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https://hdl.handle.net/1874/300649

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PROEFSCHRIFT

TER VERKRIJGING VAN DEN GRAAD VAN
DOCTOR IN DE WIS- EN NATUURKUNDE
AAN DE RIJKS-UNIVERSITEIT TE UTRECHT
OP GEZAG VAN DEN RECTOR MAGNIFICUS
Jhr. Dr. B. C. DE SAVORNIN LOHMAN
HOOGLEERAAR IN DE FACULTEIT DER RECHTSGELEERDHEID
VOLGENS BESLUIT VAN DEN SENAAT DER UNIVERSITEIT TEGEN
DE BEDENKINGEN VAN DE FACULTEIT DER WIS- EN NATUURKUNDE TE VERDEDIGEN OP MAANDAG 6 JULI 1931, DES NAMIDDAGS TE 3 UUR

DOOR

JOHANNES REKVELD
GEBOREN TE KAMPEN

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Aan mijn Ouders
Aan mijn Vrouw

Bij het beëindigen van mijn academische studie breng ik gaarne mijn oprechten dank aan U, Hoogleeraren in de Faculteit der Wis- en Natuurkunde, die tot mijn wetenschappelijke vorming hebben bijgedragen.

In het bijzonder geldt deze dank U, Hooggeleerde Ornstein, Hooggeachte Promotor, voor den voortdurenden krachtigen steun en de levendige belangstelling, die ik niet alleen bij mijn wetenschappelijken arbeid in Uw laboratorium, maar ook in andere opzichten van U mocht ondervinden. Uw voorbeeld van energie en volharding heeft een diepen indruk op mij gemaakt en steeds moge dit voorbeeld mij in mijn verder leven in herinnering blijven.

Ook betuig ik mijn dank aan allen, die mij op eenigerlei wijze behulpzaam zijn geweest bij dit onderzoek.

Ten slotte een woord van dank aan Prof. Dr. A. F. Holleman voor zijn bereidwilligheid om dit proefschrift als artikel te willen opnemen in de „Archives".

INTENSITY PROBLEMS CONNECTED WITH THE RAMANEFFECT

BY

J. REKVELD.

INTRODUCTION.

Discovery of the Ramaneffect.

After investigating the thermodynamic wave theory of light-scattering for many years Prof. C. V. RAMAN at *Calcutta* noticed for the first time in 1921 a new phenomenon in scattered light. He found that in the case of a great number of liquids the depolarisation increased very strongly when a violet filter was placed in the path of the incident light. In the summer of 1923 RAMANATHAN working on the same subject described this phenomenon as "a trace of fluorescence". He showed, that the measured depolarisation depended on the presence of a blue filter in the path of the incident beam of the scattered light, it being smaller in this case. The possibility of the effect being due to impurities was eliminated by careful chemical purification. Further investigations on 60 liquids showed the effect to be very general in character.

The well-known test of the complementary filters first applied by Stokes for detecting fluorescence was used and gave an analogous result as in the case of fluorescence. After preliminary observations with sunlight an important and decisive step was taken by using a monochromatic source of light, viz. the very powerful quartz-mercury-lamp which gives a few sharp bright lines in the visible region of the spectrum.

The first attempts were made with benzene as a liquid. In the spectrogram many lines appeared which were not present in the incident light and some of these lines disappeared when certain wave lengths of the incident radiation were cut off by suitable filters. Further researches showed similar modified lines in the case of many liquids, some of them being accompanied by diffuse bands or by a continuous spectrum. It was also found that the new lines were polarised more strongly than the unmodified scattered light.

The discovery of the phenomenon was published in the Indian Journal of Physics, Vol. II, Part III, 31st March 1928.

About the same time LANDSBERG and MANDELSTAM (1, 2), two Russian physicists at Moscou found independently of Raman the same effect in the light scattered on crystalline quartz.

Many writers however have called the new phenomenon the "Ramaneffect". In the following we will do the same.

Explanation of the Ramaneffect.

As a tentative explanation RAMAN in his first paper on the subject assumes that of the incident quantum of light ($h\nu$) the part $h\nu_{mn}$ is absorbed by the molecule and that the remaining part ($h\nu - h\nu_{mn}$) is scattered. The absorbed energy is used to enable the molecule to pass from state m into state n, the energies of which are E_m and E_n, so that, $E_n - E_m = h\nu_{mn}$.

A similar idea was first put forward by SMEKAL (3) in discussing incoherent scattering of this kind. This assumption was also used by KRAMERS–HEISENBERG (4) in deriving a quantum theory of dispersion and the wave mechanical treatment of light scattering was based upon the same idea. These theories supported the interpretation given by RAMAN.

Further observations show however that the original interpretation is not sufficient to account for many consequences of the experiments. LANGER (5) and independently DIEKE (6) pointed out, that the formule which gives the intensity of a Ramanline does not depend directly on the transition probability A_{mn} for the two states m and n concerned, but on a sum which can be written $\Sigma\, A_{mj}\, A_{jn}$ extended over all j states which can combine with m and n. As a consequence of this the appearence of Ramanlines is mainly governed by the actual existence of those j states.

From the above explanation it will be apparent that there must be a certain relation between the frequency-shifts of the modified lines and the spectrum of the molecule. RAMAN first and many others after him showed a connection between these shifts and infra-red absorption-frequencies of the examined substance. This may be understood by assuming that the above mentioned transition occurs between two oscillation- or rotation-levels of the molecule.

In all cases however a great difference has been observed between the intensities in the Ramanspectra and those in the infra-red. In some cases the infra-red absorption is quite absent, because the molecule is not a polar one, yet many Ramanlines appear which are independent of this condition.

For illustrating this fact on the basis of the explanation given by Langer and Dieke we consider the simple case of a rotation spectrum giving rise to an infra-red absorption. The appearence of absorption lines is restricted by the selection-principle. $\Delta m = \pm 1$, m being the rotational-quantum-number. In the Raman-spectrum however the lines with corresponding frequency-shifts will not appear, because there is no possibility of combining with a third state. The selection principle gives here as may be easily shown $\Delta m = 0$ or ± 2. On the other hand the corresponding transitions are forbidden in the rotational spectrum.

A very convincing proof of this explanation are the experiments on HCl made by Wood (7); the so-called missing line (R-branch) was found in the Ramanspectrum, the other lines (P- and Q-branch) were absent. Also the observations of Mc Lennan and Mc Leod (8) lead to a similar conclusion in the case of the rotation spectrum of hydrogen.

Notwithstanding this incomplete correspondence between infra-red- and Ramanspectrum the effect is a very powerful means for studying molecular spectra, because the main problems are not the rotation- but the vibration-energy-levels. In the latter case the questions about selection-principles are more complicated than in the above mentioned simple example.

Problems in the Ramaneffect.

Since the first paper of Raman very much attention has been given by physicists to the problems of modified light-scattering. In the three years since the discovery of the effect a considerable number of publications has appeared not only from the school of Raman in India, but also from other laboratories in all parts of the world, especially with regard to wave-length measurements and determination of the shifts ν_{mn}. It is impossible to give even a short account of the very interesting results within the limits of this short introduction.

We shall treat in the next chapters intensity problems arising from the Ramaneffect.

First we shall consider the ratio of energies between Stokes and

Anti-Stokes Ramanlines. It will be seen that moreover this research gives the possibility of a determination of the fundamental constant $\frac{h}{k}$.

Further we shall give a complete survey concerning the way the scattered energy in Ramanspectra depends on frequency. These experiments were suggested by the analogous problems in the classical scattering and it will be seen, that to a certain degree similar results may be obtained in the case of modified scattering.

The first problem was treated qualitatively by RAMAN and KRISHNAN (9, 10) and by DADIEU and KOHLRAUSCH (11). About the second question DAURE (12) gave quantitative results in a first paper on the subject. In a further publication (13) he called these results inexact, but did not give the corrected results; his conclusion however is that the energy increases as the fourth power of the exciting frequency.

LANDSBERG and MANDELSTAM (14) found with quartz that the energy increases more rapidly than a fourth power law in the ultra-violet. They consider however the results not to be so accurate as to draw certain conclusions about the problem.

CHAPTER I.

RATIO OF INTENSITIES BETWEEN STOKES AND ANTI-STOKES LINES AND DETERMINATION OF THE CONSTANT $\frac{h}{k}$. [1]

Introduction.

From different points of view the measurement of the ratio of intensities between Stokes and Anti-Stokes lines is of importance.

For begin with there is in these measurements a possibility of testing the validity of the distribution law of MAXWELL-BOLTZMANN in the quantum theory of light. We must take advantage of this possibility because only in a few other cases such a test can be carried out. We mention in this connection the measurements of the intensities in the bandspectrum of nitrogen recently made by ORNSTEIN and v. WIJK (15). They have found a MAXWELL-BOLTZMANN distribution among the rotation levels of nitrogen.

In the second place it will be seen that the investigation of the above mentioned ratio leads to a new optical determination of the important constant $\frac{h}{k}$ (h = PLANCK-constant; k = BOLTZ-

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[1] See: L. S. ORNSTEIN and J. REKVELD; Zs. f. Phys., 57 (1929), 539.
L. S. ORNSTEIN and J. REKVELD; Phys. Rev., Vol. 34 (1929), 720.
L. S. ORNSTEIN and J. REKVELD; Zs. f. Phys., 68 (1931), 257.

MANN-constant). The resulting value for this quantity is in a good agreement with those obtained in various other ways. Although the measurements which we are going to describe do not permit of such a high degree of accuracy as already obtained, it will be shown that the principle of the method may be used for a more exact determination. This method would be a very simple one for obtaining the important quantity.

Finally we draw attention to the fact that our experiments in combination with the theoretical formula seem to indicate an extension of the well-known summation rule so as to include the Ramaneffect. This extension points to a very general validity of the rule which is also indicated by a few other measurements in bandspectra.

We shall now first derive a theoretical formula for the ratio of intensities.

Theoretical.

In different ways several writers have already derived a theoretical formula for the ratio of intensities between Stokes and Anti-Stokes lines.

On assuming, that the probabilities of the two emission processes are equal, RAMAN (16) was the first to find for the ratio of the scattered energies the expression: $e^{\frac{h\nu_{mn}}{kT}}$ (ν_{mn} = transition frequency). The same result has been obtained by DAURE (13). In the case of crystalline matter LANDSBERG and MANDELSTAM (17) gave an interpretation of lightscattering on the basis of the BORN-theory of crystal-lattice. They arrive at a formula of the type:

$$\left(\frac{\nu-\nu_{mn}}{\nu+\nu_{mn}}\right)^4 e^{\frac{h\nu_{mn}}{kT}}.$$

The same formula was found by TAMM (18) on applying the DIRAC-theory of light-scattering. CARELLI (19) with the help of quantum-mechanics obtains the ratio: $(N_m/N_n)^2$. PLACZEK (20) also applied DIRAC-methods to solve the problem, but in a more general manner by also taking into account the dispersion of the matter. His formula therefore contains the absorption-frequencies ν_a of the substance considered. In the case of one single absorption-frequency the expression has the form:

$$\left(\frac{\nu-\nu_{mn}}{\nu+\nu_{mn}}\right)^4 \left(1-\frac{4\nu\nu_{mn}}{\nu_a^2-\nu^2}\right) e^{\frac{h\nu_{mn}}{kT}}.$$

In order to derive an expression for the ratio of intensities in a very simple way we will make use of a consideration of thermodynamical equilibrium, reasoning on the same lines as EINSTEIN did when deriving the radiation-law of PLANCK.

We therefore consider a system of molecules in thermodynamical equilibrium with radiation of the absolute temperature T. Among the different states of energy, which are possible for a molecule, we select the two states indicated by the letters m and n. Let the energies of these states be E_m and E_n.

If we assume that the distribution of the energies is according to the law of MAXWELL-BOLTZMANN, the numbers of molecules $\mathcal{N}_m$ and $\mathcal{N}_n$ in the states m and n can be represented by

$$\mathcal{N}_m = g_m \, e^{-\frac{E_m}{kT}} \text{ and } \mathcal{N}_n = g_n \, e^{-\frac{E_n}{kT}} \quad . \; . \; . \quad (\mathrm{I}),$$

(g_m and g_n are the statistical weights).

Now we suppose this system to be immersed in a field of radiation with a density $\rho(\nu)$. The way of excitation of the Ramanlines is the following: a quantum of light of frequency ν strikes the molecule and is scattered as a quantum of frequency $\nu - \nu_{mn}$, while the scattering molecule passes from state m to state n; or the scattered quantum has a frequency $\nu + \nu_{mn}$ and the molecule passes from state n to state m. The lines thus scattered are called Stokes and Anti-Stokes lines, provided that $E_n > E_m$ and the transition frequency ν_{mn} is given by $E_n - E_m = h\nu_{mn}$. We will not enter into further details about the mechanism of this transition, but only start from the experimentally given fact of the transition.

