from the fact that monochromatic visible light is split by ordinary Rayleigh scattering into a narrow triplet, we must conclude that there is already present in the liquid state a quasi-crystalline structure of the molecular arrangement which limits the molecular movement. From this it follows that just as little as the translatory motion, can the rotation of the

molecules in the liquid be considered as free. In fact, as I have tried to show, we can understand the dielectric behaviour of polar liquids if we pay attention to the limitation of the free rotation and use the well-known dielectric constants in co-operation with the measured moments in the gaseous state to estimate the potential energy which hinders free molecular rotation. Values were found<sup>21</sup> for this energy which can amount to a multiple of the thermal energy  $kT$ .

These considerations are also of particular importance for an other effect which is characteristic in general for the existence of an orientation of the molecules. Small field strengths produce a polarization through orientation which is proportional to the field strength. But if a very strong constant field is applied and then a measurement is taken of the additional polarization produced by a superimposed weak field, then according to the dipole theory we must now expect that a lower polarization effect will take place, for the molecules are in part already adjusted by the strong field. Herweg<sup>22</sup> was the first person able to show experimentally that in fact this so-called saturation effect does exist and that its order of magnitude for ethyl ether is as expected. It was found, however, in experiments by Malsch<sup>23</sup> on strongly associating liquids such as water, the alcohols, etc., that the effect was very much smaller than is to be expected from the theory of freely rotating dipoles. In this case the consideration of the quasi-crystalline structure of the liquids again gives the explanation. The partly extremely large differences observed follow quantitatively on the basis of the same values for the energy involved in the hindering of rotation as they must be introduced to explain the values observed for the dielectric constants of the liquids<sup>24</sup>.

Simultaneously with the development of the dispersion method in its application to liquids, the important question comes to the fore: how then in this case does the disappearance of the orientation take place in detail with increasing frequency? There cannot be any occurrence of sharp energy stages of a free rotation in a liquid, as there is with a gas. The idea of the polar molecule being compared to a fairly large particle, to which frictional resistances are opposed in its rotation, would correspond more to reality. But if this is the case, then it will be characteristic for the polar liquids that an orientation produced by an outer field does not adapt itself immediately to the new conditions when the field suddenly disappears, but needs some time to go over again to complete disorder. Or, in other words: there does exist a time of relaxation, and its magnitude is determined by the dimensions of the polar molecule and by the viscosity of the liquid. On this basis a

theory can be built up of orientation under the influence of any time-dependent fields. In its application to periodically changeable fields this leads on the one hand to the result that the degree of orientation will be less at higher frequencies, that is to say: an anomalous dispersion of the dielectric constant must exist for all polar liquids. The range of frequency which is decisive for the decrease of the dielectric constant, in the case of ordinary liquids of not too high a viscosity, should correspond to electric waves of a few centimetres of wavelength. On the other hand, owing to the phase difference between field strength and polarization, the anomalous dispersion should be connected with the appearance of dielectric losses<sup>25</sup>.

It was exactly these phenomena which were discovered by Drude in a series of non-conducting liquids, and there can be no doubt that they are indeed caused by the polar structure of the molecules. The marked temperature sensitivity of the anomalous dispersion and absorption corresponds to the large temperature coefficients of the macroscopically measured viscosity, as was proved particularly clearly by experiments conducted by Mizushima<sup>26</sup>. This means that the transference of the usual viscosity laws to particles of molecular dimensions is not devoid of all justification. We can make more exact quantitative predictions in particular for relatively large molecules. This is an interesting connection, for in this way, by observation of the dielectric dispersion and of the losses with high frequency, we obtain a means of determining the dimensions of large molecules. Recently experiments are being made to determine the relaxation time from the dielectric losses of diluted solutions of polar substances in non-polar solvents, and to bring it into relationship with the molecular constants. I have the impression that in these experiments as in the case of the losses shown by pure polar liquids, the theoretical approach to the actual conditions can be improved by the consideration of the quasi-crystalline structure of the liquids<sup>21,25</sup>. This thought is so much more obvious since conversely dispersion and absorption are observed in fixed bodies, as was first discovered by Errera<sup>27</sup> for ice. In this and in similar cases, as stressed by Pauling<sup>28</sup> in particular, we have to do with crystals in which atom groups can more or less freely rotate, and which are consequently internally partly "liquid".

