

## Radiation of Gas Molecules Excited by Light

This content has been downloaded from IOPscience. Please scroll down to see the full text.

1913 Proc. Phys. Soc. London 26 185

(<http://iopscience.iop.org/1478-7814/26/1/323>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 128.111.121.42

This content was downloaded on 06/09/2015 at 00:11

Please note that [terms and conditions apply](#).

XXIII. *Radiation of Gas Molecules Excited by Light.* By R. W. WOOD, *Professor of Experimental Physics, Johns Hopkins University, Baltimore.*

BEING THE FIRST GUTHRIE LECTURE, DELIVERED FEBRUARY 27, 1914.

THE emission and absorption of light by molecules, and the closely related phenomenon of dispersion, have led us to the conception of something within the atom which is capable of responding to light-waves, in much the same way as a tuning fork responds to sound-waves of the same frequency as its own. There seems to be no escape from this conclusion, and very elaborate mathematical treatments have been built up on this foundation, which explain in a more or less perfect manner many of the phenomena in question. If, however, we try to form some conception of just what is going on we find that we are still very much in the dark. Helmholtz explained absorption by the introduction of a frictional term into his equations of motion for the atom, and though this led at once to an expression which represented anomalous dispersion, it left us in ignorance of how the energy absorbed by the molecules was transformed into heat, or, in other words, how the mean velocity of the molecules was increased by the excitation of vibrations within them. Planck avoided this difficulty by considering that the energy abstracted from the beam of light is re-emitted, though at the time the only experimental evidence which could be cited was the phenomenon of selective reflection, which occurs only when the molecules are so densely packed together as to give us the liquid or solid state.

What became of the absorbed energy in the case of a gas? This is something that I have been looking for for many years. Personally I do not require a working model, but I never felt *completely* satisfied by an equation in which absorption is represented by a frictional term or selective reflection predicted by the occurrence of an imaginary quantity, as in Lord Kelvin's expression for sodium vapour, especially as no case of such selective reflection by a vapour was known. The subject which I have chosen for discussion this evening is the disposition made by the absorbing mechanism of the energy which it abstracts from the incident light, and the more complicated phenomena which occur when various absorbing mechanisms

of the atom are coupled together. All of this has, of course, a very direct bearing upon the structure of the atom, a subject which is receiving much attention at the present time. Our profound ignorance of the matter and inability to construct or imagine a model capable of representing the source of even the simplest emission spectra, make one almost regret the enormous amount of work which has been spent in tabulating the wave-lengths of the spectra of the elements. It is only within the last decade that the brilliant work of Zeeman, Lorentz, Sir Joseph Thomson and others have led to a definite conception of the constitution of the outer shell of the atom. What is inside of the egg can only be imagined at the present time.

The problem of the structure of matter is one which must be attacked simultaneously from many sides, for it is improbable that any single weapon will cause the surrender of the secret. The spectroscope alone proved itself powerless, and the first definite step in advance was made when Zeeman placed a source of light in a magnetic field.

One great difficulty lay in the fact that in all known methods of exciting spectra it was "the whole or nothing." Flames, arcs, sparks and vacuum-tube discharges set in operation simultaneously a host of vibrations within the atom and resulted in a complex of lines. While it is true that much has been learned from the circumstance that the spectra vary according to the method of excitation, our ignorance as to the forces in operation in the case of flames or sparks makes it difficult to interpret the phenomena.

My own line of attack has been to keep the molecules as cool and quiet as possible, and then excite them to radiation by the application of an alternating electromagnetic field of a definite frequency, which is more commonly referred to as monochromatic light. We can in this case be pretty sure of what we are doing to the atoms, if we are not too particular to ask for a specific definition of what we mean by an alternating electromagnetic field.

That this method of going at the thing has simplified matters somewhat you will see when I draw your attention to sodium vapour which emits only one of the yellow D lines. Much time and many experiments have been necessary to develop the technique of exciting luminescence in this way, for the conditions vary according to the element studied, some vapours emitting light only when reduced to a pressure of less than 0.001 mm., while others operate even at a pressure of several atmospheres.

The presence of a foreign gas is very detrimental, which is sufficient to explain the failure of my first experiment on the subject made over 15 years ago, the concentration of sunlight by means of a large condenser upon a flame very rich in sodium.

In the earlier part of the work the phenomena presented were very complicated, and it is only recently that simple types of emission, which could be studied quantitatively, and subjected to mathematical analysis, have come to light. It will, therefore, be best to review the subject in almost inverse chronological order, beginning with the simplest case of a vapour which exhibits a single absorption line and emits radiations similar in every respect to the exciting radiations when stimulated by a frequency equal to that of the line of absorption. This condition is very perfectly fulfilled by the vapour of mercury, which has an absorption line at wave-length 2,536 in the ultra-violet.\*

At room temperature the vapour of mercury has a pressure of about 0.001 mm. This gives us, assuming a uniform distribution, one molecule in every cube whose sides are equal to the wave-length of the ultra-violet light employed in the experiments. If a beam of monochromatic light of wave-length equal to that of the absorption line 2,536, obtained by isolating the corresponding emission line of the silica mercury arc by means of a quartz monochromator, was focussed at the centre of an exhausted quartz bulb containing a drop of mercury (the whole at room temperature), it was found that the light was powerfully scattered by the vapour, photographs of the bulb made with a quartz lens showing the cone of rays much as if the bulb were filled with smoke. The greater part of the light, however, passed through the bulb without sensible reduction of intensity even if the diameter of the bulb was sufficient to give to the luminous cone its maximum extension, for the cone is brightest where the rays enter the bulb, the intensity diminishing rapidly as we pass along the cone, owing to the removal from the incident beam of the energy of just the right frequency for exciting resonance. For a pressure of 0.001 mm. it was found that the intensity of the effective part of the incident beam was reduced to half of its original value after traversing a distance of 5 mm. in the vapour. This determination was made by passing a beam of *parallel* rays

\* "Selective Scattering, &c., by Resonating Gas Molecules," "Phil. Mag.," May, 1912.

through the vapour, and measuring the intensity of the scattered radiation along the path. If the intensity at the point of entrance is 100, the intensity after traversing a distance of 1 cm. is 25, while at a distance of 2 cm. from the point of entrance the intensity is but 6. This means that in a bulb 3 cm. in diameter the luminous cone will scarcely reach the opposite wall. Notwithstanding the astonishing stopping power of this highly attenuated metallic vapour for waves of just the right frequency, we find that a large proportion of the energy passes through the bulb without being influenced by the vapour. Experiments showed that this was due to the circumstances that the emission line had a finite width, and that its central portion only was scattered by the resonating molecules. This is made clear by Fig. 1, in which ABD represents the intensity distribution in the emission line of the arc and  $cBc'$  the central portion removed by the mercury vapour

