

Two approaches to spatial dispersion in molecular scattering of light

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Usp. Fiz. Nauk. 127, 421-450 (March 1979)

A comparative discussion is given of two approaches to taking spatial dispersion into account in the electrodynamic problem of molecular scattering of light. The first, more traditional approach, may be called the "distributed dipole" approximation (DDA) and is based on the assumption that any given molecule at a given instant of time scatters light as an electric dipole. In this approach spatial dispersion, i.e., the dependence of the spectrum on the variation of the propagation vector $q = k_1 - k_2$, is determined by the correlation of the positions of a given molecule (or of different molecules) at different times. Another approach, developed in recent years by Barron and Buckingham for the problem of light scattering by molecules with right-left asymmetry, may be called the "local multipole" approximation (LMA) and is based on taking into account the magnetic dipole and the electric quadrupole as well as the electric dipole interaction of a molecule with the field. A list is given of sets of "complete experiments" for measuring all the independent constants that determine the scattering cross section in both approaches. It is shown that the DDA approach is needed to describe the relatively large (~ 1) effects of spatial dispersion in measurements with high spectral resolution ($\delta\omega \lesssim qv$, where v is the velocity of sound in the medium) while the LMA approach is required to describe the small effects ($\sim a/\lambda$, where a is the size of the molecule and λ is the wavelength) measured with relatively low spectral resolution $\delta\omega \ll qv$. It is asserted that the right-left asymmetry of the differential (with respect to frequency) cross section for scattering in a gas containing chiral molecules need not involve the smallness parameter ka if $ql \sim 1$, where a is the size of the molecule and l is the mean free path. Also new lines are predicted in the rotational Raman scattering in a gas—transitions with $\Delta J = \pm 1, \pm 3$ in the case of noncentrally-symmetric molecules with a cross section $\sim 10^{-6}$ of the Rayleigh cross section arising in second order in a/λ due to the higher multipoles.

PACS numbers: 33.80. — b, 42.65.Cq

CONTENTS

1. Introduction	143
2. Distributed-dipole approximation in the theory of molecular scattering of light	145
3. Left-right asymmetry of the spectrum of light scattered by a gas due to collisions with chiral molecules (DDA approach)	146
4. Local multipole approximation to the scattering of light by left-right asymmetric molecules (LMA approach)	148
A. Expansion of induced multipole moments of the molecule in powers of a/λ and symmetry relationships	148
B. Differential scattering cross section in LMA	150
C. Angle integrated scattering cross section	151
D. The "complete experiment" within the framework of LMA	152
5. Ranges of validity of DDA and LMA	152
6. Rotational Raman scattering of light by non centrally-symmetric molecules	154
Appendix	156
1. Decomposition of cross polarizability tensors $\hat{\rho}$ and \hat{A} into representations irreducible under the rotation group	156
2. Expansion of radiation intensity in powers of a/λ in electrodynamic	156
3. New lines in pure rotational Raman scattering by CH_4	157
4. New lines in pure rotational Raman scattering by the isotope-substituted hydrogen molecule HD	158
References	158

1. INTRODUCTION

Most optical phenomena can be very well described by assuming that the interaction of a light wave with atoms and molecules can be considered in the electric-dipole approximation. The validity of this approximation is based on the availability of the very small parameter $a/\lambda \sim 10^{-3} - 10^{-5}$, where $a \sim 10^{-7} - 10^{-8}$ cm is the characteristic linear dimension of an atom or a molecule and $\lambda \sim 10^{-4} - 10^{-3}$ cm is the wavelength of visible or in-

frared radiation. In general, corrections that depend on the wave vector \mathbf{k} of the light wave ($|\mathbf{k}| = 2\pi n/\lambda$, where n is the refractive index), which are often referred to as spatial dispersion effects, are therefore found to be of the relative order of magnitude of $ka \sim a/\lambda$, or some higher power of this parameter. On the other hand, the condition for the validity of the dipole approximation in electrodynamic is $b/\lambda \lesssim 1$, where b is the characteristic linear dimension of the radiating system. If, by the radiating system, we understand all

atoms or molecules in the given medium (solid, liquid, or gas), we find that, in optics, the opposite condition is usually satisfied, namely, $b/\lambda \gg 1$. The resolution of this apparent contradiction is achieved by noting that, in most cases, different atoms and molecules radiate or interact with the overall radiation field in a statistically independent way. Let us examine this in greater detail.

In the case of direct radiation and in the case of scattering, the *spectral* composition of the emitted photons with wave vector \mathbf{k}_2 and frequency ω_2 is determined by the space-time correlator of the current density $\mathbf{j}(\mathbf{r}, t)$:

$$I(\mathbf{k}_2, \omega_2) \propto \int d^3(\mathbf{r}'' - \mathbf{r}') d(t'' - t') \langle j^*(\mathbf{r}', t') j(\mathbf{r}'', t'') \rangle \times \exp[i\omega_2(t'' - t') - \mathbf{k}_2 \cdot (\mathbf{r}'' - \mathbf{r}')]. \quad (1.1)$$

The *frequency-integrated characteristics* of the direct or scattered radiation are then determined by the correlator of currents at equal times:

$$\int I(\mathbf{k}_2, \omega_2) d\omega_2 \propto \int \langle j^*(\mathbf{r}', t) j(\mathbf{r}'', t) \rangle d^3(\mathbf{r}'' - \mathbf{r}') \exp[-i\mathbf{k}_2 \cdot (\mathbf{r}'' - \mathbf{r}')]. \quad (1.2)$$

However, equal-time correlation of the amplitudes of direct radiation, or the correlation of fluctuations in the parameters of the medium which govern the light scattering process, are known to extend only to distances of the order of the atomic size (this ignores certain special cases such as, for example, the neighborhoods of phase transition points). It follows that the *frequency-integrated characteristics* of direct and scattered radiation can, in fact, be calculated if we neglect corrections of the order of $\sim a/\lambda$ in the electric-dipole approximation, and turn out to be independent of \mathbf{k} for direct radiation or of $\mathbf{k}_1, \mathbf{k}_2$ for scattered radiation. It follows that spatial dispersion effects are very small-of the order of a/λ or less-for the frequency-integrated quantities.

An essentially different situation arises in the case of *frequency-differentiated characteristics*. We shall confine our attention in this paper to light scattering problems for liquids and gases (spatial dispersion in solids is examined in Ref. 1). Strong spatial dispersion effects in gases in the case of the usual single-photon absorption are discussed in our previous paper.²

The spectrum of scattered radiation is usually discussed in the approximation that may be referred to as the *distributed-dipole approximation* (DDA). In this approximation, the current density $\mathbf{j}(\mathbf{r}, t)$ at a given point \mathbf{r} in space and a given time t is given by the dipole expression

$$j_i(\mathbf{r}, t) = \frac{1}{4\pi} \frac{\partial}{\partial t} [\delta\epsilon_{ik}(\mathbf{r}, t, \omega) E_k(\mathbf{r}) e^{-i\omega t} + \text{c.c.}], \quad (1.3)$$

where $\mathbf{E}(\mathbf{r})e^{-i\omega t}$ is the incident wave and $\delta\epsilon_{ik}(\mathbf{r}, t, \omega)$ is the fluctuation in the dielectric permittivity. The essential point is that spatial dispersion is not taken into account in the relation between \mathbf{j} and \mathbf{E} given by (1.3). Substitution of $\mathbf{E}(\mathbf{r}) = \mathbf{e}_1 e^{i\mathbf{k}_1 \cdot \mathbf{r}}$ and the evaluation of the scattered field in the far zone enable us to determine the differential scattering cross section per unit volume

$$\frac{dR}{d\omega d\Omega} = \frac{1}{(4\pi)^2} \left(\frac{\omega_2}{c}\right)^4 e_{2l} e_{1k}^* e_{2l}^* e_{1m} T_{ijklm}(\delta\omega, \mathbf{q}), \quad (1.4a)$$

$$T_{ijklm}(\delta\omega, \mathbf{q}) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\tau \langle \delta\epsilon_{ik}^*(\mathbf{R}, t) \delta\epsilon_{lm}(\mathbf{R} + \mathbf{r}, t + \tau) \rangle \exp(-i\delta\omega\tau + i\mathbf{q} \cdot \mathbf{r}), \quad (1.4b)$$

$$\mathbf{q} = \mathbf{k}_1 - \mathbf{k}_2, \quad \delta\omega = \omega_1 - \omega_2, \quad (1.4c)$$

where ω_2 is the scattered frequency, $\mathbf{n}_2 = \mathbf{k}_2/k_2$, and \mathbf{e}_2 is the polarization unit vector. The characteristic feature of DDA as expressed by (1.4a) and (1.4b) is that the differential cross section per unit frequency per unit solid angle is independent of the wave vectors \mathbf{k}_1 and \mathbf{k}_2 of the incident and scattered waves separately, but is a function only of their difference $\mathbf{q} = \mathbf{k}_1 - \mathbf{k}_2$. The tensor T_{ijklm} , regarded as a function of the scattered frequency ω_2 , is also shown by (1.4b) to depend mainly on the difference $\delta\omega = \omega_1 - \omega_2$ because $\delta\epsilon(\mathbf{r}, t, \omega)$ has a smooth dependence on the frequency ω well away from resonance.

"Spatial dispersion," i.e., the dependence of the tensor T_{ijklm} which determines the spectrum of the scattered radiation on \mathbf{q} has been thoroughly investigated experimentally. This is, in fact, the polarized Mandel'shtam-Brillouin doublet with the frequency shift $\Delta\omega = \pm qv_L$, and the depolarized doublet (fine structure of the Rayleigh line wing³), which has the shift $\Delta\omega = \pm qv_T$, where v_L and v_T are the velocities of longitudinal and transverse hypersound in liquids, respectively. There are, of course, many other effects as well (see, for example, Refs. 4 and 5). Phenomenological examination of the problem, performed in the distributed-dipole approximation by Zel'dovich,⁶ has also led to the inclusion of possible effects associated with the left-right asymmetry of the scattering medium. The results obtained in this way will be briefly summarized in Sec. 2.

It is important to note that the approach which we call the distributed-dipole approximation is widely used also in the electrodynamics of absorption and refraction, for example, in various problems in plasma physics. The theory of the anomalous skin effect is a good illustration of this point. Here, spatial dispersion effects are strong in the sense that the electron mean free path l turns out to be much greater than the characteristic scale $a \sim k^{-1}$ of changes in the field, i.e., $kl \gg 1$, where k is the effective wave vector. Nevertheless, this effect is usually discussed by assuming that the electrons experience only the electric field at the given point on the electron trajectory, i.e., without taking into account the Lorentz force. This, in fact, corresponds to the spatially distributed dipole interaction. However, in the present paper, we shall confine our attention to light scattering problems and will leave absorption and refraction problems aside.

On the other hand, natural optical activity of liquids consisting of left-right asymmetric molecules (and also of gases and solids) is usually discussed as a spatial dispersion effect of the first order in a/λ . This phenomenon consists of the difference between the refractive indices (or the difference between absorption coefficients in the region of absorption bands) for right

and left polarized light. To describe this phenomenon, one must go beyond the pure dipole approximation and include *magnetic dipole* and (for solids) *electric quadrupole* interactions between the molecules and the light waves (see, for example, Refs. 7 and 8). In recent years, Barron, Buckingham *et al.* (see, for example, Refs. 9 and 10) have developed a theory of light scattering by left-right asymmetric molecules, which also involves the inclusion of *magnetic dipole* and *electric quadrupole* interactions. This approach may be referred to as the local multipole approximation (LMA). This theory predicted, and the prediction was subsequently confirmed experimentally,¹⁰ that the Raman scattering cross sections for left and right polarized incident waves should be different. The Barron-Buckingham theory (LMA) in the case of left-right scattering asymmetry^{9,10} is in roughly the same relation to the theory of natural optical activity as the theory of electric-dipole scattering (Placzek, 1930;¹¹ see also Refs. 12 and 13) is in relation to the theory of the ordinary electric-dipole refractive index. The basic points of LMA will be formulated briefly in Sec. 4 and an account will be given there of new results on the question of the "complete experiment."

It is shown in Sec. 5 that the left-right asymmetric terms in DDA, when the effect is taken into account only in the first order in $\mathbf{q} = \mathbf{k}_1 - \mathbf{k}_2$, correspond to the "two-group" mechanism¹⁴ in the left-right asymmetric terms in LMA.

