

On the Infrared Absorption Spectra of Gases

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1. According to Drude¹ the infrared emission and absorption bands found for most substances are caused by vibrations of the electrically charged molecules or atoms. This hypothesis has recently got valuable confirmation through a series of investigations from Nernst's institute^{2,3,4}. It was demonstrated that the frequencies of the atomic vibrations calculated on the basis of the quantum theory agree with the frequencies observed in the infrared spectra.

Likewise as an oscillating electrically charged atom emits and absorbs in the infrared it is also to be expected that a rotating polar molecule will emit and absorb infrared radiation. In fact, this has been shown by Rubens and v. Warthenberg⁵ who have measured the absorption of gases in the far infrared region (23μ to 314μ).

In the following I shall make an attempt to draw some new consequences from these, as it seems, now well-established theoretical aspects concerning the origin of the infrared spectra.

THE BROADENING OF A SPECTRAL LINE DUE TO THE ROTATION OF THE MOLECULE

2. First we want to ask the following question: How is the nature of the emission of an electrically charged atom which is performing a linear sinusoidal oscillation of frequency ν_1 within a molecule, when this molecule is rotating with a frequency ν_2 about an axis perpendicular to the linear oscillation? Already 20 years ago Lord Rayleigh⁶ has shown that the light emitted in a direction at right angles to the axis of rotation will split up into a double line. If the linear oscillation is resolved into two rotations about the rotational axis of the molecule it is easily seen that the light emitted in all directions can be resolved into two frequencies $\nu_1 + \nu_2$ and $\nu_1 - \nu_2$. In a direction perpendicular to the rotational axis both frequencies will be linearly polarized, whereas they will be circularly polarized in opposite directions when observed along the rotational axis. In all

intermediate directions the light will appear elliptically polarized. *A rotation of the molecule about an axis coinciding with the direction of the linear oscillation can not affect the radiation.* If, however, the rotation occurs about a random axis forming an angle, α , with the vibrational direction, we can visualize the resulting interaction by resolving the linear vibration into a vibration perpendicular to the axis of rotation (intensity proportional to $\sin^2 \alpha$) and a vibration parallel to the rotational axis (intensity proportional to $\cos^2 \alpha$). The light emitted from the two oscillators will be of the frequencies $\nu_1 \pm \nu_2$ resp. ν_1 .

3. If we have a great number of disordered molecules each with a linear vibration of frequency ν_1 , and if all these molecules are rotating with the frequency ν_2 the light emitted as a whole must be depolarized and of the frequencies $\nu_1 \pm \nu_2$ and ν_1 . Because the two opposite rotations will be equally probable for all orientations of the rotational axis within the molecule it follows that the circularly, resp. elliptically, polarized light rays will combine forming plane polarized light, and furthermore, all directions of polarization will have the same probability. If, however, all orientations of the rotational axis within the molecule are equally probable, it follows, too, that the three frequencies $\nu_1 - \nu_2$, ν_1 , $\nu_1 + \nu_2$ must appear with the same intensity.

4. In the gas the molecules will have different frequencies of rotation resulting in a broadening of the line. The rotation of a molecule may have two or three degrees of freedom. According to Maxwell's distribution law the different rotational frequencies must be distributed around a definite value of highest probability, so that as well higher as lower frequencies are less probable, and very low rotational frequencies extremely rare. This means that the broadening actually must be a splitting into three components (even if these are unresolved): one sharp central line with two equally intense, diffuse bands at both sides.

5. How do these theoretical consequences agree with observations? First we shall apply the theory to hydrogen chloride. According to Rubens and v. Wartenberg gaseous hydrogen chloride absorbs at ordinary temperature in the region round 150μ ($50\mu - 300\mu$). This absorption corresponds to a rotation with the mean frequency $2 \cdot 10^{12}$ of the electrically polar molecule. Hydrogen chloride has, however, furthermore an absorption band at 3.5μ which must be caused by a vibration of the atoms against each other with the frequency $86 \cdot 10^{12}$. According to 4, a linear vibration of this frequency in the rotating hydrogen chloride molecules must emit light not only of the frequency $86 \cdot 10^{12}$, but also at higher and lower frequencies. Because the most probable rotational frequency of the molecule is $2 \cdot 10^{12}$ there must be two maxima at the frequencies $(86 \pm 2) \cdot 10^{12}$, i.e. we must expect to observe a sharp line at 3.5μ and two diffuse lines at 3.4 and 3.6μ . From these calculations we see, that the effect should be easily observable. So far, however, only a corresponding broadening of the line has been found.

6. The infrared spectrum of carbon dioxide is thoroughly investigated^{7,8,9}. It shows bands at 2.7μ , 4.3μ , and 14.7μ which must be caused by atomic vibrations. This means that the atoms must be electrically charged. Therefore, the molecule must also emit and absorb at its rotational frequency. As Rubens and v. Wartenberg have found no absorption between 23μ and 314μ , it seems safe to conclude that the rotation of the carbon dioxide molecule is rather slow, with a rotational frequency considerably smaller than 10^{12} . From the chemical composition one should expect carbon dioxide to rotate considerably slower than hydrogen chloride because it evidently has the greater moment of inertia of the two molecules.

