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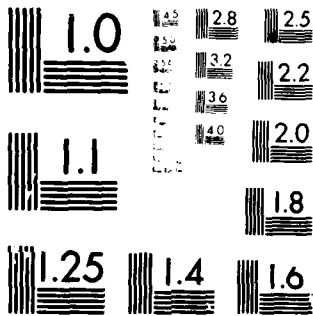
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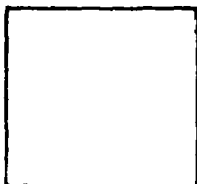


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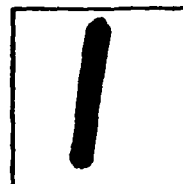
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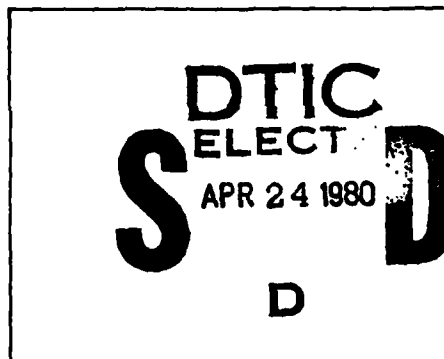
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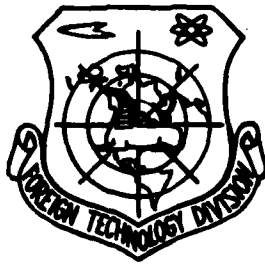
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ON THE THEORY OF THE RAMAN EFFECT

by

G. Placzek



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On the Theory of the Raman Effect

G. Placzek, Utrecht

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It is pointed out that it is not automatically possible to extend the concept of the scattering process as a result of two subprocesses (absorption of a quantum $h\nu$ and emission of a quantum $h\nu'$) to scattering processes of the second kind (Raman effect). It is further emphasized that the processes, which give rise to the emission of Stokes and anti-Stokes Raman lines, do not compensate each other in their effect upon the thermal equilibrium. From this it follows that the intensity ratio of the lines depends not only upon the number of molecules in the initial state and final state, as was previously assumed, but also upon the exciting frequency and the position of the eigenfrequencies of the molecules. Quantitative formulas for this are given and discussed.

Preliminary remark. The question of how Einstein's well-known statements on the probability of elementary processes would be modified to include the scattering of radiation by atoms was first discussed in a paper by Einstein and Ehrenfest*. It was found that the probability of a scattering process could be formally represented as the product of an absorption probability and an emission probability. From this it was concluded that it would be possible to divide the

* Zeitschrift für Physik 19, 301, 1923.

scattering process into two subprocesses (absorption and emission), and A. Smekal* in particular succeeded in making fruitful use of this concept for the quantum-theoretical description of light propagation in dispersive media. The same author has extended the Einstein-Ehrenfest statements and the division into subprocesses to the incoherent scattering which was predicted by him.

The concept can also initially be incorporated without difficulty in the conceptual system of quantum mechanics, with allowances for the refinements associated with the Heisenberg uncertainty relation. In view of these, and especially the fact that a dwell time (according to Smekal on the order of magnitude of $1/\nu$) between absorption and emission generally eludes observation here, it would seem at first, however, that the division no longer has the character of a special hypothesis about the course of the scattering process. As will be shown in what follows, this does appear to be the case for ordinary scattering; but for scattering processes which are connected with changes in the intra-atomic energy (Smekal shifts, Raman effect) the division into absorption-like and emission-like subprocesses forms a far-reaching statement about the special character of the scattering process, a statement which, moreover, is not in agreement with experience.

§1. The probability of a process in which a material system (atom, molecule) is transferred from pulse range G_1 and state m to pulse range G_2 and state n , while at the same time a light quantum with frequency ν and a certain direction becomes a quantum with frequency ν' and a different direction, can be represented by the following statement, using the findings of Dirac, who has examined the whole complex of equilibrium problems from a unified point of view**:

$$dW_{mn} = \rho(\nu) \Phi_{mn}(\nu, \nu') \left\{ 1 + \frac{c^2}{8\pi\nu^2} \rho'(\nu') \right\} d\nu d\Omega dt \quad (1)$$

* Ibid. 32, 241, 1925; 34, 81, 1925; cf. also Annalen der Physik 87, 959, 1928.

