

The Raman effect

Investigation of molecular structure by light scattering

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PART I

1. Introduction and historical

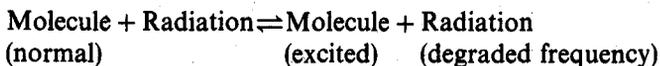
In the scheme of discussion organised by the Faraday Society, the phenomenon of the scattering of light of altered wavelength rightly occupies a position intermediate between the molecular spectra in the ultraviolet and the infrared regions because it stands in intimate relation to both these fields of research. Before dealing with these relationships and indicating the kind of information it gives regarding molecular structure, it would seem proper to give a brief historical introduction to the subject.

Eight years ago we commenced at Calcutta an extensive programme of research on the phenomena of scattering of light in gaseous, fluid and solid media. The inspiration for this scheme of research was derived in the first instance from Rayleigh's well-known theory of the blue sky, and the hope that our laboratory studies would furnish a solid experimental basis for the explanation of such natural phenomena as the colour of the sea and the colour of ice in glaciers. It soon became clear, however, from our experimental results, that the work taken up by us would go far beyond this restricted purpose, and lead us to most valuable information on such fundamental problems as the constitution of the solid and liquid states, the structure and optical properties of molecules and the nature of radiation itself. In a little essay published by the Calcutta University in February, 1922, a preliminary survey was made of the whole field. In the concluding chapter of this essay, entitled "The Scattering of Light and the Quantum Theory," it was pointed out that if the process of scattering could be regarded as a collision between a light quantum localised in space and an individual molecule, the observed laws of light-scattering would be quite different from that anticipated on the classical principles of the electromagnetic theory of light. According to the latter, the variations in the spacing and orientation of the molecules in the fluid and the consequent local fluctuations of optical density would determine the

magnitude and characteristics of scattering, while according to the extreme light-quantum point of view, the individual scattering processes would be wholly incoherent with each other, and the resulting intensity of scattering would depend on the density of the fluid as a whole, and not on its local fluctuations. Our experimental investigations in 1922 and 1923 showed that the theory of light-scattering based on the Maxwellian principles and the statistical thermodynamic concept of fluctuations were in substantial agreement with the observations. From the very first, however, evidence was encountered of the presence of a *disturbing effect*. In several *carefully purified* liquids, notably water, ether, the alcohols, and also in ice, optical glass, etc. it was unmistakably evident that the scattering of light contemplated according to the classical theories was accompanied by a radiation of altered wavelength. These observations were duly published at the time, and it may be therefore justly claimed that the existence of this new optical phenomenon had been established about the same time, and independently of the well-known work of Compton in the X-ray region. It will be recalled that Compton was inclined to attribute the softening of X-rays by scattering to what he called "a general fluorescent radiation" until his spectroscopic investigations gave an entirely different version of the matter. It is not surprising, therefore, that the optical effect brought into evidence by the Calcutta investigations was also labelled as a "*special type of feeble fluorescence*". The difficulty of explaining its excitation by incident light of frequency far removed, both from the infrared and the ultraviolet characteristic frequencies of the molecules, was obvious to me from the first. For this reason the further investigation of this phenomenon was definitely placed on the programme of research at Calcutta. Some attempts were made in 1924 and 1925 to make a spectroscopic study of the effect. Unfortunately, however, owing to the feebleness of the radiation, our attempts to photograph its spectrum were made using sunlight, with coloured glass filters as the exciting radiation, and the results obtained did not prove sufficiently encouraging.

2. The nature of the Effect

The true nature of the phenomenon became evident to me for the first time towards the end of 1927 when engaged in an attempt to explain the Compton-Effect as due to a kind of fluctuation in the state of the scattering atom in the field of radiation. The ejection of the electron from an atom is obviously a very violent kind of fluctuation in its electrical state. Much milder types of fluctuations are obviously possible, and would give rise to a change of wavelength in light-scattering by molecules according to the scheme,



The idea was vigorously followed up, and the importance of using monochromatic light as the exciting radiation soon became evident. Connected accounts of the discovery and of its history were given in a lecture delivered to the South-Indian Association at Bangalore, on the 16th March 1928, and published in the *Indian Journal of Physics*, on the 31st March 1928. All the essential features of the phenomenon were set out in this lecture, namely:

(a) Its universality, as supported by observations of it in gases, vapours, liquids, crystals and amorphous solids, also in a great variety of chemical substances, both organic and inorganic.