We will represent the transition probalities from state m to state n and inversely by Φ_{mn} and Φ_{nm}. Then the energies of the Ramanlines of frequencies $\nu - \nu_{mn}$ and $\nu + \nu_{mn}$ are given by

$$h(\nu - \nu_{mn}) \, \rho(\nu) \, \mathcal{N}_m \, \Phi_{mn}(\nu) \, d\nu \text{ and } h(\nu + \nu_{mn}) \, \rho(\nu) \, \mathcal{N}_n \, \Phi_{nm}(\nu) \, d\nu \quad (\mathrm{II}a)$$

or using formulæ I)

$$h(\nu - \nu_{mn}) \, g_m \, \rho(\nu) \, \Phi_{mn}(\nu) \, e^{-\frac{E_m}{kT}} d\nu \text{ and } h(\nu + \nu_{mn}) \, g_n \, \rho(\nu) \, \Phi_{nm}(\nu) \, e^{-\frac{E_n}{kT}} d\nu \quad (\mathrm{II})$$

In order to obtain further information about the functions Φ_{mn} and Φ_{nm} we assume that the density $\rho(\nu)$ may be represented by the law of WIEN, consequently

$$\rho(\nu) = \frac{8\pi}{c^3} \nu^3 e^{-\frac{h\nu}{kT}} \quad . \; . \; . \; . \; . \; . \quad (\mathrm{III})$$

This assumption is not an essential restriction of the generality. For under the actual experimental conditions the frequencies considered are rather high and consequently $\frac{h\nu}{kT}$ amounts to about 100. In this case we may take the law of WIEN instead of the general radiation-law of PLANCK.

As a consequence of the supposed equilibrium between radiation and matter the number of quantums having a frequency ν must be constant. This number however is changed by two processes:

a. the excitation of Stokes and Anti-Stokes Ramanlines with frequencies $\nu - \nu_{mn}$ and $\nu + \nu_{mn}$

b. the excitation of Stokes lines having a frequency ν (excited by a frequency $\nu + \nu_{mn}$) and of Anti-Stokes lines having a frequency ν (excited by a frequency $\nu - \nu_{mn}$).

By the process *a.* the energy diminishes with the amount

$$h\nu\rho(\nu)\Big[\Phi_{mn}(\nu)\,N_m + \Phi_{nm}(\nu)\,N_n\Big]\,d\nu \quad . \quad . \quad . \quad \text{(IV)}$$

This loss must be compensated by the process *b.* The energy thus obtained is represented by

$$h\nu\Big[\rho(\nu + \nu_{mn})\,\Phi_{mn}(\nu + \nu_{mn})\,N_m + \rho(\nu - \nu_{mn})\,\Phi_{nm}(\nu - \nu_{mn})\,N_n\Big]\,d\nu \quad \text{(V)}$$

Putting V equal to IV we get with I and III:

$$\nu^3 e^{-\frac{h\nu}{kT}}\Big[g_m\,\Phi_{mn}(\nu)\,e^{-\frac{E_m}{kT}} + g_n\,\Phi_{nm}(\nu)\,e^{-\frac{E_n}{kT}}\Big] =$$
$$(\nu + \nu_{mn})^3 e^{-\frac{h(\nu + \nu_{mn})}{kT}}\,g_m\,\Phi_{mn}(\nu + \nu_{mn})\,e^{-\frac{E_m}{kT}} +$$
$$(\nu - \nu_{mn})^3 e^{-\frac{h(\nu - \nu_{mn})}{kT}}\,g_n\,\Phi_{nm}(\nu - \nu_{mn})\,e^{-\frac{E_n}{kT}}$$

or in a more simple form:

$$\nu^3\Big[g_m\,\Phi_{mn}(\nu)\,e^{\frac{h\nu_{mn}}{kT}} + g_n\,\Phi_{nm}(\nu)\Big] = (\nu + \nu_{mn})^3\,g_m\,\Phi_{mn}(\nu + \nu_{mn}) +$$
$$(\nu - \nu_{mn})^3\,g_n\,\Phi_{nm}(\nu - \nu_{mn})\,e^{\frac{h\nu_{mn}}{kT}}.$$

This equation must be satisfied for all values of T, which only enters into the exponent of the *e*-power. Therefore we get the two equations:

$$\nu^3 g_m\,\Phi_{mn}(\nu) = (\nu - \nu_{mn})^3\,g_n\,\Phi_{nm}(\nu - \nu_{mn}) \text{ and } \nu^3 g_n\,\Phi_{nm}(\nu) =$$
$$(\nu + \nu_{mn})^3\,g_m\,\Phi_{mn}(\nu + \nu_{mn}) \quad . \quad . \quad . \quad . \quad \text{(VII)}$$

From the first of these equations we can obtain the second one by substituting $\nu + \nu_{mn}$ instead of ν. The two functional equations for the probabilities Φ_{mn} and Φ_{nm} are thus obviously identical.

In order to solve equation VII we use the assumption, suggested by the idea of a virtual resonator, that the energy of a Stokes line, excited by different incident frequencies, increases as the fourth power of the frequency of the modified scattered light. [1]) This energy may therefore be expressed by a formula

$$E_S = D\,(\nu - \nu_{mn})^4 \quad . \; . \; . \; . \; . \; . \quad \text{(VIII)}$$

A comparison between II*a* and VIII leads to

$$h\,(\nu - \nu_{mn})\,N_m\,\Phi_{mn}(\nu) = D(\nu - \nu_{mn})^4,$$

if we put the incident energy equal to unity. From this it results, that $g_m \Phi_{mn}(\nu)$ has the form $C(\nu - \nu_{mn})^3$, C being a constant as D, independent of ν. If we substitute this in the equation VII we obtain:

$$\nu^3\, C(\nu - \nu_{mn})^3 = (\nu - \nu_{mn})^3\, g_n\, \Phi_{nm}(\nu - \nu_{mn})$$

and this equation is satisfied by putting $g_n\, \Phi_{nm}\,(\nu - \nu_{mn}) = C\,\nu^3$ or $g_n \Phi_{nm}(\nu) = C(\nu + \nu)^3$. Putting the expressions for $g_m \Phi_{mn}$ and $g_n\, \Phi_{nm}$ in the formulæ II, the formula for the ratio between the energies of Stokes and Anti-Stokes lines as may be easily seen takes the form

$$\frac{E_S}{E_{A.S.}} = \left(\frac{\nu - \nu_{mn}}{\nu + \nu_{mn}}\right)^4 e^{\frac{h\nu_{mn}}{kT}}.$$

It must be understood, that this formula has been found on the assumption, that a fourth power law for the modified scattered light is valid. As will be shown in the next chapters, however, this is only the case in regions of the spectrum remote from absorption frequencies. It is evident that our formula has the same restrictions to its validity.

The above expression is the same as that obtained by LANDSBERG, MANDELSTAM and TAMM and also the formula given by PLACZEK is similar, if such conditions prevail that an influence of absorption may be neglected.

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[1]) This assumption has moreover been verified by the results obtained in Chapter II and IV.

Consequences of the formula.

Introducing now the usual quantity $I = \frac{E}{\nu^4}$ we get for the ratio of intensities:

$$\frac{I_S}{I_{A.S.}} = e^{\frac{h\nu_{mn}}{kT}}.$$

We have tested this expression experimentally, as will be described below.

If we assume the validity of the formula, it is evident, that the experiments may be used for another purpose, viz. for a new optical determination of the constant $\frac{h}{k}$. In this case we shall write the formula in the form:

$$\frac{h}{k} = \frac{T}{\nu_{mn}} \ln \frac{I_S}{I_{A.S.}}.$$

As all quantities in the right hand member of this equation are known from the experiments the determination of $\frac{h}{k}$ is easily possible. We have carried out this evaluation in the following.

Anticipating on the good agreement between theoretical and experimental results we shall draw a further consequence of the theoretical considerations.

We have assumed and this assumption will be verified in the next chapters, that

$$g_m \Phi_{mn}(\nu) = C(\nu - \nu_{mn})^3$$

and from this it follows with the help of the equation VII

$$g_n \Phi_{nm} = C(\nu + \nu_{mn})^3.$$

We will now replace the radiation emitted by the transition from state m to state n by the radiation of a virtual oscillator and similarly for the radiation emitted by the transition n to m. This means, that in order to describe the intensity of the radiation which actually takes place we adjoin a complex vector of amplitude to each transition process. Suppose, that the oscillator has an electric moment given by $\mathfrak{p}(t) = \mathfrak{a}\, e^{2\pi i\nu}$, ν representing the emitted frequency. Then as is generally known, the transition-probability Φ and the amplitude $\mathfrak{a}$ are connected in the following way:

$$\Phi h\nu = \frac{(2\pi\nu)^4}{3c^3} \left| \mathfrak{a} \right|^2.$$

Using the expressions for $g_m\ \Phi_{mn}$ and $g_n\ \Phi_{nm}$ we obtain:

$$\frac{g_m \Phi_{mn}\ .\ h(\nu-\nu_{mn})}{(\nu-\nu_{mn})^4}=\frac{g_n\ \Phi_{mn}\ .\ h(\nu+\nu_{mn})}{(\nu+\nu_{mn})^4}$$

and we can interprete this with the aid of the virtual oscillators by writing:

$$g_m \left| a_m \right|^2 = g_n \left| a_n \right|^2 \text{ or } \frac{\left| a_m \right|^2}{\left| a_n \right|^2}=\frac{g_n}{g_m}.$$

Consequently the intensities of the light emitted by the two transitions are proportional to the statistical weights of the final states of the molecule after the transition. This result has evidently a great analogy with the summation rule for the case of atom multiplets. By the above considerations this rule has been extented to the intensities connected with the radiation in the Ramaneffect.

Besides there are some other investigations which lead to a similar extension of the summation rule. ELLIOTT (21) found from his intensity-measurements in the bandspectrum of $B\ O$, that the assumption of the summation rule being valid in the case of bandspectra as well gives a right interpretation of the results obtained by the optical determination of the relative abundance of isotopes. A similar application of the rule has been justified by the experiments published by ORNSTEIN and BRINKMAN (22), concerning the determination of temperature from bandspectra of $C\ N$.

In conclusion we may remark, that by these extensions it is made highly probable, that the summation rule is of a very general character and may be applied in various cases.

Experimental.

We will now describe the apparatus and the method used in our experiments.

As intensity-ratios can be determined in the least complicated manner if the ratios are not too great, we have looked for a substance suitable for this purpose. It will be very clear that the intensity of a Stokes Ramanline is mainly governed by the transition probability from the normal to the excited state, whereas the value of the frequency-shift ν_{mn} has no influence on the intensity: a line for which ν_{mn} is rather large may be much stronger than a line with a small ν_{mn}.

On the other hand the appearance of Anti-Stokes lines depends on the number of molecules already in the excited state and this number will decrease with increasing ν_{mn}. For this excitation of molecules is caused by thermal motion and the greater the difference of energy between an excited state and the normal one the smaller the number of molecules in an excited state will be. Now at room-temperature the mean thermal energy of a molecule is of an amount of about 32×10^{-15} ergs, which corresponds to a frequency-shift of 160 cm^{-1} (wave-number). At this temperature Anti-Stokes lines with a transition frequency near this value will consequently appear very strongly. But the intensity of Anti-Stokes lines will fall off very rapidly with increasing value of ν_{mn}.

These considerations lead to the choice of a substance for which the values of the transition-frequencies are relatively small, so that the ratios between the intensities of Stokes and Anti-Stokes lines are alsos mall and thus favourable for the measurements. This is realized by the liquid carbon tetrachloride (CCl_4) the main lines having shifts ν_{mn} of 215, 312 and 456 cm^{-1} (wave number); moreover these lines are very strong and may be easily photographed. Before the experiments the liquid was purified carefully and distilled into the investigation tube. As a matter of fact impurities do not affect the results of all our measurements, provided that they do not give rise to absorption. For we chose our method as to be always independent of mechanical impurities; but with all investigations concerning the Ramaneffect it is of great practical importance to reduce the intensity of the disturbing back-ground obtained on the photographs to a minimum. For this back-ground besides by fluorescent light is caused mainly by the scattered energy of the continuous spectrum given by the exciting light-source and we must avoid dust-particles in the liquid, which scatter very strongly this continuous spectrum.

The tube filled with the liquid was of the type first indicated by Wood (23). It is a glass tube, having a length of 25 cm and a diameter of 4 cm. This tube is bent at the one end and has a plane window fused on the other end. The bent part of the tube is painted black on the outside, and this curvature serves to get rid of the reflexion from incident light on the back of the tube. In this way practically a black back-ground was obtained for observation which is necessary for the measurement of a such faint spectrum as the Ramanlines offer.