In Sec. 3, a model of collisions between left-right asymmetric molecules in a gas is used within the framework of the DDA to show that the left-right asymmetric terms in the *frequency differential* cross section may be quite large (of the order of 0.01–0.1) if the spectral resolution $\Delta\omega$ is better than qv_T (v_T is the thermal velocity of the molecules) and the mean free path l is such that $ql \sim 1$. At the same time, in the *frequency-integrated* cross section, the left-right asymmetric terms should, as before, be of the order of $ka \sim 10^{-3} - 10^{-4}$, in accordance with the LMA approach.

Finally, Sec. 6 suggests that it may be possible to observe new lines associated with rotational Raman scattering in gases, namely, transitions with $\Delta J = \pm 1, \pm 3$ for non centrally-symmetric molecules for which the scattering cross section is about 10^{-6} of the Rayleigh cross section. Such lines appear in the second order in a/λ because of the presence of the higher (as compared with the dipole) multipolarities in the radiation.

We note that these spatial dispersion effects, i.e., nonlocal effects, in scattering can be adequately described by only one of the above two approaches. The difference between them is connected with the difference between the very mechanisms responsible for the appearance of nonlocal behavior. In the case of LMA, one is concerned with the nonlocal response of the induced current to the field within the limits of an individual molecule. In contrast, in DDA, one is concerned with nonlocal behavior connected with the motion of the molecules and the correlations between them in space.

2. DISTRIBUTED-DIPOLE APPROXIMATION IN THE THEORY OF MOLECULAR SCATTERING OF LIGHT

As noted in the Introduction, the differential cross section per unit frequency is determined in DDA by the tensor $T_{ijkm}(\delta\omega, \mathbf{q})$ given by (1.4). To find the most general form of this tensor without using models, it is convenient to take into account⁶ the symmetry properties of the integral (1.4). In particular, for liquids or gases, i.e., media that are invariant under the rotation group, the symmetry of (1.4) corresponds to the one-parameter group of rotations around the direction \mathbf{n} of the wave vector $\mathbf{q} = q\mathbf{n}$ (we shall refer to it as the small group). In the Placzek approximation, we neglect anti-symmetric scattering,^{15,16} so that the symmetric real tensor $\delta\epsilon_{ijk}(\mathbf{r}, t)$ can be decomposed into two irreducible (with respect to the group of three-dimensional rotations) components, namely, the scalar and the zero-trace symmetry. Next, the scalar of the three-dimensional rotation group is, at the same time, the irreducible scalar representation of the small group, and the symmetric zero-trace tensor of three-dimensional space generates the vector (V_i) and the zero-trace tensor ($\tilde{\epsilon}_{ijk}$) representations of the small group:¹⁷

$$\epsilon_{ijk} = \frac{1}{3} \epsilon_{ij} \delta_{ik} + \left(\epsilon_{ijk} - \frac{1}{3} \epsilon_{ij} \delta_{ik} \right) \quad (2.1a)$$

$$= \frac{1}{3} \epsilon_{ij} \delta_{ik} + \frac{1}{6} (\epsilon_{ij} - 3\epsilon_{pi} n_p n_j) (\delta_{ik} - 3n_i n_k) + V_i n_k + n_i V_k + \tilde{\epsilon}_{ijk}, \quad (2.1b)$$

$$V_i = \epsilon_{ip} n_p - n_i \epsilon_{pi} n_p n_i.$$

Here and henceforth, we omit the symbol δ in the fluctuation $\delta\epsilon_{ijk}$. The symbol $\tilde{\epsilon}_{ijk}$ in (2.1a) represents the symmetric zero-trace tensor in the two-dimensional space orthogonal to \mathbf{n} . To evaluate the integral (1.4b) of the correlator $\langle \epsilon_{ijk}(\mathbf{r}, t) \times \epsilon_{lm}(\mathbf{r}', t') \rangle$, we can use the results of group theory, according to which only products of identical representations of the small group have nonzero averages. This yields⁶

$$T_{ijklm} = M_1 \delta_{ij} \delta_{lm} + M_2 [\delta_{ij} (\delta_{lm} - 3n_l n_m) + \delta_{lm} (\delta_{ij} - 3n_i n_j)] + M_3 (\delta_{ij} - 3n_i n_j) (\delta_{lm} - 3n_l n_m) + M_4 (n_k n_l \delta_{im}^{(2)} - n_k n_m \delta_{il}^{(2)} + n_i n_j \delta_{km}^{(2)} + n_i n_m \delta_{kl}^{(2)}) + M_5 (\delta_{il}^{(2)} \delta_{jm}^{(2)} + \delta_{im}^{(2)} \delta_{jl}^{(2)} - \delta_{ij}^{(2)} \delta_{lm}^{(2)}) + i M_6 (\epsilon_{ijp} \delta_{klm} + \epsilon_{im p} \delta_{kjl} + \epsilon_{kl p} \delta_{ijm} + \epsilon_{kmp} \delta_{ijl}) n_p + i (M_7 - M_8) (\epsilon_{ijp} n_k n_m + \epsilon_{im p} n_k n_l + \epsilon_{klp} n_i n_m + \epsilon_{kmp} n_i n_l) n_p, \quad (2.2)$$

¹⁷Strictly speaking, the two-dimensional representations (V_i) and ($\tilde{\epsilon}_{ijk}$) are irreducible only for the broader symmetry group, namely, the group $C_{\infty v}$ of rotations and reflections in planes containing \mathbf{n} . In contrast, the group C_{∞} of pure rotations (without reflections) is an Abelian group and contains only the one-dimensional irreducible representations. For example, the vector representation (V_i) is then found to split into two irreducible representations corresponding to circularly polarized vectors of the form $(e_x \pm i e_y)$, where $\mathbf{n} = e_z$; similarly, the quantities ($\tilde{\epsilon}_{ijk}$) are also found to decompose into two circular representations. This type of decomposition is particularly convenient for systems with strong left-right asymmetry. It was introduced by Brazovskii and Dmitriev²⁷ in connection with the scattering of light near the point of phase transition of an isotropic liquid into a cholesteric liquid crystal (the approach adopted in Ref. 27 was analogous to what we refer to as DDA). Conversely, for systems with weak left-right asymmetry, the decomposition (2.1a) is the more convenient. We are indebted to N. V. Tabiryan for discussions of this point.

where

$$\delta_{ik}^{(p)} = \delta_{ik} - n_i n_k. \quad (2.3)$$

The quantities $M_1 - M_5$ are scalar and M_6, M_7 pseudoscalar real functions of the scalar arguments $\delta\omega$ and $|\mathbf{q}|$, and are defined by

$$M_\alpha(\delta\omega, |\mathbf{q}|) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\tau \cdot e^{-i\omega\tau} \int d^3r e^{i\mathbf{q}\cdot\mathbf{r}} \Phi_\alpha(\mathbf{r}, \tau), \quad (2.4)$$

where

$$\Phi_1 = \frac{1}{9} \langle \epsilon_{ss}(0) \epsilon_{ll}(\mathbf{r}, \tau) \rangle, \quad (2.5)$$

$$\Phi_2 = \frac{1}{18} \langle \epsilon_{ss}(0) [\epsilon_{ll}(\mathbf{r}, \tau) - 3\epsilon_{lm}(\mathbf{r}, \tau) n_l n_m] \rangle, \quad (2.6)$$

$$\Phi_3 = \frac{1}{36} \langle [\epsilon_{ll}(0) - 3\epsilon_{st}(0) n_s n_t] [\epsilon_{ll}(\mathbf{r}, \tau) - 3\epsilon_{lp}(\mathbf{r}, \tau) n_l n_p] \rangle, \quad (2.7)$$

$$\Phi_4 = \frac{1}{2} \langle V_p(0) V_p(\mathbf{r}, \tau) \rangle \equiv \langle \epsilon_{xx}(0) \epsilon_{xx}(\mathbf{r}, \tau) \rangle, \quad (2.8)$$

$$\Phi_5 = \langle \epsilon_{xy}(0) \epsilon_{xy}(\mathbf{r}, \tau) \rangle, \quad (2.9)$$

$$\Phi_6 = -\frac{i}{2} \langle \epsilon_{xy}(0) \frac{\epsilon_{xx}(\mathbf{r}, \tau) - \epsilon_{yy}(\mathbf{r}, \tau)}{2} \rangle, \quad (2.10)$$

$$\Phi_7 = -i \langle \epsilon_{xx}(0) \epsilon_{yz}(\mathbf{r}, \tau) \rangle. \quad (2.11)$$

The above expressions for the functions $\Phi_4 - \Phi_7$ are given in the coordinate frame in which the z axis lies along \mathbf{n} .

Expansions of this kind and integrals of correlators of different components of the tensor $\delta\epsilon_{ik}$ are frequently given and discussed in the literature.^{4,5} The most important difference between our decomposition of the tensor T_{iklm} and the corresponding formulas given in the literature^{4,5} is that we admit the possibility of left-right asymmetry in the properties of the liquid or gas under consideration. This is why our decomposition contains pseudoscalar terms proportional to M_6 and $M_7 - M_6$.

It is important to note that, although, formally, the expression for T_{iklm} given by (2.2) contains the two independent left-right asymmetric terms $\sim M_6$ and $\sim (M_7 - M_6)$, only the term $\sim M_6$ comes into play in real situations.⁶ This is connected with the following point. The polarization unit vectors $\mathbf{e}_1, \mathbf{e}_2$ of the incident and scattered waves are always orthogonal to the corresponding directions of propagation $\mathbf{n}_1 = \mathbf{k}_1/k_1, \mathbf{n}_2 = \mathbf{k}_2/k_2$, so that $(\mathbf{n}_1 \cdot \mathbf{e}_1) = 0, (\mathbf{n}_2 \cdot \mathbf{e}_2) = 0$. If the frequency shift $\delta\omega = \omega_1 - \omega_2$ associated with the scattering process is small in comparison with the frequency ω_1 of the incident light, we may set $|\mathbf{k}_1| \approx |\mathbf{k}_2|$, and

$$\mathbf{n} = \frac{\mathbf{q}}{q} = \frac{\mathbf{k}_1 - \mathbf{k}_2}{|\mathbf{k}_1 - \mathbf{k}_2|} \approx \frac{\mathbf{n}_1 - \mathbf{n}_2}{|\mathbf{n}_1 - \mathbf{n}_2|}. \quad (2.12)$$

In this approximation, the tensor structure which appears in the cross section with the coefficient $M_7 - M_6$ yields a result identically zero after multiplication by the polarization unit vectors.

To determine all six functions $M_1 - M_6$ which determine the frequency differential cross sections in the DDA approach under consideration, we must have a set of not less than six independent experiments with different incident and scattered wave polarizations. To be specific, let us examine the case of scattering through 90° . It will be convenient to take the coordinate frame as shown in Fig. 1.

If the medium is left-right symmetric, we need only

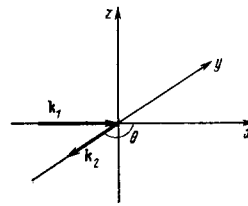


FIG. 1. Orientation of coordinate axes in the problem of light scattering at $\theta = 90^\circ$ (\mathbf{k}_1 and \mathbf{k}_2 are the wave vectors of incident and scattered light).

five experiments because $M_6 = 0$. The remaining experiments use different linear (and not elliptic) polarizations of the scattered wave for arbitrary polarizations of the incident wave, but yield only four linearly independent combinations of the five functions $M_1 - M_5$. This is also the case when the incident wave is represented by only linear polarizations and the scattered wave by arbitrary polarizations. To perform the "complete experiment," we must add a further measurement in which both the incident and scattered waves are elliptically polarized. This "complete experiment" is exemplified by the following set of scattered intensities (differential in frequency):

$$I_{zz}, I_{zx} \equiv I_{yz}, I_{yx}, I_{45^\circ/45^\circ}, I_{RL}. \quad (2.13)$$

where the first subscript indicates the polarization of the incident and the second of the scattered wave, the symbol 45° indicates linear polarization at 45° to the plane of scattering, and the subscript $R(L)$ represents right (left) circular polarization.