** Proc. Roy. Soc. 106, 581, 1924.

$\rho(\nu), \rho'(\nu')$ are the radiant energy densities before and after the process in the direction of the incoming and outgoing quantum. For the probability of the inverse process, which can be thought to arise from the defined process through reversal of the time direction and the sign of the pulses, it correspondingly holds that*:

$$dW_{nm} = \rho'(\nu') \Phi_{nm}(\nu', \nu) \left\{ 1 + \frac{c^3}{8\pi\nu^3} \rho(\nu) \right\} d\nu' d\Omega' dt.$$

The relativistic invariance requirement yields, as Pauli** has demonstrated for the special case of free electrons and Dirac*** has demonstrated in general, the following functional equation for Φ :

$$\frac{g_m \Phi_{mn}(\nu', \nu)}{g_n \Phi_{nm}(\nu', \nu)} = \frac{\nu'^3}{\nu^3} \quad (2)$$

(g_m, g_n weights of the stationary states m, n). The frequencies ν and ν' are to be measured here in the "normal coordinate system", which rests at the center of mass of atom and quantum; in this system for scattering processes of the first kind $\nu = \nu'$.

If we set

$$\begin{aligned} g_m \Phi_{mn}(\nu, \nu') &= \nu'^3 f(m, n, \nu, \nu'), \\ g_n \Phi_{nm}(\nu', \nu) &= \nu^3 f(n, m, \nu', \nu), \end{aligned} \quad (3)$$

(3) represents the most general solution of (2), if the arbitrary function f satisfies the condition that its value remain unchanged

when we replace $\begin{Bmatrix} m \\ n \\ \nu \\ \nu' \end{Bmatrix}$ by $\begin{Bmatrix} n \\ m \\ \nu' \\ \nu \end{Bmatrix}$, in the argument.

* Difficulties encountered in the quantitative discussion of the limiting case of resonance fluorescence using these statements can be dealt with - as Prof. Kramers has kindly informed me - by replacing the notion of atoms in particular states with the quantum-mechanical concept, according to which the atom is thought to be in all states at the same time, and there exists only a certain probability of finding it in a particular state during a particular experiment.

** ZS. f. Phys. 18, 272, 1923.

*** loc. cit.

If we now consider the statement of Einstein and Ehrenfest*

$$dW_{mn} = \rho(\nu) b \{a_1 + b_1 \rho'(\nu')\} d\nu d\Omega dt \left. \begin{aligned} \frac{a}{b} &= \frac{8\pi\nu^3}{c^3} \frac{a_1}{b_1} = \frac{8\pi\nu'^3}{c^3} \end{aligned} \right\} \quad (1a)$$

it first appears to be formally identical with (1). However, as soon as we interpret the quantity $\rho(\nu)b$ as the absorption probability and the quantity $(a_1 + b_1\rho'(\nu'))$ as the emission probability, we cannot avoid the requirement that the former be determined by the initial state and end state of the absorption process, and the latter by the initial state and end state of the emission process; as a consequence of this, the former can depend only upon the incoming radiation frequency and the initial state m , while the latter can depend only upon the outgoing radiation frequency and the final state n . As a result (1a) then takes the form:

$$dW_{mn} = \rho(\nu) b_{mr} \{a_{rn}(\nu') + b_{rn}(\nu') \rho'(\nu')\} d\nu d\Omega dt. \quad (1b)$$

(Here the unstable state r is already fixed by m and ν or also by n and ν' .)

We now have

$$\Phi_{mn}(\nu, \nu') = b_{mr}(\nu) a_{rn}(\nu') = \frac{8\pi\nu'^3}{c^3} b_{mr}(\nu) b_{rn}(\nu'). \quad (4)$$

If in addition we note that $g_m b_{mr} = g_r b_{rm}$, then the function f assumes the special form:

$$\left. \begin{aligned} f(m, n, \nu, \nu') &= \frac{8\pi}{c^3} g_m b_{mr}(\nu) b_{rn}(\nu') = \phi(m, \nu) \cdot \phi(n, \nu'), \\ f(n, m, \nu', \nu) &= \frac{8\pi}{c^3} g_n b_{nr}(\nu') b_{rm}(\nu) \\ &= \frac{8\pi}{c^3} g_m b_{rn}(\nu') b_{mr}(\nu) = \phi(n, \nu') \cdot \phi(m, \nu), \end{aligned} \right\} \quad (5)$$

whereby ϕ signifies an initially completely arbitrary function, which is determined by the special properties of the material system. For scattering processes of the first kind [$m = n$, $\nu = \nu'$, cf. the comment for (2)] (5) becomes

$$f = \{\phi(m, \nu)\}^2. \quad (5a)$$

* Einstein and Ehrenfest still do not specify the elementary domains. On the selection of these, cf. Dirac, loc. cit.

