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An Extension of the Polarizability Theory of Raman Effect

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The polarizability theory of Raman effect has two defects: (a) The depolarization factor ρ of Raman lines of totally symmetric oscillations of molecules can be given only by the indefinite statement $\rho<6/7$; additional utilization of the Silberstein model of optical anisotropy for a more precise prediction leads to wrong results. (b) The depolarization factor of the totally symmetric lines of calcite and aragonite should be zero for every orientation of the crystals, whereas finite values are observed for some orientations. The following cure is proposed. It is assumed that the atomic polarizability α is dependent on the exciting field strength E ($\alpha=\alpha_0+\beta E^2$). In the crystals, it is furthermore assumed that a disturbing field exists which depends on crystal symmetry. With these assumptions, it is possible to account for the observed results without changing the fundaments of the polarizability theory.

I. INTRODUCTION

THE well-known Placzek theory of Raman effect is based upon the suggestion that Raman scattering is due to changes in polarizability of molecules during vibration or rotation. This theory was very successful in describing and explaining many observed facts of importance, and it was also very helpful in giving information about molecular structure. There are, however, some topics apparently resisting this theory in its usual form. Some of these can easily be described in terms of this theory, without altering any of its main features other than by addition of such well founded concepts as anharmonic forces, quantum-resonance energy, and others. Of the remaining discrepancies, some minor ones may be due to the approximate character of some theoretical statements, but there are at least two items where observation and theory essentially disagree, so that for a long time it seemed hopeless to account for them in terms of the Placzek theory even if slight modifications or better approximations might be possible. These two main problems may be stated as follows.

(a) It is known that the depolarization factor[1] ρ of the coherent Rayleigh scattering can be computed from the assumption that scattering is produced by the induced dipole oscillating with the frequency of the incident radiation and that in addition to this the induced dipole moment is different in different directions of the molecule because of the mutual influence of the dipoles induced in the atoms of the molecule (Silberstein's model of optical anisotropy). According to theory, we should be able to compute the depolarization of Raman lines in a similar way by substituting the change of the polarizability for the induced moment into the equations of Rayleigh scattering. This treatment, though wholly in agreement with the fundamental principles of Placzek's theory and though successful in general statements, nevertheless fails if it is applied even to such simple molecules as H_2, O_2, and others.[2] E.g., for O_2 we observe $\rho=0.26$; the general theory gives $\rho<6/7$ as for all totally symmetric oscillations; computation as indicated above, with the aid of the Silberstein model, however, yields $\rho=0.63$. If it is not possible to explain this apparent failure of the polarizability theory in terms of this theory itself, we must abandon either the simple notion of mutual dipole action or the polarizability theory itself, each of which is very efficient in other respects.

An attempt to elucidate this problem in the light of existing theories has been made by Matossi,[2] in assuming that not only the molecular polarizability but also the atomic one depends on the distance between the atoms. In this purely phenomenological way, we are able to account

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[1] ρ is defined as ratio of the intensity components of scattered rays vibrating perpendicular and parallel to the direction of incident rays.

[2] Cf. J. Cabannes and A. Rousset, J. de phys. et rad. **1**, 155, 181, and 210 (1940); F. Matossi, Physik. Zeits. **45**, 304 (1945) (see supplement).

for the observed depolarization factors. The change of atomic radius during the vibration, corresponding to the change of atomic polarizability, is only two to five percent (cf. the supplement). But a stronger foundation for the just-mentioned assumption was still missing.

(b) The normal theoretical treatment of the depolarization of those Raman lines which correspond to the totally symmetric pulsation of the CO_3 group in carbonates (1087 cm^{-1}) always leads to $\rho=0$, regardless of what orientation of crystal axes with respect to directions of incidence and observation is chosen. Experimental observation, however, indicates the contrary.[3] According to Michalke, we have for calcite $\rho_x=0$, $\rho_y=0.4\pm0.1$, $\rho_z=0.2\pm0.05$, where the indices x, y, z indicate the orientation of the optic axis, this being, respectively, parallel to the direction of incidence (x), observation (y), and perpendicular to both (z).