To determine all six functions $M_1 - M_6$ (in the case of a left-right asymmetric medium), it is sufficient for example to add the measurement of I_{RR} to the five intensities in (2.13). It is interesting that the pseudoscalar term $\sim M_6$ does not contribute to any of the intensities in (2.13), but it does contribute to I_{RR} . If, on the other hand, we are interested specifically in the left-right asymmetric term M_6 , we must, for example, measure the difference:

$$M_6 \propto I_{Rx} - I_{Lx}. \quad (2.14)$$

Measurement of the difference (2.14) may be technically feasible (compare this with the experiments described in Ref. 10) if the incident-wave polarization can be rapidly switched over from right to left circular and back again without change in intensity. The quantity

$$\Delta_x = \frac{I_{Rx} - I_{Lx}}{I_{Rx} + I_{Lx}}, \quad (2.15)$$

characterizes (compare this with Ref. 10) the degree of left-right asymmetry of the scattering cross section (in this case, the frequency-differentiated cross section).

3. LEFT-RIGHT ASYMMETRY OF THE SPECTRUM OF LIGHT SCATTERED BY A GAS DUE TO COLLISIONS WITH CHIRAL MOLECULES (DDA APPROACH)

In this section, we consider the DDA approach to the problem of the left-right asymmetric terms in the Raman spectrum of light scattered by a gas containing

chiral, i.e., left-right asymmetric, molecules. To do this, we consider a rotational or vibrational-rotational Raman transition, for example, one with $\Delta J = +2$ in an arbitrary molecule. For simplicity, we shall assume that the molecule is diatomic and thus left-right symmetric. We shall suppose that a low-density gas consisting of these diatomic molecules is immersed in a denser gas of chiral molecules. Collisions with the chiral molecules perturb the rotation of the diatomic molecules and thus contribute to collisional broadening and shift $\Gamma + i\Delta\omega$. In the collisional theory of broadening of spectral lines^{17,18} it is common to express these quantities in terms of the broadening and shift cross sections $\sigma' + i\sigma''$, i.e., $\Gamma + i\Delta\omega = Nv_T(\sigma' + i\sigma'')$, where N is the density of the perturbing particles (the perturbers—in our case, the chiral molecules) and v_T is the relative velocity of the colliding particles. We shall assume that the diatomic molecules are much lighter, so that only their velocity \mathbf{v} need be taken into account.

We now introduce the most essential assumption from the point of view of our subsequent analysis, namely, that the line-broadening and shift cross sections contain left-right asymmetric terms that depend on the mutual orientation of the linear velocity \mathbf{v} and the angular velocity Ω of the diatomic molecule:

$$\Gamma + i\Delta\omega = Nv_T \left[a' + ia'' + (b' + ib'') \frac{\mathbf{v} \cdot \Omega}{|\Omega|v_T} \right] \quad (3.1)$$

where the signs of b' and b'' will change when the "right" perturbers are replaced by the "left" perturbers in accordance with the pseudoscalar character of the product $(\mathbf{v} \cdot \Omega)$.

Our aim is to find the mechanism responsible for the appearance of the left-right asymmetric scattering of light which is proportional to M_6 in (2.2) and is due to the pseudoscalar contribution to the collisional broadening cross section in (3.1). To achieve a qualitative description of this mechanism, we consider the following geometry of the experiment. Suppose the scattered light is recorded in the backward direction (180° scattering) and consider two types of experiment insofar as the polarization of the incident and scattered light is concerned, namely, $R \rightarrow R$ and $L \rightarrow L$, i.e., experiments with purely circular polarizations. It then follows from (1.4a) and (2.2) that, for backward scattering,

$$\begin{aligned} I_{RR} &= A(M_5 + M_6), & I_{LL} &= A(M_5 - M_6), \\ M_6(\delta\omega, q) &= (2A)^{-1}(I_{RR} - I_{LL}), \end{aligned} \quad (3.2)$$

where A is a constant.

The condition $\Delta J = +2$ means that scattering ensures that twice the "angular velocity" $2\Omega_{\text{rot}} = 4\pi cB(2J+3)$ is added to the frequency ω of the incident light in the case of the purely rotational transition, and to the frequency $\omega + \omega_{\mathbf{v}1\mathbf{b}}$ shifted by the vibrational quantum $\hbar\omega_{\mathbf{v}1\mathbf{b}}$ in the case of the vibrational-rotational transition. If we take the positive direction of the x axis along the incident light wave vector \mathbf{k}_1 , simple quasiclassical calculations and quantum-mechanical formulas for the matrix elements (see, for example, Ref. 19, Sec. 107) show that the $180^\circ R \rightarrow R$ scattering with $\Delta J = +2$ is mainly due to

molecules with angular velocity $\Omega_x < 0$, whereas the main contribution to $L \rightarrow L$ scattering is due to molecules with $\Omega_x > 0$. For the purposes of a qualitative discussion, we replace the true distribution of the molecules over the directions of the angular velocity Ω (or the m -components in quantum-mechanical language) by the following two-point distribution: we assume that half the molecules have $\Omega_y = \Omega_z = 0, \Omega_x = +\Omega$, and the rest $\Omega_y = \Omega_z = 0, \Omega_x = -\Omega$.

Doppler broadening of the scattered line, $\Delta\omega_D = qv_T$, due to the translational thermal motion of the molecules and the ratio of collisional to Doppler broadening will be important for the ensuing discussion. The parameter $(\Gamma/\Delta\omega_D)^{-1}$ can be rewritten in the form

$$\frac{\Delta\omega_D}{\Gamma} = \frac{qv_T}{Nv_T\sigma} = ql, \quad (3.3)$$

where $l = (N\sigma)^{-1}$ is the mean free path for the particular process. The effect in which we are interested vanishes both for very small and very large perturber densities N .

In fact, in the first case, $N \rightarrow 0$ and $ql \rightarrow \infty$. The collisions between our diatomic molecules and the perturbers are then completely turned off. If we transform to the rest system of each of the scattering molecules, we can place the target molecule at the origin $\mathbf{r} = 0$ for an infinitely long interval of time, so that the spatial dispersion effects seen in scattering because of the presence of the factor $\exp(i\mathbf{q} \cdot \mathbf{r})$ are rendered inoperative for $\mathbf{r} = 0$. All that this transformation to the moving frame and back again will yield is the Doppler frequency shift $\Delta\omega_D = \mathbf{q} \cdot \mathbf{v}$. Spatial dispersion then manifests itself only in the Doppler shape of the spectrum, but not in the polarization structure. In the other limiting case, $N \rightarrow \infty$, we have $ql \rightarrow 0$. The molecule traverses a very small distance $l \ll q^{-1}$ during the time of one free path (for this particular process). Spatial dispersion effects are then of the order of ql . We are thus left with the most interesting region of perturber pressures, for which $\Gamma \sim \Delta\omega_D$, i.e., $ql \sim 1$.

For the purposes of qualitative interpretation of the left-right asymmetry in scattering, we replace the Maxwellian velocity distribution again by the two-point distribution: half the molecules will have $v_y = v_z = 0, v_x = +v_T$ and the other half $v_y = v_z = 0, v_x = -v_T$. The qualitative model thus corresponds to the following distribution of probabilities of \mathbf{v} and Ω at a given time:

$$\begin{aligned} f(\mathbf{v}, \Omega) &= f_1(\mathbf{v})f_2(\Omega) = \left[\frac{1}{2} \delta(\mathbf{v} - \mathbf{e}_x v_T) \right. \\ &\quad \left. + \frac{1}{2} \delta(\mathbf{v} + \mathbf{e}_x v_T) \right] \left[\frac{1}{2} \delta(\Omega - \mathbf{e}_x \Omega_0) + \frac{1}{2} \delta(\Omega + \mathbf{e}_x \Omega_0) \right]. \end{aligned} \quad (3.4)$$

Consider the effect of the pseudoscalar part of the broadening b' and take $b'' = 0$. (The effect of the left-right asymmetric part of the line shift $b'' \neq 0$ for $b' = 0$ can be examined similarly.) Figure 2 shows the scattered spectra recorded in the $R \rightarrow R$ (a) and $L \rightarrow L$ (b) experiments. The broken curves show the contributions of molecules with $v_x = v_T$ and $v_x = -v_T$. To be specific, we have assumed that $b' > 0$, having thus established that, when \mathbf{v} and Ω are parallel, the given chiral perturbers produce greater broadening than

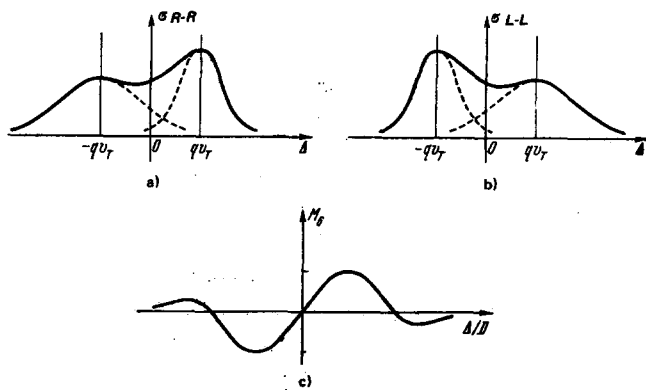


FIG. 2. Qualitative illustration of the origin of left-right asymmetry in the Raman Spectrum with $\Delta J = +2$ (see text for details).

when \mathbf{v} and $\mathbf{\Omega}$ are antiparallel. Figure 2c shows the pseudoscalar $M_6(\delta\omega, q)$, which turns out to be an odd function of detuning from the central transition frequency for $b'' = 0$.

Calculations based on a semiclassical model are analogous to those given earlier in the case of the resonance natural optical activity due to collisions.² We therefore only reproduce the final result. Assuming that (3.1) describes the broadening cross section for the transition, and that $|b' + ib''| \ll a'$, it can be shown that

$$M_1 = M_2 = 0, \quad M_7 = M_6, \quad (3.5)$$

$$3M_3 = M_4 = M_5 = \frac{A}{\sqrt{\pi}} \text{Im} F_1(\Delta, \Gamma_0, D), \quad (3.5)$$

$$M_6 = \frac{2}{3} \frac{A}{\sqrt{\pi}} \text{Im} F_2(\Delta, \Gamma_0, D); \quad (3.6)$$

where

$$F_1(\Delta, \Gamma_0, D) = i\pi^{-1/2} \int_0^{\infty} \exp\left(-i\Delta\tau - \Gamma_0\tau - \frac{D^2\tau^2}{4}\right) d\tau \\ = iD^{-1} \exp\left(\frac{\Gamma_0 + i\Delta}{D}\right) \left[1 - \Phi\left(\frac{\Gamma_0 + i\Delta}{D}\right)\right], \quad (3.7)$$

$$F_2(\Delta, \Gamma_0, D) = \frac{i}{4} D^2 \frac{b' + ib''}{a'} \frac{\Gamma_0}{D} \pi^{-1/2} \int_0^{\infty} \tau^2 \exp\left(-i\Delta\tau - \Gamma_0\tau - \frac{D^2\tau^2}{4}\right) d\tau \\ = \frac{i}{4} \frac{b' + ib''}{a'} \frac{\Gamma_0}{D} D^2 \frac{\partial^2 F_1}{\partial \Delta^2}, \quad (3.8)$$

i.e., the functions F_1 and F_2 are expressed in terms of the error integral of a complex argument and its derivative. Normalization of (3.5) and (3.6) is such that $\int M_5 d(\Delta) = A$. Moreover, in (3.5)–(3.8),

$$\Gamma_0 = N\nu_T a', \quad \Delta = \omega_1 - \omega_2 + 2\Omega, \quad D = qv_T, \quad (3.9)$$

$$\Phi(z) = 1 - 2\pi^{-1/2} \int_z^{\infty} e^{-y^2} dy.$$

In deriving (3.5)–(3.8), we retain only the first-order terms in $|b' + ib''|$. It turns out that, in this approximation, $M_6 \equiv M_7$ and the functions M_3 , M_4 , and M_5 are proportional to one another. The dimensionless quantity Δ_x in (2.15), which characterizes the left-right asymmetry of the 90°-scattered spectrum, is given by

$$\Delta_x = \pm 0.14 \frac{b'}{a'} \quad (3.10)$$

for $\Gamma_0 = D$ when $\Delta = \pm \Gamma_0$ (for simplicity, we have assumed that $a'' = b'' = 0$).

