THE STRUCTURE OF THE METHANE MOLECULE[1]

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During the last ten years a number of different methods of investigating the structure of molecules have been worked out and an almost completely new science of molecular physics has been developed. The results which have been obtained are of very general importance and the application of the theories and principles which have been derived from these studies marks a new period in the development of chemistry.

The structure of the molecule of methane is of the utmost importance to all organic chemistry involving, as it does, fundamental conceptions concerning the carbon atom and an application of these modern methods of investigation to the study of the methane molecule has given results of far-reaching significance.

Methane is a colorless, odorless gas; it shows slight deviation from the simple gas laws and can be liquefied at −164°C. It is the most important constituent of natural gas, some samples of natural gas showing as much as 99.3 per cent of methane. Since the work of Pasteur, van't Hoff and LeBel more than fifty years ago there has been very general acceptance of the *tetrahedral structure* of the methane molecule, the carbon atom being at the center of the tetrahedron and the four hydrogen atoms at the corners (fig. 1).

From the standpoint of the present-day ideas of atomic structure two of the six planetary electrons of carbon are near the nucleus and the other four are in outer orbits. The hydrogen atom has one planetary electron and the electronic structure of the methane molecule may be shown schematically by figure 2 where the dots represent electrons, the inner electrons being inclosed within the circle.

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The evidence upon which the tetrahedral structure of the methane molecule is based depends primarily upon the fact that methane does not form isomeric derivatives. For example, there is only one dichlor-methane whereas, if the structure were not a tetrahedron there should be two isomeric dichlor-methanes. The three general assumptions upon which the whole of organic chemistry has been built are:

1. The equivalence of the four valencies of carbon
2. The tetrahedral structure of methane
3. The rigidity of the structure of molecules

With the development of the science of molecular physics during the last ten years physicists have introduced new methods of

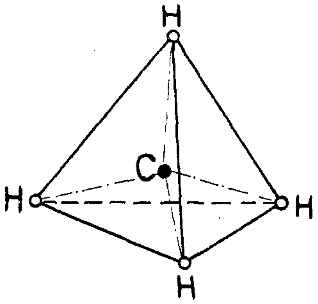

FIG. 1

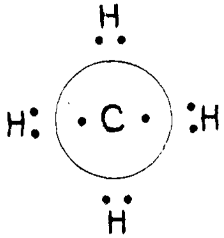

FIG. 2

investigating the structure of molecules and have made important contributions to the theoretical interpretations. These new methods were first controlled by the study of different simple molecules, such as, nitrogen, hydrogen, chlorine, hydrogen chloride, carbon monoxide and then more complicated molecules were examined and now more than seventy different molecules have been studied, of which about fifty have been investigated in my laboratory.

The results of the study of the methane molecule may be briefly summarized as follows:

1. The molecule of methane is *not* a tetrahedron but has the structure of a pyramid. The distance between two hydrogen atoms is equal to 1 Å or 10^{-8} cm. and the height of this pyramid is

equal to 0.37 Å. The relative positions of the hydrogen and carbon atoms are shown in figure 3.

2. When the four hydrogen atoms of methane are replaced by four chlorine atoms the structure changes and becomes a tetrahedron so that the molecule of carbon tetrachloride is tetrahedral. The dichlor-derivatives of methane have a tetrahedral structure whereas certain of the tetra-derivatives of methane have a pyramidal structure. For example, pentaerythritol, where each hydrogen atom is substituted by a (CH_2OH) group has a pyramidal structure as has also the molecule of tetra-phenyl-methane.

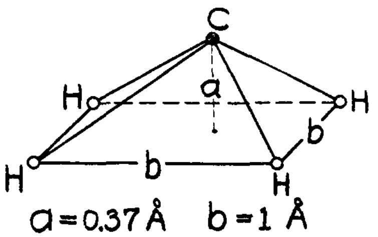

FIG. 3

3. The four valencies of the carbon atom are *not* equal. Two of them are of one kind and two of another (fig. 4). Our experimental evidence leads us to believe that the six electrons of the carbon atom are distributed in three shells. The two inner electrons are in the 1_1 orbit and of the four external electrons two are in the 2_1 orbit and two in the 2_2 orbit. This relationship is shown in figure 5.