A second tube surrounded the inner one and was fixed on it by rubber stops and provided with a supply-pipe and an outlet-pipe for a water-circulation to keep constant the temperature of the liquid during the exposures. For this purpose a very quick circulation was maintained by means of a centrifugal pump from a tank filled with water of the desired temperature.

Before beginning an exposure we waited for an equilibrium state of the temperature. Measurements of the temperature of the liquid in the tube and of the water in the tank showed, that in all cases a slight difference in temperature persisted. By means of a thermo-element this difference was observed and a correction for it applied to the measurements.

The Ramanspectrum was excited as usually by a quartz-mercury-lamp. This light source is very powerful and has the advantage of giving a relatively small number of strong lines. A polished aluminium reflector having an elliptical cross-section was put over the lamp which was placed in one focus and the tube in the other one; a reflector of the same material was put under the inner tube.

This arrangement for exciting Ramanlines can hardly be improved, because a great volume of the liquid placed at a very short distance from the light-source is exposed to a strong radiation from all sides.

The light scattered through the plane window was focussed on the slit of the spectrograph by means of an achromatic lens. This spectrograph was a Hilger-quartz-spectrograph (type E_1) with a large dispersion in the visible region of the spectrum. In order to get sharp images on the plates it proved necessary that the temperature of the room was kept constant within about one degree; the small fluctuations in temperature were damped by a heavy lagging of the spectrograph with cotton-wool. Thanks to these precautions it was possible to obtain good pictures with an exposure time of five hours.

Ilford Special Rapid plates were used being most sensitive in the region desired; moreover the grain of these plates is sufficiently fine to admit of reliable intensity-measurements. The plates were developed with Rodinal.

The densities thus obtained were measured with a Moll-selfrecording microphotometer. On each plate a set of calibration-spectra was photographed, obtained by means of a tungsten-filament lamp with a known energy-distribution. The different steps of one series of spectra were got by varying the width of the slit of the spectrograph. For each wave-length it is thus possible to draw density-curves; although the distance between the lines which we have measured is not very large (at most 200 Å) it is not allowed to neglect the variation of the plate sensitivity over this distance. A correction which can be easily found from the calibration-curve of the tungsten-lamp was always applied.

Results.

The (corrected) temperatures during the exposures were the following: 274°, 300°, 312°, 323.5° and 339.5° K. Of the incident light we used for excitation the two wave-lengths 4047 Å and 4358 Å. In the Ramanspectrum of carbon tetrachloride each of these lines gives three rather strong lines on both sides of the unmodified scattered line, corresponding to the frequency-shifts: 215, 312 and 456 cm^{-1} (wave-number). These frequency-shifts point to three absorption-bands in the infra-red spectrum near 46.5, 32.1 and 21.9 μ, which however have not yet been measured.

At the above mentioned temperatures the ratio of intensities between Stokes and Anti-Stokes lines were measured and the results are put together in the tables I, II and III.

For comparison between the experimental values and those obtained from the theoretical formula we have also given the theoretical ratios. For the calculations of the just-mentioned ratios we have used for the quantity $\frac{h}{k}$ the value obtained by Michel (24) by the measurements of isochromates. He found the value 0.476×10^{-12} degree-sec. and it seems to be a very accurate determination of the constant.

It will be evident from the tables, that a very good agreement exists between theory and experiment.

TABLE I.

Frequency-shift: $\nu_{mn} = 215\ \text{cm}^{-1}$

T (absolute)	exciting line 4047 Å	exciting line 4358 Å	mean ratio	calcul. ratio
274°	3.1	2.9	3.0	3.1
300°	3.0	2.6	2.8	2.8
312°	2.55	2.5	2.5	2.65
323.5°	2.7	2.5	2.6	2.55
339.5°	2.4	2.6	2.5	2.45

TABLE II.

Frequency-shift: $\nu_{mn} = 312\ \text{cm}^{-1}$

T (absolute)	exciting line 4047 Å	exciting line 4358 Å	mean ratio	calcul. ratio
274°	5·4	5·5	5·45	5·1
300°	4·4	4·2	4·3	4·4
312°	4·1	4·3	4·2	4·15
323·5°	4·4	3·9	4·15	3·95
339·5°	3·6	3·8	3·7	3·7

TABLE III.

Frequency-shift: $\nu_{mn} = 456\ \text{cm}^{-1}$

T (absolute)	exciting line 4047 Å	exciting line 4358 Å	mean ratio	calcul. ratio
274°	11.9	12.0	11.95	10.8
300°	9.0	9.0	9·35	8,8
312°	—	—	—	8.1
323·5°	7·4	8.1	7·75	7·5
339·5°	7.0	7.0	7.0	6.8

In order to examine more closely these results we have put for each frequency-shift:

$$ln\frac{I_S}{I_{A.S.}} = \alpha + \beta\, T^{-1}.$$

With the aid of the methods of mean squares we found, that the value of α is very near zero and that consequently the formula $ln\frac{I_S}{I_{A.S.}} = \beta T^{-1}$ holds.

This result may also be observed from the diagram given in fig. 1, where the *ln* of the intensity-ratio has been plotted against the inverse of the temperature. The three lines corresponding to the three frequency-shifts pass through the origin and thus confirm the assumption $\alpha = 0$.

It will be seen, that this fact permits us to put together in one diagram the results obtained for the different frequency-shifts. This is done in fig. 2, where $\frac{\nu_{mn}}{T}$ has been chosen as abscissa and

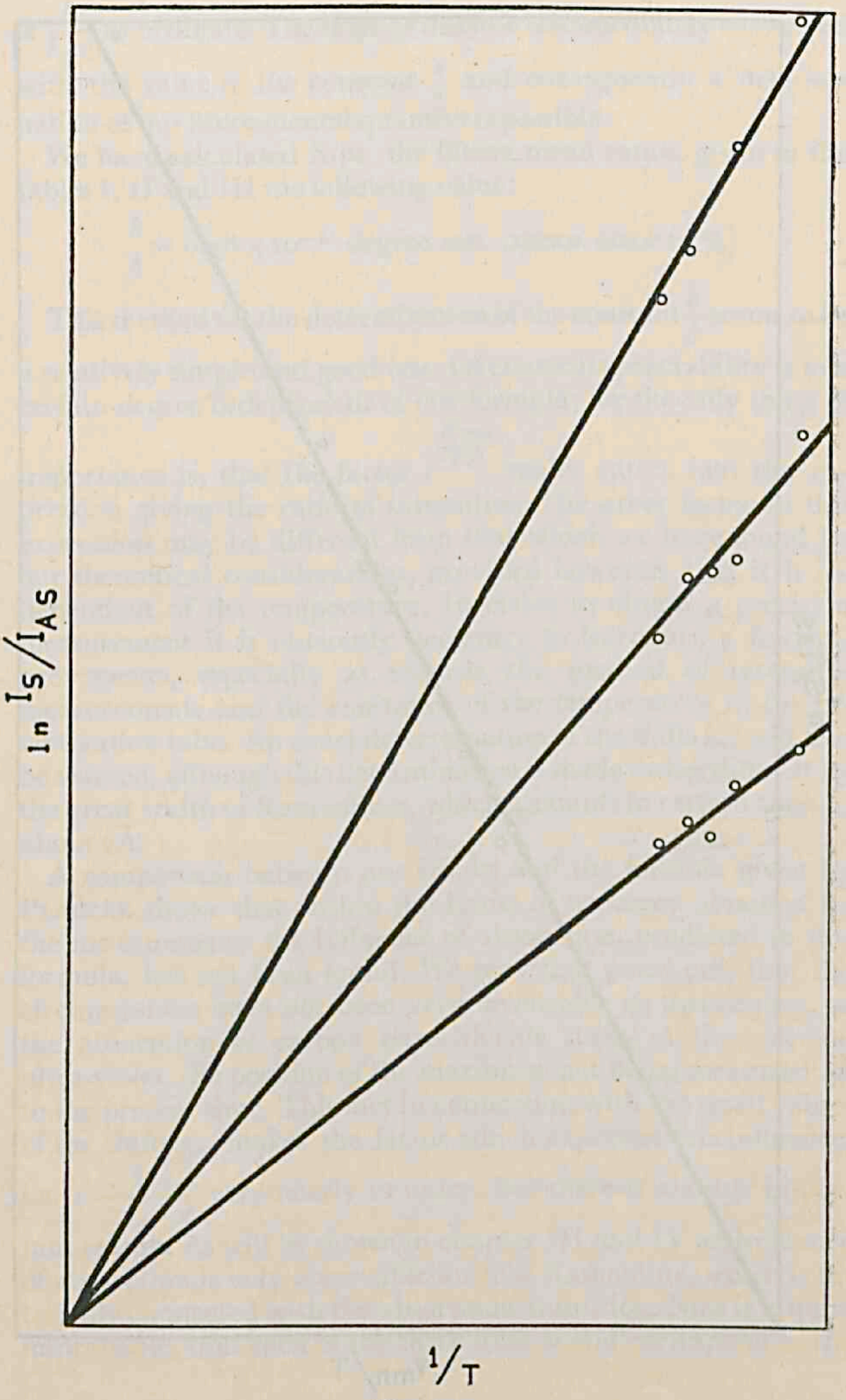

Fig. 1.

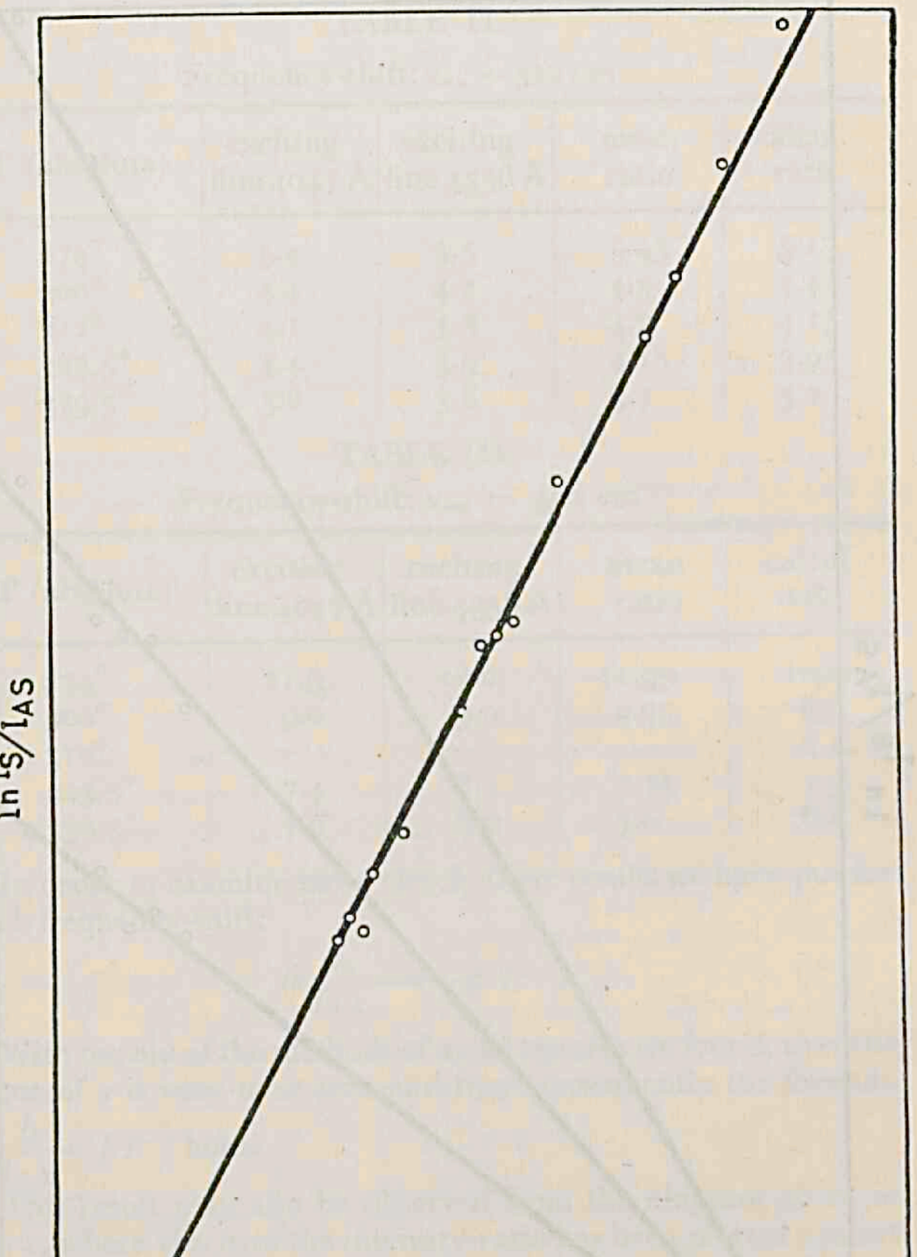

Fig. 2.