The magnitude of the asymmetry, measured for 180°

scattering in experiments of the form (3.2) for $\Delta = \pm \Gamma_0$, turns out to be greater by a factor of five:

$$\frac{I_{RR} - I_{LL}}{I_{RR} + I_{LL}} = \pm 0.7 \frac{b'}{a'}. \quad (3.11)$$

Thus, within the framework of DDA, the relative magnitude of the left-right asymmetry Δ_x in this model at the relevant pressure does not contain the small parameter a/λ , but depends on the parameter b'/a' , which characterizes the left-right asymmetry of the collision cross section.

4. LOCAL MULTIPOLE APPROXIMATION TO THE SCATTERING OF LIGHT BY LEFT-RIGHT ASYMMETRIC MOLECULES (LMA APPROACH)

In this section, we follow largely the work of Barron and Buckingham^{9,10} and survey the approach in which scattering problems are treated by including the interaction of the higher-order multipoles of the molecule (magnetic dipole and electric quadrupole) with the light-wave field. Since the behavior and orientation of the different molecules are assumed to be independent, this approach will be referred to as the local multiple approximation (LMA).

A. Expansion of induced multipole moments of the molecule in powers of a/λ and symmetry relationships

We shall suppose that the electronic state of the molecule is nondegenerate and that the frequency of the incident light lies in the transparency band of the molecule under consideration. To consider the problem of Rayleigh and vibrational-rotational Raman scattering, it is sufficient to confine our attention to the Born-Oppenheimer adiabatic approximation, which is often referred to as the Placzek approximation in the case of scattering problems. In this approximation, the scattering problem is first solved for fixed nuclei and then the dependence of the amplitude of the scattered field on the vibrational and rotational coordinates of the molecules is taken into account. As already noted, to take into account the first-order terms in a/λ in the scattered-wave amplitude, we must find the electric dipole (μ) and magnetic dipole (\mathbf{m}) as well as the electric quadrupole (θ_{ab}) moments induced in the molecule by the incident light wave. We shall use the following normalization of these moments in the cgs system of units:

$$\mu = \sum e\mathbf{r}, \quad \mathbf{m} = \frac{1}{2c} \sum e[\mathbf{r} \times \dot{\mathbf{r}}], \quad \theta_{ik} = \frac{1}{2} \sum e(3x_i x_k - r^2 \delta_{ik}). \quad (4.1)$$

In this notation, the expressions for \mathbf{m} and θ_{ik} that are linear in the amplitude of the incident wave $\mathbf{E} \exp(-i\omega t + i\mathbf{k} \cdot \mathbf{r})$ have the general form

$$m_i = i \frac{\omega}{c} \rho_{ik}^* E_k, \quad \theta_{il} = A_{kil}^* E_k. \quad (4.2)$$

Our notation is essentially the same as that used in Refs. 9 and 10 except that our tensor, ρ_{ik} , is related to the tensor G_{ik} in Refs. 9 and 10 by $G_{ik} = -i\omega\rho_{ik}$ and we use cgs units rather than SI units. In (4.2), we have confined our attention to the first nonvanishing approximation in a/λ . In other words, the right-hand sides of (4.2) contain only the field intensity E_k experienced by

the molecules and not the gradients k, E_k , etc. This is so because, already in this approximation, the tensors $\hat{\rho}$ and \hat{A} have the dimensions of L^4 and contain an extra power of the molecular size a as compared with the electric dipole polarizability $\hat{\alpha}$, which has the dimensions of L^3 .

The true tensor A_{ikh} and pseudotensor ρ_{ikh} can be referred to as the dipole-quadrupole and dipole-magnetic-dipole cross polarizabilities.²⁰ The first part of this designation (dipole) indicates that the electric field in the incident wave is looked upon as uniform. The quantum-mechanical analysis of the interaction between electrons in a molecule and the classical wave $\mathbf{E}(\mathbf{r}, t)$ in terms of the electric dipole Hamiltonian²⁾

$$\hat{V}'_{int} = -\hat{\mu} \cdot \mathbf{E}(\mathbf{r}=0, t), \quad (4.3)$$

enables us to find expressions for the tensors \hat{A} and $\hat{\rho}$; the point $\mathbf{r}=0$ corresponds here to the conventional position of the "center" of the molecule. For the non-degenerate electronic state of the molecule in the absence of a static external magnetic field, the tensors \hat{A} and $\hat{\rho}$ and the electric dipole polarizability tensor $\hat{\alpha}$ turn out to be real in the transparency region and are given by

$$\alpha_{ik} = \frac{2}{\hbar} \sum_n \frac{\omega_{n1}}{\omega_{n1}^2 - \omega^2} (\mu_i)_{1n} (\mu_k)_{n1}, \quad (4.4)$$

$$\rho_{ikh} = \frac{i}{\omega} G_{ikh} = ic \frac{2}{\hbar} \sum_n \frac{(\mu_i)_{1n} (m_k)_{n1}}{\omega_{n1}^2 - \omega^2}, \quad (4.5)$$

$$A_{ikh} = \frac{2}{\hbar} \sum_n \frac{\omega_{n1}}{\omega_{n1}^2 - \omega^2} (\mu_i)_{1n} (\theta_k)_{n1}, \quad (4.6)$$

where the sum over n of the products of the matrix elements denotes summation over the electronically excited molecular states and the subscript 1 represents the ground state. The fact that the tensors $\hat{\alpha}$, $\hat{\rho}$, and \hat{A} are real is readily understood if it is recalled that the total Hamiltonian is invariant under time reversal $t \rightarrow -t$. In fact, the nondegenerate electronic state transforms into itself under time reversal for the T -even Hamiltonian. The quantities $\hat{\mu}_i$ and $\hat{\theta}_i$ remain invariant and \hat{m}_i change sign under time reversal. The operation $t \rightarrow -t$ corresponds to transition to the complex conjugate quantities because the time dependence of the wave field is $E \sim e^{-i\omega t}$. Finally, the assumption that there is no absorption removes possible time irreversibility connected with going around the poles in the resonance denominators. In view of the foregoing, the expressions given by (4.2) turn out to be invariant under time reversal only for real ρ_{ikh} and A_{ikh} . The asterisk representing complex conjugation in (4.2) can, therefore, be omitted. We also note that all three tensors $\hat{\alpha}$, $\hat{\rho}$, and \hat{A} have finite nonzero static limits for $\omega \rightarrow 0$ (this property is not exhibited by the tensor $G_{ikh} = -i\omega_{ikh}$ discussed in Refs. 9 and 10).

The pseudotensor ρ_{ikh} is, in general, nonsymmetric in the space indices and contains nine independent components. The third-rank tensor A_{ikh} is a zero-trace sym-

metric tensor in its indices k, l , which refer to the quadrupole on the left-hand side of (4.2):

$$A_{ikh} = A_{ilh}, \quad A_{ijj} = 0, \quad (4.7)$$

so that, in general, it contains $5 \times 3 = 15$ independent components.

We have thus obtained the quadrupole and magnetic dipole induced in the molecule by the uniform electric field $\mathbf{E}(\mathbf{r}=0, t)$. The latter is present in the electric-dipole Hamiltonian (4.3). To include all first-order terms in a/λ , we must also expand in powers of a/λ the dipole moment μ_i induced by the wave in the molecule. The corresponding phenomenologic expansion is

$$\mu_i = \alpha_{ik} E_k + \beta_{ikh} \frac{\partial E_k}{\partial x_l} = \alpha_{ik} E_k + i\beta_{ikh} k_l E_k. \quad (4.8)$$

Since $\mathbf{k} \cdot \mathbf{E} = 0$ in the transverse light waves, we can add an arbitrary term of the form $c_l \delta_{lk}$ to the tensor β_{ikh} without violating (4.8). We shall always choose this term such that $\beta_{ijj} = 0$, in which case the tensor β_{ikh} will, in general, have $27 - 3 = 24$ independent components. This kind of tensor can always be decomposed into two parts, namely, an antisymmetric part and a zero-trace symmetric part in the last two indices:

$$\beta_{ikh} = \frac{1}{2} \epsilon_{ikj} (\epsilon_{jmn} \beta_{imn}) + \frac{1}{2} (\beta_{ilh} + \beta_{lkh} - \frac{2}{3} \beta_{ijj} \delta_{kl}). \quad (4.9)$$

The components of the dipole moment μ_i in (4.8) are proportional to the antisymmetric part of β_{ikh} in (4.9) and are "excited" by the magnetic field $H_i = -c/\omega e_{ikh} k_l E_k$ of the incident wave, whereas the components μ_i in (4.8) that are proportional to the zero-trace symmetric part of β_{ikh} are "excited" by the symmetric gradient

$$\frac{\partial E_k}{\partial x_l} + \frac{\partial E_l}{\partial x_k} - \frac{2}{3} \delta_{kl} \frac{\partial E_s}{\partial x_s},$$

i.e., the quadrupole part of the nonuniform electric field of the incident wave. The first term in (4.9) can, therefore, be referred to as the magnetic-dipole-dipole cross polarizability and the second as the quadrupole-dipole cross polarizability. Microscopic evaluation of the tensor β_{ikh} from (4.8) requires the inclusion of the magnetic dipole and electric quadrupole terms in the interaction Hamiltonian:

$$\hat{V}'_{int} = -\hat{\mu} \cdot \mathbf{E}(\mathbf{r}=0, t) + \hat{m} \cdot \int_{-\infty}^t c \operatorname{curl} \mathbf{E}(\mathbf{r}, t') |_{\mathbf{r}=0} dt' - \frac{1}{6} \hat{\theta}_{ie} \left(\frac{\partial E_l}{\partial x_l} + \frac{\partial E_l}{\partial x_l} \right) |_{\mathbf{r}=0}. \quad (4.10)$$

Evaluation of the induced dipole moment, which is linear in the field amplitude, with the aid of the Hamiltonian (4.10) yields (4.8) with the expression for $\hat{\alpha}$ given by (4.4) and the real tensor β_{ikh} given by (for a non-degenerate state)

$$\beta_{ikh} = -\rho_{ij} \epsilon_{jlk} + \frac{1}{3} A_{ilh}. \quad (4.11)$$

Under the above assumptions, the tensor β_{ikh} thus turns out to be uniquely related to $\hat{\rho}$ and \hat{A} . This expresses the fact that mutually symmetric cross polarizabilities are equal. It is completely analogous to the symmetry of the ordinary (dipole-dipole) polarizability tensor α_{ikh}

²⁾ We note that throughout we ignore corrections of the Lorenz-Lorentz type and similar others which are connected with the difference between the effective and macroscopic fields.

$= \alpha_{ik}$ and is a consequence of the invariance of both the Hamiltonian and the (nondegenerate) state of the molecule under time reversal.

A very important point is the covariance of the above expressions under a shift of the origin of the coordinate frame.^{20,21} In the coordinate frame K' , which is shifted relative to the original system K by a vector \mathbf{b} such that $\mathbf{r}' = \mathbf{r} - \mathbf{b}$, the quantities \mathbf{m} and θ_{ik} acquire the following additional terms:

$$\begin{aligned} \mu' &= \mu, & \mathbf{m}' &= \mathbf{m} - (2c)^{-1} [\mathbf{b} \times \dot{\mu}], \\ \theta'_{ik} &= \theta_{ik} - \frac{1}{2} [3\mu_i b_k + 3b_i \mu_k - 2\delta_{ik} (\mathbf{b} \cdot \dot{\mu})]. \end{aligned} \quad (4.12)$$

In addition, in (4.2) and (4.8), the complex amplitude of the field \mathbf{E} was interpreted as the value $\mathbf{E} = \mathbf{E}(\mathbf{r} = 0)$ at the origin of a coordinate frame attached (in general, arbitrarily) to the molecule. When we transform to the new coordinate frame, we must substitute $\mathbf{E}' \equiv \mathbf{E}'(\mathbf{r}' = 0) = \mathbf{E}(\mathbf{r} = \mathbf{b})$ in (4.2) and (4.8) at the new origin $\mathbf{r}' = 0$. Since $\mathbf{E} \sim e^{i\mathbf{k} \cdot \mathbf{r}}$, the field \mathbf{E}' takes the form $\mathbf{E}'(0) = \mathbf{E} e^{i\mathbf{k} \cdot \mathbf{b}} \approx \mathbf{E} (1 + i\mathbf{k} \cdot \mathbf{b})$. Here, we have confined our attention to the expansion that is linear in \mathbf{b} because we are only interested in the first-order terms in a/λ . To this accuracy, the corresponding transformation law for the tensors $\hat{\alpha}, \hat{\beta}, \hat{A}, \hat{\rho}$ is as follows:

$$\left. \begin{aligned} \alpha'_{ik} &= \alpha_{ik}, & \rho'_{ik} &= \rho_{ik} + \frac{1}{2} \alpha_{ij} e_{jkl} b_l, \\ A'_{kij} &= A_{kij} - \frac{1}{2} (3\alpha_{ik} b_j + 3b_i \alpha_{jk} - 2\delta_{ij} b_k \alpha_{jk}), \\ \beta'_{ih} &= \beta_{ih} - \alpha_{ih} b_l + \frac{1}{3} \delta_{kl} \alpha_{ij} b_j. \end{aligned} \right\} \quad (4.13)$$

Naturally, the symmetry relation (4.11) is also invariant under shifts of the coordinate frame. We shall now illustrate the importance of the transformation (4.13) by the following example. Consider a particle (atom or molecule) that is symmetric under inversion at some "center" $\mathbf{r} = 0$ (nuclear center in the case of an atom). In this coordinate frame, all the even-rank tensors (including A_{ikl} and β_{ikl}) and all the pseudotensors of even rank (including ρ_{ik}) that characterize the properties of the particle will vanish, i.e., $A_{ikl} = 0$, $\beta_{ikl} = 0$, $\rho_{ik} = 0$. When some other origin is chosen, non-zero components $A'_{ikl}, \beta'_{ikl}, \rho'_{ik}$ are found to appear and are given by (4.13) without assumptions about the dynamics of the system.

