CHEMICAL APPLICATIONS OF RAMAN SPECTRA*

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In the Raman or scattered-light spectra of chemical substances the differences between the frequency of the incident light and the frequencies found in the scattered light correspond in general to mechanical frequencies with which the atoms are vibrating in the molecule. The Raman spectra are therefore very characteristic of the molecular structure and are useful for qualitative identification, especially for isomers with structural differences. It is also possible in many cases to identify the individual Raman lines with the different types of motion of the molecule or special parts of it such as double bonds and substituent groups. This enables one to calculate the elastic strength of the chemical bonds and the thermal energy of the molecule, and makes possible the construction of a moving mechanical model of the molecule which reproduces on a large scale the motion of the atoms. Interpreting the Raman spectra in this manner one is able to calculate specific heats and entropies, and, using the energy of formation, free energies and equilibrium constants.

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Although modern physics has provided the chemist with a wealth of new information about the atoms and molecules with which he works, there is one outstanding deficiency in the theories of atomic and molecular structure which have been developed up to the present time, that is, their inability to deal with the molecules which contain more than two or three atoms. While it is undoubtedly of fundamental importance to understand thoroughly the simplest types of molecules, the chemist is most anxious to get some help with the problems which involve more complex molecules because it is there that he can bring to bear most effectively the vast quantity of chemical information which has been accumulated through the researches of the past one hundred years.

With this in mind it is easy to understand the enthusiasm with which the discovery of the Raman spectra was hailed. Even in the first announcements of this phenomenon it was evident that here we had a new type of spectrum, closely associated with the structure of the molecule as the chemist knows it and yielding clear-cut information even in the case of very complex molecules. Since the first paper (*1*) of Sir Chandrasekhara Raman, nearly five hundred communications have been published on the subject. It is consequently well-nigh impossible to discuss more than the outstanding features of the Raman spectra in a brief article. We shall therefore try to explain the nature and important facts regarding this type of spectrum by taking one compound as an example, namely ethyl alcohol, and showing the kind of information which can be secured that will be of particular interest for chemical research.

* Contribution to the symposium on "Mathematics in the Service of Chemistry," held under the auspices of the Division of Physical and Inorganic Chemistry, at the 81st meeting of the A. C. S., at Indianapolis, Indiana, March 31, 1931.

Experimental Technic

The experimental technic for obtaining a Raman spectrum is very simple. The most satisfactory method for general application is that developed by R. W. Wood (*2*) for liquids. It is illustrated diagrammatically in Figure 1. A mercury arc is used in order to illuminate the substance with light in which not more than two or three wave lengths are present. The light from this source (*A*) is passed through a cylindrical glass tube containing a solution which acts as a light filter in order to remove as far as possible any wave lengths of light other than those desired. This light then falls on the liquid to be studied which is contained in a glass tube about five or six centimeters long and a centimeter and a half in diameter. This tube is optically plane at one end and drawn off in a curve at the other end to avoid reflection of light.

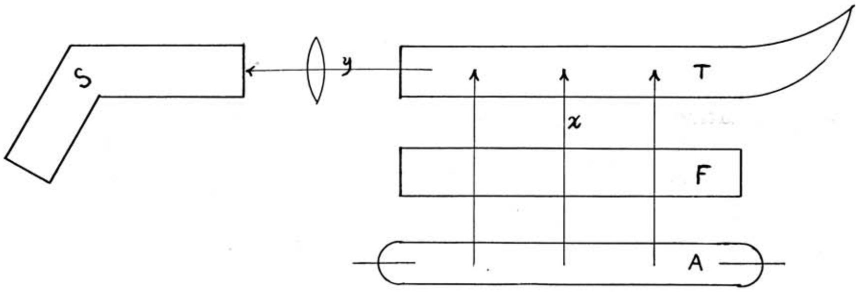

FIGURE 1.—DIAGRAM OF APPARATUS FOR OBTAINING THE RAMAN SPECTRUM

Light (*x*) passes from mercury arc (*A*) through light filter (*F*) to substance under observation in tube (*T*). There it is absorbed and scattered, and the part (*y*) coming out at a right angle to the original beam (*x*) is focused on a spectrograph (*S*).