$ln\,\frac{I_S}{I_{A.S.}}$ as ordinate. The slope of this line is immediately connected with the value of the constant $\frac{h}{k}$ and consequently a determination of this fundamental quantity is possible.

We have calculated from the fifteen mean ratios, given in the tables I, II and III the following value:

$$\frac{h}{k} = 0.48 \times 10^{-12} \text{ degree sec. (mean error: } 2\,\%)$$

This method for the determination of the constant $\frac{h}{k}$ seems to be a relatively simple and good one. Of course its practability is to a certain degree independent of our formula; for the only thing of importance is, that the factor $e^{\frac{h\nu_{mn}}{kT}}$ really enters into the expression giving the ratio of intensities. The other factor in this expression may be different from that which we have found by our theoretical considerations, provided however, that it is independent of the temperature. In order to obtain a precision measurement it is obviously necessary to introduce a few improvements, especially as regards the method of intensity-measurements and the constance of the temperature in the investigation tube. An exact determination of the shifts ν_{mn} will also be wanted, although this determination is made rather difficult by the great width of Ramanlines, which amounts in certain cases to about 2Å.

A comparison between our results and the formula given by Placzek shows that within the limits of accuracy obtained by the measurements the influence of absorption, predicted in this formula, has not been found. We may first point out, that the circumstances have not been very favourable in this respect, as the absorption of carbon tetrachloride starts in the extreme ultra-violet, the position of the maximum not being measured up to the present time. This fact in connection with the small values of the shifts ν_{mn} makes the factor which expresses this influence, i.e. $1 - \frac{4\nu\,\nu_{mn}}{\nu_a^2 - \nu^2}$ very nearly to unity. But there is another important reason. As will be shown in chapter III and IV an influence of absorption is only observable for that Ramanline, which is internally connected with the absorption-transition. Now it is quite improbable, that each of the three lines would correspond to the same absorption-frequency, provided that really one of the lines does so. It follows therefore, that it is possible that no influence of absorption will appear in this case.

By choosing a substance more suitable for detecting this influence, and taking into account the results obtained in Chapter III, the formula may be confirmed. Nevertheless, because of the predominant character of the e-power a supplementary factor will in general be hardly perceivable.

CHAPTER II.

DEPENDENCE OF THE SCATTERED ENERGY IN RAMANSPECTRA ON FREQUENCY IN NON-ABSORBING SUBSTANCES. [1]

Introduction.

The problem, which will be investigated in this chapter is the following: when we examine Ramanlines with a given frequency-shift ν_{mn}, but excited by incident lines of different frequency, what is the dependence of the scattered energy of these lines on frequency. This problem is suggested by and has to solve the same question as the investigation of the frequency dependence of classical scattering. It is wellknown, that when light of frequency ν strikes a medium, part of the incident energy is scattered into a given direction and has the same frequency ν. The part of energy thus scattered is proportional to the fourth power of the incident frequency ν. This fact is usually called the law of Rayleigh and has been stated experimentally and theoretically by a great many writers and in various ways. The validity of this rule however must be restricted to regions of frequency in which the scattering substance does not absorb or which are not very near such absorption frequencies. In both cases the fourth power law does not hold.

It seems to be very interesting to investigate this problem also for the case of modified scattering. As a consequence of the remarks just made about the validity of the law of Rayleigh for the scattered energy in the classical case, it seems necessary to divide the problem into two:

a. the dependence of the scattered energy in Ramanspectra excited in regions which are far away from absorption frequencies of the substance,

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[1] See: L. S. ORNSTEIN and J. REKVELD; Zs. f. Phys. 61 (1930) 593.

b. the same question for Ramanspectra excited in regions which are at a very short distance from absorption frequencies.

About the question whether in the absorption region itself the Ramanlines do not exist at all, or whether they are relatively very strong we cannot give any information. We can expect that certainly very long exposure times are necessary before the lines can have through the absorbing matter any effect on the plates. But we have not investigated this point .

In this chapter the problem indicated under *a.* will be treated.

Theoretical predictions about this subject have been made by Placzek (20). Taking the dispersion of the matter in question into account he arrives with the aid of quantum-mechanics to an expression for the frequency-dependence of modified scattering. The expression he gives can be simplified and written:

$$E_S = (\nu - \nu_{mn})^4 \Sigma \frac{C_{jn}}{\nu^2_{jn} - \nu^2}$$

(E_S = energy of a Stokes-line, ν_{mn} = frequency-shift, ν_{jn} = absorption-frequency, C_{jn} is a quantity connected with transition probabilities by the absorption process considered).

From this formula it follows, that we must consider three possible cases:

a. $\nu^2_{jn} >> \nu^2$; this means that the exciting frequency lies at a great distance from the absorption frequency. In this case the formula states, that in a first approximation the scattered energy will be proportional to the fourth power of the modified frequency.

b. $\nu_{jn} < \nu$; this possibility is for instance realised in regions near infra-red absorptions. The energy would decrease more rapidly than $(\nu - \nu_{mn})^4$.

c. $\nu_{jn} > \nu$; this occurs near ultra-violet absorption regions. In this case the energy according to the above formula must increase more strongly than $(\nu - \nu_{mn})^4$.

Method of Investigation.

There are two obvious ways to treat the problem.

a. The first method may be the following: the Ramanspectrum is photographed together with the scattered exciting lines. Now in the usual way the ratio of energies of each Ramanline and of the corresponding scattered unmodified line is made up. The dependence of the energy in the Ramanlines on frequency is in this way determined in connection with the energy of the unmodified lines and about this dependence we assume the Rayleigh fourth power law. From the comparison between the obtained ratios a conclusion results about the considered energies and about a possible deviation from the classical law of scattering.

This way of investigation however has in our opinion various difficulties. The substance to be considered must be made dustfree very carefully in order to avoid scattering on dustparticles which does not follow the fourth power law, as for the Ramanlines dustparticles have not direct influence. Further one has to use various screens during the exposure in order to prevent light reflected either on the walls of the tube containing the liquid or otherwise to enter into the spectrograph and spoil the results. These screens however involve an important loss of light radiated from the tube and therefore very long exposure times are necessary.

Apart from these practical objections which are at least not of fundamental importance there is according to our view a radical error in this method. We have namely assumed the validity of the fourth power law for the unmodified scattering. Now as a matter of fact this law has been stated theoretically with some discrepancies about the influence of the dispersion of the scattering substance, but strictly speaking has never been checked experimentally in a more restricted manner. The school of Raman has measured the scattering of many substances in order to make this point clear, but these measurements gave always only the integral effect of a range of wave-lengths not of individual frequencies. With each given substance we must make out first whether circumstances are such that an application of the law is allowed. This makes necessary to determine the energy of unmodified scattered lines in connection with the energies of incident lines, at least if we will not carry an uncontrolled assumption into our measurements. These considerations suggest the following method:

b. The Ramanspectrum is photographed and the energies of the lines are measured. After that the relative energies of the exciting lines are determined. The ratios of the energies of Ramanlines and of corresponding exciting lines are made up and from this the dependence on frequency is acquired in a direct manner.

Experimental.

We have chosen for our problem the liquid carbon tetrachloride ($C\,Cl_4$).

Because with this substance each exciting line gives rise to three very strong Stokes lines and to the three corresponding Anti-Stokes lines, it has the advantage of offering six objects for investigation at once. Therefore we can obtain results of a high accuracy.

The Stokes lines and the Anti-Stokes lines were photographed with different exposure times necessary to obtain suitable densities. It is evident, that for comparing the variation of energy of a given Ramanline with frequency, all the lines to be compared ought to be acquired with the same exposure: as only in that case these lines are photographed under exactly equal conditions.

The method of exciting the Ramanspectra was the same as described in Chapter I. This time however it was necessary not only to keep constant the current and voltage of the mercury lamp during the exposures but also to use the same current and voltage during all of them, in order to make sure that each time the energy of the exciting lines is exactly the same. From some preliminary researches it appeared, that in order to get the mercury lamp in a state of equilibrium the lamp had to be set going one hour or two beforehand. To reproduce equal current and voltage one must work under exactly the same circumstances as regards the mercury lamp, especially as to the placing of screens around it. The circulation of air in the room in connection with temperature fluctuations seems to influence the state of equilibrium. To prevent the continuous background on the plates from being too strong the temperature of the lamp may not be too high, which means that the energy put into the lamp may not be too much increased.

The radiation from the tube through a plane window was concentrated on the slit of the spectrograph by means of an achromatic lens. This spectrograph (Fuess) was very powerful owing to the relatively large aperture of the apparatus. The photographs were taken on Ilford Panchromatic plates.

The $C\,Cl_4$ received in a highly purified state was distilled into the investigation bulb. Further purification was superfluous for our experiments; it is sufficient that eventual fluorescing substances are eliminated as giving a disturbing strong continuous background. A few particles of dust do not harm for reasons already mentioned.

With this arrangement it was possible to get good photographs of Ramanlines excited by the mercury lines from 4047 till 5791 Å with an exposure of two hours.

Mercury lines.

Our method presupposes a knowledge of the relative energies of mercury-lines. These have been acquired in the following way:

To take a photograph of the lines as they are radiated from the mercury lamp the tube containing the liquid was replaced by a reflecting plate. For this plate we have chosen a layer of gypsum covered with magnesium-oxyde. This is applied on the gypsum by burning magnesium-ribbon under the plate; to fix it it was necessary to hold the plate into boiling steam and to repeat these manipulations several times.

The plate thus acquired will last for a long time and reflects diffusely the radiation from the lamp in the direction of the slit of the spectrograph; for this purpose the plate was made slanting at an angle of 45 degrees. Before comparing the lines thus obtained with the corresponding Ramanlines the question must be solved whether the energies thus measured are still in accordance with those actually active in the tube in exciting the Ramanlines, these energies only being of interest.

For it might be, that the light from the mercury lamp entering the tube be affected by reflexion, diffraction and eventual absorption to an amount which to a certain degree depends on wave-length. If this amount exceeds the limits of accuracy of the measurements it would appreciably alter the relative energies of the mercury lines and lead to wrong results.

For make sure we have compared the lines radiated directly from the lamp and the lines having passed through the tube.

To be quite certain about this result as regards absorption we have paid special attention to the possibility of its presence. For this purpose a tube 8 cm long with plane windows parallel to each other at the ends was filled with carbon tetrachloride. The mercury lamp was placed before a monochromator and in this way the light of the lines was made to pass successively through the tube. The energy was measured with the combined thermopile and galvanometer. Within the limits of accuracy (about a few percents) an absorption effect was not perceivable. Such an affirmation enables us to use the distribution of energies acquired from the direct radiation of the lamp, it being the same as the distribution really active in exciting the Ramanspectrum and this means an important simplification in the manipulation of the method.

The time of exposure for the mercury lines is compared with that for the Ramanspectra very short and it was therefore necessary to increase this exposure time by means of suitable screens put in the path of the light from gypsumplate to spectrograph. In this way both exposure times were made of the same order of magnitude.

Calibration of the plates.

To determine the energies of the lines from the densities on the plate, one or two sets of calibration spectra were photographed on each plate. These spectra were obtained from a tungsten-filament lamp, the alteration of energy in one set being realized by varying the width of the slit of the spectrograph. It is evident that as the shift in frequency of the Ramanlines compared with the exciting lines is small, the actual problem of intensity-measurement is not essentially different from homochromatic photometry. Therefore the exposure times necessary to obtain Ramanspectrum, mercury-lines and calibration spectra need not be the same. For it follows from the experiments carried out by v. d. Held and Baars (25), that a variation of exposure time only means a parallel shifting of density curves. Although the amount of this shift may not be the same for all wavelengths (see e.g. Chapter III), we can not go wrong by assuming, that the displacement is the same for wavelengths which are very near one another. Notwithstanding the small difference in wavelength we have corrected for the slight difference in the plate-sensitivity. Therefore a calibration of the tungsten-lamp was necessary.

The background appearing on the plates was subtracted from the energy of Ramanlines after having determined the energy of this background from the measured density. To obtain exact results it is of great importance, that the energy respectively the density of this background is neither too large nor too small; in the first case the density of the lines differs too little from that of the ground and in the other case it is impossible to determine an exact value for the background, because of the general fact, that small densities can not give reliable results in our photometry.

Results of the measurements.

On the plates appeared the Ramanlines excited by the following mercury lines: 4047, 4078, 4358, 5461, 5770 and 5791 Å. With each of these lines the following frequency-shifts gave rise to Ramanlines: 215, 312 and 456 cm^{-1} (wave-numbers), Stokes lines as well as Anti-Stokes lines, except the mercury-lines 5770 and 5791 Å (yellow lines) where the Anti-Stokes lines were apparently not strong enough to give noticeable densities during the usual exposure times. Besides some other lines are too weak for being reliably measured in comparison with other correponding lines on the same plate. Moreover the plates which we have used show a maximum of sensibility in the vicinity of the yellow lines, and these lines being very near together some of their Ramanlines coincide. Both circumstances gave particular difficulties for photometry, the first since in such regions the energy is a rapidly varying function of wavelength and the second because an analysis of the coinciding lines is necessary, which analysis is a difficult one in the case of Ramanlines of which the contour is not exactly determined. As a consequence of these considerations only the Ramanlines excited by the mercury-lines 4047, 4358 and 5461 Å are measured. This must not be thought of as a restriction, since in any case the lines excited by 4078, 5770 and 5791 Å could not give really new information, because of their close vicinity to the lines measured.