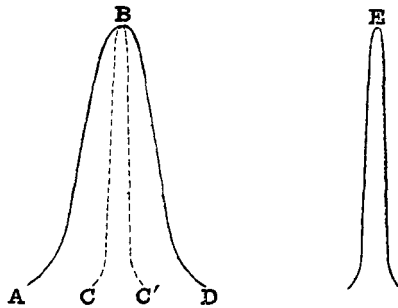


FIG. 1.

at room temperature. After passing through the bulb the emission line would appear furrowed by a fine black line of width  $cc'$  if we possessed a spectroscope of sufficient resolving power to show it. If the energy removed from the incident beam is re-emitted without change of wave-length by the vapour it is clear that the width of the spectrum line of the light given off by the cold mercury vapour in the bulb will be as shown by E in Fig. 1. In other words, we possess a method of obtaining light which is probably more homogeneous than any light obtained up to the present time. This is a matter which is being investigated quantitatively at the present time. Radiation scattered in this way without change of wave-length by resonating molecules I have named *Resonance Radiation*. We may term a bulb filled with vapour and emit-

ting light more highly monochromatic than the light which excites it a resonance lamp. With the light from a lamp of this description a photograph was made of a quartz bulb at room temperature containing a minute drop of mercury. The bulb appeared as if filled with ink, owing to the opacity of the mercury vapour for the rays. A drop of mercury placed on the top of a brass cylinder, heated to a temperature of about 5 deg. higher than that of the room, when photographed by the shadow method showed a column of vapour rising from the drop like black smoke. A lamp of this type has been used in many of the investigations of the scattering and absorbing power of mercury vapour, for the reason that it emits only waves which are in exact synchronism with the molecular resonators, whereas even the single line 2,536 isolated from the radiations of the mercury arc contains frequencies which are freely transmitted by the vapour.

*Secondary Resonance Radiation.*—It was found that the mercury vapour outside of the luminous cone traversed by the exciting rays also emitted light, a glow filling the entire bulb. Experiments showed that this was due chiefly to a secondary scattering of the light emitted by the directly excited molecules; in other words, the luminous cone of vapour acted as a light source which stimulated those portions of the vapour not actually traversed by the incident beam of light. The intensity of this secondary resonance radiation in comparison to that of the primary is surprisingly great, so great in fact that I was at first inclined to believe that it was due, in part at least, to a persistence in the luminosity of the rapidly moving molecules after they had passed through the region traversed by the exciting beam of light. Experiments showed, however, that the introduction of a thin quartz plate between the regions of primary and secondary resonance did not diminish the latter to any appreciable extent. This indicated that the phenomenon resulted from excitation by the light given out by the directly excited molecules, and did not result from a persistence of luminosity (phosphoresence), for the quartz plate is transparent to the ultra-violet light, but stops the moving molecules.

The comparatively great intensity of the secondary radiation results from the circumstance that at these low densities *no true absorption* exists; in other words, there is no transformation of energy. And now we come to a very important point, for we are at last in a position to measure the ratio of the scattered



the incident beam AB, Fig. 2, of square cross-section (plane waves), and assume that all of the energy abstracted from it is re-emitted. We require the intensity of the secondary resonance radiation from a layer immediately above the plane CDGH of the thin cross-section of the exciting beam in comparison to the intensity of the primary resonance radiation within this same cross-section. The secondary resonance is excited by the energy poured out by the resonating molecules which lie in the path of the primary beam. The energy escaping from the rectangular cross-section figured above passes out through the four sides in equal amounts, for that which escapes through the surfaces CDEF and GHIJ remains within the beam and does not contribute to the excitation of the secondary resonance.

The excitation at a point, K, immediately above the exciting beam can, therefore, be regarded as dependent upon the energy stream passing through the side CDHG, which will be approximately one-quarter of the total energy radiated *laterally* from the cross-section figured. The total amount radiated laterally represents the energy abstracted from the primary beam by the molecules lying within the cross-section, and the intensity of the primary radiation will be proportional to this quantity. We should, therefore, expect the intensity of the secondary radiation to have about one-quarter of the value of the primary, as was found to be the case in the experiment. If true absorption exists the ratio will be very different. Suppose that, of the energy abstracted from the primary beam, one-half is re-emitted and one-half absorbed. The intensity of the primary radiation will now be only one-half as great as it was before. We can, however, raise it to its original value by doubling the intensity of the exciting beam. The amount of energy escaping from the sides of the cross-section figured is now the same as before, but only half of it is effective in producing secondary radiation, the other half being lost by absorption. The secondary radiation will now be only one-half as intense as it was before, while the primary will have the same value, the ratio being  $\frac{1}{2}$  instead of  $\frac{1}{4}$ . We thus see that, by measuring the ratio of the intensities of the secondary and primary resonance radiation, we have a means of determining the ratio of scattering to true absorption. This makes a rigorous mathematical determination of the ratio which would be found in the case of complete scattering without any absorption much to be desired. The matter is peculiarly complicated,



for not only is a point lying outside of the primary beam illuminated by radiations coming from all points within the beam, but also by radiations from all points outside of the beam, and the same holds true for points within the beam. In other words, every molecule contributes, in a greater or less degree, to the illumination of every other molecule.

It would thus appear as if doubling the number of molecules in unit volume ought to more than double the intensity of the resonance radiation. This relation has not yet been investigated in the case of direct resonance radiation, but in the case of the fluorescence of iodine vapour, which is a more complicated phenomenon, a photometric study, made in collaboration with Mr. W. P. Speas, showed that doubling the vapour density by no means doubled the intensity. For example, we found that at a pressure of 3 the intensity was 24, while at a pressure of 6 the intensity was but 33. This is exactly the opposite of what is to be expected in the case of resonance radiation where all of the molecules are operating and there is no true absorption.

In the case of the iodine vapour, as the density of the vapour increases, the radiation from each molecule decreases as a result of the presence of its neighbours. The same effect is observed with a constant partial pressure of iodine, and an increasing pressure of some other gas, but iodine vapour is more effective in decreasing the luminosity of an iodine molecule than any of the other gases, and helium is the least detrimental, the gases arranging themselves in the order of their electro-negative character.