(c) It will be shown that it is possible to account for both of these discrepancies, if we assume that the atomic polarizability is not independent of the inducing electric field, but that the induced moment $\mathbf{p}$ may be written

$$\mathbf{p}=(\alpha_0+\beta E^2)\mathbf{E}, \quad \text{with} \quad \beta E^2 \ll \alpha_0. \tag{1}$$

In this equation, $\mathbf{E}$ is the electric field strength, $E=|\mathbf{E}|$. The justification (and necessity) of this hypothesis,[4] particularly the quadratic dependence of the polarizability on E, follows from the dispersion theory of anharmonic oscillators in third approximation.[5]

Furthermore, in the case of the carbonates, there must be assumed a disturbing field, homogeneous over the region of a CO_3 group, and not dependent on time (or at most slowly variable), its direction being determined by symmetry conditions. One might at first attribute the disturbance to a field emerging from the central atom of the plane CO_3 group, but here again the symmetry prevents an influence of this nonhomogeneous field on the depolarization factor—hence the assumption of a homogeneous field, which may alter its strength and direction slowly compared with the time of oscillation.

We may imagine the disturbing field as representative of the deviations of the central field from exactly trigonal symmetry or as the resultant field of the neighboring atoms, these never being perfectly regularly distributed because of their vibrations and the non-ideal lattice.

We shall show that in the case of the crystals it will be sufficient to take notice only of the disturbing field without considering the mutual influence of the atoms. Taking the latter condition also into account would make computation very laborious and difficult to survey. We shall be content to obtain at least a possibility of explaining the above-mentioned results of observation without going into a too detailed quantitative treatment.

II. DIATOMIC MOLECULES

A simple calculation in a first approximation applied to Eq. (1) according to Silberstein's procedure,[6] leads to the following expressions for A_1 and B_1, the polarizabilities of the molecule of type X_2 parallel and perpendicular to its axis, respectively (we omit the index 0 at α_0 for sake of simplicity):

$$A_1=A_0\left\{1+\epsilon\left(1+\frac{A_0}{r^3}\right)\times\left[E_r^2\left(1+\frac{A_0}{r^3}\right)^2+E_n^2\left(1-\frac{B}{2r^3}\right)^2\right]\right\}, \tag{2a}$$

$$B_1=B_0\left\{1+\epsilon\left(1-\frac{B_0}{2r^3}\right)\times\left[E_r^2\left(1+\frac{A_0}{r^3}\right)^2+E_n^2\left(1-\frac{B}{2r^3}\right)^2\right]\right\}, \tag{2b}$$

in which $A_0=[2\alpha/1-(2\alpha/r^3)]$ and $B_0=[2\alpha/1+(\alpha/r^3)]$ are the polarizabilities for $\epsilon\equiv\beta/\alpha=0$, i.e., the normal Silberstein formulae. E_r and E_n are the components of the field strength of the

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[3] D. Osborne, Thèses (Paris 1932); H. Michalke, Zeits. f. Physik **108**, 748 (1938). These authors disagree in the details but agree in the statement that ρ is not always vanishing. We use Michalke's data.

[4] Originally (cf. Naturwiss. **33**, 190 (1946)), we had used a linear function for α, $\alpha=\alpha_0+\beta E$, for which there is no theoretical foundation. The results (not published) are different only in quantitative respect.

[5] Cf. F. Matossi, Physik. Zeits. **40**, 323 (1939); the underlined terms of Eq. (8) of this paper, neglected there, are essential now.

[6] L. Silberstein, Phil. Mag. **33**, 92, 521 (1917); cf. also S. Bhagavantam, *Scattering of Light and the Raman Effect* (Chemical Publ. Company, Inc., New York, 1942), p. 101 ff.

In deriving the Eqs. (2), the induced dipole moment is given its value for $\epsilon=0$ in all terms containing ϵ as a factor.

incident wave parallel and perpendicular to the molecular axis; r is the distance between the two atoms.