(b) Its spectral character, consisting of lines in some cases, more or less diffuse bands in others, and in addition, a more or less diffuse continuous spectrum accompanying the lines or bands.

(c) The theoretical explanation of the phenomenon, as involving an exchange of energy between the quantum and the molecule, and the equality of the change of frequency (positive or negative) to a characteristic frequency of the molecule, and the consequent utility of the phenomenon as an aid to the exploration of molecular spectra—especially in the infrared.

(d) The possibility of an enhancement in the frequency in addition to the degradation of it, but the greater probability of the latter.

(e) The *strong* polarisation of the radiations scattered with altered wavelength.

(f) The distinctness of the new phenomenon from fluorescence, though in obvious relationship with it.

(g) Its analogy to the Compton-Effect, and the indicated existence of an X-ray scattering with altered wavelength of a more general type than the Compton-Effect.

(h) The incoherent nature of the radiation.

Since the publication of the paper, the subject has been extensively studied in other countries, and admirable contributions have been made to the subject, notably by Wood, Pringsheim, McLennan, Rasetti, Cabannes, Daure and others. A bibliography of the subject with 160 references and abstracts has been compiled by Dr Ganesan, and has just been published in the *Indian Journal of Physics*.

3. Gases

In the case of gases the intensity of the scattered light is very weak, but by the use of very high pressures, spectrographs of great light-gathering power, and intense intrinsic illumination, the difficulties of investigation may be successfully overcome. The great importance of working with gases is obviously that here the molecular freedom, both for rotation and vibration, is greatest, and hence the possibility arises of getting sharper lines and greater resolution than in the liquid state. The rotational frequencies in liquids manifest themselves as a diffuse spectrum or wings accompanying the principal lines. In gases and especially with

light molecules, the rotational effects can be clearly resolved. Notable success in this direction has been achieved by McLennan, Wood and Rasetti. The importance of this development cannot be over-estimated as the moments of inertia of the molecule, and the coupling of rotation with vibration, are capable of determination from the measurements. So far, detailed reports have been made on HCl, NH₃, H₂, O₂, and N₂. Even in the case of large molecules, by using spectrographs of sufficient resolving power, important progress in this direction remains to be achieved.

4. Liquids

Liquids are by far the most convenient to study the effect with, and a fair number, especially organic chemicals, have been examined so far. Amongst the investigators who have drawn important conclusions concerning the relation between chemical structure and the molecular frequencies, as determined by the method of light-scattering, I would mention Daure in France, Kohlrausch and Dadieu at Graz, Petrikaln in Riga, Venkateswaran and Ganesan at Calcutta. Reference will be made later to this question, but I would like here to emphasise the great importance of a critical comparison of the data obtained in the liquid and the corresponding vapours. Ramdas' early work on ether vapour appeared to suggest the identity of the frequencies of the molecular vibration in the two states. It must be remembered, however, in the case of polar molecules, we have reason to believe that association occurs in the liquid state, and hence we cannot assume without critical examination that a vapour and a liquid would give identical frequencies. Indeed, some discrepancies have been noted already in NH₄ and HCl. Water presents a very notable example of molecular association. The structure of the band obtained with water and the change that occurs with rise of temperature has been studied by several investigators. The most detailed investigation appears to be that of Venkateswaran and Ganesan at Calcutta. These authors have also attempted to correlate the effects observed with water and with ice. It would be of interest to investigate water-vapour and connect the three together by quantitative study. The field for the study of the effect in liquids offered by organic chemistry is so vast that only a small fraction of the substances offering themselves have been studied as yet.

5. Mixtures and solutions

The important physicochemical problem of the nature of solutions naturally offers itself for investigation by the method of light-scattering, and several investigators have already commenced work on the subject. The most promising question is that of the completeness (or otherwise?) of dissociation of electrolytes

in solution. The subject has received attention from Carelli, Pringsheim and Rosen, Daure, Venkateswaran and Ganesan, and others. Perhaps the most interesting results are those of Daure, who examined a number of chlorides. He found that CCl_4 , PCl_3 , etc. give sharp lines corresponding to the M—Cl bond. The results obtained with bismuth and antimony chlorides in solution showed a broadening of the lines with increased dilution until they finally disappeared. Ganesan and Venkateswaran similarly find that the well known bands due to water in aqueous solutions of H_2SO_4 , HCl , HNO_3 acids become sharper and sharper with increasing concentration of acid. These results appear very significant.