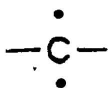

FIG. 4

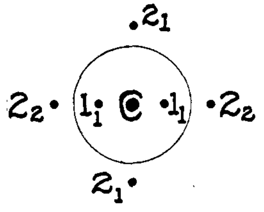

FIG. 5

These three conclusions are in absolute contradiction to the classical theories upon which organic chemistry has been built and in the light of this new experimental evidence there should be a complete revision of the chemistry of carbon compounds. It is with pleasure that I acknowledge the very important contributions made by American physicists to the science of molecular physics.

The experimental methods by which these important results have been achieved may be classed into five different groups:

1. The scattering of light
2. The absorption spectra
3. The structure of crystals as determined by x-rays
4. The calculation of the potential energy of molecules
5. The emission spectra of atoms and molecules

These various methods will be examined briefly and the results summarized.

1. THE SCATTERING OF LIGHT

The very familiar example of the effect of the scattering of light is the production of the blue color of the sky by the scattering of the sun's rays by the molecules of the atmosphere. Tyndall (1) was the first to investigate thoroughly the scattering of light and the phenomenon has since been called the Tyndall effect. J. W. Strutt (Lord Rayleigh) (2) developed the theory by which it is shown that when a beam of light of intensity I_0 falls on a gas inclosed in a tube, a portion of this beam is scattered by the molecules of the gas and the intensity of this scattered light, I_1, (fig. 6) in one direction is dependent upon the kind of molecule, the volume of the molecules and the number of them per cubic centimeter. This amount of scattered light is very small, varying from two to five millionths of the intensity of the incident light. If the molecules are isotropic the scattered light is totally polarized, the plane of polarization being determined by the directions of the two beams I_0 and I_1.

During the last seven years a number of experimental investigations of the scattering of light by various sorts of gases have been made by R. J. Strutt (Lord Rayleigh) (3), Cabannes (4), Gans (5), and Raman (6) and these results have shown that for the rare gases, helium, neon and argon which are monatomic there is a total polarization of the scattered light. These molecules are all isotropic. In the case, however, of the diatomic and triatomic gases, nitrogen, hydrogen, oxygen, carbon monoxide, hydrogen chloride, carbon dioxide, water etc., there is only a partial polarization produced in the scattered light. This incomplete polarization is due to the anisotropic character of these molecules. A complete theory has been derived by Gans (5) according to which it is possible to calculate the degree of anisotropy of a molecule from the proportion of the scattered light which is non-polarized. It is thus possible to show that the structure of these different di- and triatomic molecules can be represented by an ellipsoid. A special study of the molecule of methane and of other hydrocarbons was made by Cabannes (7).

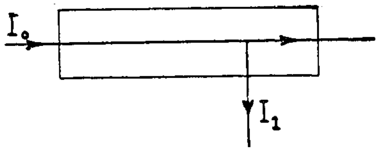

FIG. 6

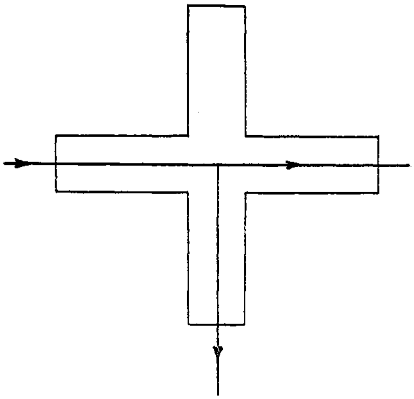

FIG. 7

The actual measurement of the amount of scattered light which is polarized involved great difficulties in technique. The pure gas was dried and filtered so that it contained no dust and was then introduced into a tube having the form of a cross (fig. 7). An intense beam of monochromatic light was allowed to fall on the gas and a photograph made at right angles to the plane of the incident light. The amount of polarized light was determined by a system of nicols. The results obtained with methane showed that there was a considerable proportion of non-polarized light thus showing that the methane molecule is anisotropic. This result excludes the possibility of a tetrahedral structure inasmuch as the molecule must have two different moments of inertia. In the case of carbon tetrachloride Cabannes found *isotropic* molecules.