*True Absorption.*—The factor of true absorption makes itself manifest as soon as we admit air or some other foreign gas to the bulb containing the mercury drop. Even if the pressure is only a millimetre or two the effect is very marked. The intensity of the primary radiation is diminished to a certain extent, while that of the secondary radiation is reduced to a much greater degree for the reason mentioned a few moments ago. At a pressure of 6 mm. there is scarcely any trace left of the secondary resonance radiation, though the intensity of the primary is only reduced to one-third of its value in the complete absence of air, Fig. 3 (opposite page 201).

*Huygens' Principle and Resonance Radiation: Selective Reflection.*—Another point of considerable interest is the determination of the conditions under which it is possible to apply the principle of Huygens to the secondary waves emitted by

the molecular resonators. In certain theoretical discussions of absorption, the resonators are regarded as giving out waves which interfere destructively with the primary wave in the direction in which it is travelling, while in the opposite direction, there being no energy stream with which they can interfere, they unite into a wave which travels back towards the source, the phenomenon constituting selective reflection. While there is no doubt but that the resonators are close enough together to make the application of Huygens' principle justifiable, there are certain other factors which, it seems to me, must be taken into account.

In the first place, in a vapour at low pressure, the wave is obliged to pass by an enormous number of molecules before its intensity is much reduced. To give a numerical illustration, it was found that in the case of mercury vapour at room temperature the intensity was reduced to one-half its original value after the light had traversed a layer of the vapour 5 mm. in thickness. The pressure at room temperature is about 0.001 mm., which gives us about one molecule in every cube the sides of which are equal to the wave-length of the ultra-violet light. The light thus has to pass through 16,000 layers of molecules before losing one-half of its intensity, if we assume the molecules arranged in cubic order. If the radiations emitted by the molecules combined by Huygens' principle to form a regular wave, it would, in this case, constitute what we might term "volume reflection" as contrasted to surface reflection. It appears to me to be inconceivable that a reflection of this nature can occur, for the same reason that reflection cannot occur at the boundary between two media of different optical densities, if the transition is gradual instead of abrupt. The question may perhaps be raised as to why the molecules diffuse the light at all if there are many of them to the wave-length. We are accustomed to regard a medium in which the structure (so to speak) is small in comparison to  $\lambda$  as a homogeneous medium.

There is, however, in the present case another factor which doubtless has some bearing on the problem, namely, the circumstance that every molecule is excited to a greater or less degree by the radiations from its neighbours, all of which are moving at high velocities in all directions. This, it appears to me, would cause a random distribution of phase among the vibrations coming from the molecules, and would prevent

completely interference of the type considered in Huygens' principle.

*Selective Reflection by a Dense Gas.*—I have, however, observed that if the pressure of the mercury vapour is raised to several atmospheres regular reflection of a selective nature occurs at the inner surface of the bulb. The wave-length most strongly reflected is not quite in coincidence with the centre of the absorption line, but lies slightly on the short wave-length side of it. This is probably due to the circumstance that the refractive index of the vapour has an abnormally low value at this point, for the absorption line shows very strong anomalous dispersion. For a reflection from the inner surface of a quartz bulb we should expect a marked increase in the reflecting power for those values of  $\lambda$  for which the refractive index of the medium in the bulb was less than unity. The selective reflection of mercury vapour for wave-lengths in the vicinity of the 2,536 line should be investigated quantitatively. I have made only a qualitative investigation up to the present time, but as I have now learned how to control the intensity and width of the emission line of the mercury arc I feel certain that this can be done in a satisfactory manner.

*I wish also to emphasise again the desirability of having a rigorous theoretical treatment of the emission of radiant energy, by resonating molecules, which give out again all of the energy which they abstract from the primary beam, both for a highly rarefied and a very dense gas.* Much of the value of the experimental work will be lost if this is not done. Most important is the calculation of the relative intensity of the primary and secondary resonance radiation, under some condition verifiable by experiment. The best condition appears to me to be the case of an exciting pencil of parallel rays, of square cross-section, passing through the gas parallel to and almost grazing the window through which the observations are made.

Next in importance is the determination of what happens when the gas is dense enough to practically stop the incident rays before they have penetrated to a depth of more than one or two wave-lengths; if the intermediate condition can be examined, that too would be desirable. By this I mean the manner in which we pass from diffusion to regular or specular reflection, which I have examined experimentally. The regular reflection is not, however, nearly as powerful as we should

expect it to be if there were no absorption. As we increase the density of the vapour the intensity of the diffused radiation decreases and it is finally replaced by regular reflection. I do not, however, believe that the selective reflecting power is over 20 per cent., which means that the factor of true absorption has been introduced by the increase in the vapour density. I have not yet determined quantitatively the effect of increasing the density of the mercury vapour, as compared with the effect of raising the pressure in the same proportion by the introduction of some other gas. I am very sure, however, that true absorption is introduced to a greater degree in the latter case—that is to say, that collisions with foreign molecules are more effective in introducing absorption than collisions with mercury molecules. These questions I am now about to investigate; now that I am able to work with a source of constant intensity.

*Case of Sodium Vapour.*—Many of the phenomena which were discovered by photography in the case of the ultra-violet resonance of mercury vapour can be rendered visible by employing the vapour of sodium. The resonance radiation of this vapour I discovered in 1905,\* heating the metal in an exhausted tube, illuminated by the rays from an oxy-hydrogen sodium flame brought to a focus by means of a large condensing lens. On gently heating the tube the path of the rays through the vapour was marked by a yellow glow, which drew back towards the side of tube through which the rays entered, as the vapour density increased, until only a thin skin of yellow light remained, which lined the inner wall of the tube, the image of the sodium flame appearing on the surface layer of vapour. Attempts to obtain regular selective reflection by increasing still further the vapour density failed, as a result of the chemical action of the vapour on the glass at high temperatures.