For the Ramanlines just mentioned we have obtained the energies in the above mentioned manner and each of these energies has been divided by the energy of the corresponding exciting line. The ratios thus formed have been normalized in such a way, that the reduced energy of all the lines excited by 4047 Å are put equal to 100. This normalization has only a practical signification. The numbers acquired for the relative energies are given in table IV and V. For comparison the relative values of ν_{Hg}^4 and ν_R^4 are put into the tables, equally normalized on 100 for the lines excited by 4047 Å. (the frequencies of the lines are respectively: 24705, 22938, 18308 cm^{-1} (wave-number)).

TABLE IV.

Frequency-shift: $\nu_{mn} = 215$ (Stokes lines)

ν_{Hg}	exp.	ν^4_{Hg}	ν^4_R
24705	100	100	100
22938	72	74·3	74·1
18308	32	30.2	29.8

Frequency-shift: $\nu_{mn} = 312$ (Stokes lines)

ν_{Hg}	exp.	ν^4_{Hg}	ν^4_R
24705	100	100	100
22938	74	74·3	74·0
18308	30	30.2	29.6

Frequency-shift: $\nu_{mn} = 456$ (Stokes lines)

ν_{mn}	exp.	ν^4_{Hg}	ν^4_R
24705	100	100	100
22938	73	74·3	73·9
18308	31	30.2	29.4

TABLE V.

Frequency-shift: $\nu_{mn} = 215$ (Anti-Stokes lines)

ν_{Hg}	exp.	ν^4_{Hg}	ν^4_R
24705	100	100	100
22938	70	74·3	74·5

Frequency-shift: $\nu_{mn} = 312$ (Anti-Stokes lines)

ν_{Hg}.	exp.	ν^4_{Hg}	ν^4_R
24705	100	100	100
22938	74	74·3	74.6

Frequency-shift: $\nu_{mn} = 456$ (Anti-Stokes lines)

ν_{Hg}	exp.	ν^4_{Hg}	ν^4_R
24705	100	100	100
22938	75	74·3	74·7

Each of the results, mentioned in these tables is the mean value of repeated measurements. A comparison between the ratios obtained for the same exciting frequency but for different shifts ν_{mn} shows, that there is a relatively small spreading of the values. The evidence of an analogous behaviour of different Ramanlines authorizes us to make up the mean of the energies from different lines excited by the same mercury line. We get therefore the following mean ratios:

exciting freq.	24705	22938	18308
mean ratio	100	73	31

To find the function, which gives the dependence of the ratio of energy (E) on the exciting frequency (ν), we try: $E = A\nu^x$ where A is a constant and x the exponent to be examined. To solve this equation with respect to x we have made a diagram in

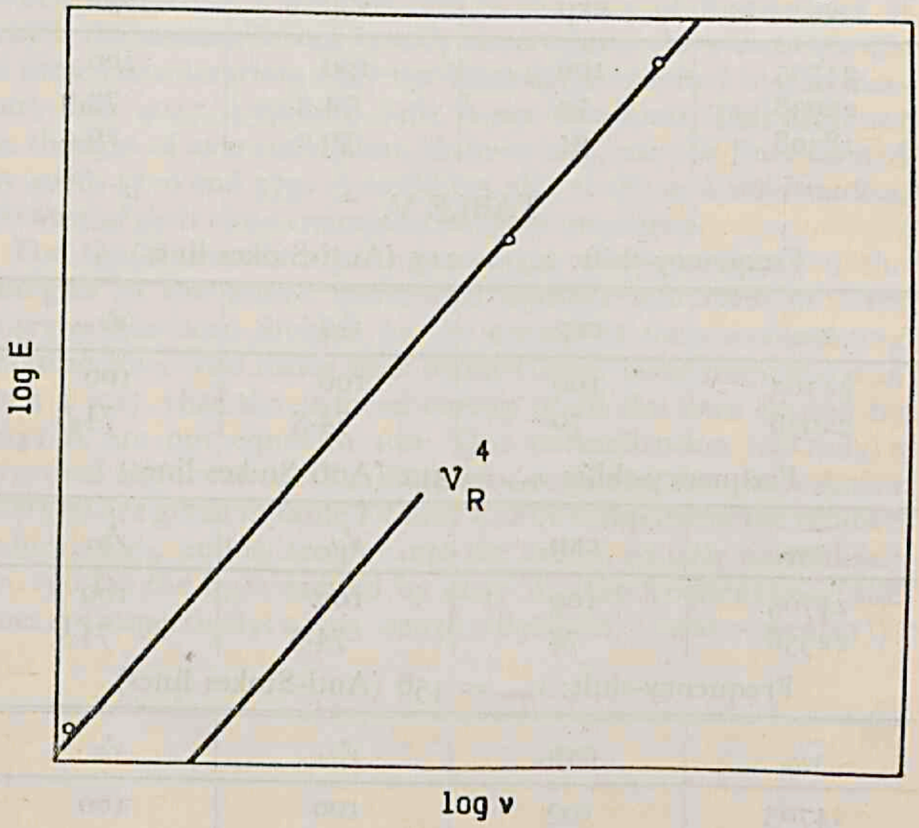

Fig. 3.

which $lg\ \nu$ is the abscissa and $lg\ E$ the ordinate. It is evident, that the slope of the line in this diagram immediately gives the value of the exponent x. A reproduction of this diagram is given in Fig. 3 and for comparison the line having a slope corresponding to $x = 4$ is also drawn in the diagram. It is very clear that the line, drawn through the experimental values is parallel to the line showing the slope for $x = 4$ and from this it follows, that the energy of Ramanlines increases as the fourth power of the exciting frequency.

This result obtained we can divide each value of the relative energy by the fourth power of the exciting frequency. Doing so we get for all lines numbers which are in good agreement with each other.

Discussion of results.

On assuming the validity of this fourth power law we have put into the tables IV and V the relative values of ν^4_{Hg} and ν^4_R. Now we have stated the dependence deduced from our experiments to be a fourth power law of exciting frequencies.

On comparing however the values of the fourth power of the frequencies of the mercury-lines and those of the Ramanlines we see at a glance, that there is only a very slight difference between the relative numbers. As a matter of fact a decision between the two assumptions is impossible. A dependence corresponding to the fourth power of the frequency of Ramanlines signifies a different behaviour for different frequency-shifts. This however is not apparent from the tables, no systematic progress being detectable for different lines. It is very clear that the difference just mentioned falls within the limits of error, obtainable by intensity measurements, because this difference is only of the order of about 1%. So all things considered we must leave open the possibility for both assumptions. Measurements with a substance where the frequency-shifts are much larger could possibly give a decision. We shall return to the question in the next chapter.

We choose the substance $C\,Cl_4$ because no absorption occurs in the visible or ultra-violet region. In the results no influence of an absorption can be detected. We are obviously too far away from the proper frequencies of the substance to perceive this influence. We will conclude this chapter with the remark, that the results of our experiments confirm the theoretical predictions about this question given by Placzek in the above mentioned formula.

In the next chapter we shall try to continue the researches about this problem especially as regards the influence of absorption frequencies of the substance.

CHAPTER III.

DEPENDENCE OF THE SCATTERED ENERGY IN RAMANSPECTRA ON FREQUENCY IN ABSORBING SUBSTANCES. 1)

Introduction.

We have shown in the foregoing chapter that in the case of $C\,Cl_4$ the scattered energy of a Ramanline increases according to a fourth power law just as with the classical phenomenon of unmodified scattered light. As has been shown there, however, the problem is not solved completely with this result.

We have namely pointed out, that the whole of the investigation must be divided into two parts by the occurence of absorption frequencies.

Now in the case of carbon tetrachloride we have made our experiments in a region far away from the absorption of this substance. In the following the second part of the question will be examined, viz.: the dependence of the scattered energy in Ramanspectra on frequency in a region which is fairly close to a proper frequency of the substance. The expectation that in this case a different law will hold has been suggested by the analogous case of the unmodified scattering, where in the regions just mentioned the fourth power law breaks down.

As we have made clear already, the formula given by Placzek (20)

$$E_S = (\nu - \nu_{mn})^4 \, \Sigma \frac{C_{jn}}{\nu^2_{jn} - \nu^2}$$

predicts an influence of absorption. The way the frequencies enter into this expression may be understood by the following considerations:

To explain the Ramanlines we assume a quantum of light with frequency ν to strike a medium. Part of the energy falling upon a molecule of the scattering substance will be absorbed by the molecule, the remaining energy being scattered as light of a

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1) See: J. Rekveld, Zs. f. Phys. 68 (1931), 543.

frequency differing from ν. The energy absorbed is used by the molecule for the transition from state m to state n, the latter state having the higher energy.

We must now assume as has been stated theoretically and also has been made clear by the experiments giving a selection principle for the Ramanlines, that this transition between the states m and n is not a direct one, but is performed via an intermediary state j which can combine with both states m and n.

To deduce the formula for the intensity of a Ramanline we must therefore consider all transitions m to n combined with all intermediary states j provided they are not forbidden transitions. In order to arrive at an expression representing this intensity we can use anyone of the dispersion theories given by LADENBURG, KRAMERS or SCHRÖDINGER which do not differ essentially. The probabilities of all possible transitions will enter in the formula.

It will be very clear that an influence of absorption frequencies will occur in the expression for the scattered energy of the Ramanline and this will take the form as is usual in dispersion-formulæ, i.e. the well-known resonance-denominators of the type $\nu^2_{jn}-\nu^2$.

This means, however, that in the vicinity of the absorption frequency the energy of the modified scattering will increase more rapidly than according to a fourth power law.

Experimental.

For the problem under investigation at first sight one might think that a great many substances be suitable. On second thoughts, however, conditions arise from experimental point of vieuw.

In the first place the Ramanspectrum must be fairly strong, but absorption may not be too strong, because in that case the lines would become too weak in the vicinity of the region of the absorption.

The absorption line must be narrow, so as to enable us to get very near the maximum of absorption. It is further desirable that the absorption line occurs either in the infra-red or in the remote ultra-violet parts of the spectrum. Further it is of great importance that the substance in question is not altered by photochemical reaction particularly when using ultra-violet light. For this reason it was impossible to use the liquid carbon tetrachloride for this investigation as was obvious from some preliminary experiments.

Most of the conditions mentioned are fulfilled rather well with methyl-alcohol. In his publication about ultra-violet absorptions Henri (26) gives the position of an absorption maximum of methyl-alcohol near the wave-length 2200 Å, the intensity of the absorption not being very strong. The Ramanspectrum has been measured by several scientists and they found that only one very strong line appears on the photographs. The frequency-shift of this line amounts to 2832 cm^{-1} (wave number). The line is a doublet with components of equal intensity, but being a very narrow one we get only one point for our determination of the dependence of scattered energy on frequency.

As the mercury-lamp itself gives a great many lines in the ultra-violet region, the fact that only a few or even only one Ramanline arise from each exciting line is of great practical importance.

Method of exciting Ramanlines.

Being forced to work in the ultra-violet region of the spectrum, we had to alter the apparatus and the method described in the foregoing chapters accordingly.

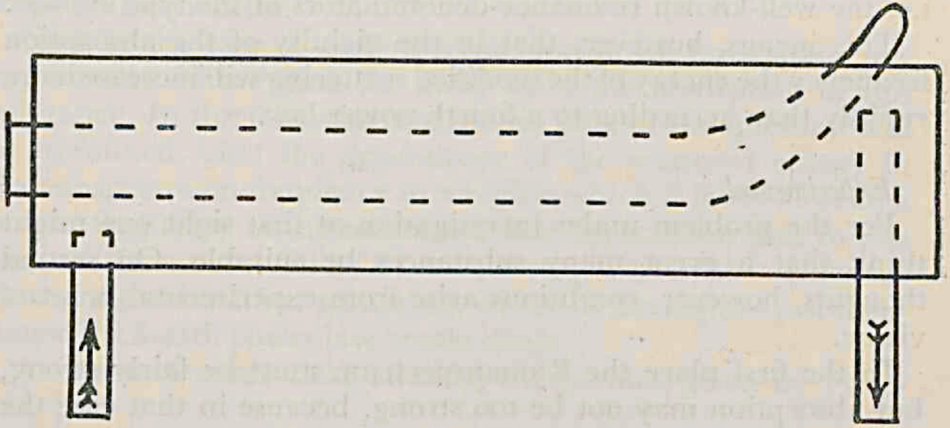

Fig. 4.