Of the light which passes through the liquid, part is absorbed by the molecules and re-emitted as scattered light. If we focus this scattered light which comes out of the end of the tube on a slit of the spectrograph and observe its frequencies by means of a photographic plate, we find that in addition to the one or two wave lengths originally present in the light from the arc there are also a number of other new wave lengths. This is illustrated in Figure 2 which shows the sort of plate we would get if we took a photograph of the scattered light from ethyl alcohol illuminated by a mercury arc (*3*).

Nature of Raman Photographs

We presume in this case that we have filtered out all the light except that from the two lines in the mercury arc which have wave lengths 4046 A. U., and 4358 A. U., or in terms of frequency, the reciprocal of the wave length, 24,715 cm.$^{-1}$ and 22,946 cm.$^{-1}$. In our photograph we find these two lines coming through with the greatest intensity as shown in the diagram. We also find a number of other lines of varying faintness. If the photograph is observed carefully one finds that these lines can be divided into two similar groups, one group coming from 4046 A. U., and the other from 4358 A. U. The arrows in the diagram show how the different Raman lines have originated from these two lines. The shift of the Raman line from the exciting line is indicated by the number on the arrow. It is simple to see that the shifts for the two sets of lines are the same. Experiments with the other sorts of exciting light show that the values of the shift are independent of the sources of excitation and depend only on the nature of the molecule which is doing the scattering. So it is evident that we have here a very powerful tool for investigating molecular structure.

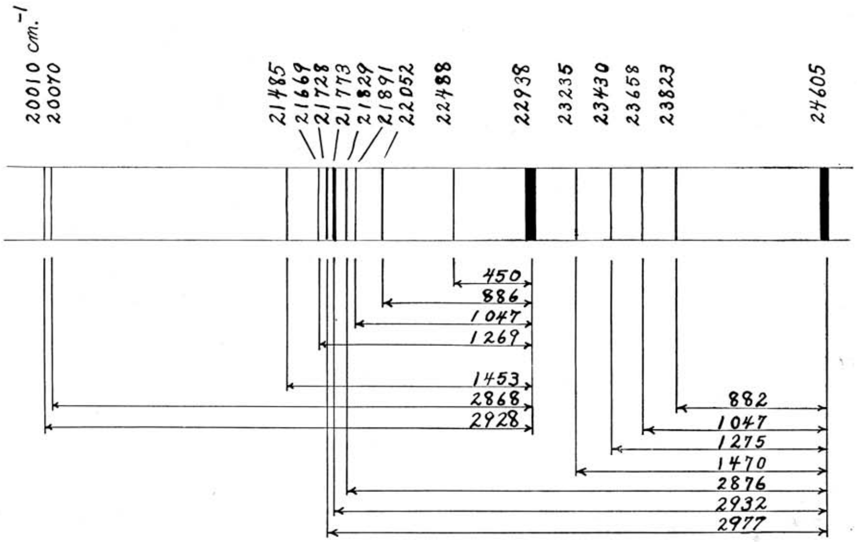

Figure 2.—Showing How the Raman Lines of Ethyl Alcohol Originate from the Two Lines (22,938 and 24,605) of the Mercury Arc

The shifts in frequency are indicated by the arrows and are practically independent of the wave length of the line of origin as may be seen by comparing to two groups. [From Ganesan and Venkateswaran, Ref. (*3*).]

To what process, then, are these shifts due? If we compare the numbers associated with the shifts to the numbers in the scale of frequencies which physics has associated with light or other electro-magnetic vibrations we find that the numbers for the shifts are the same as the frequencies in the infra-red (*4*) which have been shown to correspond to the frequencies of the vibrating motion of the different atoms in the molecule. It therefore looks as if we should investigate the nature of the motion of the atoms in the molecule in order to understand the Raman spectra.

Molecular Vibration

It has been recognized for a great many years that the atoms in the molecule are in constant motion due to the heat present in the molecule. Since we know that the same atoms always stay associated together in a particular molecule, it is evident that their motions must be vibratory in nature, for they move about some mean position while they retain essentially the same form of structure. We would expect therefore that the forces which are holding them together would be elastic in character so as to permit this vibration. It also appears that in a homo-polar molecule such as ethyl alcohol (*5*) these forces are due almost entirely to the chemical bonds and that they operate along lines connecting the atoms which have hitherto been associated with the chemical bond in a vague sort of way. It has been possible in the simplest cases to find the actual values of these elastic forces and to calculate the way they vary as the molecule is pulled to pieces. A diatomic molecule, like hydrogen for example, behaves very much like two balls joined together by a spiral spring, and in a more complex molecule we can arrive at a fair mechanical picture (*6*) of the forces and masses present by imagining the nuclei as small balls containing the appropriate masses and the chemical bonds as spiral springs which join these together.