The similarities exhibited by solutions of carbonates of different radicals and similarly of the sulphates and nitrates amongst each other appear to support the idea that the characteristic frequencies are those of the ionised acid radical. Much, however, remains to be done in this field of research, particularly in the direction of the exact quantitative study of the mixtures of liquids, the constituent molecules of which are believed to associate or combine with each other.

6. Crystals and amorphous solids

As already mentioned, ice was the first crystal in which the spectral character of the scattered radiation was examined and reported. It has a special interest, as it is perhaps the only substance in which direct comparison of the solid and the liquid state has been published so far. Subsequently, observations of the effect in various other crystals have been reported upon, notably quartz, calcite, gypsum, topaz and Rochelle salt. The case of gypsum, which has been examined by K S Krishnan, is perhaps the most interesting of all. As is well known, this substance contains two molecules of water of crystallisation. Krishnan found, from photographs taken with large dispersion, that in addition to the wavelengths which could reasonably be attributed to the SO_4 radical, three sharp lines, at 2.8, 2.9, 3.0 μ respectively, were obtained. These evidently are due to the water of crystallisation, and it is worthy of note that they are practically in the same position as the components of the band observed with water and ice though considerably sharper than even in the case of ice. The relative intensities in the three substances are, however, different. The comparison with the data for strong H_2SO_4 solutions given by Ganesan and Venkateswaran is also of interest. It would seem that even in concentrated acid solutions, an approach is made towards the state of H_2O in the solid crystal.

Another point of great interest is as regards the degree of sharpness of the lines obtained with the crystals. In the photographs taken with calcite and quartz by Krishnan in July, 1928, this is the most striking feature. With rise of temperature, however, the lines become diffuse, and in amorphous quartz becomes so diffuse that Pringsheim failed to observe them. Recently, however, Gross and Romo-

nova have succeeded in photographing the diffuse bands with fused quartz and optical glass. The latter had been previously observed visually at Calcutta in the very first studies. Langer reports having obtained very diffuse lines with Rochelle salt. All these facts of observation may, perhaps, be connected by the general idea which I entertained from the first that the more perfect and ordered the arrangement of the molecules in a space lattice, the sharper would be the lines in the scattered-spectrum. It is well known from X-ray work that only relatively few crystals really give perfect X-ray reflections, and that in order to account for the facts, a mosaic theory of crystal structure is now generally believed in. The theory of imperfection of crystals developed by Šmekal, Zwicky, and others may be recalled in this connection. It would seem that the scattered light furnishes with a measure of the perfection or otherwise of crystals, just as X-ray diffraction does. This idea, however, requires further investigations for complete establishment. The failure to obtain the evidence of the effect in rock salt, sylvine, etc. has been explained as due to the ionic nature of the lattice of the crystals. How far the well-known imperfections of the rock-salt as a crystal contributes to failure is a matter for consideration. It is not unlikely that many crystals will offer themselves for investigation for light scattering. The difficulty of course is to grow a sufficiently large and clear crystal.

7. Intensity and polarisation

It cannot be over-emphasised that measurements of the frequencies of the radiations appearing in light scattering do not, by themselves, give the maximum of information available by such studies. It is necessary also to obtain quantitative information regarding the intensity of the new lines, both relatively to the lines of unaltered wavelength and to the incident radiation. Further, the state of polarisation of the lines is also a matter of great importance. In the first report, and also more fully in the papers contributed in collaboration with K S Krishnan, the principal features were clearly emphasized. In the first place, the intensity of the new lines (absolutely) increases rapidly with the decreasing wavelength of the incident radiations. This increase is analogous to the well-known Rayleigh fourth-power law of the classical scattering, and appears in some cases at any rate to be more pronounced. The different lines appear to be polarised to very different extents. Further, some of the lines corresponding to well-known infrared absorption frequencies fail to appear in the scattered light. The absolute intensity of the scattered radiation with altered wavelength is much smaller than of the classical scattering.

While these qualitative results are of general application, obviously much more precise statements are essential, and it is here that there is the greatest scope for future research. The subject has received attention also from Pringsheim, Cabannes and Daure and others. As yet, however, the information available is very meagre.