The experiment has been recently improved by L. Dunoyer, who employs a Bunsen flame charged with a spray of a solution of chloride of sodium, which is blown into the base of the burner by means of an atomiser. A chimney of sheet iron, with a square window, surrounds the flame, and an image of the window is projected upon the wall of the sodium bulb, by means of a quadruplet condenser, free from aberration if mono-

\* Wood, "Phil. Mag.," August, 1905.

chromatic light is employed.\* The bulb contains a little metallic sodium, carefully freed from hydrogen by distillation in vacuo, and is very highly exhausted. It is heated in a column of hot air rising from a tall chimney which surrounds a large Meker burner. The resonance radiation first appears at a temperature of about  $125^{\circ}\text{C}$ ., a faint cone of yellow light appearing in the bulb. As the temperature is increased, it becomes brighter, and presently the secondary resonance radiation appears, a yellow glow filling the entire bulb. At a temperature of  $180^{\circ}\text{C}$ . the cone of primary resonance radiation disappears and with it the secondary radiation, and there remains only a brilliant square of yellow light on the front surface of the bulb, an image of the illuminated window thrown upon a resonating gas. It is as sharply defined as if thrown upon white paper, but has an intensity of only about one-tenth of the intensity obtained when a paper screen receives the rays coming from the condenser. In other words, the greater part of the light from the sodium flame passes through the vapour unhindered, the narrow cores only of the D lines being operative in causing resonance precisely as was the case with mercury vapour. If the bulb is allowed to cool slowly the first change observed is a fuzziness of the edges of the square image of the window, the appearance being as if the image suddenly went "out of focus." This is due to secondary radiation, and in its first stages it is confined to a shallow layer of vapour close to the wall. As the bulb cools down the cone of yellow light appears again, the phenomena previously described taking place in inverse order.

If, now, no absorption occurs in the case of sodium vapour, as appears to be the case with mercury vapour, we ought to obtain as brilliant an image on the vapour as on white paper, *provided our light source emits only light capable of exciting resonance.*

This subject has been investigated in collaboration with M. Dunoyer during the past winter. We fed the flame of the Meker burner with the spray of a solution of NaCl of varying concentration and measured the ratio of the diffusive power of a patch of MgO, formed on the outer wall of the bulb, to that of the diffusive power of the vapour within. It was found that the intensity of the resonance radiation from the sodium vapour was practically independent of the amount of

\* L. Dunoyer "Sur l'Aberation de Sphéricité dans les Objectifs" ("Journal de Physique," 1913).

sodium in the flame, *i. e.*, of the total intensity of the source. This means, of course, that the *cores* of the D lines, which are alone effective in exciting resonance, do not increase much in intensity as we increase the amount of sodium in the flame. The ratio above referred to varied enormously however. With a solution made by diluting a saturated solution with 30 parts of water the ratio was 15 : 1—that is, the MgO was 15 times brighter than the surface layer of resonating sodium molecules in the bulb. With the solution diluted with 1,000 parts of water the ratio was 4 : 1 and with a still more dilute solution 3 : 1. The ratio could not be made smaller than this on account of the feeble intensity of the flame. The decrease in the ratio

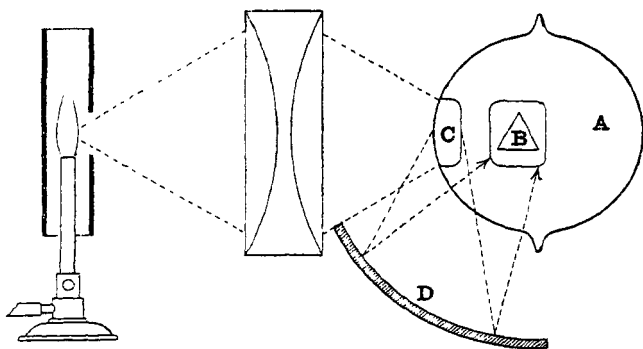


FIG. 4.

Experiment showing that the diffuse reflecting power of sodium vapour is equal to that of magnesium oxide for the highly homogeneous light of a sodium resonance lamp. A is a glass bulb, highly exhausted, containing sodium vapour. C is the image of the sodium flame thrown upon the vapour by the condensing lens. This image has an intensity of about one-fifth of the intensity shown by MgO under the same illumination. B is a triangular patch of MgO upon which an image of C is thrown by the concave mirror D. The MgO triangle cannot be distinguished from the luminous sodium vapour.

results from the circumstance that the width of the exciting lines (D lines) decreases as the amount of sodium in the flame is decreased; in other words, we are working with light more nearly in exact synchronism with the resonators. It is very important to know what the ratio would be if our exciting light were still more homogeneous. In this case we should have a ratio of 1 : 1, if the sodium vapour exhibits complete scattering with no trace of true absorption. It is impossible to accomplish anything in this direction by reducing further the amount of sodium in the flame, but by making use of the principle of the resonance lamp we can investigate the matter.

A single bulb was made to serve both as a resonance lamp and as a screen for measuring the reflecting power of the vapour, Fig. 4. An image of the sodium flame was thrown upon the side of the bulb and by means of a concave reflector, which had an effective aperture represented by F. 1 (formed by silvering one surface of double convex lens), an image of the spot of resonance radiation was thrown back upon the bulb of sodium vapour, one half of it being received by a small triangle of magnesium oxide, the other half by the vapour. Under these conditions it was found that there was absolutely no difference in the diffusive reflecting power. This means that the vapour of sodium at a pressure of probably less than 0.001 mm. has a reflecting power as great as that of the whitest paper or MgO, for light of exactly the right wavelength.

These experiments make it seem probable that absorption, as we usually understand the word, is a secondary action, resulting from reciprocal actions between the molecules. M. Dunoyer has made experiments on the effect of hydrogen on the intensity of the sodium resonance radiation and has found that the intensity is reduced practically to zero if hydrogen is present at a pressure of 10 mm. With helium at a pressure of half an atmosphere there is still considerable luminosity.

This indicates that the sodium molecule is far more sensitive to disturbances from neighbouring molecules than iodine, for which vapour the intensity of the fluorescence is reduced only from 100 to 35 by hydrogen at a pressure of 10 mm.

Now, the intensity of the iodine fluorescence decreases tremendously as the vapour density increases. From photometric observations made in collaboration with Mr. Speas I have calculated that the intensity of the radiation from an iodine molecule is reduced from 100 to 35 by a pressure increment of 0.25 mm. produced by increasing the density of the iodine vapour.\*

Sodium is probably much more sensitive still, and the factor of true absorption is undoubtedly introduced by the reciprocal action between the molecules at even the very low pressure used in the experiments which have been described.

Thus far we have considered the type of resonance which results in the re-emission of radiant energy of the same type (*i.e.*, wave-length) as that of the exciting radiations. It has been studied for two cases, mercury vapour and sodium vapour,

\* "A Photometric Study of the Fluorescence of Iodine Vapour." ("Phil. Mag.," March, 1914.)

the ultra-violet absorption (so-called) line of Hg at wavelength 2,536 and the D lines of sodium operating in this way. It appears probable that what is commonly spoken of as absorption results from some action upon the molecules of neighbouring molecules, for in both cases we find that an increase of vapour density or the presence of some chemically indifferent gas diminishes the resonance radiation and increases the factor of true absorption. It is to be clearly understood that by examination of the transmitted light we are powerless to discriminate between the two cases. The appearance of the spectrum is the same regardless of whether the molecules re-emit or absorb the radiations which they remove from the exciting beam.