2. THE ABSORPTION SPECTRA

When a beam of light containing all wave-lengths from the infra-red to the ultra-violet is passed through a gas or vapor

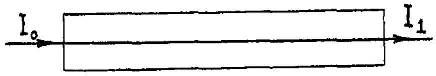

FIG. 8

contained in a tube with quartz ends, analysis of the beam of light I_1 (fig. 8) after passage through the gas shows that certain wave-lengths are missing or have been absorbed by the gas. If the beam I_1 falls on the slit of an infra-red spectrometer or of a spectrograph the absorption spectrum of the gas or vapor may be determined. Each substance has a very characteristic absorption spectrum made up of a large number of absorption lines and bands. Although the number of these absorption bands is always in the thousands they can all be arranged in groups and series in which the distribution may be formulated mathematically and it is now possible to understand the physical significance of this mathematical formulation.

According to the Bohr theory the absorption of light of definite frequency takes place whenever the internal energy of the molecule increases in the form of jumps. In the case of molecules, three kinds of motion must be considered: (1) the orbital motion of the electrons, (2) the vibration of the atoms or groups of atoms, (3) the rotation of the molecule. From this point of view the internal energy W° of a molecule in the normal state may be expressed as the sum of three quantities:

$$W^\circ = E_e^\circ + E_v^\circ + E_r^\circ$$

where E_e°, E_v° and E_r° are the values of the electronic, the vibrational and the rotational energies. When the molecule is activated under the influence of light the energy of the activated molecule will be

$$W' = E_e' + E_v' + E_r'$$

and according to the second postulate of Bohr the frequency v of the absorbed light is

$$\nu = \frac{W' - W^\circ}{h}$$

where h is Planck's constant and equal to $6.55.10^{-27}$ erg. sec.

If only the rotational energy of the molecule is considered it can be shown that this is dependent on two factors,—the quantum number of rotation and the moments of inertia of the molecule. If the molecule is isotropic there is only one moment of inertia J. The successive states of rotation of the molecule correspond to successive values of the internal energy E_r°, E_r', E_r'', . . . E^m, E_r^{m+1} . . . the general formula for a molecule with one moment of inertia being

$$E_r^m = \frac{h^2\, m(m + 1)}{8\pi^2\, J}$$

The transition from one state m to the next (m + 1) or to the preceding (m − 1) state absorbs light of definite frequency. The general distribution of these absorption lines is given by the formula

$$\nu = \nu_o + \frac{E_r^{m+1} - E_r^m}{h} \qquad \text{or} \qquad \nu = \nu_o + \frac{E_r^m - E_r^{m-1}}{h}$$

This distribution depends upon only *one* value which is characteristic of a particular molecule, that is the moment of inertia. This means that in all parts of the absorption spectrum, the fine structure, which is determined by the rotation of the molecule, must be the same. The rotational spectrum of a molecule with one moment of inertia shows a series of equidistant lines in which the distance between two successive lines is equal to

$$\Delta \frac{1}{\lambda} = \frac{h}{4\pi^2 J} = \frac{55.5 \, .10^{-40}}{J} \text{ cm}^{-1}$$

If therefore the distance between successive lines is measured the moment of inertia can be readily calculated. This conclusion has been confirmed by a great number of measurements on different molecules with only one moment of inertia,—nitrogen, hydrogen, sulphur, hydrogen chloride, carbon monoxide, etc.