After having tried in the preceding part to give a survey of the methods of determining the dipole moments and their part in the elucidation of the dielectric phenomena, we must now discuss their significance for problems of the actual molecular structure. In view of the extension which this branch has assumed it is impossible to offer a comprehensive presentation. I must

be satisfied with pointing out the guiding principles by means of some characteristic examples<sup>17,18</sup>.

The atoms of the inert gases are non-polar, corresponding to the centrally symmetrically structure of their electron clouds. In the same way diatomic molecules consisting of two equal atoms ( $N_2, O_2$ ) have been proved to be non-polar. On the other hand, polarity immediately appears as soon as the two atoms are different. This polarity is small if both atoms are close to each other in the periodic table (CO) and it only becomes large in the case of molecules like HCl. The magnitude of the moment, however, does not in any way correspond to the value which would be proper to a structure which would consist of a H-ion and a Cl-ion at their actual nuclear distance. The actual moment,  $\mu = 1.04 \cdot 10^{-18}$ , is only about  $\frac{1}{6}$  of that value. If we consider a HCl molecule as having been created by two ions brought into close proximity, there is then a considerable penetration of the H-nucleus into the electron cloud of the Cl-ion, by which 5/6 of the originally existing moment is compensated. An actual quantum-theoretical calculation of the moments does not appear to be easy. In any case, up to now the calculation of Kirkwood<sup>29</sup> for the molecules HF, HCl, HBr and HI is the only one which has led to a result.

Molecules which consist of three atoms can be divided into two groups:  $CO_2$  and  $CS_2$  are non-polar, but the molecules  $H_2O$ ,  $H_2S$  and  $SO_2$  have a permanent moment. The explanation is that in the first case the arrangement of the atoms in the molecule is linear, whereas in the second case the atoms are situated at the corners of a triangle. The moments of inertia, resulting from the analysis of the band spectra, provide an independent proof of those structures. Similarly, the observed polarity of the molecules  $NH_3$ ,  $PH_3$  and  $AsH_3$  leads to a structure in which N, P, or As are placed at the apex of a three-sided pyramid and the three H atoms at the corners of its base.

From the measurements by Sanger<sup>7</sup> on the series  $CH_4$ ,  $CH_3Cl$ ,  $CH_2Cl_2$ ,  $CHCl_3$ , and  $CCl_4$ , it follows that the first and also the end members of this series are non-polar, but the intermediate members are all polar. This fits in beautifully with the views introduced into organic chemistry by Van 't Hoff on the carbon valencies.

In the case of the ethylenes doubly substituted with Cl or Br, the *cis*-form has a considerable moment, as shown by Errera<sup>30</sup>, whilst the symmetrical *trans*-form is non-polar, again in agreement with the structural formula. The measurement of the polarity, generally speaking, in many cases of *cis-trans*-isomerism forms an excellent and easy means of determining the two forms.

For the rest, it should be stressed that neither the double bond nor the triple bond between two C atoms has in itself any polarity. Both ethylene and acetylene are non-polar.

In the same way all saturated hydrocarbons are non-polar, whether with branched or non-branched chains. We shall certainly have to award a moment to the CH bond as such, but nevertheless all the molecules are non-polar, as Smyth stresses<sup>15</sup>, if we adhere to the tetrahedral valency orientations, because then every CH<sub>3</sub> group is precisely able to compensate a CH bond electrically.

Thus we have made a start with a division of the entire moment into individual moments of the bonds, which are combined by means of vectorial addition to a resultant moment, like forces. (Absolute values for the individual bonds were given in detail for the first time by Eucken<sup>31</sup>). This construction, stipulated by the nature of the electric moment, has proved reliable throughout all the discussion of the molecular structure based on moment measurements. It is true that this description is only an approximation in so far that on more intimate inspection due consideration must be given not only to an additional influence of the adjacent valency orientations, but also to the electrical influence of the molecular structure arising from the moments. This does not, however, prevent the simple method from being a highly valuable means of achieving a first and good approximation.