On the other hand, according to (3), $f(m, \nu)$ also becomes completely arbitrary for these processes. Therefore (1b) signifies no specialization of statement (1) for the case of ordinary scattering. But for scattering processes of the second kind equation (4) and equation (5) represent a substantial specialization of the general solution (3) to the functional equation (2). From the physical standpoint this means that the division into subprocesses for the case of modified scattering is equivalent to a special hypothesis about the nature of the elementary process or about the properties of the material system concerned. Only experience can decide if this is justified.

In order to permit a comparison with experience, let us first turn to the energies scattered per unit of time in a specified direction:

$$\left. \begin{aligned} E_{mn}(\nu, \nu') &= N_m h \nu' \Phi_{mn}(\nu, \nu') \varrho(\nu) \left\{ 1 + \frac{c^2}{8\pi \nu'^2} \varrho'(\nu') \right\} \\ &= \frac{N_m}{g_m} h \nu'^4 \varphi(m, \nu) \cdot \varphi(n, \nu'), \\ E_{mm}(\nu) &= N_m h \nu \varrho(\nu) \Phi_{mm}(\nu) \left\{ 1 + \frac{c^2}{8\pi \nu^2} \varrho'(\nu) \right\} \\ &= \frac{N_m}{g_m} h \nu^4 (\varphi(m, \nu))^2. \end{aligned} \right\} \quad (6)$$

Now we can proceed in two different ways. We can refer to the thermodynamic relationship, which connects the scattered energy and the refractive index*; it is then seen that the quantities $\phi(m, \nu)$, $\phi(n, \nu')$ become proportional to the refraction equivalents $R_m(\nu)$, $R_n(\nu')$ in state m or n . From (2) and (5) it then follows that

$$g_m \Phi_{mn}(\nu, \nu') = c R_m(\nu) R_n(\nu'). \quad (7a)$$

Or we can express ϕ_{mn} by ϕ_{mm} and ϕ_{nn} with the aid of (2) and (4), and then

$$g_m \Phi_{mn}(\nu, \nu') = \sqrt{\frac{\nu'^3}{\nu^3}} g_m \Phi_{mm} \cdot g_n \Phi_{nn}. \quad (7b)$$

These two (identical) expressions can be tested empirically, since they represent the intensity of the modified scattered radiation by the refraction equivalents in the initial state and end state, or by

* A. Einstein, Ann. d. Phys. **33**, 1275, 1910.

the intensity of the unmodified scattered radiation in these states. If we compare them first with the Kramers-Heisenberg formula* (which can happen, for example, through substitution for R or for Φ_{mm}, Φ_{nn}), it is seen that (7) is not identical with the latter. (7) in particular leads to other selection rules for the Raman effect. Since the selection rules resulting from the Kramers-Heisenberg formula have been largely confirmed by the experiments of Wood and Rasetti, (7) can be considered disproved by experience.

Hence, it is to be concluded that the division of the elementary process of scattering into simple absorption-like and emission-like processes cannot be extended to scattering processes of the second kind.

§2. In connection with the reflections in the preceding section, it is now proposed to discuss a special case, which is important from the experimental point of view: the intensity ratio of Stokes and anti-Stokes Raman lines. The question has already been discussed by various authors. While Raman**, assuming the processes connected with emission of the lines to have equal probability, finds $e^{-\frac{h\nu_{mn}}{kT}}$ for the intensity ratio, Landsberg and Leontovich*** have arrived at the expression $\frac{1}{2c \frac{h\nu_{mn}}{kT}}$ using the same assumption. Carrelli**** obtains $\left(\frac{N_m}{N_n}\right)^2$ from quantum mechanics, and Ornstein and Rekveld***** obtain $\frac{\nu + \nu_{mn}}{\nu - \nu_{mn}} e^{-\frac{h\nu_{mn}}{kT}}$ by considering equilibrium. Since all of these

* ZS. f. Phys. **31**, 681, 1925.
 ** Proc. Roy. Soc. **122**, 23, 1928.
 *** ZS. f. Phys. **53**, 439, 1929.
 **** Rend. Lincei (6) **8**, 155, 1928.
 ***** ZS. f. Phys., forthcoming.

derivations are open to doubt*, while on the other hand quantitative measurements of intensity are now available in the work of the last-mentioned authors, it appears to be of interest to deal with the question here.