In the case of the molecule of methane the measurements made by Cooley (8) in the infra-red have shown that there are two different sets of fine structure. For the band $\lambda = 3.3\mu$ there are many narrow lines in which $\Delta\frac{1}{\lambda} = 5.51$ cm^{-1}, but for the band $\lambda = 7.7\mu$ the lines are more widely spaced and $\Delta\frac{1}{\lambda} = 9.77$ cm^{-1}. This structure of the absorption spectrum cannot be that of a molecule with only one moment of inertia. During the last year these results have been discussed quite fully by Dennison (9) and particularly by Guillemin (10) from the laboratory of Sommerfeld in Munich.

The absorption spectrum of formaldehyde has been studied in my laboratory with Dr. Schou (11) and we have found a double rotational spectrum with two sorts of fine structure. The particular importance of these results depends upon the fact that if the molecule has two moments of inertia, J and K, it is possible to calculate these values from the distribution of the fine lines in the absorption spectrum.

When a molecule has two moments of inertia, J and K, the energy of rotation depends on two quantum numbers m and q. The energy of rotation in any state E_r^{mq} is expressed by

$$E_r^{mq} = \frac{h^2}{8\pi^2}\left[\frac{m(m+1)}{K} + q^2\left(\frac{1}{J} - \frac{1}{K}\right)\right]$$

in which q is constant in the transition from the state m to (m ± 1) and m remains constant in the transition from q to (q ± 1), thus giving rise to two sorts of absorption lines. By application of this formula the values for the two moments of inertia may be calculated. For the methane molecule $J = 3.64 \,.10^{-40}$ and $K = 5.65 \,.10^{-40}$ and for the formaldehyde molecule $J = 1.41 \,.10^{-40}$ and $K = 25 \,.10^{-40}$. These results show that the molecule of methane cannot be a tetrahedron and the simplest structure which is in accord with these values is that of a pyramid. From the values of the two moments of inertia, corresponding to the rotation around the two axes, it is possible to calculate the distance between the different atoms. Guillemin's calculations (10) show that the distance between the hydrogen atoms in methane is $1.05 \,.10^{-8}$ cm. and the distance between the carbon and hydrogen atoms is $1.15 \,.10^{-8}$ cm., the height of the pyramid being equal to $0.375 \,.10^{-8}$ cm. For formaldehyde we have found the distance between the carbon and oxygen atoms to be $1.02 \,.10^{-8}$ cm. and between the two hydrogen atoms $1.34 \,.10^{-8}$ cm.

3. THE STRUCTURE OF CRYSTALS AS DETERMINED BY X-RAYS

It is not possible to examine the crystal structure of solid methane but different derivatives of methane have been examined. The crystal structure of pentaerythritol ($C(CH_2OH)_4$) has been studied by Mark (12) and his results have been confirmed by Huggins and Hendricks (13). The results show that this compound cannot have cubic symmetry and that the most probable structure of the molecule which is in agreement with the experimental values is that of a pyramid. Similar results have been obtained with tetraphenyl methane and on the basis of these results Weissenberg (14) and Reis (15) have developed a whole new stereochemistry based on the conception of the pyramidal structure of the methane molecule.

4. POTENTIAL ENERGY OF THE MOLECULE OF METHANE

The theoretical study of the stability of different configurations of a molecule formed by one negative ion and one or more hydrogen ions has been investigated recently by Heisenberg (16), Born (17), Kornfeld (18), Hund (19), and the molecule of methane in particular by Guillemin (10). This theoretical study is based upon the following considerations: (1) between the carbon atom, or rather the carbon ion, and each hydrogen ion there is first an attractive force proportional to $1/r^2$ and secondly, a repulsive force proportional to $1/r^n$, where $n = 5$ or 7 or 9; (2) between the different hydrogen atoms there are forces proportional to $1/s^2$ and to $1/s^n$; (3) inasmuch as the carbon ion is polarized or deformed by the intramolecular electrical field, the resulting dipole exerts an additional action on the hydrogen ions and this action is dependent upon the deformation coefficient α of the carbon ion ($\alpha = 1.34 .10^{-24}$). The potential energy of a configuration such as is shown in figure 9 can be expressed as the sum of terms depending upon $1/r$, $1/s$, and α:

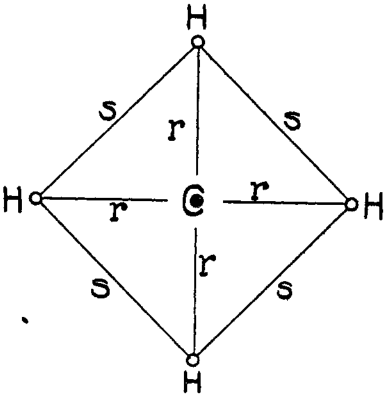

FIG. 9

$$P = F(1/r) + G(1/s) + H(\alpha,1/r)$$

This potential energy has a minimum value for a certain definite configuration and the conditions for this minimum value can be calculated. The form corresponding to the minimum of the potential energy is dependent upon the value of the deformability coefficient α. The results of these calculations show that the potential energy of the tetrahedral configuration is larger than that of the pyramidal form since for the tetrahedral form $P = -136 . 10^{-12}$ erg and for the pyramidal $P = -175 . 10^{-12}$ erg.

These results show therefore that the stable form of the methane molecule is that of a pyramid and not of a tetrahedron. The same method of calculation when applied to the structure of the water molecule shows a triangular structure (fig. 10) with an angle of 66° and to the molecule of ammonia a pyramidal form (fig. 11).

Another important result derived from the mathematical treatment of potential energy is obtained when this method of calculation is applied to the molecule of carbon tetrachloride. In this case the structure of minimum potential energy is the tetrahedral form and not the pyramidal. These conclusions are of particular significance inasmuch as they show not only that the structure of the methane molecule is pyramidal but also that the form of a molecule cannot be considered as rigid and fixed. It is incorrect to conclude that because a molecule has a certain definite structure that this same type of structure would be maintained in all derivatives. On the contrary, a molecule is a mobile system of atoms in which the stability of the structure is determined by the minimum value of the potential energy. Instead of assuming the *rigidity* of the molecule, which has been the assumption upon which organic chemistry has been developed in the past, there must be a recognition of the *lability* of every molecule. This

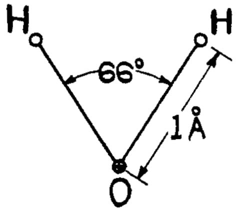

FIG. 10

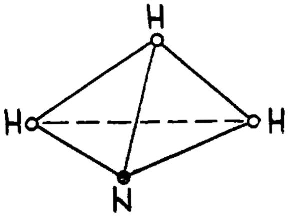

FIG. 11

lability of structure determines the chemical reactivity and if the values of the potential energy for different molecular structures are known it is possible to predict the chemical reactivity.

5. EMISSION SPECTRA OF THE CARBON ATOM

The carbon atom contains two inner K-electrons which have circular orbits and correspond to the quantum notation 1_1, and four external or valence electrons. Until 1922 it was assumed that these external electrons were all of the same type, with circular or 2_2 orbits. In 1924, however, Fowler (20) in studying the emission spectra of ionized carbon (C_+) found that this spectrum had the same structure as that of boron. Analysis of the boron spectrum had already shown that the boron atom contained two external electrons with 2_2 orbits and one electron with a 2_1 orbit. It would follow therefore that the ionized carbon (C_+) must have the same two types of external electrons. The structure of the carbon spectrum for the normal carbon atom (C) and the successive ions, C_{+}, C_{++}, C_{+++}, and C_{++++} has been studied recently by Millikan and Bowen (21) and the general result of their work shows that there must be two types of valency electrons in the carbon atom. Two of these electrons have circular or 2_2 orbits and two have elliptical or 2_1 orbits. It would follow therefore that the four valencies of carbon would not be equivalent and there must be a distinction made between the two types of valencies. Further analysis of the emission spectra of carbon gives a method of determining values of the energy required to bring about the successive ionizations of the carbon atom. The results are as follows:

$$C \rightarrow C_+ + e - 184{,}000 \text{ calories}$$

$$C_+ \rightarrow C_{++} + e - 560{,}000 \text{ calories}$$

$$C_{++} \rightarrow C_{+++} + e - 1{,}060{,}000 \text{ calories}$$

$$C_{+++} \rightarrow C_{++++} + e - 2{,}300{,}000 \text{ calories}$$

SUMMARY

By the application of the modern methods of molecular physics to the study of the structure of the methane molecule, the following conclusions, based on five completely independent methods have been established:

1. The four valencies of carbon are not equivalent but consist of two different types.
2. The structure of the molecule of methane is pyramidal in form and not tetrahedral as previously assumed.
3. The molecule of methane is a labile system of atoms and is capable of change to other structures in its derivatives.

REFERENCES

(1) Tyndall, J.: Phil. Mag. (4) **37**, 384 (1869).
(2) Strutt, J. W.: Phil. Mag. (4) **41**, 107, 274, 447 (1871).
(3) Strutt, R. J.: Proc. Roy. Soc. **95A**, 155 (1918); **97A**, 435 (1919); **98A**, 57 (1920); **102A**, 190 (1922); Compt. rend. **171**, 1002 (1920).
(4) Cabannes, J.: Compt. rend. **171**, 852 (1920); J. phys. radium **1**, 129 (1920).
Cabannes, J., and Lepape, A.: Compt. rend. **179**, 325 (1924).
Cabannes, J., and Granier, J.: J. phys. radium **4**, 429 (1923).
(5) Gans, R.: Ann. Physik. **65**, 97 (1921).
(6) Raman, C. V.: Nature **109**, 75 (1922); **114**, 49 (1924).
Raman, C. V., and Ramanathan, K. R.: Phil. Mag. **45**, 113 (1923).
Raman, C. V., and Rao, K. S.: Phil. Mag. **46**, 426 (1923).
(7) Cabannes, J., and Gauzit, J.: J. phys. radium **6**, 182 (1925).
Cabannes, J., and Granier, J.: Compt. rend. **182**, 885 (1926).
(8) Cooley, J. P.: Astrophys. J. **62**, 73 (1925).
(9) Dennison, D. M.: Astrophys. J. **62**, 84 (1925).
(10) Guillemin, V.: Ann. Physik. **81**, 173 (1926).
(11) Henri, V., and Schou, S. A.: Compt. rend. **182**, 1612 (1926).
(12) Mark, H., and Weissenberg, K.: Z. Physik. **17**, 301 (1923).
(13) Huggins, M. L., and Hendricks, S. B.: J. Am. Chem. Soc. **48**, 1647 (1926).
(14) Weissenberg, K.: Ber. **59B**, 1526 (1926).
(15) Reis, A.: Ber. **59B**, 1543 (1926).
(16) Heisenberg, W.: Z. Physik. **26**, 196 (1924).
(17) Born, M., and Heisenberg, W.: Z. Physik. **23**, 388 (1924).
(18) Kornfeld, H.: Z. Physik. **26**, 205 (1924).
(19) Hund, F.: Z. Physik. **31**, 81 (1925).
(20) Fowler, A.: Proc. Roy. Soc. **105A**, 299 (1924).
(21) Bowen, I. S., and Millikan, R. A.: Phys. Rev. **25**, 594 (1925); **26**, 150 (1925); **26**, 310 (1925); Proc. Nat. Acad. **10**, 199 (1924); Nature, **114**, 380 (1924).