The first instance which I know of as arising from this point of view, and which was indeed discussed by J. J. Thomson<sup>32</sup>, was that of the disubstitution products of benzene. If, for example, the moment of monochlorobenzene is known, we should be able to calculate the moments of ortho-, meta- and paradichlorobenzene by combining to a resultant two equal monochlorine moments vectorially with angles of 60°, 120°, and 180°, based upon the structure of benzene characterized by the regular hexagon of the C atoms. It is correct that the para-substitution product is in fact non-polar; on the other hand, the calculated numerical values of the two other products, and particularly those of the ortho-substituted benzene, are not quite in agreement with the experimental findings. Obviously we have to deal in this instance with a reciprocal influence of closely adjacent groups, which leads to a spreading-out of the valence directions.

If two different atoms or groups are substituted in para-position, the resultant moment can be both equal to the sum and equal to the difference of the individual moments. One would expect this, for whether the sum or the difference occurs, will depend on whether, in the substituted groups,

like or unlike charges show externally. A means is thus obtained of distinguishing positive and negative groups (in the purely electrostatic definition) one from another.

Finally, it can even happen in the substitution of two equal groups in para-position that a polar molecule does occur, nevertheless. For instance, the moment of hydroquinone-dimethylether, in which two O-CH<sub>3</sub> groups are substituted in para-position at the benzene ring, is  $1.73 \cdot 10^{-18}$ . Such and similar results are explainable by the fact that the moment of the individual groups does not lie in the plane of the benzene ring. It is clear that the two valence directions of the O atom form a smaller angle than 180°, as is the case with the H<sub>2</sub>O molecule. This, together with the more or less free rotatability of each group around the axis, which is present from the C atom of the benzene nucleus to the O atom, means that apart from entirely special positions of the two O-CH<sub>3</sub> directions the molecule will always have a resultant moment, and therefore in the experiment a mean moment must be observed. It is clear that by combinations of measurements on suitable substitution products we can draw valuable conclusions both regarding the valency angle and the greater or lesser freedom of the rotation, and in fact in many cases polarization measurements have been used for this purpose.

A particularly interesting case occurs when the potential energy which restricts the freedom of rotation is comparable with the thermal energy of the surrounding temperature. Such a case is, *inter alia*, 1-2-dichloroethane, in which a rotation of the two CH<sub>2</sub>Cl groups can take place round the C-C bond. The position with the least potential energy in this instance is the *trans*-position, to which as such the moment zero is proper. With increasing temperature the amplitudes of distortion become increasingly greater and finally, with a sufficiently high temperature, all the distortion angles are equally justified. A moment is however associated with this situation and hence we must expect that the "permanent" moment of the molecule observed at different temperatures will not be constant, but will increase with increasing temperature to a limiting value. In fact that is the result of the observation; the temperature curve can be utilized to deduce quantitative statements regarding the amount of work required for the rotation of the groups<sup>33</sup>.

The conviction of chemists that the structural formula is in fact a representation of the spatial arrangement of the atoms in the molecule which corresponds to nature is obviously brilliantly confirmed by the previous discussion. Often the only thing lacking is that the representation is not ac-

cording to scale. A method should therefore be sought to carry out measurements of the distances within the molecule. Since the discovery by von Laue<sup>34</sup> of crystal interferences we know that the wavelengths of X-rays are small enough to be suitable for this purpose. If, however, we wish to examine free molecules, the difficulty arises that we have to operate with particles which cannot be fixed in a definite orientation in space, like a crystal. Fortunately, however, I was able to show<sup>35</sup> that every atomic structure irradiated with X-rays must produce recognizable interferences in its scattered radiation, even when it changes its orientation in space continuously and uncontrollably. I was led by this consideration, when together with Scherrer<sup>36</sup>, the interferences of crystalline powders and of liquids were discovered. These experiments were a preliminary step to the first attempt to produce interferences by scattering on  $\text{CCl}_4$  vapour, carried out in 1928 together with Bewilogua and Ehrhardt<sup>37,42</sup>.