Now although the quantum theory shows that we cannot treat the energy present in the molecule by means of classical mechanics, it is still true that the masses and forces behave in a manner almost exactly similar to the forces and masses with which we deal in large-scale mechanics. We can, therefore, tell quite easily the types of motion to be expected in a mechanical system such as that found in the molecule (*7*). For example, in a diatomic molecule the two masses will vibrate toward and away from each other with a constant frequency. This frequency (ν) will depend only on the force (k) binding the two atoms together and the masses (m_1 and m_2) of the two atoms, and the relation can be expressed in a very simple way as follows:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \mu = \frac{m_1 m_2}{m_1 + m_2} \qquad (1)$$

In a more complex molecule such as ethyl alcohol it will still be possible to calculate (*8*) the frequencies if we know the masses and the strength of the forces which are tying them together, although the problem is, of course, more complicated. It has been known for some time (*6*) that the elastic strength is very nearly the same for all the bonds with which we are dealing here. Since the hydrogens are so light, this means that they will vibrate very much faster than the carbon and oxygen atoms so that we can treat their types of motion as being independent of the motion of the heavier atoms and vice versa. We would, therefore, expect the hydrogen to have two types of frequency, one very fast in which the hydrogen atom moves directly out along the line of the bond, and the other quite a bit slower in which the hydrogen moves perpendicular to the direction of the bond and bends it without stretching it.

As may be seen in the diagrams of Raman spectra which are included later in this article, there appear to be two groups of frequencies always associated with hydrogen, one at about 3000 cm.$^{-1}$ and the other at 1200 to 1500 cm.$^{-1}$. These are always found when hydrogen is present in the compound and are always absent when there is no hydrogen. It is apparent that these two groups are present in the ethyl alcohol spectrum. Besides this we have three lines of lower frequency.

It has been shown from a study of the classical mechanics (*8*) for such a mechanical system that we would expect the three heavy atoms to have three types of motion. These are illustrated in Figure 3. The elastic constants which have been found for the chemical bond would lead us to expect two of these to occur at about 1000 cm.$^{-1}$ and the other at about 450 cm.$^{-1}$. This is exactly what is found in the case of ethyl alcohol, so that our concept of the molecule as a system of masses (the nuclei) and forces (the chemical bonds) accounts very satisfactorily for the observed Raman spectra, if we assume that the values of the frequency shifts in the spectra correspond to the frequencies of motion of the atoms in the molecule.

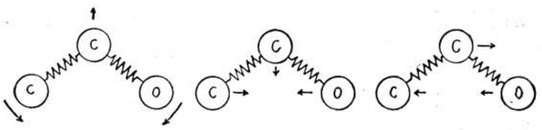

FIGURE 3.—THE THREE TYPES OF MOTION OF THE CARBON AND OXYGEN ATOMS IN ETHYL ALCOHOL
The hydrogens are not shown.

Such a simple and direct explanation seemed almost too good to be true in the early days of Raman spectra and the first theoretical treatments pointed to a more complicated explanation. As observations accumulated, however, the evidence in favor of this simple correspondence appeared quite convincing (*7*) and Van Vleck (*9*) has recently shown that it is in accord with the quantum theory for the process. There may be some few exceptions to the rule but in general we may expect a one-to-one correspondence between the Raman shifts and the frequencies of mechanical vibration in the molecule.

The nature of the Raman scattering can thus be stated very simply. According to the fundamental postulate of the quantum theory the energy in a beam of light is present in small units, the quanta. The energy of any one quantum E_i will be related to the frequency of vibration (ν_i) of the light by the equation

$$E_i = h\nu_i \tag{2}$$

where h is the universal constant known as Planck's constant.