The action of a molecule in destroying the resonance radiation of a neighbouring molecule appears to depend upon the electronegative quality of the molecule only. If the gas is strongly electronegative, resonance radiation only appears at very low pressures (bromine) or not at all (chlorine). If less strongly electronegative (iodine) we have radiation even when the pressure amounts to several millimetres, while with an electropositive molecule (mercury) resonance radiation persists even when the pressure is as high as several atmospheres.

Of all the gases, helium appears to be the least destructive in its action upon molecular radiation; at least this is true for iodine vapour, and M. Dunoyer and I have recently found that it is possible to have a fairly bright resonance radiation of sodium in helium at a pressure of half an atmosphere.

The addition of a chemically indifferent gas not only changes the phenomenon of resonance radiation into absorption, but also increases the width of the absorption line as observed with a spectroscope. The line becomes fuzzy and is less black at the centre. I have not yet examined the action of different gases upon the absorption lines to see whether helium at, say, 50 mm. and CO<sub>2</sub> at 2 mm. have the same effect upon the absorption lines, which are the pressures which produce the same destructive action upon the fluorescence in the two cases. It is my belief, however, that the electronegative quality of a gas will not have much effect upon the change produced in the appearance of the absorption lines.

We now come to the second part of our subject. In many cases the molecule, when excited by monochromatic radiation, emits not only radiation of this same wave-length, but also



other wave-lengths which form what I have named Resonance Spectra. It seems as though there were numerous vibrating systems in the atom, the excitation of one system being communicated to the others in some way. Even the mercury 2,536 line and the D lines of sodium cannot be considered as due to a simple isolated vibrator, for I have found that mercury vapour can be caused to emit the 2,536 line when excited by extremely short ultra-violet waves, below wave-length 2,000 in the spectrum, and sodium vapour can be caused to emit a yellow band at wave-length 5,890 when excited by blue-green light.

We will consider first an experiment which I suggested in the Paper of 1905 already referred to, and which I have just brought to a successful conclusion in collaboration with M. Dunoyer. The question which we wished to solve was whether the mechanisms which produce the D lines are connected; in other words, if sodium vapour is excited to radiation by monochromatic light of the wave-length of  $D_2$  only, will it emit light of the wave-length of  $D_1$  as well as that

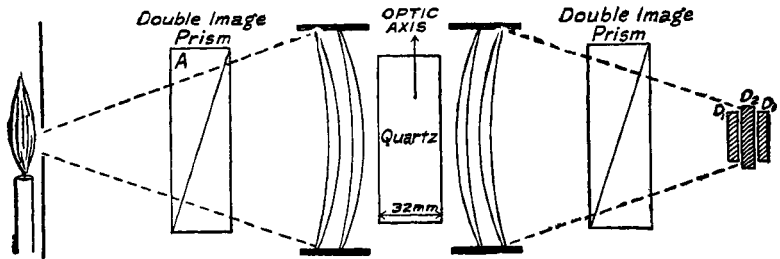


FIG 5

of the exciting radiation ( $D_2$ )? For this experiment we require some means of obtaining a powerful beam of light containing only the radiations of one of the two sodium lines. This was accomplished by means of a device which I described many years ago, depending upon the double refraction of quartz.

I have since improved this polarisation method, so that practically no light is lost (see Fig. 5).

Double-image prisms are used instead of nicols, and the two images which contain only  $D_2$  light are united by a suitable rotation of the second prism, the  $D_1$  images lying to the right and left. The separation of the two wave-lengths is effected by a block of quartz 32 mm. in thickness, cut parallel to the

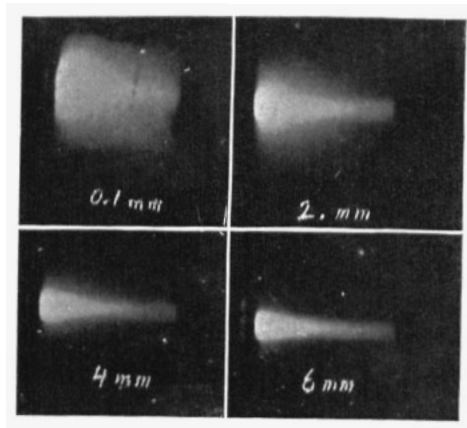


FIG. 3.

Cone of primary resonance radiation surrounded by the glow of the secondary resonance radiation. The latter has disappeared in the fourth picture as the result of admitting air at a pressure of 6 mm. "Phil. Mag.," May, 1912.

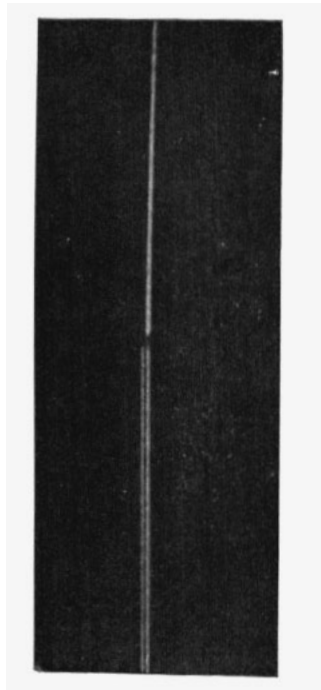


FIG. 6.

*To face page 201.*]

axis, which causes the two D lines to emerge polarised at right angles to each other. The monochromatic light obtained in this way is represented in Fig. 6, in which the upper portion of the slit is illuminated by  $D_2$  light and the lower by the light of the sodium flame.\*

With this apparatus we succeeded in exciting a bright resonance radiation of the sodium bulb by the light of  $D_2$ , and with an exposure of five hours obtained the spectrum of the emitted light, a single line only ( $D_2$ ) with no trace of  $D_1$ . *It is thus possible to have sodium vapour emitting one only of the D lines, and the experiment is a very good illustration of how spectra may be simplified by exciting them by means of light-waves.*

We have also photographed the spectrum of the resonance radiation of sodium vapour excited by the two D lines, and have found that the emitted lines have practically the same intensity. Now, it is well known that in the sodium flame (which was used for the excitation)  $D_2$  is much stronger than  $D_1$ , and it is very surprising to find that this same difference does not appear in the case of the resonance radiation. I have made a study of the relative intensity of the two lines in the case of flames, and have found that, with a flame very feebly coloured with sodium,  $D_2$  is fully four times as intense as  $D_1$ . With a flame very heavily charged with the vapour  $D_2$  is certainly not over 1.3 times as bright as  $D_1$ . Two photographs were made in coincidence simultaneously, with an exposure of half an hour, the light of the very intense flame passing through a piece of densely smoked glass before entering the instrument. The light from the feeble flame was reflected by the comparison prism. The smoked glass was so chosen that the intensity of the bright flame was reduced to almost exactly that of the feeble flame. To obtain the large ratio it is necessary to use a flame much less coloured than the flames commonly employed.