Because of the smallness of ϵ, the terms containing ϵ are irrelevant for the computation of A_1 and B_1 themselves; therefore, the depolarization factor of Rayleigh scattering still is practically determined by A_0 and B_0. But for Raman scattering, the depolarization factor of which is given by the derivatives of A and B with respect to the normal coordinate, the case is different.

Abbreviating

$$\epsilon\left(1+\frac{A_0}{r^3}\right)=\epsilon_1,\quad \epsilon\left(1-\frac{B}{2r^3}\right)=\epsilon_2,$$
$$E_r/E=v,\quad E_n/E=w, \tag{3}$$

we obtain

$$A_1=A_0\left(1+\frac{{\epsilon_1}^3}{\epsilon^2}v^2E^2+\frac{\epsilon_1{\epsilon_2}^2}{\epsilon^2}w^2E^2\right), \tag{4a}$$

$$B_1=B_0\left(1+\frac{{\epsilon_1}^2\epsilon_2}{\epsilon^2}v^2E^2+\frac{{\epsilon_2}^3}{\epsilon^2}w^2E^2\right). \tag{4b}$$

Differentiating these expressions with respect to the normal coordinate q of the vibration and denoting these derivatives by a prime, we have

$$A_1'=A_0'+2\left[\frac{{\epsilon_1}^3}{\epsilon^2}v^2+\frac{\epsilon_1{\epsilon_2}^2}{\epsilon^2}w^2\right]A_0EE', \tag{5a}$$

$$B_1'=B_0'+2\left[\frac{{\epsilon_1}^2\epsilon_2}{\epsilon^2}v^2+\frac{{\epsilon_2}^3}{\epsilon^2}w^2\right]B_0EE'. \tag{5b}$$

In these equations, we have neglected all terms of higher order which do not contain E' because of their smallness compared with A_0' and B_0'. However, it is not permissible to neglect terms with ϵ_1E' and ϵ_2E', since it is possible that $E'A_0$ and $E'B_0$ may become large relative to EA_0' and EB_0'. For if we have

$$E=E_0|\sin\omega t|,\quad q=q_0\sin(\omega_0t+\Delta), \tag{6}$$

E_0 and q_0 being the amplitudes of light-wave and molecular vibration and Δ being an arbitrary phase constant, we obtain

$$E'=(dE/dq)_{q=0}$$
$$=(E_0\omega/q_0\omega_0)\cos(\omega/\omega_0)(n\pi-\Delta), \tag{7}$$

in which n is an integer. By comparing E' with $E_{q=0}=E_0|\sin(\omega/\omega_0)(n\pi-\Delta)|$, we obtain for the ratio $E'A_0/EA_0'$ the expression $\omega A_0/\omega_0q_0A_0'\approx10^2$ to 10^3, ignoring the sine and cosine functions.

To compute the depolarization factor of a gas consisting of molecules with the polarizability components (5), we proceed as usual;[7] however, we have to consider that A_1 and B_1 are themselves dependent on the orientation of the molecule on account of the factors v and w. But it is a sufficient approximation, to substitute for v^2 and w^2 their mean values, $\frac{1}{3}$ and $\frac{2}{3}$, respectively; then A_1' and B_1' are constant polarizability components, and the result of Born can be adopted immediately.

The result is:

$$\rho=(6\Omega/5\Omega_0+7\Omega), \tag{8}$$

with

$$\Omega=\langle(A_1'-B_1')^2\rangle_{\mathrm{Av}}=(A_0'-B_0')^2$$
$$+\epsilon'^2E_0^4(\epsilon_1A_0-\epsilon_2B_0)^2(\omega^2/\omega_0^2q_0^2), \tag{9}$$

$$\Omega_0=\langle(2B_1'+A_1')^2\rangle_{\mathrm{Av}}=(2B_0'+A_0')^2$$
$$+\epsilon'^2E_0^4(2\epsilon_2B_0+\epsilon_1A_0)^2(\omega^2/\omega_0^2q_0^2). \tag{10}$$