First of all, the following is to be said about the assumption of Raman: if the transition $m \rightarrow n$ produced by the frequency ν of the incoming radiation is connected with the emission of an anti-Stokes line $\nu + \nu_{mn}$ (a process hereinafter designated I.), then it is clear that the inverse of this process is in no way linked with the emission of the corresponding Stokes line $\nu - \nu_{mn}$. Instead, the inverse of I. is that process in which a light quantum of the frequency $\nu + \nu_{mn}$, with direction and polarization** of the outgoing quantum in I., is transformed by a transition $n \rightarrow m$ into a quantum of the frequency ν , with direction and polarization of the incoming quantum in I. On the basis of considerations of equilibrium, only one statement can be made about the intensity ratio of the $\nu + \nu_{mn}$ and ν Raman lines excited by the defined processes. It is necessary to think of the experiment as being carried out so that we first have radiation with the frequency ν and measure the intensity of Raman line $\nu + \nu_{mn}$, and then have radiation at $\nu + \nu_{mn}$ and measure the intensity of Raman line ν . (The inversion of the direction of observation and the direction of radiation, which is still to be carried out, proves to be superfluous because of the random distribution of molecular axes, as closer analysis reveals.) Under these conditions the intensity ratio relative to equal incoming radiation becomes, according to (2)

* The first two are discussed in the text. Carrelli's paper gives only the order of magnitude. It is true that Ornstein and Rekveld, on the basis of Wien's law, also finally arrive at equation (62); however, they solve the latter not with the general function (3), but

with a special one intended to correspond to the statement $f = \frac{1}{\nu^3 \nu'^3}$. Since this statement leads to a proportionality of ordinary scattered radiation with $1/\nu^2$, it cannot also, in the author's opinion, have a physical significance for any limiting case.

** On the term "polarized light quantum" cf., for example, B. P. Jordan, ZS. f. Phys. 44, 292, 1927. For the sake of simplicity, the discussions in the previous section do not specify the directions of polarization. This can be easily done; instead of going into details, let us say only that f is to be generally understood as a function of all variables which determine the state before the process, and then it must satisfy the condition of remaining unchanged when the values

and (6):

$$\frac{\frac{1}{c\nu} E_{mn}(\nu, \nu')}{\frac{1}{c(\nu')} E_{nm}(\nu', \nu)} = \frac{N_m \nu' \Phi_{mn}(\nu, \nu')}{N_n \nu \Phi_{nm}(\nu', \nu)} = \frac{N_m \nu'^4 g_n}{N_n \nu^4 g_m} = \frac{\nu'^4}{\nu^4} e^{-\frac{h\nu_{mn}}{kT}} \quad (8)$$

However, the intensity ratio of Stokes and anti-Stokes lines which are assigned to the same exciting frequency can no longer be determined by general approaches, because for this it is necessary to know the frequency dependence of the quantity Φ . Everything which can be stated about this from considerations of equilibrium is in equation (3).

In the following section, therefore, we intend to undertake determination of the intensity ratio according to quantum mechanics.

§3. If we presuppose $\nu_{mn} < \nu$, the transitions $m \rightarrow n$ give rise only to scattered radiation with the frequencies $\nu + \nu_{mn}$, $\nu - \nu_{mn}$. Their intensity is calculated for*

$$\left. \begin{aligned} q_{+1mn}(\nu) &= \frac{E}{2h} \sum_j \left(\frac{q_{mj} x_{jn}}{\nu_{jn} + \nu} + \frac{x_{mj} q_{jm}}{\nu_{jm} - \nu} \right) e^{2\pi i(\nu + \nu_{mn})t}, \\ q_{-1mn}(\nu) &= \frac{E}{2h} \sum_j \left(\frac{q_{mj} x_{jm}}{\nu_{jm} + \nu} + \frac{x_{mj} q_{jm}}{\nu_{jn} - \nu} \right) e^{2\pi i(\nu - \nu_{mn})t}. \end{aligned} \right\} \quad (9)$$

x_{kj} and q_{kj} are the ordinary matrix elements in the direction of polarization of the impinging light and in the direction of polarization in which observation conducted. The scattered energy is connected with q_{+1} in a well-known way by

$$E_{mn}(\nu) = (\nu + \nu_{mn})^4 \cdot \frac{64\pi^4}{c^3} \{ |x_{+1mn}|^2 + |y_{+1mn}|^2 + |z_{+1mn}|^2 \}$$

First let us establish that (9) satisfies the general condition (3). Because we replace m with n , ν with ν' , and vice versa, and we invert the direction of radiation and the direction of observation

of all variables before the process are replaced with their values after the process.