In the case of the D lines there seems to be no connection between the two vibrating systems, and I have never been able to get the D lines by ultra-violet excitation at the point of the spectrum occupied by the second members of the principal series. It may, however, be possible to do this with the improved methods.

\* A full description of the apparatus will be found in the "Phil. Mag." for March, 1914, from which Figs. 3 and 6 are taken.

We will now examine some cases in which we have a connection between the vibrators.

*Resonance Spectra.*—It will be impossible to give anything more than a very brief outline of the extremely complicated relations which exist in the case of these remarkable spectra, which appear to become more and more involved the more we study them. A very complete account of what is known at the present time regarding the case which has received the fullest study, will be found in the "Philosophical Magazine" for November, 1913, and the "Phys. Zeit.," December 1, 1913.\*

The discovery of resonance spectra was made in the course of some experiments on the fluorescence of sodium vapour. It was found that if the vapour was illuminated with monochromatic light of wave-length corresponding to that of one of its many thousand absorption lines, it emitted a spectrum consisting of widely separated lines spaced with remarkable regularity along the spectrum. The phenomenon is exhibited only by sodium vapour of considerable density, *i.e.*, at a pressure of the order of magnitude of a millimetre or two. Its absence in the case of vapour at such low pressures as are used for the study of the resonance radiation (D line emission) may be due to its relative faintness, or perhaps to the circumstance that it results from molecular aggregates which do not form at the low pressures. This is a point which will probably be settled by some investigations now in progress.

The absorption spectra of iodine and bromine are very similar to that of sodium. With my plane grating spectrograph at East Hampton, the focal length of which is nearly 14 metres, I have found that there are about 35,000 absorption lines in the visible spectrum, 115 having been counted in a region no wider than the distance between the D lines of sodium.

Now, since we obtain a different emission spectrum for each absorption line which we excite by monochromatic light, we are confronted with the case of an element which can theoretically be made to emit *many thousands of spectra, no two of which are precisely alike*. The number of spectra possible is vastly in excess of the total number of absorption lines, for we may excite two or more lines simultaneously, in all possible combinations, so that *the total number of different spectra possible*

\* Wood, "Resonance Spectra of Iodine under High Dispersion."

*is practically infinite.* In fact, it is only by taking special precautions that a single absorption line can be excited, for the lines are so close together that most of the emission lines of metallic arcs, which are used for the excitation of the vapour, have a natural width of such magnitude that they cover from two to a dozen of the absorption lines. The study of these resonance spectra has appeared to me to be of the greatest importance, for it is practically the only case in which we have any exact knowledge of the nature of the excitation. In flame, arc and spark spectra we know practically nothing about the forces which are at work upon the molecule, while in the case of resonance spectra we can be reasonably sure that we are subjecting the molecule to alternating electromagnetic forces of a definite frequency, and nothing else. Of course, these forces may bring other factors into play by dissociating the molecules or breaking up molecular aggregates, though I regard the fact that the emitted light is strongly polarised as evidence against this. Experiments made in Prof. Pupin's laboratory at Columbia University have shown that if an armature, free from current initially, is rotated in an alternating magnetic field the armature will deliver a current made up of a large number of different frequencies increasing by constant increments, and furnishing an interesting analogy with the resonance spectra.

I will now give a brief résumé of the results which have been obtained with iodine vapour, omitting most of the experimental details, which are very fully described in the Papers already referred to.

The vapour is used at room temperature in highly exhausted tubes, the excitation being by the radiations from a quartz mercury arc, sorted out by suitable ray-filters. The most careful study has been made in the case of the excitation by the green line (5,461), which can be made to cover from one to 10 absorption lines, by varying the watt consumption of the lamp. By interposing a ray-filter of bromine vapour it is even possible to remove some of the frequencies of the broadened green line, and so "throw out of action" the iodine absorption lines which happen to coincide with the bromine lines. The resonance spectra excited in this way have been photographed in the fourth order spectrum of a 6 in. plane grating used in conjunction with a collimator and a specially constructed Cooke portrait objective of about 130 cm. focus.

The vapour of iodine was contained in long glass tubes,

blown out to a small bulb at one end, an image of the mercury arc being formed along the axis by means of a large condenser.

It was found in the earlier work, that if the resonance spectrum, excited by the green mercury line emitted by the quartz arc operating under normal conditions, was photographed under high dispersion, the resonance lines were resolved into close groups. This was found to result from the circumstance that the green line was wide enough to cover seven absorption lines. By operating the lamp at a lower temperature—that is, with a small voltage drop across its terminals—the width of the green line can be reduced until it covers but a single absorption line, or at most two. The resonance spectrum is now found to be much simpler, the complicated groups being replaced by single lines or by pairs of lines. By raising the voltage of the exciting lamp, the number of lines in the groups can be gradually increased, for the green line broadens and covers other absorption lines as the watt consumption increases.

The groups are spaced at nearly equal distances along the normal spectrum, the distance between them increasing by a nearly constant amount as we pass from group to group towards the red end of the spectrum. There are slight variations, however, from the law of constant second difference, which cannot be explained by errors of measurement, for the wave-lengths have been determined to within 0.02 A.°E. in the case of the photographs made in the fourth order spectrum.

In my last Paper I gave a table of wave-lengths for the lines in all of the groups for the excitation by the broadened green line. The wave-lengths for the single lines and pairs, which replace the groups, when the excitation was by the narrowed green line (covering one absorption line only), were recorded on the photograph only, and the differences and second differences were not given. It may, therefore, be well to record them here in the form of a table.

The study of this comparatively simple spectrum is somewhat complicated by the circumstance that at two or three points we have single lines instead of pairs, and one or two of the pairs are made up of components of very unequal intensity, the components being a little closer together than is the case with the majority of the pairs. The spectrum which we are now considering is reproduced in Fig. 1, Plate XV., of the Paper referred to above. Some of the fainter lines result from excitation by the yellow mercury lines, which were not screened

off in this case. Two pairs in the series are missing altogether, and I have divided the difference in  $\lambda$  between the adjacent pairs by 2 in these cases.

