

MOLECULAR STRUCTURE

Third Robert A. Welch Foundation Conference

By C. F. Squire

ABOUT forty years ago, the Solvay Conferences were started in Belgium under the guiding influence of Peter Debye and other well-known European scientists. Those conferences have been most valuable throughout the years in stimulating fundamental research in physics and in chemistry. When The Robert A. Welch Foundation was started some six years ago and obtained Prof. Debye as a member of its Scientific Advisory Board, one of the first things which he instigated was the valuable Welch Foundation Conferences. This year was the third such conference and the topic was "Molecular Structure". There were a total of just seven papers and these were given by the following world-famous scientists: *G. P. Thomson* (FRS, Nobel Laureate, master of Corpus Christi College, Cambridge University), *H. B. G. Casimir* (Royal Academy of Amsterdam, director of research at the Philips Company, Eindhoven), *Gerhard Herzberg* (director of Physics Division at the National Research Council in Canada), *Manfred Eigen* (professor at Göttingen University and director of a division of the Max Planck Institut), *Henry Eyring* (US National Academy and dean of the Graduate School of the University of Utah), *E. Bright Wilson* (US National Academy and Theodore W. Richards Professor at Harvard University), *Charles H. Townes* (US National Academy and professor of physics at Columbia University). The Conference lasted for three days, November 16, 17, and 18, 1959, and thus much of the valuable exchange of ideas and information came in the active discussion periods. The discussion leaders were the following: W. O. Baker, Jacob Bigeleisen, Lawrence O. Brockway, Bryce L. Crawford, Jr., Raymond M. Fuoss, Walter Gordy, Joseph O. Hirschfelder, H. A. Levy, F. A. Matsen, Joseph E. Mayer, Robert S. Mulliken, Lars Onsager, J. Th. G. Overbeek, and Charles P. Smyth. There were about 400 scientists who registered for the Conference and listened to the experts speak about the molecule. Let us repeat some of the high points of what was said.

VAN der Waal's forces between molecules arise from those molecules having no permanent dipole or quadrupole moments. Dr. Casimir regards the forces between neutral atoms or molecules as arising from induced dipoles caused by an instantaneous dipole of the central atom. This gives rise to the well-known potential of attraction proportional to $1/R^6$. As Fritz London

once theorized, the central atom is regarded as a harmonic oscillator which is loosely coupled to a neighbor oscillator. Now these oscillators have certain zero-point energies and excited states with the coupling energy between them given by:

$$U = -\frac{2}{3R^6} \sum_{k,p} \frac{|q_{0k}|^2 |q_{0p}|^2}{h(\nu_k + \nu_p)}$$

This energy can be expressed in terms of the polarizability, α , of the atom k and the atom p by:

$$U = -\frac{3}{2} \frac{hc}{R^6} \sum_{k,p} \frac{\alpha_k \alpha_p}{\lambda_k + \lambda_p}$$

where the wavelengths λ_k and λ_p are associated with the oscillators' frequencies. Recent experiments with colloidal particles give evidence that the Van der Waal's forces are indeed somewhat different than supposed because of a new effect. At distances between particles comparable to the wavelengths used for the oscillators, λ_k and λ_p , a phase relation can exist so as to reduce the effect of the induced dipole acting back on the first dipole. This requires quantum electrodynamics and Dr. Casimir found a correction factor to the above equation which went from unity at short distances to a term $1/R$ at larger distances. At long distances the energy becomes:

$$U = -\frac{23}{8\pi^2} \frac{hc}{R^7} \alpha_1(0) \alpha_2(0)$$

where α_1 and α_2 are the static polarizabilities and the factor 23 is *not* an error in the computation! These polarizabilities are proportional to the cube of the radius of the atom. If we take the two atoms as perfectly conducting spheres of radius $\alpha_1^{1/3}$ and $\alpha_2^{1/3}$, then classical electrodynamics of two such spheres placed in a cavity with perfectly reflecting walls will give exactly such an expression as the one above. Each atom reduces the electric field to zero at its surface and this is an effect of reducing the electromagnetic energy in the cavity by a little bit. So there is a kind of attractive energy between the atoms. Efforts have been made to observe the attractive force predicted here by using two metal

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plates and agreement has been found. Even dielectric slabs have shown these attractive forces, i.e., several dynes/cm² at distances of 3/4 of a micron. The approximation is good only for the distance between the particles (or plates) taken as being small.