The fact that the different lines are differently polarised is obviously fundamental. The question of intensity is essentially related to that of polarisation. If we understand completely why some lines are strongly polarised and why others are weakly polarised, we would at the same time get a clear comprehension of why some infrared absorption lines fail to appear in scattering and *vice versa*. Incidentally, it may be remarked that the lines corresponding to vibration frequencies of the molecule would stand on a different footing from rotation lines, or from rotation-vibration combination lines. Each of these classes would have to be separately studied. Then, again, the question arises, how the intensity and polarisation would be influenced by change of state. The work of Ramdas seems to suggest that probably we have merely an enhancement of the intensity in proportion to density, without a change of polarisation in the new lines. This, however, is far from being established, and it may even prove to be untenable. The impedance to free rotation in the liquid state must profoundly influence the rotational transitions, and hence also the intensity of the scattered radiation in general. In this connection work with liquids at low temperatures or under high pressures would be of value. It is not unlikely that a broadening of the lines and a development of a continuous spectrum may be noticed. An effect of this kind has, indeed, already been observed by Venkateswaran in glycerine, even after careful purification.

It may be pointed out that even as regards the polarisation of light scattered without change of wavelength, the information available is not adequate. Some recent work by P V Krishnamoorthy at Calcutta seems to indicate that in liquids at any rate, the depolarisation of the classically scattered light shows a very rapid increase as we approach towards the ultraviolet. The theory of anomalous dispersion, indeed, leads us to anticipate the existence of some such effect. Further investigations on this topic, however, would seem very desirable. Mr Krishnamoorthy has also found that the ratio of intensity of the new lines to the old lines is considerably larger than was previously supposed. Daure has also reported results supporting Krishnamoorthy's work. It may be remarked here that in liquids the ratio would be considerably larger than in vapours. This is a consequence of the thermodynamic theory of the classical scattering.

8. Relationship with ultraviolet and infrared spectra

It is obvious that having ascertained the characteristic molecular frequencies—rotational, vibrational, rotational—vibrational and also electronic transitions, if any, we can proceed to utilise the data for an interpretation of the molecular spectra of the ultraviolet, and also for understanding infrared absorption and emission data. The question of possible alternative formulations of the fundamental energy levels of the molecule will naturally arise here. The evidence, however, seems fairly clear that the vibrational frequencies observed in light

scattering are really fundamental frequencies, and *not* due to inter-combination between the fundamental vibrational frequencies of the molecule. This would seem to be fairly clear from the comparative data for substances with similar chemical constitution, but with atoms of differing weight in the molecule. Daure's results with a series of chlorides and Ganesan and Venkateswaran's results on bromoform, as compared with chloroform, show a remarkable and parallel shifting of the frequencies observed in light scattering towards longer wavelengths with increasing weight of the substituent atoms. It would be incredible that such beautiful parallelism would be observed if the frequencies were differences of the fundamental frequencies of the molecules, and not the latter themselves.

Several papers have already appeared on the interpretation of ultraviolet absorption and fluorescent spectra, and of the infrared absorption spectra with the aid of the results from light scattering. Obviously, however, an immense amount of work remains to be accomplished.

The data already obtained with organic liquids show how, in quite a number of cases, it is possible to identify particular frequencies with vibration of particular chemical bonds in the molecule. Apart from the frequencies as measured, it is fairly certain that a study of the polarisation character of the new lines would enable a further advance to be made in this direction. It is found, for instance, that the frequency corresponding to the C—H bond in aliphatics and aromatics is different, and that the polarisation is even more strikingly so.

9. Theory of the effect and its relation to molecular structure

The theory of dispersion in the form which it takes on the wave-mechanics formally explains the phenomena of light scattering. Several attempts to formulate the theory in a more concrete form so as to fit in with facts observed in particular cases have already been made. Special reference may be made here to Professor Kemble's explanation of Wood's observations with hydrochloric acid gas. The Dirac theory has also been used by two Italian writers, Amaldi and Segre, to give a general interpretation of light scattering and its relation to fluorescence. In a separate communication, I shall endeavour to indicate what would seem to me to be a promising line of further attack on the whole question of the relationship between molecular scattering of light, infrared absorption, and the theory of dispersion.