From the slower rotation of the carbon dioxide molecule it follows that the absorption bands must be rather sharp. In fact, this is the case. I have tried to estimate the rotational frequency of the carbon dioxide molecule from the width of the bands. The difficulty is, however, to find a proper measure for the broadening of the line. I have used the interval between the two points in which the absorption coefficient has just decreased to one half of its maximum value. If the absorption in the maximum is x per cent it will be:

$$(1 - \sqrt{1 - x/100}) \cdot 100 \text{ per cent}$$

for an absorption coefficient of half the magnitude.

In this way I have calculated the width of the bands using Hertz's measurements of the absorption⁹. For the band at 14.7μ the width is about 1μ , and for the band at 4.3μ about 0.1μ . The values found from absorption curves for different partial pressures and different thicknesses of the absorption path agree satisfactorily. If one assumes that the distance between the two components produced by the rotation, is equal to the width, the rotational frequencies are found to be $0.7 \cdot 10^{12}$, resp. $0.8 \cdot 10^{12}$. These frequencies correspond to a band at about 400μ which agrees with the findings of Rubens and v. Wartenberg that the absorption must be at longer wave-lengths than 314μ .

The carbon dioxide band at 2.7μ is much broader than it should be according to the rotational frequency calculated above. On both sides of the principal maximum at 2.67μ it has a secondary maximum. One of these is distinct and situated at 2.75μ , the other is very little pronounced at 2.59μ ⁹. These maxima may be explained by assuming a rotation with the mean frequency $3.5 \cdot 10^{12}$. The structure of this band might be explained in another way because it corresponds to such a high rotational frequency. It is possible that the linear vibration, causing the 2.7μ band, is orientated at right angles to an axis in the molecule about which the moment of inertia is particularly small and, consequently, the rotation fast.

7. Owing to the low mass of the hydrogen atom, one must expect the water molecule to rotate rather fast because of its small moment of inertia. Rubens

and v. Wartenberg⁵ have found a strong absorption at 52μ in water vapour. I estimate the maximum of the absorption to be at about 60μ because the absorption is weaker at 23μ than it is at 110μ . The position of this maximum corresponds to the rotational frequency $5 \cdot 10^{12}$. This fast rotation must strongly influence the water spectrum in the region between 1 and 10μ (the bands of atomic vibrations). For example, the vibration of the frequency $52 \cdot 10^{12}$ (5.8μ) must absorb light of the frequencies $47 \cdot 10^{12}$ and $57 \cdot 10^{12}$ due to such a rotation. Table 1 shows the wave-lengths of the absorption maxima calculated in this way and the maxima observed in this region⁷. It thus seems as if we are able

Table 1

λ calc.	5.3μ	5.8μ	6.4μ
λ obs.	5.25μ	5.90μ (strong)	6.07μ

to explain the absorption of water between 5 and 6μ by assuming a single vibration in the rotating water molecule. The asymmetrical absorption in this region is, however, left unexplained, but it may be due to the superposition of a secondary effect.

The absorption bands of water in the near infrared are, according to the theory, less broadened. There exist, however, no accurate measurements of the structure of these bands. The water bands in the far infrared are probably not caused by vibrations in the water molecule and shall therefore not be dealt with in this connection (cp. 11).

8. I realize fully that the experimental evidence supporting the proposed theory is rather weak. Therefore, I would not have dared to present the above considerations right now had it not been for the reason that they really only are new consequences from old well-established theories derived without the aid of any new hypothesis.

In the following I shall state further consequences which we arrive to, if we proceed in the above way using the quantum hypothesis.

APPLICATION OF THE QUANTUM HYPOTHESIS TO MOLECULAR SPECTRA

9. The problem whether Planck's radiation law and Einstein's formula for the specific heat derived from it, really are to be explained as due to a quantization of the energy, as assumed by Planck, or whether the energy does vary continuously, but that it is the equations of motion of the atoms that must be changed, is one of the most interesting problems of physics at present. A minor contribution to a solution of this question may be given by means of the viewpoints proposed above.

10. As shown by Nernst¹⁰ it is a necessary consequence of the quantum hypothesis that as well the *vibrational energy of the atoms* as the *rotational energy of the molecule* must vary discontinuously. There is, however, at present a certain difficulty in an exact use of the quantum hypothesis to the rotational energy because the quantum distribution of this energy is unknown. It is possible that every fraction of the rotational energy, referring to the different degrees of freedom (momentum coordinates), is quantized. It may be, however, that only the entire rotational energy is quantized. In the following it is assumed that the entire rotational energy is quantized and that the moments of inertia of the molecule about all axes through the centre of gravity are the same. In this case we must have the following equation for the rotational frequency ν

$$\frac{1}{2} \mathcal{J}(2\pi\nu)^2 = n h \nu,$$

where \mathcal{J} = moment of inertia, $h = 6.548 \cdot 10^{-27}$ (Planck's constant) and n is any integral number. This equation results in

$$\nu = \frac{n h}{2\pi^2 \cdot \mathcal{J}}$$

According to this the rotational frequencies must vary *discontinuously* and constitute an arithmetical progression*.