Now it is also true that the energy present in the *molecular* vibrations must also exist in units where the energy of a unit (E_m) is related to the frequency of vibration of the molecule (ν_m) by

$$E_m = h\nu_m \tag{3}$$

The theory which we have just postulated states that in nearly all cases a quantum of light will be absorbed by the molecule and then re-emitted, leaving behind just enough energy to give the molecule one unit of vibrational energy. Since the law of conservation of energy must hold we will have for the process

$$E_i - E_r = E_m \tag{4}$$

where E_r is the energy left in the quantum re-emitted with frequency ν_r.

Combining with equations (2) and (3) we shall have then the relation that the shift in frequency $\nu_i - \nu_r$ must be equal to the frequency with which the molecule is vibrating ν_m, *i. e.*,

$$\nu_i - \nu_r = \nu_m \tag{5}$$

Sometimes if the quantum is absorbed by a molecule which already has a quantum of vibrational energy, the light is re-emitted with its energy increased by the amount E_m. This gives rise to the so-called anti-Stokes lines where the frequency is increased instead of decreased.

A Mechanical Model of the Molecule

Since the mechanical system which has been postulated obeys macroscopic mechanical laws, it seemed worthwhile to try to construct a macroscopic model actually using spiral springs for the chemical bonds and balls of appropriate weight for the nuclei of the atoms. Such a model might show, for example, the frequencies which depended on the action of a number of atoms at once and which are very difficult to calculate from a purely mathematical consideration of the system. Such a model was constructed by Kettering, Shutts, and Andrews (*10*) as follows. With the help of the frequencies observed in the simple diatomic and triatomic molecules, it was possible to calculate quite exactly the bending and stretching constants for the average chemical bond. A spiral spring was then constructed which had the same ratio for the bending and stretching constants as the bond. Using these springs, models were made of a number of molecules and it was found that they exhibited elastic spectra very similar to the Raman spectra. A photograph of the model of ethyl alcohol is shown in Figure 4.

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FIGURE 4.—PHOTOGRAPH OF THE DYNAMICAL MODEL OF ETHYL ALCOHOL

The method of study was as follows. The model was suspended from rather weak elastic bands, and a somewhat stronger elastic band was attached to the model at some point and pulled by a reciprocating arm driven by a variable speed electric motor. Only those impulses at frequencies which were in tune with the natural periods of vibration of the model would cause any action. When the model was agitated at one of these frequencies, however, it would go through the type of motion corresponding to that frequency. It could be observed by means of a stroboscope so arranged that the apparent motion was slow enough to be followed visually. Thus, for ethyl alcohol the analysis which had been made on the basis of the spectra was confirmed. Three types of motion corresponding to the three lowest lines in the Raman spectra were found. In these motions the two carbons and the oxygen behaved as is shown in Figure 3. The two groups of frequencies were also found for the hydrogen as may be seen in Figure 5, the lines marked *B* corresponding to the bending of the bond and those marked *S* to the stretching.

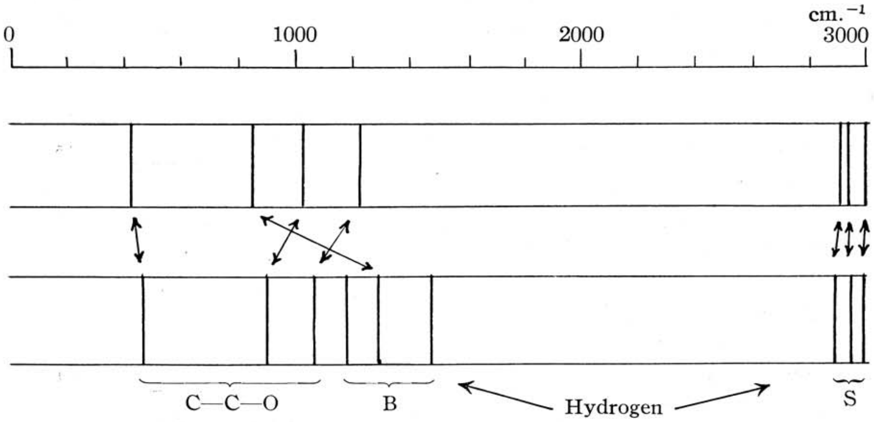

Figure 5.—Comparison of the Frequencies Observed in the Model (*upper*) and in the Raman (*lower*) Spectrum of Ethyl Alcohol

The frequencies of the model observed in r. p. m. have been converted to wave numbers for comparison with the spectrum by multiplying with appropriate constants.