It is well known that the usual polarizability tensor $\alpha_{ik} = \alpha_{ki}$ is conveniently decomposed into irreducible components with respect to the group of rotations of three-dimensional space, namely, the scalar and symmetric zero-trace components. Similarly, the tensor A_{ikl} can be decomposed into three representations of rank $l = 3$ (irreducible third-rank tensor), $l = 2$ (irreducible second-rank pseudotensor) and $l = 1$ (vector). The pseudotensor ρ_{ik} is decomposed into representations with $l = 2$ (irreducible pseudotensor of rank two), $l = 1$ (vector), and $l = 0$ (pseudoscalar) (see Appendix 1). Such decompositions are convenient for the subsequent evaluation of quantities averaged over the molecular orientations.

B. Differential scattering cross section in LMA

The scattered-field amplitude in the far zone is given

by the following standard expression which corresponds to the sum of the amplitudes of dipole, magnetic dipole, and electric quadrupole radiations:

$$\mathbf{E}_2(\mathbf{R}, t) = -\frac{1}{c^2 R} \left[\left[\ddot{\mu} + \frac{1}{3c} (\dot{\theta} n_2) n + [\dot{m} n_2] n \right] n_2 \right]; \quad (4.14)$$

where n is the refractive index of the medium and the value of the right-hand side in (4.14) is taken at time $t' = t - n|\mathbf{R} - \mathbf{r}_0|/c$. Here \mathbf{R} is the point of observation, $|\mathbf{R} - \mathbf{r}_0| \approx R \gg \lambda$, $\mathbf{n}_2 = \mathbf{R}/R$, \mathbf{n}_2 is the unit vector in the direction of scattering, and $\mathbf{k}_2 = n\omega\mathbf{n}_2/c$. Quantities referring to the incident wave are indicated by the subscript 1. Thus, for the wave vector, we have $\mathbf{k}_1 = n\omega\mathbf{n}_1/c$. We must now substitute into (4.14) the expressions for μ , \mathbf{m} , and $\hat{\theta}$, induced in the molecule by the incident waves:

$$\mu_i = \left(\alpha_{ik} + i\rho_{ik} e_{shk} k_{1j} + i \frac{1}{3} A_{ikj} k_{1j} \right) E_k \exp(-i\omega t + i\mathbf{k}_1 \cdot \mathbf{r}_0), \quad (4.15a)$$

$$m_i = i \frac{\omega}{c} \rho_{ki} E_k \exp(-i\omega t + i\mathbf{k}_1 \cdot \mathbf{r}_0), \quad (4.15b)$$

$$\theta_{il} = A_{kil} E_k \exp(-i\omega t + i\mathbf{k}_1 \cdot \mathbf{r}_0). \quad (4.15c)$$

Further results can conveniently be written in terms of the projection A_2 of the amplitude \mathbf{E}_2 along the polarization unit vector \mathbf{e}_2 of the scattered wave: $A_2 = (\mathbf{e}_2^* \cdot \mathbf{E}_2)$. The scattering cross section per unit solid angle for a wave with polarization \mathbf{e}_1 , i.e., $\mathbf{E}_1 = A_1 \mathbf{e}_1$, into a wave with polarization \mathbf{e}_2 and with propagation directions \mathbf{n}_1 and \mathbf{n}_2 , respectively, is given by

$$\frac{d\sigma}{d\Omega}(\mathbf{n}_1, \mathbf{e}_1 \rightarrow \mathbf{n}_2, \mathbf{e}_2) = \frac{R^2 |A_2|^2}{|A_1|^2} = \left(\frac{\omega_2}{c} \right)^4 e_{2i} e_{1k}^* e_{2l}^* e_{1m} P_{iklm}. \quad (4.16)$$

In our particular approximation, the tensor $(4\pi)^2 N P_{iklm}$ in the LMA approach has the same significance as the tensor $\int T_{iklm} d(\delta\omega)$ introduced above [(see (1.4a)] in the DDA approach. In the present expression, N is the number of scattering molecules per unit volume. When the expression for $|A_2|^2$ is evaluated to the required accuracy, we retain only the zero-order terms in a/λ , terms proportional to α^2 , and interference terms of the first order in a/λ , which are proportional to the products $\alpha\rho$ and αA . In these small interference terms, we neglect corrections of the order of $(|\omega_1 - \omega_2|/\omega_1)$, which are relatively small even for the vibrational Raman scattering of light. The final result is

$$\begin{aligned} P_{iklm} &= \left\langle \left[\alpha_{ik} - i \frac{\omega n}{3c} (A_{ikp} n_{1p} - A_{kip} n_{2p}) \right. \right. \\ &\quad \left. \left. - i \frac{\omega n}{c} (\rho_{ik} e_{shk} n_{1p} - \rho_{ks} e_{sip} n_{2p}) \right] \left[\alpha_{lm} + i \frac{\omega n}{3c} (A_{lmt} n_{1t} - A_{mlt} n_{2t}) \right. \right. \\ &\quad \left. \left. + i \frac{\omega n}{c} (\rho_{lq} e_{qmt} n_{1t} - \rho_{mq} e_{qlt} n_{2t}) \right] \right\rangle; \end{aligned} \quad (4.17)$$

where the angle brackets represent averaging over the orientations of the molecules. It is well known that this averaging is most conveniently performed by decomposing the tensors into irreducible (with respect to the rotation group) components. The only nonzero averages are then those of the products of irreducible representations of equal dimensionality l . The final result is the well-known expression for the correlator of the tensors $\hat{\alpha}$:

$$\langle \alpha_{ik} \alpha_{lm} \rangle = C_1 \delta_{ik} \delta_{lm} + C_2 \left(\delta_{il} \delta_{km} + \delta_{im} \delta_{kl} - \frac{2}{3} \delta_{ik} \delta_{lm} \right), \quad (4.18a)$$

and the expressions for the terms of the first order in a/λ :

$$\langle \alpha_{ik} \rho_{lm} \rangle = C_3 \delta_{ik} \delta_{lm} + C_4 \left(\delta_{il} \delta_{km} + \delta_{im} \delta_{kl} - \frac{2}{3} \delta_{ik} \delta_{lm} \right), \quad (4.19a)$$

$$\langle \alpha_{ik} A_{lmn} \rangle = C_5 (e_{ilm} \delta_{kn} + e_{klm} \delta_{in} + e_{iln} \delta_{km} + e_{kln} \delta_{im}), \quad (4.20a)$$

where

$$C_1 = \frac{1}{9} \langle \alpha_{ii} \alpha_{jj} \rangle, \quad C_2 = \frac{1}{10} \left(\langle \alpha_{ij} \alpha_{ij} \rangle - \frac{1}{3} \langle \alpha_{ii} \alpha_{jj} \rangle \right), \quad (4.18b)$$

$$C_3 = \frac{1}{9} \langle \alpha_{ii} \rho_{jj} \rangle, \quad C_4 = \frac{1}{20} \left(\langle \alpha_{ij} \rho_{ij} \rangle + \langle \alpha_{ij} \rho_{ji} \rangle - \frac{2}{3} \langle \alpha_{ii} \rho_{jj} \rangle \right), \quad (4.19b)$$

$$C_5 = \frac{1}{30} e_{jik} \langle \alpha_{kp} A_{jlp} \rangle. \quad (4.20b)$$

The tensor P_{iklm} then assumes the form

$$\begin{aligned} P_{iklm} = & C_1 \delta_{ik} \delta_{lm} + C_2 \left(\delta_{il} \delta_{km} + \delta_{im} \delta_{kl} - \frac{2}{3} \delta_{ik} \delta_{lm} \right) \\ & + i \frac{\omega}{c} n C_3 (\delta_{ik} e_{lmj} - e_{ikj} \delta_{lm}) (n_{1j} + n_{2j}) \\ & + i \frac{\omega}{c} n C_4 \left[n_{1j} (2\delta_{il} e_{kmj} + \delta_{lm} e_{klj} + \delta_{kl} e_{imj}) \right. \\ & \left. - n_{2j} (2\delta_{km} e_{ilj} + \delta_{im} e_{klj} + \delta_{kl} e_{imj}) - \frac{2}{3} (\delta_{ik} e_{lmj} - \delta_{lm} e_{ikj}) (n_{1j} + n_{2j}) \right] \\ & - i \frac{\omega}{c} n C_5 [n_{1j} (2\delta_{km} e_{ilj} + \delta_{im} e_{klj} + \delta_{kl} e_{imj}) \\ & - n_{2j} (2\delta_{il} e_{kmj} + \delta_{kl} e_{imj} + \delta_{im} e_{klj}) \\ & + n_{1j} (\delta_{ij} e_{klm} - \delta_{jl} e_{ikm}) + n_{2j} (\delta_{kj} e_{ilm} - \delta_{mj} e_{ikl})]. \quad (4.21) \end{aligned}$$

The expression for the scattering cross section is obtained by multiplying this tensor by the polarization unit vectors [see (4.16)]. In the case of Raman scattering, the tensor α_{ik} must be replaced by its variation with respect to the molecular coordinate Q , i.e., $\alpha_{ik} \rightarrow (\partial \alpha_{ik} / \partial Q) Q$ in all these formulas. This also applies to the tensors ρ_{ik} and A_{ik} .

We note particularly that the above expressions do not depend (to within terms of the order of $\sim a/\lambda$, inclusive) on the choice of the origin in the molecule if we take into account the transformation rules given by (4.13).

The differential scattering cross section per unit angle is characterized by five constants: two are of zero order in a/λ and three are first order in this ratio. The zero-order terms (electric dipole) are well known: they correspond to scalar and symmetric zero-trace scattering. At the same time, since the electronic term is nondegenerate in the adiabatic approximation, there is no antisymmetric scattering (see Refs. 15 and 16 in this connection). It may be said that scattering of zero order in a/λ corresponds to the process where a photon corresponding to the spherical vector of the field of electric-dipole type (see Ref. 13, Sec. 46) is removed from the incident plane wave and a similar photon is emitted into the scattered wave, i.e., we have the $D \rightarrow D$ process. Scalar scattering then proceeds without a change in the m -components of the spherical vector whereas symmetric zero-trace scattering does, in general, involve this change.

To avoid misunderstanding, we note the following. It is well known (see, for example, Ref. 11) that the selection rule for symmetric zero-trace and antisymmetric $D \rightarrow D$ scattering is the same as for the infrared absorption due to quadrupole and magnetic-dipole transitions, respectively. This is why the above types of

pure dipole scattering are frequently colloquially referred to as "quadrupole and magnetic-dipole scattering." In our case, this terminology will only confuse the situation because we shall have to consider scattering with an actual participation of electric quadrupoles and magnetic dipoles. We shall therefore avoid this terminology.