The basis for the interpretation and evaluation of such scattering curves is based on the following calculation. The intensity of the scattered X-ray light decreases gradually with increasing angle  $\theta$  between the primary and secondary ray as well for atomic as for molecular gases and it does so as a result of an interference effect. In the case of the atoms, this decrease follows a smooth curve, but in the case of molecules, on the other hand, actual maxima and minima occur in the scattering curve occasionally reduced to undulations only. Such a scattering curve can be constructed by superposition of as many individual curves as there are atomic distances in the molecule. If the molecule consists, for instance, of  $N$  atoms, for which an enumeration  $1 \dots m$  or  $n \dots N$  is assumed, then for the intensity the following expression is obtained, neglecting a factor, which here is unessential:

$$I = \sum_{m=1}^N \sum_{n=1}^N \psi_m \psi_n \cdot \frac{\sin x_{mn}}{x_{mn}}$$

The magnitude  $x_{mn}$  is here proportional to the distance  $l_{mn}$  from atom  $m$  to atom  $n$  and, if the primary wavelength  $\lambda$  is used for irradiation, it is defined by the relation:

$$x_{mn} = 4\pi \frac{l_{mn}}{\lambda} \cdot \sin \frac{\theta}{2}$$

The magnitudes  $\psi_m$  or  $\psi_n$  are the so-called atomic form factors of the atoms  $m$  or  $n$  respectively, and represent the amplitudes dispersed by those atoms.

Every atomic distance in the molecule therefore produces for itself an intensity which increases and decreases with the increasing angle  $\vartheta$ , in accordance with the function  $\sin x/x$ . For large atomic distances, the maxima lie close together, they get farther apart for small distances. The relative importance of the different atomic distances is measured by the product of the atomic factors  $\psi$ . These can be calculated by various methods (Thomas-Fermi, Pauling-Sherman<sup>38</sup>) or they can be taken with greater accuracy from the tables drawn up by Hartree<sup>39</sup>. For small angles such an atomic form factor is simply proportional to the number of electrons contained in the atom. Consequently, for the distribution of intensity, the distances between the atoms of fairly large atomic weight have the most importance; the distances between the light and heavy atoms are of less importance and the least important are the distances between light atoms.

We must also take into consideration that with scattering, polarization of the radiation occurs, and so the intensity in the neighbourhood of the  $90^\circ$  direction is reduced. Furthermore, each diagram has a background of incoherent radiation which in accordance with the Compton effect has changed its wavelength and does not contribute to the interferences. No allowance was made in the formula for these circumstances, which are to be considered more as corrections.

The fact that the first experiment was conducted on  $\text{CCl}_4$  gas was not an accident. If we take the tetrahedron as the basis for the structure of this molecule there occur in it four equal distances between the heavy Cl atoms beside four distances which are equal between the light C and the heavy Cl atoms, though according to what we stated above, these latter distances are much less important. It could therefore be hoped that there would be a distribution of intensity which would show relatively pronounced maxima and minima of intensity, and the experiment confirmed this expectation. To determine the atomic distances in the molecule, we need only compare the observed angular position of the maxima and the minima with that resulting from the theoretical representation. With a known wavelength of the primary radiation, a proper choice of the atomic distances has to be made in order to obtain agreement between theory and experiment. This is particularly simple in the case of  $\text{CCl}_4$ , as the tetrahedron is completely determined by a single length, the length of edge for instance. In making an exact comparison we must of course require that not only attention is paid to the position of the maxima and minima, but that the intensity curve throughout its entire length coincides with the theoretically calculated curve. Careful

experiments in this direction, using purely monochromatic primary radiation obtained by crystal reflection, were carried out by Van der Grinten in the Leipzig laboratory<sup>40</sup>. The excellent agreement shown in this instance can be regarded as direct experimental proof of the regular tetrahedral structure of the  $\text{CCl}_4$  molecule.