The tube containing the liquid was of the usual type first indicated by Wood (23) and was made of quartz with a plane window of quartz fused on at one end. To cool the liquid the tube was placed in a small receptacle of tin-sheeted iron with in- and outlet-pipes for watercirculation from the main (see e.g. Rao (28) and fig. 4).

This receptacle was open at the top and the inside was painted dull-black to avoid reflexions from the incident light; for this reflected energy would to an unknown extent form part of the energy giving rise to the Ramanlines which part can not be taken into account in determining the relative energies of the mercury-lines radiated from the lamp.

In accordance with the size of the mercury-arc we painted a part of the tube, which has a total length of about 20 cm and a diameter of 2 cm, leaving thus only $12^1/_2$ cm open for the incident light.

We may therefore assume if we wish to take the absorption corrections into account that pro unit of volume the incident and therefore also the scattered energy is a constant for a given wavelength.

The aluminium-reflector placed over the mercury-lamp was covered with a layer of magnesium-oxyde in order to obtain a diffuse, non metallic reflexion. The purpose of this will be explained in the following.

The photographs were taken with a Hilger-quartz-spectrograph (type E_2) which is very powerful and gives a good dispersion in the ultra-violet necessary for avoiding a too strong continuous background on the plates. This spectrograph was placed directly in front of the plane window of the investigation-tube, without lenses. The lenses of the spectrograph being entirely filled by this arrangement we have no loss of intensity in the exposures and moreover we are able to work without the usual lenses which are not achromatic for the whole region, as is required for our measurements.

The exposure time for obtaining suitable densities was about 7 hours. These photographs were taken on Ilford Special Rapid Plates.

Determination of the energy of the mercury-lines.

As the principle of the method used in this investigation is quite the same as that described in Chapter II we must now determine the relative energies of the mercury-lines. This is done in the following way:

The tube filled with liquid was replaced by a thin plate of black-backed amorphous quartz reflecting the light from the mercury-lamp in the direction of the slit of the spectrograph. The amount of the reflexion must, of course, be known. This can be easily calculated by means of the formulæ given by FRESNEL, assuming that the light falling upon the quartz-plate is unpolarized.

To make sure of the correctness of this assumption we covered the reflector of the lamp with magnesium-oxyde, then getting rid of the metallic polarized reflexion and obtaining a diffuse unpolarized reflexion of the mercury lines.

To avoid complicated calculations necessary for the evaluation of the reflexion of cristalline quartz we used a plate of amorphous quartz.

The time of exposure, though increased through the use of reflected instead of direct light, would of course have been still exceedingly small. But as we must take density-marks with the same time of exposure (see further on) this must at least amount to a measurable duration. So, to reduce the light to the intensity required we applied a diaphragm of which the holes were big enough to avoid diffraction.

Because of the fairly great distance between the exciting line and the Ramanline with each wave-length, the method of photometry is essentially different from that described in the preceding chapter.

There we could apply the method of homochromatic photometry because the distance of the Ramanlines from the exciting lines amounts at the most to about 100 Å. Of course a correction must be applied for the variation of plate sensitivity, even over this short distance.

In the case however of methyl-alcohol the distance between Ramanlines and exciting mercury-lines varies from 200 to 300 Å. Taking into account the strongly decreasing sensitivity of the plate and other properties which are of importance in photometry, e.g. the variation of the Schwarzschild-constant p, it is necessary to measure the lines separately and to combine the measured intensities. This means however that it is necessary to apply a method of heterochromatic photometry. We have determined the relative energies of the mercury lines and also those of the Ramanlines; the ratios between corresponding energies give values which represent the energy of a Ramanline in the energy of the exciting line as a unit.

We will now give a more detailed description of the way followed in our experiments in order to carry out the heterochromatic photometry in the ultra-violet region of the spectrum.

Heterochromatic photometry in the ultra-violet.

The problem is as follows: of the photographs of two or more spectral lines of different wave-lengths the densities, arising in the same time, on the same plate and using the same apparatus, are given. Determine the ratio of the energies of these lines.

If the lines do not differ in wave-length it is sufficient to take on the same plate, with an exposure-time which may vary within certain limits with regard to that of the lines, a series of density marks, caused by a light source which gives a continuous spectrum when one prefers to graduate the steps with the aid of the method of slit-widths variation. This light source need not be constant if only the different steps of one series are taken simultaneously.

In the problem of heterochromatic photometry, however, the distribution of the energy in the source of light must be known as we need a definite radiation which we can reproduce at will, knowing its dependence on external conditions. We used for this purpose a quartz-lamp with tungsten-ribbon in order to have a source also suitable for the ultra-violet part of the spectrum. For calibrating this lamp we used the Utrecht-method which gives the true temperature of the lamp as a function of the current used. To obtain the various steps of energy required to get a series of density marks with a fixed temperature of the lamp, we used the method of slit-widths-variation. We assume that the energy thus active on the plate is proportional to the width of the slit, provided the latter is not so narrow that diffraction-effects occur. As will be explained further on, it is necessary to use the same time of exposure for the calibration-spectra as for the spectrum under investigation. Since for our experiments the exposure time for the Ramanlines was several hours we have tried to find out a method for obtaining a set of density marks in one single exposure. For this purpose we made use of a "step-slit", first applied by ELLIOTT (21).

This consists of six short slits of different widths which form a geometric progression. The widths of these steps were determined by direct measurements with a comparator. This step-slit was placed immediately in front of the proper slit of the spectrograph, which was opened as far as possible. This method has the same advantages as that with the so-called step-reducers but without the complication of being dependent on wavelength. Of course care must be taken to prevent the light passing through the step-slit from filling the lenses and the prism of the spectrograph, for then the proportion between the energies falling on the plate would not be the same as that of the slit-widths.

It is also of fundamental importance to have a homogeneous distribution of light on the slit of the spectrograph. As we have not used lenses during the exposures, this homogeneity is easily obtained by putting the tungsten-lamp at a relatively great distance from the slit of the spectrograph. Moreover, a distribution at random was made of the widths over the step-slit in order to detect irregularities of this kind or of those caused by other circumstances such as sensitivity or treatment of the plate. Since we have investigated a rather large range of wavelengths one series of calibration spectra is, for two reasons, not sufficient. First, the sensitivity of the plate decreases with shorter wavelengths, and secondly the energy of the lamp falls off very rapidly towards the region of shorter wavelengths. Generally speaking a given set of density marks can therefore be used for one single wavelength only, and for the whole range different sets must be taken on the plate.

To obtain the other series various ways are open to us.

a. The placing of a diaphragm in front of the constant light-source. This way may be convenient for a narrow range of wave. lengths, but when an alteration is necessary within a wider range the margin of the variation is not sufficient, especially considering that when the opening of the diaphragm is too small, diffraction effects may occur and, because of their dependence on wavelength, may alter the distribution of energy.

b. Variation of the distance between light source and slit of the spectrograph. This arrangement has also the disadvantage of not being applicable over the wider ranges occurring in our experiments. Moreover, the way in which the light fills the spectrograph would be different for various distances if the same apparatus is used.

This can give rise to errors in the comparison between lines and marks as in both cases the light must fill the spectrograph in the same way.

c. Variation of the time of exposure.

This method would be fundamentally wrong, although it has often been applied by others. The reason for this may be traced to a wrong interpretation of the facts published by v. D. HELD and BAARS (25) about parallelism of density-curves with variation of exposure-time. Their experiments show that if the variation does not exceed a factor 1000, the density-curves are parallel. From this it is obvious that in homochromatic photometry the exposure time may differ for spectrum and density marks as this means only an additional factor for the energy in all the measured lines which is not essential in making up their ratio. For heterochromatic photometry the circumstances are totally different. In the latter case not only the parallelism is of great importance but also the question whether for different wavelengths the curves are shifted to the same amount or not. It can easily be seen that the shift is not determined by the same factor for different wavelengths, if we assume, for instance, the law of SCHWARZSCHILD to be valid. According to this law the density D is given by the equation $D = C\,E\,t^p$ or $lg\,D = lg\,C\,E + p\,l\,g\,t$. The above mentioned facts are easily understood from this formula: alteration of t only enters into an additional term and means a parallel shift of the curve which gives $lg\,D$ as a function of $lg\,E$, the amount of the shift being $p\,l\,g\,(t_2 - t_1)$. The question whether this shift depends on wavelength is now reduced to the dependence of the exponent p on wavelength.

As may be generally known, however, p varies fairly strongly with wavelength. In order to illustrate this fact we have determined for a number of wavelengths the value of p for a given plate. These values have been obtained by drawing isochromates (density curves for one definite wavelength) with different exposuretimes; the factor of shifting gives at once a determination of the value of p using the formula of SCHWARZSCHILD as given above. The results are given in the table VI and in figure 5.

TABLE VI.

Wavelength	2450 Å	2532 Å	2667 Å	2850 Å	3062 Å
Value of p	.76	.77	.80	.88	.90

These results will probably vary with the treatment of the plate, certainly they do so when using other plates. It would therefore be necessary to determine for each plate the values of p by this method, which would be tedious work and moreover a source of errors that had better be avoided. From these considerations and experiments it is very clear that to obtain accurate results the times of exposure for calibration-marks and spectrum must be equal in heterochromatic photometry, and that in any case an alteration of exposure time without further ado is not allowed.

d. Variation of the current of the lamp, i.e. of the temperature. This method leaves enough room for very large ranges of wavelength, because of the strong increase of energies with rising temperatures. In our case, with a variation between the limits 10 and 15 Ampères we could obtain good density curves over the whole range. We may explain this method more in detail, especially as regards the question of how to find the energy distribution with a given temperature, and how to combine the distributions corresponding to different temperatures.

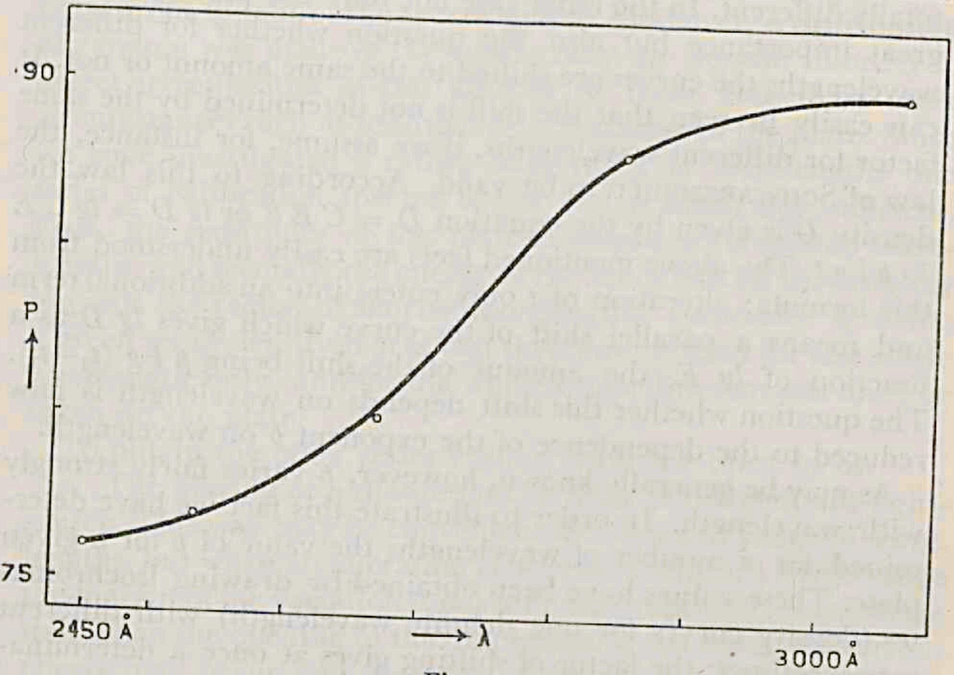

Fig. 5.

If we consider the radiation to be sent out by a black body the law of Planck gives the energy $E(\lambda, T)$ as a function of λ and T in the form $E(\lambda, T) = C_1 \frac{\lambda^{-5}}{e^{C_2/\lambda T} - 1}$ or remembering that $E_{max}(T) = C_3 T^5$ $\Big[$$E_{max}(T)$ means the maximum of energy for a given $T$$\Big]$: $\frac{E(\lambda, T)}{E_{max}(T)} = C_4 \frac{(\lambda T)^{-5}}{e^{C_1/\lambda T} - 1} = f\}(\lambda T)\{$.

This expression gives the energies, with E_{max} as a unit, as a function of the product λT. This function may be drawn once for all. In the case of a black body and various temperatures, the energy corresponding to a given wavelength is easily found by multiplying the energy from the diagram by a factor proportional to T^5.