In these equations, it is written

$$\langle E^2E'^2\rangle_{\mathrm{Av}}=\tfrac{1}{4}E_0^4(\omega^2/\omega_0^2q_0^2),$$

according to (6) and (7). Furthermore,

$$\epsilon'=({\epsilon_1}^2+2{\epsilon_2}^2)/3\epsilon^2.$$

Estimating the value of q_0 for oxygen[8] to be $q_0=7\times10^{-10}$ cm and supposing $x=\epsilon E_0^2$ to be 0.01 and $\omega/\omega_0=16$ (for violet light), we calculate $\rho=0.27$, whereas $\rho=0.26$ is observed with oxygen. $\epsilon=0$ would give the result $\rho=0.63$. That $x=0.01$ is not too large a value is demonstrated by comparing the computed depolarization factors of Rayleigh scattering for $x=0.01$ and for $x=0$. We obtain with $\alpha=0.73\times10^{-24}$ cm^3, $r=1.5\times10^{-8}$ cm

for $x=0.01$: $\rho_{\mathrm{Rayl}}=0.084$,
for $x=0$: $\rho_{\mathrm{Rayl}}=0.082$,

i.e., only an alteration by two percent, not exceeding the deviations of different measurements. In the case of Raman scattering, the assumption

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[7] Cf. M. Born, *Optik* (Verlag Julius Springer, Berlin, 1933), pp. 81 and 82.

[8] Cf. K. W. F. Kohlrausch, *Ramanspektren, Hand- und Jahrbuch d. chem. Physik* (Becker und Erler, Leipzig, 1944), Vol. 9, Part IV, p. 65.

TABLE I.

	$\alpha \times 10^{24}$ (cm^3)	$r \times 10^8$ (cm)	$q_0 \times 10^{10}$ (cm)	ω_0 (cm^{-1})	$\rho_{obs.}$[2]	$\rho_{calc.}$ ($x=0.01$)	$\rho_{calc.}$ ($x=0$)
N_2	0.88	1.6	6.4 [8]	2330	0.19	0.26	0.63
O_2	0.73	1.5	7.3	1555	0.26	0.27	0.63
H_2	0.40	1.44	17	4160	0.05	0.11 ($x=0.1$)	0.74
CO_2	1.0	2.0 (O—O)	7.0 estimated	1335	0.21	0.10 [0.21 for $x=0.0022$]	0.75
CS_2	3.2	2.52 (S—S)	7.0	660	0.15	0.23	0.65

$x=0.01$, however, leads to changing the depolarization factor by about 50 percent and therefore to a far better agreement with observation.

The results for those diatomic molecules, for which data are available, are recorded in Table I, which includes also CO_2 and CS_2, these molecules being treated as diatomic ones, because their C atom can be considered as unpolarizable. For the computation, ω is always taken as about 25000 cm^{-1}. There is, in principle, a dependence of ρ on ω but only in a very small amount. The values of α and r are taken from data for Rayleigh scattering for sake of consistency.

In general, the calculated values are still too high, but the agreement between observation and theory seems to be satisfactory.

Only the absolute value of ϵ is determined by Eqs. (7) to (9). In the next section, we find a negative ϵ; therefore here ϵ may be negative too.

Another interesting example is OCS. This molecule has two symmetric vibrations, at 860 and 2050 cm^{-1}. The former one has a very strong Raman line with $\rho=0.10$; it corresponds to the totally symmetric vibration of CO_2 (S and O in opposite phases).[9] But for the much weaker Raman line at 2050, we have $\rho=0.77$; this vibration corresponds to the antisymmetric one of CO_2 (S and O in equal phases). It is understandable that the theory developed here applies only to the 860 line, in which the distance O—S changes appreciably. The other vibration approximately lets this distance unchanged. We can assume that only this distance is relevant for Raman effect, treating OCS as a diatomic molecule OS because of $\alpha_C=0$, and that for 2050 the normal theory with $\epsilon=0$ will be accurate enough. Then the theoretical value of ρ for this line is $\rho=0.80$, in sufficient agreement with the experiment. The lower value for the other line may be explained qualitatively in the same manner as above for the diatomic molecules.