First-order terms in a/λ in this scattering cross section arise due to interference of the $D \rightarrow D$ process with the $M \rightarrow D$, $D \rightarrow M$, $Q \rightarrow D$, and $D \rightarrow Q$ processes. Here, M and Q represent spherical photons of the magnetic-dipole and electric-quadrupole type (see Ref. 13, Secs. 46 and 47). The fact that the M and Q photons have positive parity whereas the D photon has a negative parity shows immediately that terms of the first order in a/λ change sign under space reflection during scattering by freely rotating systems. In other words, such terms have different signs for the right-handed and left-handed molecules, whereas, for left-right symmetric molecules, they are zero. The first-order correction in a/λ is also found to vanish for the racemic (50%/50%) mixture of left- and right-handed molecules.

Specifically, the two constants C_3 and C_4 are due to interference between the $D \rightarrow D$ process and the $D \rightarrow M$ and $M \rightarrow D$ processes. The constant C_3 appears as a result of interference of the scalar α_{ii} with the pseudo-scalar ρ_{jj} and C_4 originates in the interference of the irreducible symmetric tensors of rank two, $\hat{\alpha}_{ik}$ and $\hat{\rho}_{ik}$. The further constant C_5 corresponds to interference of $D \rightarrow D$ with $D \rightarrow Q$ and $Q \rightarrow D$ processes, in which only the symmetric zero-trace part of the tensor A_{ikl} (irreducible tensor of rank two) and a similar representation of α_{ij} are involved.

C. Angle integrated scattering cross section

In order to evaluate the scattering cross section summed over the scattered wave polarizations, we must replace the tensor $e_{2i} e_{2i}^*$ by the projection operator $e_{2i} e_{2i}^* \rightarrow \delta_{ii} - n_{2i} n_{2i}$. It is then a relatively simple matter to obtain the integrated cross section by integrating with respect to the solid angle $d\Omega_{n_2}$. A still simpler procedure is to use the general expression for the radiation intensity integrated with respect to the angles. Neglecting second-order terms in a/λ (see Ref. 22 or Appendix 2), we find that the integrated intensity is given by the usual dipole formula

$$I \text{ (erg/sec)} = \frac{2}{3c^3} \ddot{\mu}^2 = \frac{\omega^4}{3c^3} (\mu_i \mu_i^*). \quad (4.22)$$

Substitution for μ_i from (4.8), averaging over the angles, and division by the flux density $c |E|^2 / 8\pi$ (erg/cm²·sec) yields the following total cross section:

$$\sigma = \frac{8\pi}{3} \left(\frac{\omega a}{c} \right)^4 \left[\left(C_1 + \frac{10}{3} C_2 \right) + 2 \frac{\omega}{c} \left(C_3 + \frac{10}{3} C_4 \right) P_c \right]; \quad (4.23)$$

where $P_c = i \langle n_i [e_i^* e_i] \rangle$ is the degree of circular polarization of the incident wave; $P_c = +1$ and $P_c = -1$ for right- and left-polarized radiation, respectively. We note that, in contrast to the differential cross section $d\sigma/d\Omega$, the total cross section σ does not include the quadrupole term C_5 . This is so because the quadrupole

photon has $J=2$ and cannot, therefore, interfere with the dipole photon (in the incident wave) during averaging over orientations. In contrast to this, the magnetic dipole photon in the incident wave ($J=1$) does interfere with the electric dipole ($J=1$) and the parity restriction is removed by the left-right asymmetry of the molecule.

In conclusion, we note the following curious point. Consider a one-component gas of left-right asymmetric molecules of low density, so that the refractive index is very close to unity. Suppose further that the symmetry of the molecules allows the presence of only the scalar part of the polarizability α_{it} , i.e., the anisotropy of the dipole-dipole polarizability α_{it} is zero. We thus arrive at a situation that was examined long ago by Rayleigh. It was, in fact, Rayleigh who appears to have been the first to point out that, in the case of molecules with a purely isotropic electric dipole polarizability, the Rayleigh scattering cross section of a gas can be expressed in terms of its refractive index. We now draw attention to the fact that terms of the first order in a/λ in the scattering cross section are then also expressed in terms of the refractive properties of the gas:

$$\sigma_{\pm} = \frac{4}{3\pi} \left(\frac{\omega}{c}\right)^4 \frac{n_{\pm}^{-1}}{N} \frac{n_{\pm} + n_{\pm} - 2}{2N}; \quad (4.24)$$

where the subscripts (+) and (-) refer to the right- and left-polarized waves, respectively. The most convenient way of deriving (4.24) is to use the optical theorem from wave theory (see, for example, Ref. 23), according to which the refractive index is determined by the zero-angle scattering amplitude. We note, finally, that (4.24) cannot be written as a simple generalization of Rayleigh's formula $\sigma_{\pm} = \text{const} \cdot (n_{\pm} - 1)^2$. This type of "generalization" would yield $(\sigma_{+} - \sigma_{-})/\sigma$ greater by a factor of two than the correct value given by (4.24).

D. The "complete experiment" within the framework of LMA

Although the existence of left-right asymmetry in light scattering has itself been reliably confirmed by experiment,¹⁰ actual measurements of this asymmetry carried out to-date have not, unfortunately, been very accurate. Nevertheless, it is basically interesting to consider the question of the "complete experiment" within the framework of the LMA approach.

Left-right asymmetric terms $\sim C_3$, C_4 , and C_5 in the scattering cross section have no effect if both polarizations, i.e., the polarization of the incident and scattered waves, are plane (linear). It is, therefore, sufficient to have two experiments to determine C_1 and C_2 ; for example, one can measure I_{xx} and $I_{xx} = I_{yy} = I_{zz}$ for scattering at $\theta = 90^\circ$ (Fig. 1).

The essential difference between the LMA approach as exemplified by (4.21) and the DDA approach represented by (2.2) is that the polarization measurements of the cross section at a single angle are no longer sufficient to enable us to determine all five constants $C_1 - C_5$ in the LMA approach. In particular, calcula-

tions similar to those performed in Ref. 6 show that, for any fixed scattering angle in the LMA approach, there are only four linearly independent experiments, for example, I_{xx} , I_{yy} , I_{zz} , I_{xx} . In order to determine all five constants $C_1 - C_5$, one must perform polarization measurements for at least two different values of the scattering angle.

The following is an example of such a "complete experiment":

$$\begin{aligned} I_{zz}(\theta = 90^\circ), \quad I_{yz}(\theta = 90^\circ), \quad I_{Rz}(\theta = 90^\circ), \\ I_{Rx}(\theta = 90^\circ), \quad I_{RR}(\theta = 180^\circ). \end{aligned} \quad (4.25)$$

Accordingly, measurements of only the left-right asymmetric constants C_3, C_4, C_5 in the LMA approach can be achieved within the framework of the following experiments:

$$\left. \begin{aligned} \theta = 90^\circ: (I_{Rz} - I_{Lz}) &= 2 \left(\frac{\omega}{c}\right)^5 (C_3 + \frac{7}{3}C_4 - C_5), \\ (I_{Rx} - I_{Lx}) &= 2 \left(\frac{\omega}{c}\right)^5 \cdot 2(C_4 + C_5), \\ \theta = 180^\circ: (I_{RR} - I_{LL}) &= 2 \left(\frac{\omega}{c}\right)^5 \cdot 16(C_4 - C_5). \end{aligned} \right\} \quad (4.26)$$

Measurements of the cross section differences (4.26) are quite difficult. Such measurements are, nevertheless, to be preferred as compared with measurements selected from (4.25) with subsequent subtraction of the small differences between large quantities recorded for (4.25) under appreciably different experimental conditions.

5. RANGES OF VALIDITY OF DDA AND LMA

We have examined two approaches to taking spatial dispersion into account in molecular scattering of light. The problem now naturally arises as to what is the relationship between these two approaches and what is the range of validity of each.

Let us begin by considering the limiting case in which these two regions of validity overlap. As noted in the Introduction, DDA means that we can use the dipole permittivity $\epsilon_{ik}(\mathbf{r}, t)$ or polarizability α_{ik} at each point. The corresponding approximation in the local multipole approach is the so-called two-group mechanism.¹⁴ It involves the following model of the interaction between a molecule and a light field. Let us suppose that a molecule of size $\sim a$ consists of K structural units of size $b \ll a$, located at the points $\mathbf{r} = \mathbf{r}^{(j)}$ ($j = 1, \dots, K$), so that $|\mathbf{r}^{(j)}| \sim a$. We shall now suppose that each structural unit has only the dipole polarizability tensor $\alpha_{ik}^{(j)}$ and all the higher-order tensors $\rho_{ik}^{(j)}$, $A_{ikl}^{(j)}$ are zero. More precisely, this may be formulated in the form of the following approximate expressions:

$$\alpha^{(j)} \sim b^3, \quad \rho^{(j)} \sim b^4 \approx 0, \quad A^{(j)} \sim b^4 \approx 0. \quad (5.1)$$

However, the assertion that the tensors $\rho_{ik}^{(j)}$ and $A_{ikl}^{(j)}$ are zero and the estimates (5.1) can be made for each structural unit only in its "own" coordinate frame with origin at the point $\mathbf{r} = \mathbf{r}^{(j)}$. The transformation to a coordinate frame that is common to all the components of the molecule can be based on (4.13), which gives

$$\left. \begin{aligned} \alpha_{ik} &= \sum_j \alpha_{ik}^{(j)}, \\ \rho_{ik} &= \frac{1}{2} \sum_j x_p^{(j)} \alpha_{il}^{(j)} e_{ikp}, \\ A_{ikl} &= -\frac{3}{2} \sum_j \left(x_k^{(j)} \alpha_{il}^{(j)} + x_l^{(j)} \alpha_{ik}^{(j)} - \frac{2}{3} \delta_{kl} x_p^{(j)} \alpha_{ilp}^{(j)} \right). \end{aligned} \right\} (5.2)$$

This still depends on the choice of the origin but, if we evaluate the coefficients C_3, C_4, C_5 , which determine the scattering cross section, we find that they are no longer functions of the choice of the origin. In particular, it follows from (5.2) that

$$C_3 = 0, \quad C_4 = -3C_5 = \frac{1}{20} \cdot \frac{1}{2} \sum_{i,p} \alpha_{ik}^{(i)} \alpha_{ilm}^{(p)} e_{ilm} (x_m^{(j)} - x_m^{(p)}), \quad (5.3)$$

which involves the sum of the contributions of different pairs j, p of structural units and this is the origin of the phrase, "two-group mechanism." If we rewrite this sum over all j, p in the form of a sum, subject to the condition $j < p$, we can remove the coefficient $1/2$ from (5.3). As noted in Ref. 10, the scalar part ρ_{ii} of the tensor $\hat{\rho}$ (which is known to determine the natural optical activity of liquids) in the "two-group approximation" is zero. This is easily verified on the basis of (5.2). The "two-group mechanism" is, therefore, a possible mechanism for the left-right asymmetry, but only in the case of scattering (through nonzero angle!). It is not suitable for the refractive index. This is why the constant C_3 is also zero in this mechanism.

Since $C_4 = -3C_5, C_3 = 0$, the left-right asymmetric terms in the tensor P_{iklm} in (4.21) assume the form

$$\delta P_{iklm} = i \frac{\omega}{c} n C_4 \left\{ \left[\frac{4}{3} (n_{1j} - n_{2j}) (\delta_{il} e_{kmj} + \delta_{im} e_{klj} + \delta_{kl} e_{imj} + \delta_{km} e_{ilj}) \right] + \left[\frac{2}{3} (n_{1j} + n_{2j}) (\delta_{il} e_{kmj} - \delta_{km} e_{ilj} + \delta_{im} e_{klj} - \delta_{ik} e_{lmj}) \right] + \frac{1}{3} n_{1j} (\delta_{ij} e_{klm} - \delta_{jl} e_{ikm}) + \frac{1}{3} n_{2j} (e_{ilm} \delta_{kj} - \delta_{jm} e_{ikl}) \right\}. \quad (5.4)$$

This expression is written in the form of two terms. The term in the second pair of brackets is arranged so that, when it is multiplied by the polarization unit vectors $e_{2i} e_{1k}^* e_{2l}^* e_{1m}$, subject to the transversality conditions $(\mathbf{n}_1 \cdot \mathbf{e}_1) = 0$ and $(\mathbf{n}_2 \cdot \mathbf{e}_2) = 0$, the result is identically zero.