* A. Kramers and W. Heisenberg, ZS. f. Phys. , 681, 1925. Because of the notation in the quantum mechanical form used here cf. for example M. Born, Probleme der Atomdynamik; refer also to a work in preparation by Manneback. (I am indebted to Prof. Manneback for sharing and discussing his findings.)

at the same time, the absolute value of (9) remains unchanged. The validity of (8) follows immediately from this.

For further analysis let us first assume the molecule to be isotropic; then x is replaced with q , (9) becomes

$$|q_{1mn}(\nu)| = \frac{E}{2h} \left| \sum_j g_{mj} g_{jn} \frac{(\nu_{jm} + \nu_{jn})}{(\nu_{jn} + \nu)(\nu_{jm} - \nu)} \right|$$

and we obtain identically with (8):

$$\frac{J_{mn}(\nu)}{J_{nm}(\nu)} = \frac{\nu'^4 |g_{mn}(\nu)|^2}{\nu'^4 |g_{nm}(\nu')|^2} \cdot \frac{N_m}{N_n} = \frac{\nu'^4}{\nu^4} e^{-\frac{h\nu_{mn}}{kT}} \quad (8a)$$

Since (9) holds for non-degenerate states, it is necessary to set

$g_m = g_n$ here, and therefore $\frac{N_m}{N_n} = e^{-\frac{h\nu_{mn}}{kT}}$. It is easily discovered, however, that (8a) agrees with (8) for the degenerate case as well. Because one imagines the degeneracy to be removed and sums over the individual substates (designated by the indices m' , n'), then, with consideration of the fact that $|q_{1m'n'}(\nu) = |q_{1n'm'}(\nu')|$, one obtains

$$\begin{aligned} \frac{J_{mn}(\nu)}{J_{nm}(\nu')} &= \frac{N_m \nu'^4 |g_{1mn}(\nu)|^2}{N_n \nu^4 |g_{1nm}(\nu')|^2} \\ &= \frac{\nu'^4 \sum_{m',n'} \frac{N_{m'}}{g_{m'}} |q_{1m'n'}(\nu)|^2}{\nu^4 \sum_{m',n'} \frac{N_{n'}}{g_{n'}} |q_{1n'm'}(\nu')|^2} = \frac{\nu'^4 \sum_{m',n'} \frac{N_{m'}}{g_{m'}} |q_{1m'n'}(\nu)|^2}{\nu^4 \sum_{m',n'} \frac{N_{n'}}{g_{n'}} |q_{1m'n'}(\nu)|^2} \\ &= \frac{\nu'^4}{\nu^4} e^{-\frac{h\nu_{mn}}{kT}} \quad (\nu' = \nu + \nu_{mn}). \end{aligned}$$

Let us now proceed to the calculation of the intensity ratio

$\frac{J_{mn}(\nu)}{J_{nm}(\nu)}$ of anti-Stokes and Stokes lines with the frequencies $\nu + \nu_{mn}$ and $\nu - \nu_{mn}$. For this the value $\frac{|q_{1mn}(\nu)|}{|q_{1nm}(\nu)|}$ is characteristic.

If we assume

$$\left. \begin{aligned} \nu_{mn}^2 &\ll (\nu_{jn} + \nu)^2 \\ \nu_{mn}^2 &\ll (\nu_{jn} - \nu)^2 \end{aligned} \right\} \quad (10)$$

which is always true for the ordinary experimental conditions, then

$$\left. \begin{aligned} \frac{|q_{+1mn}(\nu)|}{|q_{+1nm}(\nu)|} &= \frac{\left| \sum_j q_{mj} q_{jn} \frac{\nu_{jm} + \nu_{jn}}{\nu_{jn}^2 - \nu^2} \left(1 + \frac{\nu_{mn}}{\nu_{jn} + \nu} \right) \right|}{\left| \sum_j q_{nj} q_{jm} \frac{\nu_{jm} + \nu_{jn}}{\nu_{jn}^2 - \nu^2} \left(1 + \frac{\nu_{mn}}{\nu_{jn} + \nu} \right) \right|} \\ &= 1 + 2\nu \nu_{mn} \frac{\left| \sum_j \frac{\nu_{jm} + \nu_{jn}}{(\nu_{jn}^2 - \nu^2)^2} q_{mj} q_{jn} \right|}{\left| \sum_j \frac{\nu_{jm} + \nu_{jn}}{\nu_{jn}^2 - \nu^2} q_{mj} q_{jn} \right|} \end{aligned} \right\} \quad (11)$$