Other unsymmetric linear molecules, as ClCN, have both symmetric Raman lines strongly polarized ($\rho=0.20$ and 0.24, respectively). Probably they cannot be treated in the same manner as OCS, because the assumption $\alpha=0$ for C might not be fulfilled in this case (different bonds at the C atom).

III. CALCITE AND ARAGONITE

As mentioned in the introduction, the assumption that the polarizability is dependent on the field strength is not sufficient to account for the observed results concerning the depolarization factors of the Raman lines of the totally symmetric vibration of the CO_3 group. This arises from the trigonal symmetry of this group, the general theory here giving unequivocal results independent of assumptions about the polarizability. Therefore, a field-dependent α alone cannot help, and we have assumed the disturbing field, also mentioned above, neglecting here the mutual influence of the atoms because, on one hand, the greater distance of the O atoms in the CO_3 group reduces this mutual action and because, on the other hand, it is unnecessary for explaining the main features of the observations. In any case, the polarizability of the central atom can be considered as small enough to be irrelevant. The experimental data are not yet sufficiently reliable to justify going into greater detail.

We characterize the calcite crystal by one of its CO_3 groups. The x axis of the coordinates may be one of the altitudes of the CO_3 group, the y axis being parallel to the corresponding triangle side. The normal of the group plane corresponds to the optic axis of the crystal. The incident light-wave may have the components E_y and E_z of the electric field strength $\mathbf{E}$; the disturbing field $\mathbf{E}_d$ may have the components E_{dx} and E_{dy}, $\mathbf{E}_d$ being in the CO_3 plane. Denoting the components of the total moment of all three oxygen atoms as $P_x=p_{1x}+p_{2x}+p_{3x}$, P_y, P_z, we have $\rho_z=\langle P_x'^2\rangle_{Av}/\langle P_z'^2\rangle_{Av}$, the primes indicating differentiation with respect to the normal coordinate of vibration, the bars indicating aver-

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[9] J. Wagner, Zeits. f. physik. Chemie 193, 55 (1943).

aging. Interchanging y axis and z axis, we obtain $\rho_y = \langle P_z'^2\rangle_{\text{Av}}/\langle P_y'^2\rangle_{\text{Av}}$. Interchanging x axis and z axis, we obtain $\rho_x = \langle P_z'^2\rangle_{\text{Av}}/\langle P_x'^2\rangle_{\text{Av}}$.

However, in this case, $\mathbf{E}$ has only the components E_x and E_y. Hence $\rho_x = 0$, because P_z is proportional to E_z. $\rho_x = 0$ is also the result obtained by all observers.

The assumptions mentioned above lead to

$$\begin{aligned} P_x &= 3\{\alpha+\beta|\mathbf{E}+\mathbf{E}_{\mathrm{d}}|^2\}E_{dx}, \\ P_y &= 3\{\alpha+\beta|\mathbf{E}+\mathbf{E}_{\mathrm{d}}|^2\}(E_y+E_{dy}), \qquad (11) \\ P_z &= 3\{\alpha+\beta|\mathbf{E}+\mathbf{E}_{\mathrm{d}}|^2\}E_z, \end{aligned}$$

in which α and β refer to a single atom.