The left-hand table gives the wave-lengths of the longer wave-length components of the doublets, the right-hand table the components of shorter  $\lambda$ . Absent members are indicated thus . . . . ., and in the case of the single lines I have placed them in the left-hand table as this appears to be their proper place.

$\lambda$ Differences.			$\lambda$ Differences.	
6560.7	..... —	.....	6558.4	..... —
.....	..... 82.0	.....	.....	..... 82.0
6396.3	..... —	.....	6394.3	..... —
—	..... 79.7	.....	—	..... 79.9
6316.6	..... —	.....	6314.4	..... —
—	..... 78.6	.....	—	..... 78.3
6238.0	..... —	.....	6236.1	..... —
—	..... 77.1	.....	—	..... 77.0
6160.9	..... —	.....	6159.1	..... —
.....	..... 75.0	.....	.....	..... 75.0
6010.8	..... —	.....	6009.1	..... —
—	..... 73.0	.....	—	..... 73.9
5937.6	..... —	.....	5935.2	..... —
—	..... 71.7	.....	—	..... 70.7
5866.1	..... —	.....	5864.5	..... —
—	..... 70.1	.....	.....	..... 69.1
5796.0	..... —	.....	—	..... —
—	..... 69.4	.....	.....	..... —
5726.6	..... —	.....	5657.1	..... —
—	..... 67.8	.....	—	..... 67.6
5658.8	..... —	.....	5589.5	..... —
—	..... 66.8	.....	—	..... 64.5
5592.0	..... —	.....	5525.0	..... —
—	..... 65.5	.....	—	..... 64.3
5526.5	..... —	.....	5460.7	..... —
—	..... 65.8	.....	—	..... —
5460.7	..... —	.....	—	..... —

As will be seen from the table, the second differences vary in an irregular manner. The doublets are very clearly defined in the red and orange of the spectrum, but in the region between the green and yellow mercury lines they are not so pronounced, being replaced by single lines in two cases, and by a single line with a fainter series on the short wave-length side in the case of the one at 5726.6.

*Multiplex Excitation.*—By raising the terminal voltage of the lamp (by gradually cutting out the resistance in series with it) other lines make their appearance to the right and left of each doublet, until we finally have groups containing as many as a dozen lines. This occurs when the green mercury line has covered eight iodine absorption lines.

The total width of each group of lines is about 30 times as great as the width of the group of absorption lines covered by the mercury line. The groups in the immediate vicinity of the exciting lines are very similar in appearance, and the regularity of their disposition along the spectrum reminds one of the diffraction spectra exhibited by a grating of small dispersion. For convenience in referring to them we may designate them as groups of the +1st, +2nd, +3rd, &c., *orders*, adopting the same nomenclature as in the case of grating spectra. Those on the short wave-length side of the exciting line we may designate -1st, -2nd, -3rd orders.

I have observed as many as 20 orders on the red side (*i.e.*, + orders) and two or at most three on the short wave-length side (*i.e.*, - orders). These latter orders constitute exceptions to what is known as Stokes's Law. In the case of the excitation by the green line the -order groups are extremely faint, while in the case of the excitation by the yellow lines they are very strong. In other words the exception to Stokes's law become more conspicuous as we excite with vibration of lower frequency. The same thing was found in the case of sodium vapour.

*Origin of the Groups.*—The key to the question as to how the groups originate lies in the fact that a group appears at the point of the spectrum occupied by the exciting line. This group we may call the group of zero order, and as I have already said it is about 30 times as wide as the group of eight iodine absorption lines, which we are stimulating and which lie at the centre of the zero order group.

It is a little difficult to express in words the rather complicated phenomena involved. In the Paper referred to I have attempted to account for the formation of the groups, but as explanation may be found somewhat long-drawn-out and difficult to follow, I will try to give it in a simplified form in the present report. Let us suppose that we are stimulating three iodine absorption lines instead of eight. These lines are the lines 1, 2 and 3 of Fig. 7. They are so close together that the spectroscope used for photographing the resonance spectra could not possibly resolve them. The width of the group of lines 1, 2, 3 and A, B, C, should be about  $\frac{1}{30}$ th of the distance between B' and A' to have the diagram in correct scale. The stimulation of absorption line 1 causes the vapour to emit the same wave-length which gives us line A (immediately below



line 1 in the diagram). This is what we call resonance radiation, and we may designate this line as the RR line. The vapour emits in addition the lines A of 1st order group and A of 2nd order group, &c. If this were all, we should have a resonance spectrum of the simplest type, consisting of a series of equidistant single lines.

In the earlier investigations I was of the opinion, that resonance spectra were of this nature, but it is now certain that such is not the case, for we should have, under these conditions, each of the absorption lines 1, 2 and 3 giving a series of equidistant lines, which, if the spacing were the same, would coincide, while if the spacing were different for the three series arising in this way we should have groups of three lines each, similar in appearance but with their components separated by increasing amounts as we pass from group to group. There would, in this case, be no group but only a single line (in reality three close unresolved lines at the position of zero order).

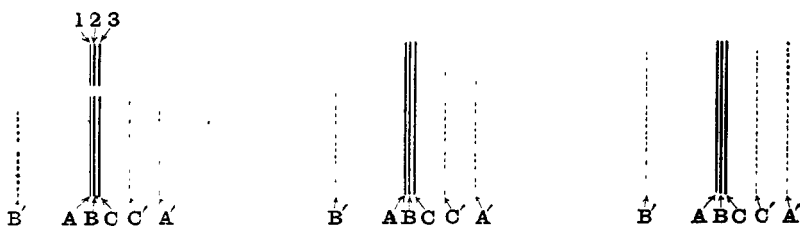


FIG. 7.

I am forced to the conclusion that absorption line 1 gives us, in addition to the lines A, the companion lines A'. Absorption line 2 gives us the lines B and the fainter companions B', which we will assume to lie to the left of the strong lines in this case.

In the same way absorption line 3 gives us the lines C and the companions C', the companions, in this case, lying to the right of, and nearer to, the main line. The main lines A, B and C of each group appear superposed with the resolving power obtained in the first order spectrum of the grating, and form what I termed the core of the group in the Paper referred to. In the photographs made in the 4th order spectrum they appear slightly separated, showing that the spacing of the three series is not quite the same. This explanation accounts for the similarity in the appearance of the groups, the fact that the distance between the components is essentially the same,

and the fact that we have a similar group (zero order) at the position of the exciting line.