It was even possible to distinguish the atoms principally affected by the three frequencies corresponding to the stretching of the C—H bond. The frequency at 2876 cm.$^{-1}$ caused the three hydrogens of the CH_3 group to vibrate while the others remained quiet. The frequency at 2932 cm.$^{-1}$ made the CH_2 vibrate and at 2977 cm.$^{-1}$ the O—H. The behavior of the model thus confirms the picture of the molecule which has been drawn from Raman spectra.

Determination of Molecular Structure

It is thus seen that the Raman spectra add one more step to the evolution of the chemical formula which has been taking place in the last one hundred years. We have gone from the old idea of a molecule as representing a sort of vague association of atoms in integral numerical ratios, through the first organic formula which recognized the importance of placing bonds in definite relations to the atoms, through the extension of this formula into three-dimensional space, through the confirmation of the space picture by means of X-rays, to a dynamic picture of the molecule in which we can tell the way the parts of the molecule move and the strength of the forces which are directing these movements.

The usefulness of this to chemistry will indeed be apparent in many ways. In the first place it is extremely valuable for qualitative analysis to have an easily obtained spectrum which is so characteristic for each type of molecular structure. Again in solving the puzzle of the structure (*7*) of an unknown compound it is extremely valuable to have a means of determining the presence of such things as double bonds (*11*), secondary and tertiary hydrogen, ring structure, length of chains, and other similar points. The charts of Raman spectra in Figures 6, 7, and 8 show to some extent how this may be done. Table I gives some of the values which have been calculated from Raman spectra for the strength of the bonds.

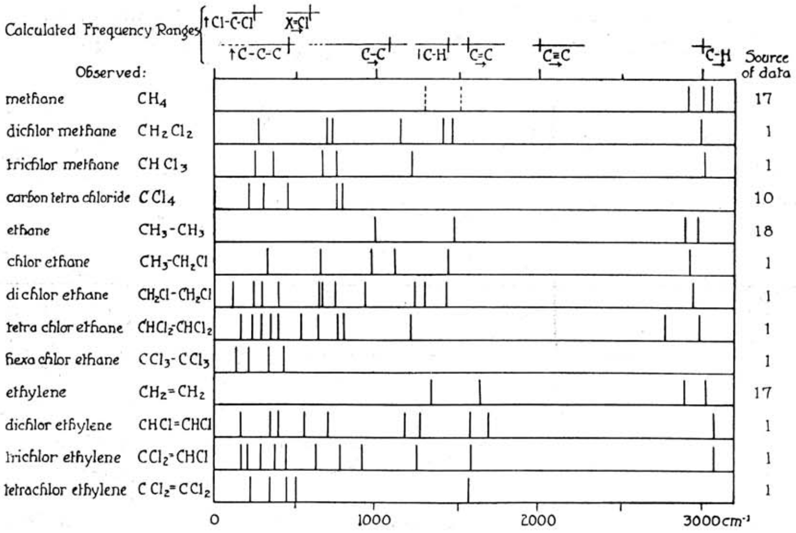

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FIGURE 6.—RAMAN FREQUENCIES OF SOME METHANE, ETHANE, AND ETHYLENE DERIVATIVES

Sources of data: DADIEU AND KOHLRAUSCH, *Physik. Z.*, **30,** 384 (1929); *Ber.*, **63,** II, 251 (1930); *Wiener Ber.*, IIa, **138,** 41, 336, 420, 607, 635, 799 (1929); **139,** 77 (1930). (10) See Ref. (*3*). (17) See Ref. (*14*), second paper. (18) DAURE, *Compt. rend.*, **188,** 1492 (1929).

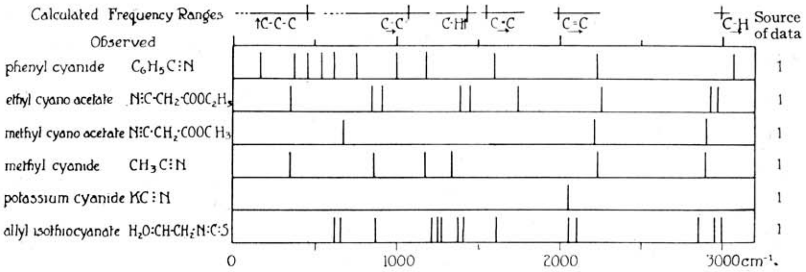

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FIGURE 7.—RAMAN FREQUENCIES OF SOME COMPOUNDS CONTAINING DOUBLE AND TRIPLE BONDS