After the scattering experiments with X-rays<sup>37,42</sup> had shown that interferences can be obtained from the individual molecule, Mark and Wierl published in 1930<sup>41</sup> the first results of similar experiments with cathode rays. Since, according to de Broglie, electron rays can interfere with one another with the wavelength  $\lambda = h/p$  ( $h$  = Planck's quantum constant,  $p$  = electron impulse), this method was also successful. If both methods are compared, the advantage of the cathode-ray method lies in the fact that, because of the much stronger interaction of the electrons with the electric charges in the atom, the exposure times here are much smaller (of the order of one second), whereas in the case of X-rays they amount to hours. Secondly, with the usual voltages the wavelength of the cathode rays (0.07 Å with 30,000 volts) is essentially smaller than that of the X-rays utilized (about 1 Å). As a result, the interferences can be taken and followed up to higher orders. On the other hand, the X-rays have the advantage that recordings for complete intensity curves can be obtained without much difficulty. In addition, there is the fact that the background arising from the incoherent radiation increases with increasing angle starting from zero at zero angle in the case of X-rays, whereas in the electron-case the largest intensity occurs for small angles. Consequently, with X-rays the maxima are more strongly pronounced.

The question now arises, with what accuracy the distances in the molecule can be determined from the maxima which are only indistinct in any case because of the low number of the interfering atoms. We can establish this very well on the basis of experiments of both kinds on the  $\text{CCl}_4$  molecule, which has gradually become a kind of standard substance. Bewilogua<sup>42</sup> finds 2.99 Å for the Cl-Cl distance in 1931 with X rays, and Wierl<sup>43</sup> 2.98 Å shortly afterwards with cathode rays. The next two years, 1932 and 1933, bring three further publications with cathode rays, which lead to the values 2.98, 2.97, and 2.98. Work with cathode rays is continued in more places; in 1933 one publication gives the smaller value 2.91, and then in 1934 there are four further results with cathode rays which yielded the still smaller values 2.87, 2.86, 2.85, and 2.87<sup>47,48,49,50</sup>. This induced me, when I was Francqui Professor at Liège to build an X-ray and a cathode-ray apparatus in order to check the problem of the exact value of the distance again.

Degard and Van der Grinten<sup>44,45</sup> find 2.86Å in 1935 with cathode rays, and Piérard and Van der Grinten<sup>44,46</sup> obtain 2.85Å with X-rays. It is therefore quite certain that the value found at the start of the development was about 4% too high, and that the value 2.86 Å, with a tolerance of  $\pm 0.01$  Å, is to be regarded as the correct one. The above-mentioned measurements from 1934 by Brockway and Pauling<sup>47</sup>, Cosslett and de Laszlo<sup>48</sup>, by Cosslett<sup>49</sup> and by Brockway and Wall<sup>50</sup> are also in agreement with this.

In the seven years which have elapsed since 1929 many other molecules besides  $\text{CCl}_4$  have been investigated interferometrically; in a handbook article by Hengstenberg and Wolf<sup>51</sup> in 1935, a list of 66 substances has been given, and in an article by Brockway in the *Review of Modern Physics*<sup>52</sup> in 1936, there is a list of 143 substances. Exact distance details, as contained in such tables, are of special interest, because they allow interesting conclusions on the nature of the bond as emphasized for instance by Pauling. Moreover, the picture we receive of the spatial structure is of importance. Here we have only space for a few incomplete details which should be enough to create a general impression.

Bewilogua, in publication of 1931<sup>42</sup>, had already shown for the series  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CH}_3\text{Cl}$  how with decreasing Cl-content the diagram changes as expected from the tetrahedral structure. At the same time the conclusion was drawn that an increase of the Cl-Cl distances goes together with a reduction of the number of Cl substitutions. The latter result has been doubted at times, but newer measurements with both methods show unambiguously<sup>53,54</sup> that, to begin with, in the case of chloroform the Cl-Cl distance is in fact 3.5% greater than in  $\text{CCl}_3$ , i.e. by the same relative amount which Bewilogua deduced. There is therefore a repulsion between the Cl atoms, as one would expect from the observed dipole moments.