From (11), we get

$$\begin{aligned} P_x' &= 6\beta E_{dx}(EE'+E_{dy}E_y'), \\ P_y' &= 3\alpha E_y' + 6\beta(E_y+E_{dy})(EE'+E_{dy}E_y') \\ &\quad + 3\beta(E_d^2+E^2+2E_{dy}E_y)E_y', \qquad (12) \\ P_z' &= 3\alpha E_z' + 6\beta E_z(EE'+E_{dy}E_y') \\ &\quad + 3\beta(E_d^2+E^2+2E_{dy}E_y)E_z'. \end{aligned}$$

In calculating the mean squares of these components, the average values with respect to t (in E), to Δ (in E'), and to the orientation (in E_y, E_z) are taken independently. Then, after some elementary calculations, the depolarization factors ρ_y and ρ_z are

$$\begin{aligned} \rho_y &= \frac{4\beta^2E_{dx}^2(E_0^2+E_{dy}^2)}{\alpha^2+\beta^2(E_d^4+(27/8)E_0^4+4E_{dy}^4+3E_d^2E_0^2+4E_d^2E_{dy}^2+24E_0^2E_{dy}^2)+2\alpha\beta(E_d^2+\frac{3}{2}E_0^2+2E_{dy}^2)}, \\ \rho_z &= \frac{4\beta^2E_{dx}^2(E_0^2+E_{dy}^2)}{\alpha^2+\beta^2(E_d^4+(27/8)E_0^4+3E_d^2E_0^2+2E_0^2E_{dy}^2)+2\alpha\beta(E_d^2+\frac{3}{2}E_0^2)}. \end{aligned} \qquad (13)$$

It is seen at once that ρ vanishes if $E_{dx}=0$. This is quite understandable, since only a component of the disturbing field in the x direction may cause an induced moment in this same direction, if mutual action is neglected. If $E_{dy}=0$, it is $\rho_y=\rho_z$.

A difference of ρ_y and ρ_z, as it is observed experimentally, may only occur if E_{dy} does not vanish. Indeed, it must be supposed that the disturbing field does not remain parallel to the x direction, the direction of one altitude of the triangle. It will rather change its direction irregularly, or the field direction may be different at different CO_3 groups. Therefore, we should average with respect to all possible field directions. According to the individual features of the disturbing field, which might be different for each individual crystal, these mean values of ρ might be different also in different samples.

$\mathbf{E}_{\mathrm{d}}$ may be supposed to remain constant in value, only the direction varying. If the field assumes all directions in the CO_3 plane or only those parallel to the altitudes of the CO_3 triangle, as it seems natural for a calcite crystal, we have, with the abbreviations

$$\epsilon E_0^2 = x, \quad \epsilon E_d^2 = y; \qquad (14)$$

$$\begin{aligned} \bar{\rho}_y &= \frac{2xy+\frac{1}{2}y^2}{1+(27/8)x^2+(9/2)y^2+15xy+3x+4y}, \\ \bar{\rho}_z &= \frac{2xy+\frac{1}{2}y^2}{1+(27/8)x^2+y^2+4xy+3x+2y}. \end{aligned} \qquad (15)$$

With $x=-0.02$ and $y=-0.35$, we obtain, in sufficient agreement with the observations

$$\bar{\rho}_y = 0.39, \quad \bar{\rho}_z = 0.19$$
$$(\text{observed:} \quad 0.4, \quad 0.2\ ).$$

Slight changes in y cause great changes in $\bar{\rho}_y$. The numerical value of y seems to be reasonable, but in view of the qualitative character of the treatment, its exact value is not of essential importance. As is seen from Eq. (11), it is not necessary to assume $\epsilon|\mathbf{E}+\mathbf{E}_{\mathrm{d}}|^2$ to be very small because, in the approximation expressed by (11), β does not influence the depolarization of the Rayleigh scattering at all.[10]

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[10] Equation (11) does not give correct values of ρ for Rayleigh scattering (cf. the complete theory of Rayleigh scattering in crystals, F. Matossi, Zeits. f. Physik **92**, 425 (1934) and the observations of S. Bhagavantam and J. V. Narayana, Proc. Ind. Acad. Sci. **A16**, 366 (1942); therefore, it may be doubted, whether (11) should be used in the treatment of Raman effect. But what is important in our considerations is the influence of β, which nevertheless may be obtained in a fair approximation.