Now in our lamps the ideal case of black-body-radiation is not realized and some corrections must be applied to the energy thus determined. This is usually done for the visible part of the spectrum by introducing for each temperature of the lamp a so-called colour temperature. This colour temperature represents the true temperature of a black body to which the same distribution of energy would correspond as the lamp actually possesses at its true temperature. Up to the present time the possibility of introducing a colour temperature for the ultra-violet has not been tested experimentally, and anyhow it is certainly impossible to render the whole range of the spectrum from the utra-violet to the visible part by assuming a colour temperature.

Therefore we have used the true temperatures of the lamp, but have also applied corrections for the emission of tungsten. This emission coefficient $e\ (\lambda, T)$ is also a function of λ and T and its value as a function of wavelength and temperature have been measured by many physicists, the results being in good agreement with each other. By multiplying the energies from the diagram above mentioned by T^5 and by $e(\lambda, T)$ the distributions of energy for all currents of the lamp and all wavelengths are known. Finally, the usual correction for the varying dispersion of the spectrograph must be taken into account. If we take this dispersion d to be Ångström per millimeter, it is very clear that the energies mentioned above must be multiplied by a factor proportional to this dispersion. Summing up, we have thus for the relative energy at a given wavelength active on the plate

$$\frac{E(\lambda, T)}{E_{max}} \cdot T^5 \cdot e\,(\lambda, T) \cdot d$$

The densities were measured with the Moll self-registering microphotometer and so for each wavelength the relation between energies and densities is known, and the energies as function of the wavelength as well. From the densities of the lines given by these curves the relative energies of the lines were deduced.

To check the entire method, especially the corrections which have been applied as described above, we made several tests in the following way. Isochromates were made, i.e. for two temperatures of the lamp the density curves are drawn, obtained from the two corresponding sets of density marks at the same wavelength. When all corrections have been carried out these two curves ought to be identical. This check has given satisfactory results in many cases.

Finally we must draw attention to the fact that it is not necessary to carry out this work for all wavelengths occurring in our measurements. It is sufficient to pick out a few wavelengths from the range to be examined, being careful as to where the sensitivity of the photographic plate has an extreme value. The curves obtained for these few wavelengths enable us to draw diagrams representing the energy as a function of wavelength for each density. The density curve for a given wavelength may be easily found afterwards by interpolation from the energy-wavelengths diagrams.

Corrections.

We have thus determined the relative energies of both the mercury-lines and the Ramanlines.

Now the following corrections must be applied to these energies:

a. All mercury-lines have been measured by means of reflexion on quartz. Therefore it is necessary to calculate the coefficients of reflexion of amorphous quartz, which is easily done, using the FRESNEL-formulæ. The measured energies of the lines must be divided by these coefficients. The values thus corrected represent the relative energies of the lines as they fall on the investigation-tube.

b. For some of the mercury-lines a small correction must be applied in order to account for the slight weakening by the absorption of the light on its path from the wall of the tube to the axis. As already mentioned, the shape of the scattering volume of the substance is nearly cylindrical, the diameter of it being a fraction of that of the tube. So in taking the absorption-correction just mentioned, we have a sufficient mean for the whole diameter. This correction amounts to only a few percents.

c. The measured energies of the Ramanlines must be corrected for the absorption of the scattered energy of each element of volume, on its way from this element to the window of the tube. To obtain these corrections we first remark that by our method of investigation the whole scattering volume of the tube is exposed to homogeneous radiation. The diffuse reflexion from the reflector covered with magnesium-oxyde does not depend on wavelength. And therefore we may assume that the distribution of energy over the wavelengths is the same for each element of volume of the tube, which is under irradiation and that for each wavelength the incident energy is the same for each element of volume. Therefore the energy scattered by each element per unit of incident energy is independent of the position of the element, and depends only on the law of scattering, holding for the particular wavelength considered.

If we consider a unit of volume at distance x from the window, the intensity I of the light passing through the window will be connected with the intensity I_0 scattered per unit of volume by the formula

$I = I_0 \,.10^{-\varepsilon c x}$ ($\varepsilon =$ molecular coefficient of extinction, $c =$ concentration of the substance in mol/liter). Thus, the relative energy I_R falling on the slit per unit of area is given by

$$I_R = \frac{I_0 \; 10^{-\varepsilon c x}}{x^2}$$

Therefore, the total amount of relative energy, scattered by the whole volume is expressed by integrating the foregoing formula over the axis of this volume. By dividing the energies obtained for the Ramanlines by the value of this integral, the influence of the absorption is eliminated. We have calculated the integrals graphically.

Results.

The exciting mercury-lines have the following wavelengths: 2537 Å, 2652 Å, 2894 Å, 2967 Å, 3022 Å, 3126 Å.

As already mentioned, each of these lines gave rise to one strong Ramanline with a frequency-shift $\nu_{mn} = 2832$ cm^{-1} (wave-number) corresponding to an infra-red absorption band near to 3.5 μ. The positions of the Ramanlines which we have measured are therefore: 2733 Å, 2866 Å, 3152 Å, 3239 Å, 3305 Å, 3430 Å.

The corrected ratios for the energies of Ramanlines and exciting lines are given in Table VII.

TABLE VII.

Wavelength of *R*-line	2733 Å	2866 Å	3152 Å	3239 Å	3305 Å	3430 Å
ratio (*E*)	17.0	10.0	3.4	2.6	2.4	2.0

In order to make clear the meaning of these results we have drawn the diagram reproduced in fig. 6. where *lg E* has been chosen as ordinate and $lg\ \nu_R$ as abscissa. For comparison a line is drawn in the figure showing the function $E = C\nu_R^4$. The diagram shows that for the first two or three lines the fourth power law holds, but at shorter wavelengths, i.e. with greater frequencies the ratio increases much more rapidly than according to the

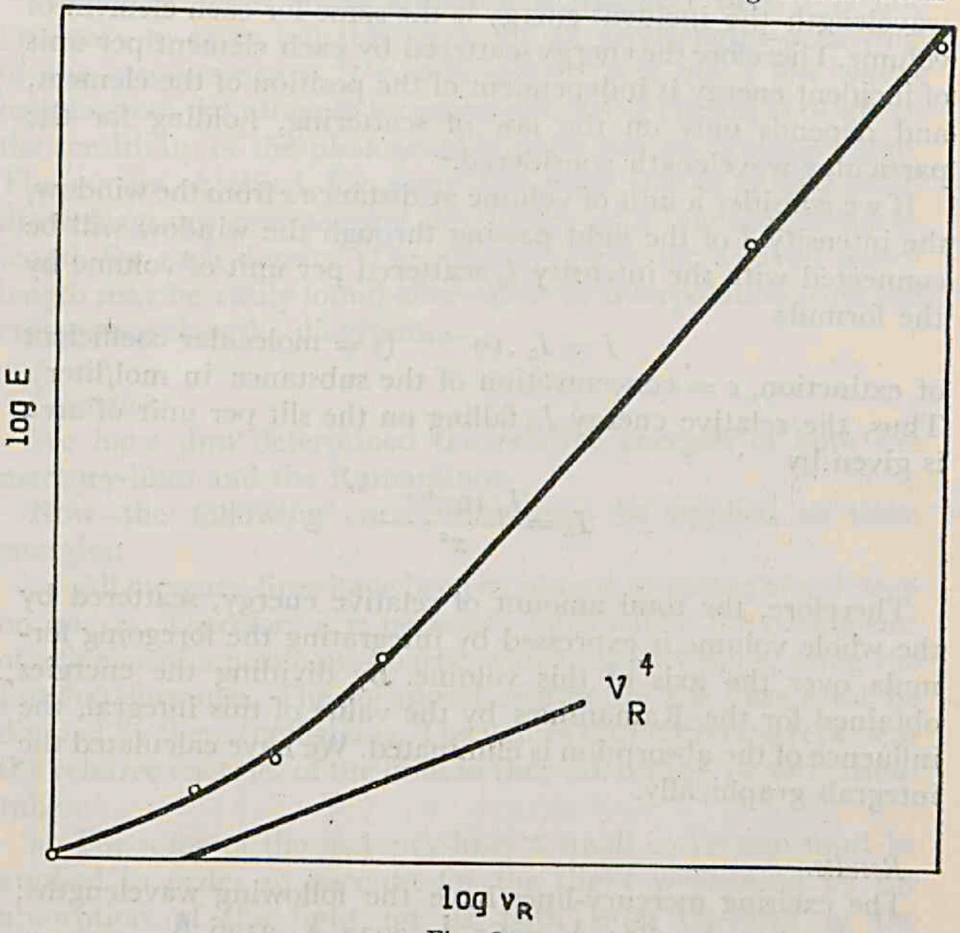

Fig. 6.

fourth power of the frequency. Although in this case, too, the values of ν_R^4 and ν^4 do not differ very much, the position of the first points of the diagram are decidedly in favour of the ν_R^4. We can hardly expect a still more convincing indication, for the differences between ν_R^4 and ν_{Hg}^4 will always remain relatively small.

We may, for this reason draw a conclusion which settles the question left open in the foregoing chapter and state that: in regions far from absorption frequencies the energy of a Raman-line increases as the fourth power of its own frequency.

If we now consider the formula given by Placzek (20) it is easily seen that qualitatively our results are in agreement with the theory. To examine this agreement more closely in a quantitative manner too, we assume that in the vicinity of one absorption-frequency the above given formula is simplified to:

$$E = (\nu - \nu_{mn})^4 \frac{C}{\nu_a^2 - \nu^2}$$

(ν_a = absorption-frequency and C is a constant). It must be mentioned however that this simplification involves a sharp maximum of absorption which does not occur in the case of methyl-alcohol and also that the other absorptions are remote from this one.

Moreover, the formula is, properly speaking, deduced for regions where absorption of the substance is absent.

We may assume for a moment the validity of the above expression, especially in the vicinity of the absorption-frequency considered. It must be possible to determine an approximate value of this absorption-frequency ν_a by computing the quotient of two ratios (E) representing the scattered relative energies.

We have carried out this division for the ratios obtained for the exciting lines 2537 Å and 2652 Å. We thus get the following calculations:

$$\frac{E_{2537}}{E_{2652}} = 1.7 = \left(\frac{\nu_{2537} + \nu_{mn}}{\nu_{2652} + \nu_{mn}}\right)^4 \frac{\nu_a^2 - \nu_{2652}^2}{\nu_a^2 - \nu_{2537}^2}$$

ν_a being the only unknown quantity. We found in this way

$$\nu_a = 43.900 \text{ cm}^{-1} \text{ or } \lambda_a = 2280 \text{ Å}.$$

This result agrees satisfactorily with the position of an absorption-maximum of methyl-alcohol indicated by Henri (26) near the wavelength 2200 Å. As no other absorption-maxima occur in this region we must identify both frequencies and assume that the transition giving rise to the Ramanline is connected with this proper frequency of the substance. Now the absorption-maximum just mentioned appears in the case of a great many substances and has been ascribed by HENRI to the group *C-H* which these substances have in common.

We conclude, therefore, that the Ramanline under consideration is characteristic for the group *C-H*. This fact has already been shown in different ways by several writers (see e.g. VENKATESWARAN and KARL (27)).

From these experiments an influence of the absorption-frequencies is made very clearly. We may state that, generally speaking, on approaching an absorption frequency of the substance, the scattered energy of a Ramanline, connected with the same group of the molecule as the absorption process, increases much more rapildy than according to a fourth power law.

In conclusion we draw attention to the fact that by our method a decision is possible about the question to which group of a molecule a Ramanline must be ascribed when the absorption spectrum of the substance is known and its frequencies have been ascribed to certain groups of the molecule.

CHAPTER IV.

DEPENDENCE OF THE SCATTERED ENERGY IN RAMANSPECTRA ON FREQUENCY FOR ACETON.

Introduction.

In the preceding chapters we have given the method and results of our experiments concerning the dependence of the scattered energy in Ramanspectra on frequency in two cases:

a. working with six Ramanlines of which the frequencies differ greatly from the absorption-frequency of the substance.

b. working with one Ramanline of which the frequency is close to the absorption-frequency of the substance.

To settle this question definitely we felt the necessity of examining the second problem once more, and this time with a substance in which each exciting line gives rise to two rather strong Ramanlines with each exciting frequency, whereas the lines do not belong to the same group of the molecule. For it was found in Chapter III that the line influenced by the absorption must be ascribed to the same group as the absorption process, and we have to show that other lines, not related with this absorption process, do not undergo such an influence. Moreover a confirmation will be obtained in this way for both cases because in the investigation which we are now going to describe the two parts of the problem are, to a certain extent, combined.

Experimental.