In order to compare this expression with the left-right asymmetric terms in the DDA approach, we assume that the correlation between the fluctuations $\langle \delta \epsilon_{ik}(\mathbf{0}) \delta \epsilon_{lm}(\mathbf{r}) \rangle$ extends to distances $|\mathbf{r}| \sim a$, much shorter than the wavelength. More precisely, $a \ll |\mathbf{q}|^{-1}$, where $\mathbf{q} = \mathbf{k}_1 - \mathbf{k}_2$ is the change in the wave vector of the photon after scattering. If in (2.4) we confine our attention to the first approximation in qa , we find that $M_7 = M_8$,

$$\int M_8(q, \delta\omega) d(\delta\omega) = -\frac{1}{30} q e_{ilp} \int \langle \delta \epsilon_{ik}(\mathbf{0}) \delta \epsilon_{lm}(\mathbf{r}) r_p \rangle d^3r, \quad (5.5)$$

and the corresponding terms in T_{iklm} are

$$\delta T_{iklm} = i M_8 (e_{ilp} \delta_{km} + e_{imp} \delta_{kl} + e_{klp} \delta_{im} + e_{kmp} \delta_{il}) n_p. \quad (5.6)$$

If we compare (5.3)–(5.6), and use the transversality condition, we find that the results are quantitatively the same if the fluctuations in the permittivity tensor $\delta \hat{\epsilon}(\mathbf{r})$ in the DDA approach are taken in the form

$$\delta \epsilon_{ik}(\mathbf{r}) = 4\pi \sum_j \delta^{(j)}(\mathbf{r} - \mathbf{r}^{(j)}) \alpha_{ik}^{(j)}. \quad (5.7)$$

This, in fact, corresponds to the basis of the "two-group mechanism" in the LMA approach.

We note that the above comparison cannot be looked upon as an argument either for or against the validity of the two-group mechanism in the case of real molecules, and simply serves as an aid to a better understanding of the physical assumptions used in LMA and DDA.

To establish the differences between the two approaches, we turn now to DDA and consider the form of the *integrated* cross section (with respect to the frequency of the scattered light) in the DDA approach. We must first define our terms. We must establish the frequency interval over which the cross section must be integrated in order to obtain some useful result for some particular variable. For example, it is clear that the intensity of the scalar part of the Rayleigh line, integrated with respect to the frequency, which was calculated long ago by Einstein from thermodynamic considerations, is not directly related to the intensity of the individual lines in the vibrational Raman spectrum, which are separated from the Rayleigh line by $100\text{--}1000 \text{ cm}^{-1}$. This shows that an integral over a much smaller frequency interval should already exhibit certain definite invariance properties, i.e., a kind of spectroscopic stability. We shall now show that $\delta\omega = |\mathbf{q}|v$, can be taken as this minimum frequency interval, where v is the characteristic velocity of propagation of perturbations in the medium under consideration. We begin by considering the expression for the scattering cross section measured with a spectroscopic device with an instrumental function $g(\Delta\omega)$, normalized so that $\int g(\Delta\omega) d(\Delta\omega) = 1$. Apart from numerical coefficients and factors such as the polarization unit vectors, the DDA approach yields

$$\begin{aligned} I_{\text{meas}}(n_2, \omega_2) &\propto \int \frac{dR(\omega_2 + \Delta\omega)}{d\omega} g(\Delta\omega) d(\Delta\omega) \propto \\ &\propto \int T_{iklm}(\mathbf{q}, \omega_1 - \omega_2 - \Delta\omega) g(\Delta\omega) d(\Delta\omega). \end{aligned} \quad (5.8)$$

If we take the Fourier transform of the instrumental function

$$G(\tau) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega g(\Delta\omega) e^{-i\Delta\omega\tau}, \quad G(0) = 1, \quad (5.9)$$

we find that the scattered intensity at frequency ω_2 , as measured by the instrument, is determined not by the original tensor $T_{iklm}(\mathbf{q}, \omega_1 - \omega_2)$ given by (1.4b), but by the tensor

$$\begin{aligned} T'_{iklm}(\mathbf{q}, \omega_1 - \omega_2) &= \frac{1}{2\pi} \int \langle \delta \epsilon_{ik}^*(\mathbf{R}, t) \delta \epsilon_{lm}(\mathbf{R} + \mathbf{r}, t + \tau) \rangle \\ &\times G(\tau) \exp[-i(\omega_1 - \omega_2)\tau + i\mathbf{q}\mathbf{r}] d^3r d\tau. \end{aligned} \quad (5.10)$$

In other words, \hat{T}' differs from \hat{T} as given by (1.4b) by the fact that the space-time correlator $\langle \delta \hat{\epsilon} \cdot \delta \hat{\epsilon} \rangle$ is multiplied by the function $G(\tau)$. General properties of Fourier transforms show that $G(\tau) \sim 1$ only for $\tau \leq \Delta\omega_0^{-1}$, where $\Delta\omega_0$ is the width of the instrumental function $G(\Delta\omega)$. The function $G(\tau)$ falls off rapidly for

larger values of τ [if the function $g(\bar{\Delta}\omega)$ is smooth the reduction in $G(\tau)$ for $|\tau| \rightarrow \infty$ is exponential].

We now assume that the correlator $\langle \delta\hat{\epsilon}(\mathbf{R}, t) \times \delta\epsilon(\mathbf{R} + \mathbf{r}, t + \tau) \rangle$ is nonzero only within the sphere $r \leq a_0 + v|\tau|$, where v is the characteristic velocity of perturbations in the medium, and a_0 is the simultaneous correlation length:

$$\langle \delta\hat{\epsilon}(\mathbf{R}, t) \cdot \delta\hat{\epsilon}(\mathbf{R} + \mathbf{r}, t + \tau) \rangle = 0 \quad \text{for } |\mathbf{r}| \geq a_0 + v|\tau|. \quad (5.11)$$

Far from the phase transition points the parameter a_0 is of the order of a few molecular dimensions and measures the short-range order. To within an order of magnitude, v is equal to the velocity of sound, i.e., $v \sim 10^4 - 10^5$ cm/sec. In the case of elementary excitations such as excitons, v may turn out to be of the order of $10^7 - 10^8$ cm/sec.

When the integral in (5.10) is evaluated subject to (5.9) and (5.11), two limiting cases may be encountered, namely, high and low resolution $\Delta\omega_0$ of the spectroscopic instruments. In the case of high resolution, when $\Delta\omega_0 \ll qv$, we have $q\mathbf{r} \sim qv/\Delta\omega_0 \gg 1$ in the region where both factors, i.e. $\langle \delta\epsilon \cdot \delta\epsilon \rangle$ and $G(\tau)$ are appreciably different from zero. Spatial dispersion, i.e., the q -dependence of T'_{iklm} , is then important and one must use the expansions of the DDA approach given by (2.2)–(2.11). If, on the other hand, we have low resolution, $\Delta\omega_0 \gg qv$, the exponential $\exp(i\mathbf{q} \cdot \mathbf{r})$ can be replaced by unity over a large portion of the integration range. The result is the simple Placzek theory with the q -independent tensor T'_{iklm} , i.e., without spatial dispersion:

$$T'_{iklm}(\omega_2, \omega_1) \approx M'_{scal}(\omega_2) \delta_{ik} \delta_{lm} + M'_{sym}(\omega_2) \left(\delta_{il} \delta_{km} + \delta_{im} \delta_{kl} - \frac{2}{3} \delta_{ik} \delta_{lm} \right). \quad (5.12)$$

Moreover, we can use (5.9)–(5.11) to estimate the degree of approximation involved in (5.12). It is convenient to do this by writing down the expressions for the functions M'_i ($i = 1-6$) from (2.2) as measured by the instrument with spectral resolution $\Delta\omega_0 \gg qv$:

$$M'_1 = M'_{scal} \left[1 + O(ka)^2 + O\left(\frac{qv}{\Delta\omega_0}\right)^2 \right], \quad (5.13)$$

$$M'_2 = \sqrt{M'_{scal} M'_{sym}} \left[O(ka)^2 + O\left(\frac{qv}{\Delta\omega_0}\right)^2 \right], \quad (5.14)$$

$$M'_3 = \frac{1}{3} M'_{sym} \left[1 + O(ka)^2 + O\left(\frac{qv}{\Delta\omega_0}\right)^2 \right], \quad (5.15)$$

$$M'_4 = M'_{sym} \left[1 + O(ka)^2 + O\left(\frac{qv}{\Delta\omega_0}\right)^2 \right], \quad (5.16)$$

$$M'_5 = M'_{sym} \left[1 + O(ka)^2 + O\left(\frac{qv}{\Delta\omega_0}\right)^2 \right], \quad (5.17)$$

$$M'_6 = M'_{sym} \left[O(ka)^4 + O\left(\frac{qv}{\Delta\omega_0}\right)^4 \right], \quad (5.18)$$

$$M'_7 - M'_8 = M'_{sym} \left[O(ka)^3 + O\left(\frac{qv}{\Delta\omega_0}\right)^3 \right]; \quad (5.19)$$

where $O(x)$ represents small quantities of the order of x .

Roughly speaking, the LMA approach considered in Sec. 4 is concerned with the polarization structure of the small terms represented by $O(ka)$ in (5.18).¹ In this sense, the LMA approach may be said to have the higher precision of the order of a/λ , inclusive. At the same time, LMA does not enable us to take into account fine spectral effects due to the spreading of the fluctua-

tion correlator with time over large ($\geq \lambda$) distances. In this sense, the LMA approach has lower precision because it is only concerned with scattered intensities averaged over the spectral interval $\Delta\omega_0 \geq qv$.

The limiting value of the spectral resolution $\Delta\omega_{lim} = qv$ can be written in the form $\Delta\omega_{lim} = \omega_0(v/c_{ph})^2 \sin^2(\theta/2)$, where $c_{ph} = c/n$ is the phase velocity in the medium and θ is the scattering angle. Thus, in the typical situation $\Delta\omega_{lim}/\omega_0 \sim 10^{-3} - 10^{-6}$, since the velocity v is much smaller than the velocity of light (see above).

We note that spatial dispersion, i.e., the dependence on the wave vectors \mathbf{k}_1 and \mathbf{k}_2 of the incident and scattered waves appears in different ways in LMA and DDA. In particular, in DDA, we must take into account the complicated functional dependence on \mathbf{k}_1 and \mathbf{k}_2 , but only through the difference $\mathbf{q} = \mathbf{k}_1 - \mathbf{k}_2$. Conversely, in the LMA approach, we have the dependence on each of the vectors \mathbf{k}_1 and \mathbf{k}_2 separately, but in the form of a polynomial in $\mathbf{k}_1, \mathbf{k}_2$ of degree not higher than one.

To describe low-resolution experiments ($\Delta\omega_0 \gg qv$) that are not too accurate, i.e., if we neglect corrections of the order of $(a/\lambda)^n$ and $(qv/\Delta\omega_0)^n$, it is sufficient to use a still simpler approach, namely, the *local-dipole approximation* (LDA) which is described in all textbooks on electrodynamics, quantum electrodynamics and molecular optics. In the LDA approach, the polarization dependence of the scattering cross section is given by the well-known expression (5.12). The parameter n then characterizes the inadequacy of the LDA approach: $n = 2$ for left-right symmetric terms and $n = 1$ for left-right asymmetric terms.

Conversely, measurement of the polarization characteristics of scattering performed with very high precision (better than a/λ) and very high spectral resolution (better than qv) would already need the *distributed multipole approximation* (DMA) for their interpretation. Since this problem is very difficult both experimentally and theoretically, we shall not discuss DMA here. All the foregoing may be summarized in the following table:

TABLE I.

Measurement precision	Spectral resolution $\Delta\omega_0$	Worse than qv	Better than qv
	~ 1		LDA
$\sim \frac{a}{\lambda}$		LMA	DMA

6. ROTATIONAL RAMAN SCATTERING OF LIGHT BY NON CENTRALLY-SYMMETRIC MOLECULES

We have seen that observed effects of the first order in a/λ are wholly determined by the left-right asymmetry of the ensemble of scattering molecules. For left-right symmetric molecules, effects $\sim a/\lambda$ are therefore absent and corrections to dipole processes are of the order of $(a/\lambda)^2$ (in the local approximation). Since, in the visible range, $a/\lambda \sim 10^{-3}$, the corresponding corrections are of the order of 10^{-6} of the dipole-dipole

scattering cross sections. Such small corrections are practically impossible to observe against a large background. However, the exception is the situation where some particular frequencies are forbidden in the scattered radiation for $D \rightarrow D$ processes. The $D \rightleftharpoons Q$ and $D \rightleftharpoons M$ processes then have a relatively low probability, but can be observed without a background.