There may be one objection more: $\alpha+\beta|\mathbf{E}+\mathbf{E}_{\mathrm{d}}|^2$ is the

The depolarization factors for polarized excitation may be obtained starting from (12) in the same manner as above. The final formulae are for $E_z=0$:

$$\rho_y=E_{dx}^2/E_{dy}^2,$$

$$\rho_z=\infty$$

and for $E_y=0$:

$$\rho_y=\frac{4\beta^2E_{dx}^2(\tfrac{1}{2}E_0^2+E_{dy}^2)}{\alpha^2+\beta^2(E_d^4+(27/8)E_0^4+4E_{dy}^4+3E_d^2E_0^2+4E_d^2E_{dy}^2+24E_0^2E_{dy}^2)+2\alpha\beta(E_d^2+\tfrac{3}{2}E_0^2+2E_{dy}^2)},$$

$$\rho_z=\frac{2\beta^2E_0^2E_{dx}^2}{\alpha^2+\beta^2(E_d^4+(27/8)E_0^4+3E_d^2E_0^2)+2\alpha\beta(E_d^2+\tfrac{3}{2}E_0^2)};$$

or, after averaging with respect to the directions of $\mathbf{E}_\mathbf{d}$ in the CO_3 group as above,

for $E_z=0$:

$$\bar{\rho}_y=1,$$

$$\bar{\rho}_z=\infty;$$

for $E_y=0$:

$$\bar{\rho}_y=\frac{xy+\tfrac{1}{2}y^2}{1+(27/8)x^2+(9/2)y^2+15xy+3x+4y},$$

$$\bar{\rho}_z=\frac{xy}{1+(27/8)x^2+y^2+3xy+3x+2y}.$$

With the same values of x and y as before, calculated ρ values are

for $E_z=0$:

$$\bar{\rho}_x=0, \qquad \bar{\rho}_y=1 \qquad \bar{\rho}_z=\infty;$$

observed is,[11] respectively:

$$0.4, \qquad 2, \qquad 10;$$

for $E_y=0$:

$$\bar{\rho}_x=0, \quad \bar{\rho}_y=0.35, \quad \bar{\rho}_z=0.02;$$

observed respectively:

$$0.05, \qquad 0.6, \qquad 0.5.$$

Considering the approximative character of the theory, the utilization of only two adjustable magnitudes (x and y) and the difficulty of measuring depolarization factors of crystals, the agreement between theory and experiment is not inacceptable. The values measured by Bhagavantam do not seem to be very reliable; at least the first one is certainly too high ($\rho=\infty$ and $\rho=10$ are quite compatible values).

Also for aragonite there are observations[12] which are anomalous for the Raman line at 1087 cm^{-1}. Because of the rhombic symmetry (D_{2h}) of aragonite, we have six different crystal positions with respect to the x-y-z system. Designating with ζ the axis perpendicular to the CO_3 groups, with ξ, a direction parallel to one altitude of a CO_3 triangle perpendicular to a symmetry plane of the crystal, the different positions may be characterized by the following scheme, which at the same time contains the observed ρ values:

1	2	3	4	5	6
$x\ y\ z$	$x\ y\ z$	$x\ y\ z$	$x\ y\ z$	$x\ y\ z$	$x\ y\ z$
$\zeta\ \xi\ \eta$	$\zeta\ \eta\ \xi$	$\xi\ \zeta\ \eta$	$\eta\ \zeta\ \xi$	$\xi\ \eta\ \zeta$	$\eta\ \xi\ \zeta$
$\rho=0$	0	0.3	0.3	0.3	0.3

According to the D_{2h} symmetry, we assume $\mathbf{E}_\mathbf{d}$ to have finite values approximately only in directions 90° apart ($E_{dx}=0$ or $E_{dy}=0$). Then we obtain the following theoretical expressions for ρ, in the same manner as above:

$$\bar{\rho}_1=\bar{\rho}_2=0,$$

$$\bar{\rho}_3=\bar{\rho}_4=\frac{2xy}{1+(27/8)x^2+5y^2+15xy+3x+4y},$$

$$\bar{\rho}_5=\bar{\rho}_6=\frac{2xy}{1+(27/8)x^2+y^2+4xy+3x+2y}.$$

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polarizability of the molecule in the solid state, which differs from that in gaseous state, $\alpha+\beta E^2$, appreciably, if y is not very small. Normally, the difference of polarizabilities, determined by the Lorentz-Lorenz-formula, is only small; but just in the cases we are dealing with, it is not possible to measure the refractive indices for gaseous and fluid states without destroying the substance. Therefore, we cannot finally decide this question from observational data.