If the influence of an eigenfrequency ν_{jn} is predominant, it becomes

$$\frac{|q_{+1mn}(\nu)|}{|q_{+1nm}(\nu)|} = 1 + \frac{2\nu \nu_{mn}}{\nu_{jn}^2 - \nu^2}$$

and the intensity ratio becomes

$$\frac{J_{mn}(\nu)}{J_{nm}(\nu)} = \left(\frac{\nu + \nu_{mn}}{\nu - \nu_{mn}} \right)^4 \left(1 + \frac{4\nu \nu_{mn}}{\nu_{jn}^2 - \nu^2} \right) e^{-\frac{h\nu_{mn}}{kT}} \quad (12)$$

From formula (12) and also generally from (11) we learn the following: the anti-Stokes/Stokes intensity ratio depends not only upon the number of molecules in states m and n , but also upon the exciting frequency ν , the infrared frequency ν_{mn} , the absorption frequencies ν_{jn} , and the transition probabilities q_{jn} , q_{jm} , with the last dropping out in (12). It is to be represented as the product of a ν^4 factor, a Boltzmann factor, and the square of expression (11). This square is larger or smaller than one, depending on whether the influence of the absorption frequencies predominates in the ultraviolet region ($\nu_{jn} > \nu$) or the infrared region ($\nu_{jn} < \nu$). If, as usual, the exciting frequency lies in the blue or violet region, the first case is realized.

In order to extend the formulas to the anisotropic case, it is necessary to average (9) over all directions and then to proceed by analogy, as in the derivation of (11) and (12). This will be taken up in a subsequent paper, dealing with the degree of depolarization of Raman lines; however, in the approximation with which the frequency-dependence of the degree of polarization can be disregarded (no such dependence has been found experimentally up to now in the entire frequency range investigated)*, nothing new is yielded.

* C. V. Raman, loc. cit., P. Pringsheim, B. Rosen, and A. Carrelli, ZS. f. Phys. 51, 515, 1928.

For comparison of the formulas with experience let us confine ourselves to the measurements performed by Ornstein and Rekveld* on CCl_4 . The absorption points of this substance have not been measured precisely, but are rather far into the ultraviolet region. If we set $\nu_{jn} = 40,000$ (nr. of waves/cm)** , then for the Hg 4047 excited Raman

line 458 the $e^{-\frac{h\nu_{mn}}{kT}}$ factor in (12) becomes approximately 1.20, and the ν^4 factor alone becomes 1.15, while Ornstein and Rekveld conclude from their measurements that the intensity ratio is represented within their accuracy of measurement by the Boltzmann factor. It must be borne in mind, however, that the predominant influence of the exponential function causes low accuracy in the measurement of an additional factor; but in this case measurements at higher temperatures could soon bring clarification. It would be more advantageous to study a substance whose absorption is in the near ultraviolet.

In conclusion, I would like to make one more comment about the frequency dependence of the Raman effect. From the expression [cf. (9):]

$$|g_{+jmn}(\nu)| = \left| \sum_j \left\{ g_{mj} g_{jn} \frac{\nu_{jm} + \nu_{jn}}{\nu_{jn}^2 - \nu^2} \left(1 + \frac{\nu_{mn}}{\nu_{jn} - \nu} \right) \right\} \right|$$

it is readily apparent that the sum terms with $\nu_{jn} > \nu$ increase as the frequency rises, while the terms with $\nu_{jn} < \nu$ decrease. Depending upon the predominance of the former or the latter, the intensity is therefore stronger or weaker than with $(\nu + \nu_{mn})^4$. [This is also the reason for the behavior of (11) which was discussed.] Because of the far greater influence of the absorption points in the ultraviolet, this seems to be a satisfactory theoretical explanation for the qualitative observations of Raman* and Landsberg and Leontovich*, according to which the intensity of Raman lines with an increasing exciting wavelength decays faster than that of ordinary scattered radiation.

I would like to thank Prof. Ornstein most sincerely for the kind reception at his institute and for sharing the findings of the work cited.

Utrecht, Physics Laboratory of the Rijksuniversiteit, Sept. 1929.

* loc. cit.

** Cf. Gillam and Morton, Proc. Roy. Soc. **129**, 609, 1929.

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