PART II*

Faraday was not only the greatest experimental physicist of the nineteenth century, but by his discovery of benzene can claim to be regarded as one of the founders of modern chemistry. It is therefore very appropriate that the Faraday Society should offer itself as a forum for the discussion of a new phenomenon which forms a kind of bridge between the sciences of physics and chemistry. As explained in my written paper, its discovery was no accident, but was the result of systematic research on the subject of the molecular scattering of light continued for several years in the hope that results of a fundamental character would be reached. It is proposed in this address to deal with the explanation of the phenomenon and with its relation to molecular structure, problems of deep interest to physicist and chemist alike.

In the first day's discussion we heard a good deal about spectroscopic nomenclature and especially about the very large number of symbols necessary to describe the physical state of a molecule in its electronic, vibrational, and rotational energy levels. It may not, therefore, be superfluous to emphasise that a molecule, in spite of this apparent complexity of structure, is after all a single physical entity, and that its properties should be capable of being described in a simple manner. The study of the phenomena of light-scattering and also certain related investigations conducted at Calcutta on electric and magnetic birefringence of fluids disclose that many of the polyatomic molecules familiar to the chemist possess very remarkable properties. Chief amongst them is the possession, in many cases, of extraordinary degrees of optical, electrical and magnetic anisotropy.

As an instance of the new results reached at Calcutta in this direction we may refer to the cases of the aromatic hydrocarbons, benzene, naphthalene, and anthracene. The crystalline birefringence exhibited by the two latter substances has been recently measured by Mr Bhagavantam and has been found to be about twice and thrice as great respectively as that of calcite. High as is the degree of optical anisotropy indicated by these measurements, even more remarkable is their magnetic anisotropy established by observations with the crystalline solids. The naphthalene and anthracene molecules have a diamagnetic susceptibility about four and five times respectively greater in a direction normal to the plane of the carbon rings than the minimum value in a direction parallel to the plane. The aromatic and aliphatic series of compounds of carbon offer a most interesting contrast in this respect. As was found several years ago by Cotton and Mouton, benzene and the aromatic compounds of carbon generally in the fluid state show strong magnetic birefringence similar to that of a *positive* uniaxial crystal. By

*Substance of an oral address given at the Bristol meeting by way of supplementing the written paper bearing the same title (see Part I above) which was printed and circulated in advance. Part I was mainly historical in character.

means of a specially constructed electromagnet, we have been recently able to detect the magnetic birefringence of the aliphatic hydrocarbons, and Mr Ramanathan's measurements with them show the birefringence to be very feeble and similar to that of a *negative* uniaxial crystal. These observations indicate that the well-known chemical differences between the aromatic and aliphatics correspond to a difference in their magnetic characters which is so striking and significant that it may not be too much to say that the ultimate explanation of the facts of organic chemistry may be found *via* the studies of magnetic behaviour of carbon compounds.

In the case of the benzene molecule, our studies of light-scattering and of magnetic birefringence enable us definitely to assert that a direction normal to the plane of the carbon atoms is an axis of *minimum* optical polarisability and of *maximum* diamagnetic susceptibility. On the other hand, we have convincing reasons for believing that in the triatomic molecules of CO_2 and CS_2 , the line joining the centres of the atoms coincides with the direction of the *maximum* optical as well as of the *maximum* diamagnetic susceptibility. The explanation of such facts concerning the optical and magnetic characters of different types of polyatomic molecules in terms of the electronic configurations in them offers itself as an important problem for the spectroscopists to solve.

It was in the attempt to investigate experimentally how the optical anisotropy of molecules varied with the wavelength of the incident radiation that we were led at Calcutta to the discovery of the existence of scattered radiations with altered wavelength. Before dealing with this phenomenon, we may venture to turn from the problems of spectroscopy to some physical considerations regarding the scattering of light by molecule.

Investigations on the molecular scattering of light of the classical kind show very clearly that the intensity of such secondary radiation stands in the closest quantitative relationship with the refractivity of the molecules. The classical theory of dispersion also teaches us that the refractivity of molecules for visible rays and for radiations in the near ultraviolet is determined by the existence of characteristic molecular frequencies lying mainly in the far ultraviolet region of the spectrum.