[11] S. Bhagavantam, Proc. Ind. Acad. Sci. **A8**, 345 (1938).

[12] L. Couture, Comptes Rendus **218**, 669 (1944).

It is not possible to regain the observed values exactly. One of the best theoretical values is reached for $x=y=-0.22$. Then $\bar{\rho}_3=0.16$ and $\bar{\rho}_5=0.32$. In spite of the discrepancy for $\bar{\rho}_3$, which is not too serious (Couture does not give the limits of accuracy, she only states $\rho=\sim 0.3$), these results may be accepted as another qualitative indication that the theory is able to account in principle for anomalous depolarization factors.

It should be mentioned, however, that the total intensities of the Raman lines are not described accurately by this theory. But there might be other factors influencing the excitation of Raman lines in different crystal orientations, affecting the absolute values but not the ratios of the scattered intensity components. These factors are not yet understood. Another possibility of explaining the anomalies of ρ in calcite and aragonite, deviation of the CO_3 group from strictly trigonal symmetry, is unable as well to account for the intensities.[13] It is uncertain whether a combination of both theories (field dependency and deviation of symmetry) would give better results in this respect.

There remain at least two questions: Why do such anomalies or such disturbing fields occur just in calcite and aragonite, while for other crystals we have no indication for a similar behavior? Is the neglection of mutual influence really justified? A negative answer to the last question might change the numerical conclusions but hardly the qualitative result, the necessity of a field-dependent polarizability and of a disturbing crystal field.

IV. SUMMARY

Assuming a small dependence of atomic polarizability on inducing field strength and utilizing the Silberstein concept of mutual interaction of induced dipoles, it is possible to compute the depolarization factors of Raman lines of diatomic molecules as well as those of Rayleigh scattering in agreement with observation.

Furthermore, assuming a disturbing field in $CaCO_3$ crystals, it is possible to account for the observed non-vanishing depolarization factors of the Raman lines of the totally symmetric vibration.

SUPPLEMENT

Because the issue of the Physikalische Zeitschrift cited in reference 2 is not easily available, the results of that paper may be reviewed shortly.

It was assumed that α be dependent on the distance r between the atoms of linear molecules, α being the *atomic* polarizability. Then

$$\rho=\frac{6b^2}{45a^2+7b^2}$$

with $b^2=(A'-B')^2$, $a=\frac{1}{3}(A'+2B')$, and

$$A'=\frac{2(d\alpha/dr)[1-(2\alpha/r^3)]}{[1-(2\alpha/r^3)]^2},$$

$$B'=\frac{2(d\alpha/dr)[1+(\alpha/r^3)]}{[1+(\alpha/r^3)]^2}.$$

From the observed ρ values and these formulae, $d\alpha/dr$ is computed. The result is contained in the following table, together with the relative change of atomic radius R which corresponds to the change of α for $dr=q_0$, the amplitude of the oscillation. dR/R is small enough to justify the procedure.

	H_2	O_2	CO_2	CS_2
$10^{16}(d\alpha/dr)$	0.27	0.6	0.76	3.3 cm^2
dR/R	0.05	0.02	0.02	0.02

Dr. G. B. Sabine and Dr. L. Mundie have given valuable aid in the English formulation.

Note added in proof.—Independent from us, H. Senftleben and H. Gladisch recently [Naturwiss. **34**, 187 (1947)] suggest the same hypothesis as we to explain some results about the dependence of heat transfer on electric fields.

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[13] H. Michalke, see reference 3; F. Matossi, Zeits. f. Physik **64**, 34 (1930).