TABLE I

The Force Required to Stretch the Chemical Bond by One Ångstrom Unit

C—H	4.7×10^{-3} dynes
C—O	4.9
C—C	4.2
C=C	10.2
C≡C	14.1

Application to Inorganic Chemistry

Although in explaining the nature of Raman spectra we have discussed organic compounds only, the range of the phenomenon includes practi-

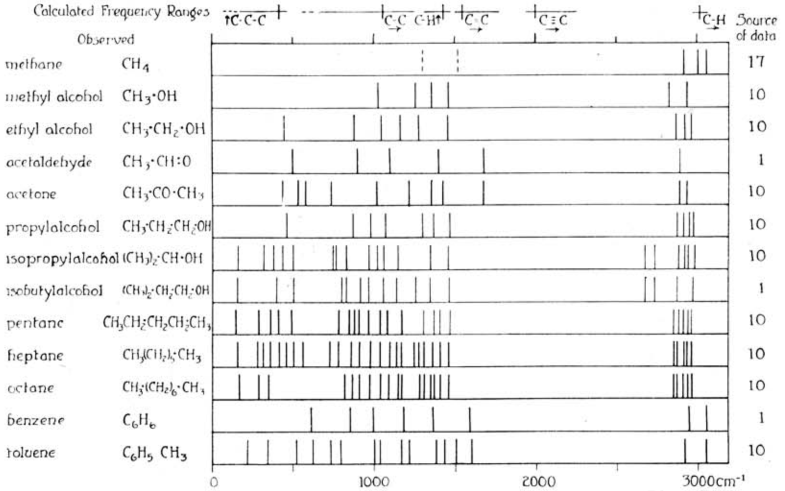

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FIGURE 8.—RAMAN FREQUENCIES ILLUSTRATING THE VARIATION WITH COMPLEXITY OF THE MOLECULE

The lines above the diagram show in what region the frequencies associated with different types of bonds may be found.

cally every state and kind of matter. It has been observed in crystals (*12*), liquids, solutions (*13*) and gases (*14*) for both organic and inorganic compounds. The chief limitation seems to be that only those motions which take place under the influence of homo-polar bonds appear to give Raman lines. Thus, for example in KCN solution (*15*) we get a strong line for the vibration of the C and N against the force of the triple bond but no line for the vibration of the K, while in CH_3CN we find lines for the vibrations of all the atoms.

The Raman spectra appear to be largely independent of the nature of the environment and in solution the lines for all substances present including the solvent appear just as they would in the pure compounds (*16*). Some research has been done to see how lines might be affected by dissociation, and there is evidence that there is an effect (*17*). When more work has been done we may expect valuable information in these fields.

Calculation of Specific Heats

One of the most important chemical applications is in the calculation of specific heats (*18*). It has been shown that as a good approximation we can treat each type of motion in a molecule as behaving like a so-called ideal harmonic oscillator. By using the expression of Einstein for the specific heat of such an oscillator in terms of its frequency and temperature we can calculate (*6*) the amount of heat which any particular type of motion would absorb merely by knowing its frequency and number of degrees of freedom. Since, from the analysis of the Raman spectrum, particularly with the help of the model, we can identify the lines with the various types of molecular motion it is possible to calculate the amount of heat absorbed by each type of motion and, summing these together, to get a value which we can compare with the observed specific heat of the molecule. By integrating the specific heat we can secure values for the entropy and from this and the heat of formation, we can calculate the free energy. Knowing the free energy it is possible to estimate the equilibrium constant for any reaction of the substance with other compounds for which the free energy is known. While there is not space enough to cover the details of such calculations at this time it may be seen that we have here the possibility of investigating chemical reactions for which it might be very difficult to obtain direct experimental data.

This brief sketch may suffice to give an idea of the usefulness to chemistry of this spectrum which tells us so much about the inside of the molecule. As our picture of the nature of the molecule becomes more vivid and clear we may hope that in addition to the ordering of previously known chemical facts we shall have a stimulus toward the discovery of new realms of chemistry which otherwise might never have been dreamed of.

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