When light is scattered by a molecule, the incident radiation has usually a frequency less than the characteristic ultraviolet frequencies of the molecules; hence the energy of the incident quantum of radiation is insufficient to cause the electrons in the molecule to pass definitely into a higher energy level. Nevertheless, it is the tendency of the incident radiations to disturb these electrons that is responsible for the classical scattering of light. As the characteristic *infrared* molecular vibrations or rotations contribute to a negligible extent to the refractivity for visible light, it follows that they do not play any important part in the process of light-scattering as conceived in the classical theory.

We may, at this stage, ask ourselves, how are we to explain the fact that the classical type of scattering is actually accompanied by radiations of altered

wavelength? In my very first report, I suggested a simple and easily understood picture of the process involved in this new phenomenon. The quantum of radiation exchanges energy with the molecule on which it is incident. Part of the energy of the quantum is taken over by the molecule which thus passes into an excited condition. *Vice versa*, an excited molecule may give up its energy to the quantum which then goes off with increased energy. The first process naturally occurs more frequently, as there are more unexcited molecules than excited ones. The process pictured is one which can actually occur, for the incident quantum of energy is greater than the quantum of energy absorbed by the molecule; that the interpretation is a valid one is shown by the fact that the difference between the frequencies of the incident and scattered radiations is characteristic for the molecule, and in not a few cases agrees with known infrared absorption frequencies.

Several writers have criticised this simple picture of the process of light scattering as inadequate. I believe these criticisms are based on a misapprehension. It is true that the theory of dispersion in the form which it takes in the quantum theory involves the consideration of three different levels of energy *A*, *B* and *C* of the scattering system, and that the change of frequency which occurs in the scattering process is the difference between the energy quanta required from a transition from *A* to *C*, and from *B* to *C*. The ultimate result is, of course, a transition of the system from *A* to *B*. The critics have, it seems to me, overlooked the fact that in the cases with which we are actually concerned, the introduction of the third level *C* is merely a mathematical device. The fact that the scattering with altered wavelength is usually only a feeble addition to the classical type of scattering, and that its intensity increases rapidly with increasing frequency of the incident radiation, indicates that the third level *C* with which we are chiefly concerned is an electronic level corresponding to a characteristic frequency of the molecule in the far ultraviolet. When the incident light is in the visible or near ultraviolet, its quantum of energy is insufficient actually to cause the molecule to pass over into the state *C*, and the transition of the molecule assumed for the purpose of the calculation is a purely virtual one which cannot actually occur. There is an interchange of energy between the molecule and the quantum only if the initial and final states of the former are different, and the frequency of the scattered radiation depends only on the difference of these two states.

We may at this stage, endeavour to picture to ourself in greater detail the process which causes the molecule to go over into a different state of energy as the result of the radiation falling upon it. There are two types of physical theory which experience proves to be useful in the exploration of a new field of research. The first is the *a priori* or fundamental type of theory based upon a deep analysis of all the elements involved in the problem. The second is the phenomenological theory which accepts the observed facts and endeavours to connect them with other observed facts in a coherent manner. The former type of theory is the more ambitious, and we may venture to hope that some day it will be possible to work it

out in full detail, for our phenomenon. Meanwhile, however, and especially in the case of the polyatomic molecules so important to the chemists generally, it seems probable that progress will be achieved more quickly with the aid of theories of the phenomenological type.

In the first place we may ask ourselves, why does the impact of radiation cause the molecule to change its energy-level of vibration or rotation? The answer to this is, very probably, that while the effect of the light on the molecule is primarily to disturb the electrons in it, there must be a tendency to alter at the same time also the rotational and vibrational energy-levels. The spectroscopist knows very well that it is only an approximation to regard changes in electronic, vibrational and rotational energy-levels of a molecule as independent of each other. In reality, all three are connected with each other, and it is impossible for the incident light to disturb the electrons in the molecule without at the same time tending to disturb the atomic nuclei and also the molecule as a whole and thereby altering its state of vibration and spin. If the classical notions of mechanics were valid, all three types of disturbance would occur simultaneously. In the newer physics, we should say that the probabilities of the three types of transition occurring in any given molecule are definitely related to each other. If the interconnections of the three types of transition are known empirically from the spectroscopic data for any given molecule, we could proceed from them to calculate the behaviour of the molecule in light-scattering or *vice versa*.