The substance used for these experiments was aceton ($C\ H_3\ C\ O\ C\ H_3$). Its absorption has also been measured by HENRI who found a strong absorption in the near ultra-violet with a maximum near 2700 Å. On one hand, therefore, the conditions of working are more favorable than in the case of methyl-alcohol because we can carry out the experiments for the greater part in the visible region of the spectrum and in the near ultra-violet. But on the other hand only a few exciting lines can be used because of the relatively strong absorption which prevents going below the wave-length 3650 Å. The light of each of the mercury-lines incident on the substance gives rise to two fairly strong Ramanlines, the corresponding shifts being 795 and 2925 cm^{-1} (wave-number).

The method followed in this research is exactly the same as that described in Chapter III, the apparatus, too, being similar. Of course, in order to get an idea of the different behaviours of the two lines, appearing with each exciting line, it would be sufficient to make up their ratio and then to see how it varies with different frequencies. If the ratio is not constant it means for our problem, that the influence of absorption differs with each Ramanline. A more quantitative result however showing the actual dependence for each line would not be obtainable on applying this method.

The method of photometring the plates and the evaluation of the densities has been the same as in the case of methyl-alcohol. Only one detail has been altered. To avoid the tedious calculations necessary for combining the several sets of density marks obtained by different currents of the quartz ribbon-lamp, we have taken one set giving in only a few steps at each wavelength of the whole range densities fit for use e.g. with longer wavelengths the narrower steps, with shorter wavelengths the wider ones must be used. In this way we have a few points at each wavelength and we can combine these points in the way described in the preceding chapter. In order to obtain the density curve passing through these points we have, moreover taken a few sets of marks giving at each desired wavelength densities enabling us to draw this curve. And thus the calibration of the plate is carried out completely.

Contrary to the case of methyl-alcohol the measurements on aceton did not require corrections for absorption.

Results.

We could measure the Raman-lines excited by the following mercurylines: group 3650 Å (i.e. 3650 Å, 3655 Å and 3663 Å), 4047 Å and 4358 Å. As the frequency-shifts are 795 cm^{-1} and 2925 cm^{-1} the Ramanlines appeared for the first shift near 3758 Å, 3763 Å, 3771 Å 4180 Å and 4514 Å and for the second shift near 4086 Å, 4093 Å, 4103 Å, 4595 Å and 4990 Å. Making up the ratio between the energies of a Ramanline and its exciting mercury-line we get the values given in table VIII and table IX. For the sake of comparison the relative values of ν^4_R are added to the tables. It must be remarked that some of the lines are in a very unfavorable position for the measurements because of their overlapping with other lines, or because of their being at a too short distance from mercury-lines. The results for these lines not being reliable, they have been omitted:

TABLE VIII.

Frequency-shift $\nu_{mn}=795\ \text{cm}^{-1}$

Wavelength of Ramanline	ratio (E)	ν^4_R
3758 Å	—	—
3763 Å	20.	20.7
3771 Å	—	—
4180 Å	14.	13.6
4514 Å	10.	10.

TABLE IX.

Frequency-shift $\nu_{mn}=2925\ \text{cm}^{-1}$

Wavelength of Ramanline	ratio (E)	ν^4_R
4086 Å	—	—
4093 Å	30.	22.1
4103 Å	28.	21.9
4595 Å	14.	13.9
4990 Å	10.	10.

We have given these results in the diagrams reproduced in fig. 7 and fig. 8, in which the lines corresponding to ν^4_R have also been drawn. We can gather from these diagrams that, in the case of the frequency-shift 795 cm^{-1} the fourth power law holds, but not with the other frequency-shift. Here with increasing exciting frequency the energy increases much more rapidly than according to a fourth power law. The different behaviours of the two Ramanlines are shown very convincingly in these results.

We might try, as we did in the case of methyl-alcohol, to determine the maximum of absorption indicated by the strong increase of the energy. The circumstances are, however, very unfavorable for this purpose. As already mentioned the absorption is very strong and prevents us from approaching nearer than 3650 Å. Now the position of the maximum as given by HENRI (26) is 2700 Å and in the case of the exciting line 3650 Å, too, we, are at a fairly great distance from the maximum, whereas in the case of methyl-alcohol we could approach the maximum to within about 350 Å.

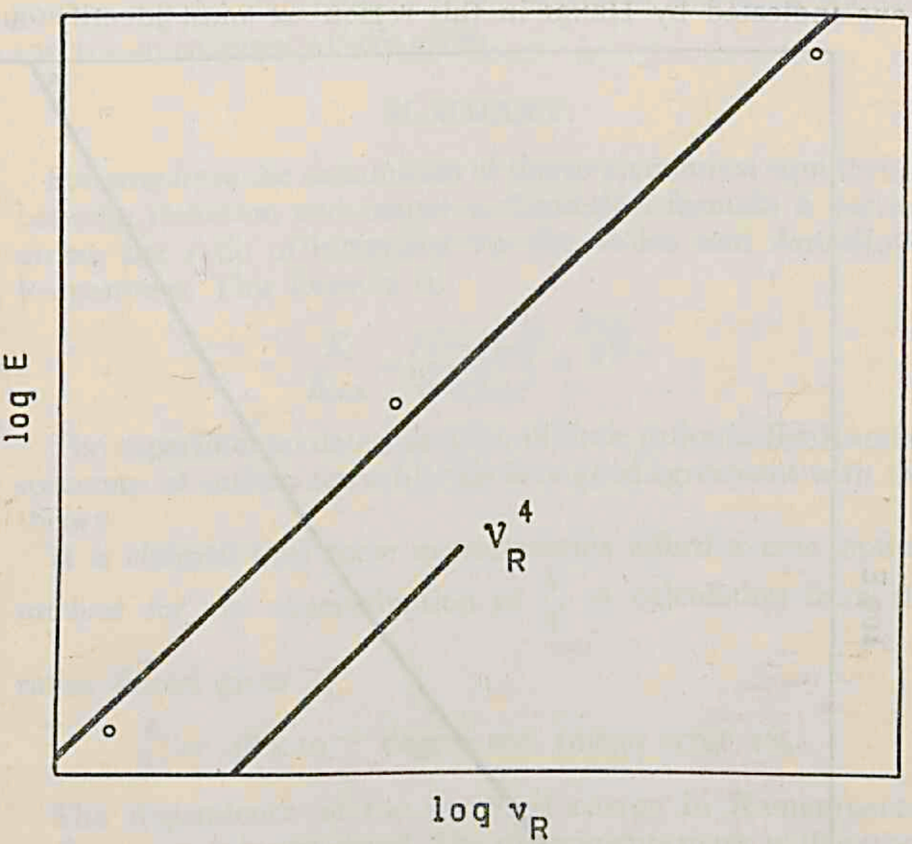

Fig. 7.

Yet we made an estimation of the influencing absorption wavelength by proceeding in the same way as described in Chapter III.

We have thus calculated the following expression:

$$\frac{E_{3663}}{E_{4047}} = 2.0 = \left(\frac{\nu_{3663} + \nu_{mn}}{\nu_{4047} + \nu_{mn}}\right)^4 \frac{\nu_a^2 - \nu_{4047}^2}{\nu_a^2 - \nu_{3663}^2}.$$

From this we get the value $\nu_a = 35.500$ cm^{-1} or $\lambda_a = 2820$ Å.

As no other absorption-maximum has been found but the one indicated by **Henri** in this region we must identify our

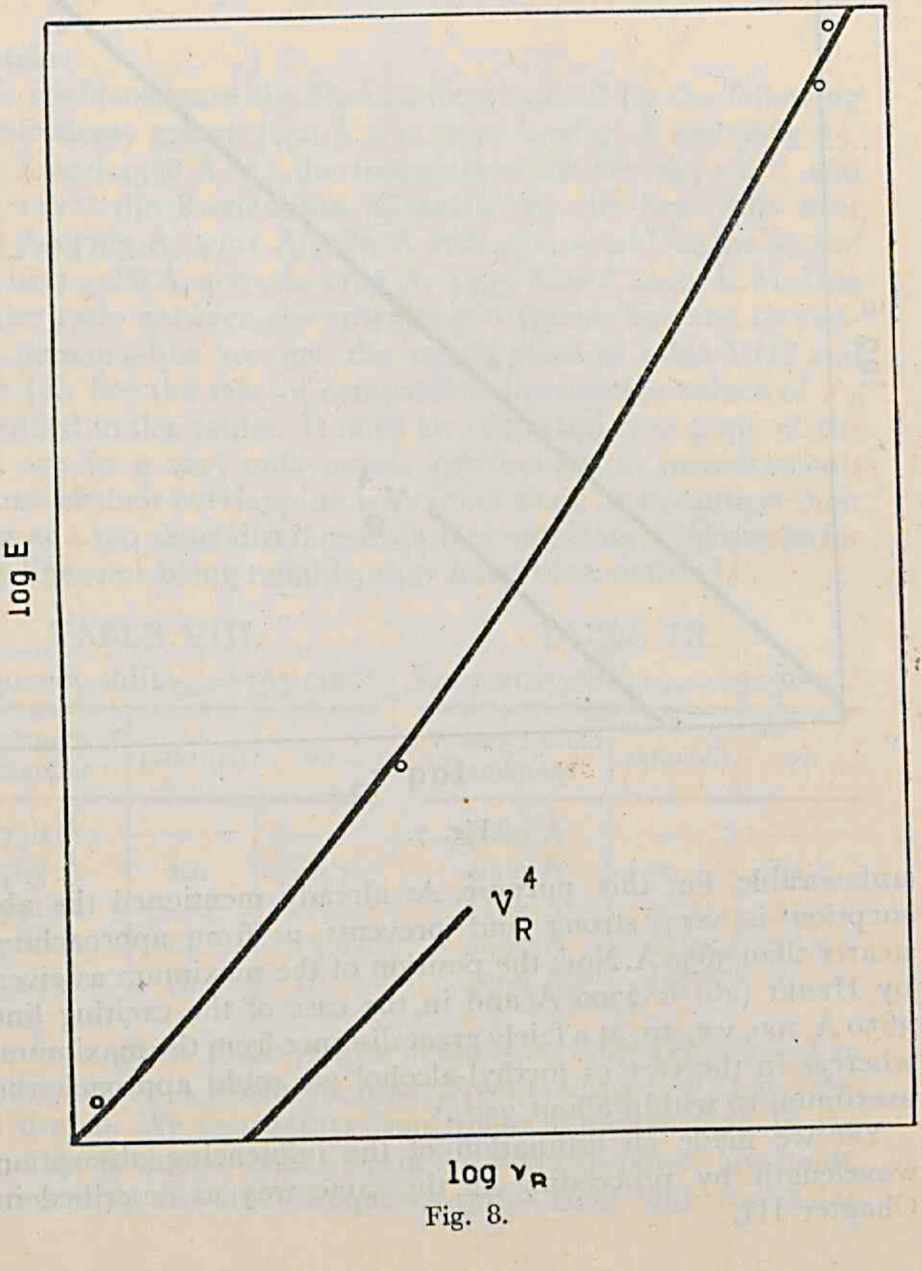

Fig. 8.

value with that given by him. This absorption has further been ascribed to the group *C-H* of the molecule aceton just as the Ramanline with a frequency-shift 2925 cm^{-1} is characteristic for the same group.

The experiments just described confirm strongly the results obtained in Chapters II and III and justify once more the laws concerning the dependence of the scattered energy in Ramanspectra on frequency there given.

SUMMARY.

Starting from the assumption of thermodynamical equilibrium between radiation and matter a theoretical formula is derived giving the ratio of intensities for the Stokes and Anti-Stokes Ramanlines. This formula is:

$$\frac{E_S}{E_{A.S.}} = \left(\frac{\nu - \nu_{mn}}{\nu + \nu_{mn}}\right)^4 e^{\frac{h\nu_{mn}}{kT}}.$$

The experimental determination of these ratios in the Ramanspectrum of carbon tetrachloride is in good agreement with this theory.

It is claimed that these measurements afford a new optical method for the determination of $\frac{h}{k}$. A calculation from the ratios found gives

$$\frac{h}{k} = .48 \times 10^{-12} \text{ degree sec. (mean error } 2\%).$$

The dependence of the scattered energy in Ramanspectra on frequency is investigated. The experiments made with carbon tetrachloride, methyl-alcohol and aceton show the existence of two regularities in this dependence.

a. When the exciting line lies in a region of the spectrum remote from an absorption-frequency of the substance, the scattered energy of a Ramanline increases as the fourth power of the modified frequency.

b. In the region of the spectrum near an absorption-frequency of the substance the scattered energy of a Ramanline increases much more rapidly than according to a fourth power of the modified frequency.

In the latter case, an estimate is made of the position of the

absorption-frequency, using a theoretical formula given by Placzek (20). The value found is in fairly good agreement with that given by Henri (26) which he obtained from absorption measurements. Moreover the results confirm the theoretical assumption, that the energy of a line is only influenced by an absorption-frequency when connected with the same group of the molecule as the absorption process itself.

A method for heterochromatic photometry in the ultra-violet is described.

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