In the communication to the "Philosophical Magazine" there will be found a diagram of the changes which occur in the groups resulting from the addition of new companion lines as the broadening mercury line covers more and more of the iodine absorption lines.

One of the most important questions, which I hope to solve next year, is whether the nature of a resonance spectrum is the same when the exciting line falls on the right-hand edge of an absorption line as when it falls on the other edge; in other words, when the frequency of the light is very slightly greater or less than the frequency of the absorption line.

*Polarisation of the Light of Resonance Spectra.*—The circumstance that the light emitted by the iodine vapour is strongly polarised, and that the polarisation is equally marked in all of the lines of the resonance spectrum, indicates that the emission of light is the direct result of vibrations forced in the molecule by the light waves, and does not depend upon dissociation and recombination. A short communication of this subject will be found in the "Phil. Mag." for November, 1913, illustrated by photographs of the resonance spectrum crossed by the Savart fringes, which give the measure of the polarisation.

*Radiation of Gases produced by Ultra-Schumann Waves.*—We come now to another side of the subject of which I should like to make brief mention.

Several years ago I made some experiments with a view of ascertaining whether the absorption of Schumann waves by air or oxygen was accompanied by an ultra-violet fluorescence. A powerful condenser spark was allowed to play against the under side of a metal plate perforated with a small hole\* at the point against which the spark played. It was found that if a photograph of the region above the plate was photographed in a dark room, with a quartz lens, a luminous "squirt" appeared in the pictures issuing from the hole. The spectrum of the squirt showed that the light was made up chiefly of the so-called "water band" of the oxy-hydrogen flame, together with a number of the stronger nitrogen bands, *with no trace whatever of any of the spark lines*, showing that the "squirt" was not the light of the spark diffused by dust in the air. It

\* "A New Radiant Emission from the Spark." "Phil. Mag.," Oct., 1910.

was found to be much more intense in nitrogen than in air, and much less intense in oxygen. If the hole was covered with a very thin (1 mm.) plate of fluorite, however, all trace of the squirt disappeared, which made it appear as if the luminosity must be produced by some emission from the spark other than the Schumann waves, which are transmitted by lenses and prisms of fluorite.

During the past winter the subject has been investigated again in collaboration with G. Hemsalech and many new and very remarkable phenomena have come to light. In the first place we have found that even a rather feeble air blast across the "squirt" destroys its luminescence at the spot traversed by the jet, though it is quite as bright both below *and above* the jet as before. This shows that *air in motion* does not become luminous. We are unable to explain this phenomena to our complete satisfaction; at first we thought that the air might remain luminous after the passage of each spark (phosphorescence) as in the beautiful vacuum tube experiments made by Strutt, the action of the air-blast being the continuous sweeping away of the luminous gas, but long exposures, with feeble air jets, failed to show any evidence of luminosity in the air jet after its passage across the squirt.

With nitrogen, however, the reverse is true. The luminosity is much more intense (perhaps 10 times) in the jet, and the spectrum of the light from the moving jet shows the nitrogen bands, with no trace of the "water-band," which predominates in the "squirt" (in air) above and below the moving jet of nitrogen. If oxygen is added to the nitrogen the luminosity becomes much less, which agrees with the powerful influence of oxygen in destroying the fluorescence of iodine. If we place a quartz prism in front of the quartz lens, in making our photographs we find that the luminosity in the moving nitrogen jet is displaced to one side of the monochromatic image of the squirt (water-band image). This displacement results from the difference of the wave-length of the light emitted by the nitrogen (the nitrogen bands). Similar displaced images were obtained with jets of hydrogen, carbon dioxide and coal-gas, each gas giving a characteristic spectrum. The phenomena are too complicated to be given in much detail in the time at my disposal and I shall have to refer you to the Paper published by Mr. Hemsalech and myself which will appear shortly.\*

\* "Phil. Mag.," May, 1914.

I have still more recently endeavoured to find some vapour or gas which would emit visible radiations when passed through the squirt, as the phenomena could be much more satisfactorily investigated if we were not obliged to work always in the dark with photographic methods. The first substance which I tried was iodine, and as the detrimental effect of oxygen was well known the vapour was carried across the squirt in a jet of nitrogen. A few iodine crystals were placed in the glass tube which delivered the nitrogen jet to the "squirt." Even at room temperature a faint bluish-green fluorescence was visible, which became quite bright if the tube was slightly warmed.

If air was used instead of nitrogen, the iodine vapour refused to respond.

A fluorite plate was now placed over the hole above the spark, and the green fluorescence at once appeared, but faded away very rapidly, disappearing entirely in about 15 seconds. The fluorite plate was moved a trifle and the fluorescence at once appeared again. It was at once apparent that the spark vapours formed a deposit on the fluorite plate which made it opaque to the rays which excited the fluorescence.

It is rather remarkable to find iodine vapour fluorescing brightly when mixed with nitrogen at atmosphere pressure when we remember that the fluorescence excited by blue-green light is reduced practically to zero by nitrogen at a pressure of only 8 cm. I have not yet examined the spectrum of the iodine vapour excited by the spark rays. The colour of the light is bluish-green, in contrast to the yellowish-green fluorescence excited by visible light, and it is evidently much less affected by the presence of a foreign gas. The discovery of the deposit formed upon the fluorite plate suggested at once that the failure to observe any trace of the "squirt" in air (even with long exposures) when the fluorite was used was in all probability due to the formation of this deposit.

I accordingly repeated the experiments with air and nitrogen, cleaning the fluorite plate every 15 seconds, and succeeded in getting the "water-band" squirt, as well as the one of nitrogen. It was found, however, that it was necessary to give an exposure about 80 times as long as that necessary without the plate to obtain an image of equal intensity. This indicates that a plate of fluorite 1 mm. thick transmits only a trifle over 1 per cent. of the energy of the radiation which excites these gases to ultra-violet fluorescence. The waves are thus undoubtedly shorter than those discovered by Schumann, since these pass readily through lenses and prisms of fluorite.

Attempts are being made at the present time to develop a method of measuring, at least roughly, the wave-length of these radiations.

In conclusion, let me say that I have endeavoured to show what has been learned from the study of these vibrations, forced in the molecule by means of light waves.

It is my hope that the study of resonance spectra and related phenomena may, in time, furnish one number in the "combination" necessary to unlock the secret of molecular radiation.