The case of radiation inducing a change in the spin-energy of the molecule is the one in which it seems most hopeful to obtain a quantitative picture of the phenomenon. It would be quite inappropriate to regard this as a simple case of mechanical collision between two particles resulting in a spin being set up in one of them. What is actually involved is the mechanical action of the field of the light-wave on the electric charges contained in the molecule. If we assume that the molecule has no permanent electric moment, or decide to ignore the latter if it be present, the mechanical action on the molecule would be due to the reaction of the field with the oscillating electric doublet induced by it in the molecule. The resulting couple would vanish completely if the molecule were optically isotropic, as the direction of the field and of the doublet would then be coincident. Actually, however, it is known that all molecules are optically anisotropic, some molecules such as benzene, CO_2 , CS_2 , etc. strongly so. Hence such optical anisotropy of the molecule makes it possible for the field of the light-wave to exert a couple on the molecule and alter its state of spin. It is interesting to notice that the available experimental evidence indicates the intensity of the rotational effect to be much greater in the case of strongly anisotropic molecules such as those mentioned above, than for molecules which are known to be more nearly isotropic optically, e.g. CH_4 , CCl_4 , etc. It is believed that the considerations set out above, when more fully developed with the aid of the new mechanics will furnish a basis for quantitative comparison with experiment.

We may now pass on to consider changes in the vibrational state of the

molecule induced by the incident radiation. From thermodynamical considerations it is evident that the great majority of the molecules in a substance would be in the zero vibrational state at ordinary temperatures, and hence it is clear, especially in view of what has been said above regarding the nature of the transitions induced by light, that they must correspond to the fundamental vibration frequencies of the molecules. [In exceptional cases, harmonics of such vibrations, and summations of two fundamental frequencies may occur with low intensities]. It appears desirable to emphasise this point particularly because the contrary opinion expressed by Langer in a note to *Nature* dealing with the case of CCl_4 , appears to have gained currency in certain quarters and is quoted by Prof. R W Wood with approval in his communication to the *Faraday Soc.* The figures given by Langer in his note in *Nature* do not prove his contention, as the observed absorption frequencies of CCl_4 in the infrared can be explained with equal numerical accuracy and physically in a much more acceptable way by taking the frequencies in the far infrared observed in the light-scattering as the fundamentals, and the absorptions in the near infrared as summationals derived from them. [Indeed this has been done recently by another American writer in a paper in *Phys. Rev.*]. The view that the vibration frequencies observed in light-scattering are really the fundamentals is supported by very cogent and convincing evidence. Particularly striking in this connection is the fact that the frequencies found move further and further into the region of the remote infrared with increasing atomic weights, as we should expect them to do if they were fundamental frequencies. The diagram given by Prof. Pringsheim in his recent article in the *Handb. Phys.* (Band XXI, p. 612, Abb. 5) from the observations of Daure is specially instructive in this respect.

To enable us to understand why the light in disturbing the electrons also tends to set the atomic nuclei in vibration, it appears advantageous to adopt the method of representation used by Prof. Franck in his well known theory of photochemical dissociation of molecules, and by Prof. Victor Henri in the beautiful discourse which we have listened to on the work of the Zürich school of physical chemists with polyatomic molecules. For simplicity, we may consider a diatomic molecule and draw a graph connecting the potential energy of the atoms as a function of their nuclear separation. The graph exhibits a minimum at a distance of separation of the atoms corresponding to their position of equilibrium. If now the molecule passes into an excited electronic state, we have to draw a new graph corresponding to such greater energy, and the distance of the nuclei at the lowest point of the new graph will be different from the first. In other words, if we excite the electrons, there is an inherent probability that we also alter the nuclear separation of the atoms in the molecule. In the experiments on light-scattering, the incident radiation quantum has insufficient energy to make the electron actually pass into an excited state. But the tendency to do so is there, and hence it is to be expected that in a certain proportion of the encounters with the

radiation-quanta, the molecules will absorb energy and pass into a higher vibrational state.

If the form of the potential energy graphs were known, it should be possible to express this tendency in a quantitative form and thus to determine the intensity of the light scattered with changed wavelength.

In the case of polyatomic molecules, our one-dimensional picture may be, in general, too simple and may require elaboration into a three-dimensional scheme connecting the excitation of the electrons in different directions with the probabilities of excitation of different types of nuclear vibration. In this way, the remarkable variation in the polarisation of the scattered radiations of different wavelengths may receive a satisfactory explanation.