If the rotational frequencies are assumed to vary discontinuously it follows that a band originating from a linear vibration of the rotating molecule must consist of a series of fine lines. Many investigators^{9, 12, 13, 14, 15, 16} have noticed that the infrared bands of gases possess such a fine structure. This line-structure speaks in favour of a discontinuous rotational energy as claimed by the quantum hypothesis.

11. Some calculations based on measured frequencies in the water vapour bands from 10 to 20 μ are of some interest. They seem to confirm that the rotational frequencies of the water molecule really form an arithmetical progression consistent with the formula in 10. The frequencies of these bands actually form an arithmetical progression with the common difference $1.73 \cdot 10^{12}$. If we put

$$\lambda = \frac{3 \cdot 10^{14}}{\nu} = \frac{3 \cdot 10^{14}}{n \cdot 1.73 \cdot 10^{12}}$$

and let n vary from 10 to 16 we get the wave-lengths, λ calc., of table 2. The observed wave-lengths, λ obs., are the band maxima found by Rubens and Aschkinass⁸ between 10 and 20 μ in the absorption spectrum of water vapour.

* I want to mention that the interesting work by Eucken¹¹ on the molecular heat of hydrogen seems to indicate that the rotational frequency is constant. However, the difficulties in the interpretation of the experiments by Eucken are so great that hardly too much emphasis can be given to this.

Table 2

<i>n</i>	16	15	14	13	12	11	10
λ calc.	10.8	11.6	12.4	13.3	14.4	15.8	17.3
λ obs.	10.9	11.6	12.4	13.4	14.3	15.7	17.5

The absorption bands become stronger and stronger toward the long wavelength region and overlap more and more. For wave-lengths higher than 17.5μ , where the experimental technique is less satisfactory, only intensive absorption without structure has so far been found.

Thus it seems permissible to assume that these bands originate from the rotation of the water molecule.

From the difference $1.73 \cdot 10^{12}$, the moment of inertia of the water molecule can be calculated. One has

$$\frac{6.548 \cdot 10^{-27}}{2\pi^2 \cdot \mathcal{J}} = 1.73 \cdot 10^{12}; \quad \mathcal{J} = 1.92 \cdot 10^{-40}$$

A homogeneous sphere of the same mass as the water molecule ($18/[62 \cdot 10^{22}]$) has this moment of inertia if its radius $r = 0.4 \cdot 10^{-8}$ cm.

$$\mathcal{J} = \frac{2}{5}r^2 \cdot m = 1.92 \cdot 10^{-40}$$

$$r = 0.4 \cdot 10^{-8}.$$

It is seen that the calculated moment of inertia has a magnitude compatible with molecular dimensions.

It is easy to compute the *rotational energy* of one mole water vapour from the calculated moment of inertia and the observed average rotational frequency $5 \cdot 10^{12}$:

$$\frac{1}{2} \cdot 1.92 \cdot 10^{-40} (2\pi \cdot 5 \cdot 10^{12})^2 \cdot 62 \cdot 10^{22} / (0.419 \cdot 10^8) = 1400 \text{ cal.}$$

If it is assumed that the rotational energy of water vapour is $\frac{3}{2}RT$ it follows that the temperature must be 200° C. The experiments of Rubens and v. Wartenberg were carried out at 110° C. The agreement must be regarded as satisfactory, considering the somewhat inaccurate determination of the maximum.

The rotational frequency calculated from the bands between 10 and 20μ is 3 to 6-fold greater than the most frequently occurring rotational frequency of the water molecule which corresponds to an absorption near 60μ according to part 7 of this paper. The bands between 10 and 20μ must, therefore, originate from small fractions of the total number of molecules because velocities that are that much in excess of the average are rare, according to the law of distribution of velocities. This explains why these bands have no influence on the broadening of the absorption bands of water vapour from 2 to 6μ .

The rotation of the water molecule does not result in sharp lines, but in bands. This may indicate that the quanta are of different magnitude, or, what seems more likely to me, that there are different moments of inertia about the molecular axes of rotation. The formula

$$\nu = \frac{nh}{2\pi^2\mathcal{J}}$$

shows that rotations about different axes take place with different frequencies.

Thus a closer discussion of the structure of the infrared spectrum of water vapour in two ways leads to the inference that the discontinuity of the rotational energy of the water molecule, as predicted by the quantum hypothesis, seems to be at hand.

12. Before ending the discussion concerning molecular rotation, I may add that it is possible to conclude with great certainty from the sharpness of several spectral lines, resp. from a missing symmetrical arrangement of lines required by the quantum hypothesis, that the radiating *atoms* do not rotate, or, at least not with frequencies comparable with molecular rotational frequencies. In this way we get evidence for the fact, established by investigations of specific heats, that the rotational energy of atoms must be very small.

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