The field of microwave spectroscopy was reviewed by Prof. E. Bright Wilson and some of the recent results from Harvard were presented. The molecules (as a gas) are placed in the very high-frequency radio fields and information is obtained about molecular structure through an analysis of the energy levels coming from rotation, vibration, etc. The spectral frequencies can be measured with great accuracy (one part in 10⁶) and by use of isotopes even asymmetric rotors can be understood. Of course, isotopes have different zero-point energy of vibration and so interatomic distances are not identical when taken from the raw data. But differences and even double differences of moment of inertia can be used and so interatomic distances can be accurately deduced. Thus the carbon-carbon distance may be observed to vary from 1.53 Å in ethane where the bond is "single" to 1.50 Å in the single bond C-C in the ethyl aldehyde. The so-called "hybridization" of the carbon has been changed and shortened the distance between the C-C. The rotation of a methyl group about the C-C bond can be observed in the spectra and a barrier to the rotation can be deduced. Generally then there is a sort of torsional motion but by a tunnel effect there is complete rotation observed. The height of the potential barriers is deduced (see Fig. 1) and they are between about 1 and 3 calories per mol for the methyl group. The theory for these barriers is either at a standstill or not very satisfactory, according to one's taste. Use of electric fields on the gas in the cavity produces splitting of the rotational energy levels in the way quantum mechanics predicts. The results give accurate dipole moments of the molecule. Isotope substitution has little effect on the dipole moments observed in the molecules studied.

Prof. Charles Townes dealt with microwave spectroscopy and spoke about the interaction between a nucleus

in the molecule and the rest of the molecule: that is to say, interaction between a given nucleus and all the other electrons around the nucleus and all the other atoms. The potential at the nucleus depends on electric fields from the electron and if the nucleus is not spherical then a nonspherical distribution of the electron can give rise to a quadrupole electric field interaction. The magnetic dipole of a nucleus also interacts with neighboring magnetic fields caused by other magnetic dipole nuclei, by electron magnetic dipoles, by the rotation of the molecule as a whole, and by other smaller effects from induced dipoles. For example, the hydrogen-hydrogen nuclei in the methyl group of an organic molecule give an interaction causing a splitting of some 30 kilocycles when microwave studies of rotation spectra are made and from this the internuclear distances are computed. The interaction with electron spin dipole is of the order of 1 Mc/sec.

Prof. Townes spoke of the work on quadrupole coupling of the nucleus with electrons having *p*-wave functions. For Cl₂ the splitting is 109.6 Mc/sec and for ionic type bands like KCl there is no splitting at all. In this way the ionic character manifests itself in the molecule like KI, LiI, KCl by having a very small quadrupole coupling—i.e., the electron charge about the nucleus of the iodine or the chlorine is spherically symmetrical. The use of O¹⁷ in molecules like NO will be most valuable for future work in the field of work involving quadrupole coupling.

In the future there may be the possibility of an infrared or optical region maser. Prof. Townes believes it possible to build such a device with a multiple reflecting cavity for infrared and the optical region by a type of Fabry-Perot mirror which will reflect at low loss a single mode of oscillation. The maser will, it is hoped, emit extremely monochromatic radiation I.R. at 3μ with a band width of 5 kilocycles/sec and with a power of some few milliwatts. The intensity of the plane waves of coherent radiation is thus extremely high. These new, exciting ideas and calculations were done with Dr. Schawlow and hopes are high that experiments will prove them to be satisfactory.

Finally, a word about the most interesting research under Prof. Eigen. The conference learned of the measurements of high-speed motions going on in molecules at speeds requiring time intervals of 10⁻¹⁰ seconds to describe them. These motions bring about relaxation effects (absorption of energy) just as in other forms of spectroscopy but the motions are associated with a sort of chemical reaction—i.e., motions of atoms or groups of atoms associated with the readjustment of the system to equilibrium conditions. The techniques used included sound waves at 100 megacycle/sec frequency and a study of sound energy absorption in liquids.

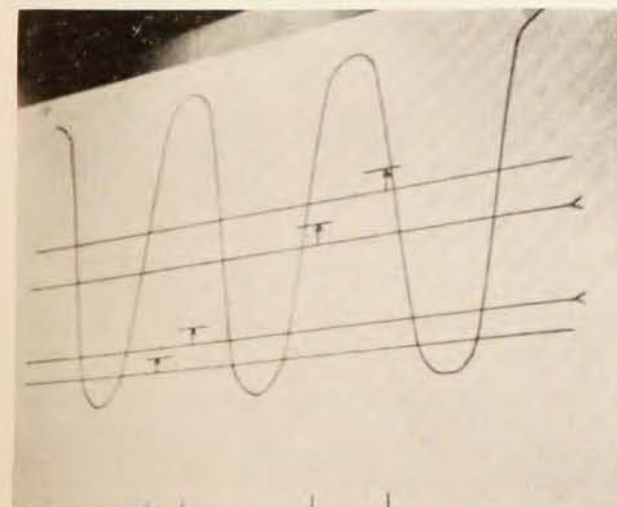


Fig. 1. Methyl group spectra showing rotation energy levels with arrows pointing to them from torsion energy levels.