Wierl<sup>43</sup> has shown, and other observers have confirmed, that besides  $\text{CCl}_4$  the analogous molecules  $\text{SiCl}_4$ ,  $\text{TiCl}_4$ ,  $\text{GeCl}_4$ , and  $\text{SnCl}_4$  possess the tetrahedral structure. It is interesting that the same applies for  $\text{Ni}(\text{CO})_4$ , as recently found by Brockway and Cross<sup>55</sup>. The molecules  $\text{CO}_2$  and  $\text{CS}_2$  are shown by interferometric measurements to be linear, in agreement with the fact that their dipole moment is zero. It has also been possible to prove that in the molecules  $\text{SF}_6$ ,  $\text{SeF}_6$ , and  $\text{TeF}_6$  the fluorine atoms occupy the corners of a regular octahedron<sup>51,52</sup>.

That the interferometric methods are able to distinguish between *cis-trans* isomers has been shown for the dichloroethylenes. The *trans*-form has substantially larger Cl-Cl distance than the *cis*-form, which is what it ought to

have. If there is a single bond between the two C atoms, instead of a double bond, the question again comes to the fore, as in the case of the dipoles, of the freedom of rotation around the C-C bond. It is of particular interest that it is also possible to prove interferometrically the preference of the *trans*-position, as was likewise inferred from the temperature dependence of the dipole moment<sup>56</sup>.

For the benzene molecule, and particularly beautifully for hexachlorobenzene, it can be proved that the six-membered ring is planar and that it corresponds to the carbon ring of graphite and not to that in the diamond<sup>57</sup>. This is also indicated by the C-C distance itself, which has a value of 1.54 Å in aliphatic compounds, but only 1.41 Å in aromatic compounds. It becomes still smaller with double or even triple bonds<sup>51,52</sup>.

Finally, two general questions may be raised which so far have not been answered in full.

Is it possible by using interferometric methods to measure the thermal oscillations of the atoms in the molecule? Experiments and measurements by James<sup>58</sup> led to the result that in the molecule  $\text{SiCl}_4$ , which was selected because the Cl atoms are somewhat more loosely bound than in  $\text{CCl}_4$ , the oscillations are too small to allow certain proof with the aid of X-ray interferences. From Raman-effect measurements the conclusion can be drawn that in most molecules the elastic constants are in fact relatively large; for instance, the C-C bond in aliphatic hydrocarbons is as hard as it is in the diamond. Recently Van der Grinten<sup>44</sup> has explained the flattening of the intensity curve for  $\text{CCl}_4$  in the vicinity of the 5th maximum (obtained with electrons) as due to the influence of atomic oscillations. So it seems possible that by the investigation of the intensity curve of electron recordings in the neighbourhood of suitably selected interference maxima of high order, the atomic oscillations can be traced.

Can we determine by interferometric methods the position of the hydrogen atoms? It will hardly be possible to do so with X-rays, for as the X-ray scattering is due to the electrons, it is necessary for these to be present in a satisfactory concentration in concentric distribution around the nucleus whose position is to be measured. This is, however, not the case with the H-nucleus. On the contrary, as recent experiments by Thomer<sup>59</sup> show, the molecules Ne,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and  $\text{CH}_4$  with the same total nuclear charge all scatter almost like monatomic gases. The only thing clearly indicated is, that the electron cloud is the more extended, the more the total nuclear charge of 10 unit charges is distributed on individual nuclei. It has not yet been

decided experimentally whether the electron scattering, which with larger angles chiefly takes place at the nucleus, can be better utilized here. Provisionally it is in any case more practical to replace such hydrogen atoms (the position of which is of particular interest) chemically by heavier atoms, such as Cl.

In summary I would like to emphasize that the physical methods discussed here besides furnishing a precise definition of atomic positions have given a brilliant confirmation of structures obtained by purely chemical means.

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