We note that the appearance of new Raman lines corresponding to a change in the parity of the state of the scatterer due to the $D \rightleftharpoons Q$ and $D \rightleftharpoons M$ processes appears to have been discussed for the first time in Ref. 24. However, the discussion given in that paper was, from our point of view, exceedingly complicated and laborious because the adiabatic Born-Oppenheimer approximation, i.e., the Placzek approximation in scattering theory, was not used, and all the formulas were written down directly for the quantized rotational states of the molecule. In contrast, our discussion is based, as in Sec. 4, on the preliminary evaluation of the induced multipole moments, followed by averaging over translational, rotational, and vibrational motion of the nuclei. This, i.e., the adiabatic, approximation turns out to be much more convenient in the discussion of such important questions as covariance with respect to the choice of the origin of the reference frame, the two-group mechanism, and so on. Let us consider some specific examples.

a) The methane molecule, CH_4 . This molecule has symmetry planes and is left-right symmetric. The terms of the first order in a/λ are therefore absent from the scattered intensity. The electric dipole polarizability $\alpha_{i\hbar}$ for this molecule in the vibrational ground state reduces to the scalar $\alpha_{i\hbar} = \alpha_0 \delta_{i\hbar}$ because of the presence of four third-order symmetry axes. As is well known, rotational Raman scattering by this molecule is therefore absent (the rotation of the molecule does not modulate the induced dipole moment $\mu = \alpha_0 \mathbf{E}$). However, this conclusion is valid only for $D \rightleftharpoons D$ processes. Since CH_4 does not have an inversion center, the process $D \rightleftharpoons Q$ is not, in general, allowed. In this approximation, the rotation of the molecule is accompanied by the modulation of the components of the induced current (μ and $\theta_{i\hbar}$) at the ordinary and tripled rotational frequencies. In quantum-mechanical language, this corresponds to transitions with $\Delta J = \pm 1$ and $\Delta J = \pm 3$. The cross section may amount to $\sim (a/\lambda)^2 \sim 10^{-6}$ of the Rayleigh cross section. Since, however, the Rayleigh background is absent at the rotational lines of methane, one would hope that this scattering would not be too difficult to detect, especially since the rotational constant of methane in the vibrational ground state is relatively large ($B \approx 5 \text{ cm}^{-1}$). The dependence of the cross section for the rotational $Q \rightleftharpoons D$ Raman scattering by methane on the polarization and propagation directions ($\mathbf{e}_1, \mathbf{e}_2, \mathbf{n}_1, \mathbf{n}_2$) is written out in Appendix 3.

b) Linear molecules. In the case of scattering by asymmetric linear molecules, for example, HCL or HD, we have both the well-known lines with $\Delta J = 0, \pm 2$ ($D \rightarrow D$ process) and the very weak lines with $\Delta J = \pm 1, \Delta J = \pm 3$ ($M \rightleftharpoons D$ and $Q \rightleftharpoons D$ processes). The intensity of the latter lines is lower by a factor of 10^4 – 10^6 as com-

pared with the allowed lines with $\Delta J = 0, \pm 2$.

The isotope-substituted hydrogen molecule HD is also interesting because it can be analyzed exactly. Thus, within the framework of the adiabatic approximation, the electronic properties of this molecule are the same as those of H_2 . If we take the origin of the coordinates at the mid-point between the nuclei (which are fixed in the adiabatic approximation), then for both molecules, i.e., HD and H_2 , the tensors $\beta_{i\hbar}, A_{i\hbar}$, and $\rho_{i\hbar}$ are all zero because of the presence of a center of inversion. However, to achieve the correct description of the time dependence of the scattered-wave amplitude, i.e., of its spectrum, we must place the origin at the center of gravity of the molecule which is free from periodic displacements at the rotation frequency. In this new coordinate frame, the tensors $\rho_{i\hbar}, A_{i\hbar}$, and $\rho_{i\hbar}$ of the HD molecule assume nonzero values, in complete correspondence with the fact that, when the motions of the nuclei, i.e., their masses, are taken into account, the HD molecule does not have a center of symmetry. The essential point is that the values of the tensors $\hat{\beta}, \hat{A}, \hat{\rho}$ can be expressed through (4.13) in terms of well-known variables such as the displacement vector \mathbf{b} , which is equal to $1/6$ of the separation between the nuclei, and the electric dipole polarizability tensor $\alpha_{i\hbar}$, which is known from various experiments.²⁵ The large value of the rotational constant ($B \approx 46 \text{ cm}^{-1}$) means that one can use spectroscopic instruments with relatively low resolution and, therefore, high luminosity. Appendix 4 lists the corresponding expressions and numerical values for scattering by HD molecules with $\Delta J = \pm 1$ and $\Delta J = \pm 3$.

Since the anisotropy of the electric-dipole polarizability of the hydrogen molecule is low (see, for example, Ref. 25), $3(\alpha_{\parallel} - \alpha_{\perp})/(\alpha_{\parallel} + 2\alpha_{\perp}) \approx 0.377$, it is instructive to consider the limiting case obtained for $\alpha_{\parallel} = \alpha_{\perp}$. In this limiting case, the rotation of the molecule does not modulate the electric dipole polarizability $\alpha_{i\hbar} = \alpha_0 \delta_{i\hbar}$. The appearance of rotational lines with the selection rule $\Delta J = \pm 1$ in the case of the HD molecule is due to the simple fact that the position $\mathbf{r}(t)$ of the "electric-dipole center of gravity" (compare with Ref. 26) rotates around the mechanical center of gravity. The complex scattering amplitude which contains the phase factor $\exp[i(\mathbf{k}_1 - \mathbf{k}_2)\mathbf{r}(t)]$, then acquires, because of the rotation $\mathbf{r}(t) \sim \sin(\Omega t + \varphi)$ terms of the first degree in $\mathbf{r}(t)$:

$$\exp[i(\mathbf{k}_1 - \mathbf{k}_2)\mathbf{r}(t)] \approx 1 + i(\mathbf{k}_1 - \mathbf{k}_2)\mathbf{r}(t). \quad (6.1)$$

The first term in this expression corresponds to the usual unshifted scattering and the second corresponds to scattering with selection rules $\Delta J = \pm 1$. In this approximation with $\alpha_{\parallel} = \alpha_{\perp}$, scattering with $\Delta J = \pm 3$ does not appear. It is interesting to note that, for polarization with $\alpha_{\parallel} = \alpha_{\perp}$, both types of scattering ($\Delta J = 0$ and $\Delta J = \pm 1$) are scalar. In other words, the scattering cross section corresponding to $\Delta J = \pm 1$ is proportional to $(\omega/c)^4 |\mathbf{e}_1 \mathbf{e}_2^*|^2 |\mathbf{k}_1 - \mathbf{k}_2|^2$. The scattered intensity with $\Delta J = \pm 1$ is then a maximum for 180° scattering, and zero for zero-angle scattering. The scattered intensity with the selection rule $\Delta J = \pm 3$ is also a maximum for 180° scattering and tends to zero as $\sim |\mathbf{k}_1 - \mathbf{k}_2|^2$ for

small scattering angles although its polarization dependence no longer reduces to $1 + |\mathbf{e}_1 \cdot \mathbf{e}_2|^2 - (2/3)|\mathbf{e}_1 \cdot \mathbf{e}_2^*|^2$, and can have a more complicated form.

APPENDIX

1. Decomposition of cross polarizability tensors $\hat{\rho}$ and \hat{A} into representations irreducible under the rotation group

The true tensors α_{ik} and A_{ikl} and the pseudotensor ρ_{ik} can be decomposed into the following irreducible representations:

$$\alpha_{ik} = \alpha_{ik}^{(0+)} + \alpha_{ik}^{(2+)} = \alpha_0 \delta_{ik} + \frac{1}{2} (\alpha_{ik} + \alpha_{ki} - \frac{2}{3} \alpha_{jj} \delta_{ik}), \quad (\text{A1.1})$$

$$A_{ikl} = A_{ikl}^{(3+)} + A_{ikl}^{(3-)} + A_{ikl}^{(1-)} = A_{ikl}^{(3+)} + \frac{1}{3} (e_{kij} 2A_{jl}^c - e_{kij} A_{ji}^c) + \delta_{il} A_k + \delta_{ik} A_l - \frac{2}{3} \delta_{kl} A_i, \quad (\text{A1.2})$$

$$\rho_{ik} = \rho_{ik}^{(0-)} + \rho_{ik}^{(2-)} + \rho_{ik}^{(1-)} = \rho_0 \delta_{ik} + e_{ikj} \rho_j + \rho_{ik}^c, \quad (\text{A1.3})$$

where the superscript in parentheses represents the "quantum number l " corresponding to the given representation and the signs (+) and (-) indicate the nature of the corresponding irreducible tensor of rank l : ($l+$) corresponds to the true tensor and ($l-$) to the pseudotensor. Moreover, we use the following notation:

$$\left. \begin{aligned} A_{ikl}^{(3+)} &= \frac{1}{3} [A_{ikl} + A_{lik} + A_{kli} - \frac{4}{3} (\delta_{il} A_k + \delta_{kl} A_i + \delta_{ik} A_l)], \\ \alpha_0 &= \frac{1}{3} \alpha_{jj}, \quad \rho_0 = \frac{1}{3} \rho_{jj}, \\ \rho_i &= \frac{1}{2} e_{ikj} \rho_{kj}, \quad A_i = \frac{3}{10} A_{ssi}, \\ \rho_{ik}^c &= \frac{1}{2} (\rho_{ik} + \rho_{ki} - \frac{2}{3} \delta_{ik} \rho_{jj}), \\ A_{ik}^c &= -\frac{1}{2} (e_{ijl} A_{jlk} + e_{kjl} A_{jli}), \end{aligned} \right\} \quad (\text{A1.4})$$

where α_0 is a true scalar, ρ_0 is a pseudoscalar, A and ρ are true vectors, A_{ik}^c and ρ_{ik}^c are irreducible (zero-trace symmetric) pseudotensors of rank 2 and $A_{ikl}^{(3+)}$ is an irreducible true tensor of rank 3. This classification enables us to reduce very substantially the number of independent components of these tensors for molecules with a particular symmetry group.

Finally, it will be useful to write out the relationships between the components of the tensors $\hat{\rho}$, \hat{A} , $\hat{\beta}$, that are the analogs of the Hermitian condition for the tensor α_{ik} and that follow only from the condition that there is no absorption (but, in general, without the condition of time symmetry):

$$\alpha_{ik} = \alpha_{ki}^*; \quad \beta_{ilk} = -\rho_{li}^* e_{ijk} + \frac{1}{3} A_{ilk}^*. \quad (\text{A1.5})$$

In general, α_{ik} , β_{ilk} , ρ_{ik} , A_{ikl} are complex numbers. The relationships given by (A1.5) are also invariant under the transformation (4.13) if it is assumed that the Hermitian condition $\alpha_{ik} = \alpha_{ki}^*$ holds.

2. Expansion of radiation intensity in powers of a/λ in electrodynamics²²

In subsection c) of Sec. 4, we used the formula for the usual electric dipole approximation to calculate the

intensity integrated with respect to the angles. In this Appendix, we shall show that this formula is, in fact, valid to within terms of the order of $\sim a/\lambda$, inclusive, and thereby obtain a (more complicated) expression for the intensity integrated with respect to the angles and valid to within terms of the order of $\sim (a/\lambda)^2$. This problem is important because standard textbooks on electrodynamics²⁸⁻³⁰ contain an error and give expressions that are incorrect and non-covariant with respect to the choice of the origin of the coordinate frame.

We recall that the dipole moment of a set of charges is independent of the choice of the origin, but only if the total charge $\sum e$ of the system is zero. When this charge is not zero, the dipole moment μ' in a new frame shifted by \mathbf{b} relative to the old is given by

$$\mu' = \mu - \mathbf{b} \sum e. \quad (\text{A2.1})$$

However, this result does not affect the expression $(2/3c^3)(\ddot{\mu})^2$ for the intensity of dipole radiation because the total charge does not change with time and the shift \mathbf{b} is also time-independent.

Similarly, if the dipole moment μ of the system of charges is nonzero, the magnetic dipole moment \mathbf{m} and the electric quadrupole moment tensor θ_{ik} depend on the choice of the coordinate frame:

$$\theta'_{ik} = \theta_{ik} - \frac{1}{2} (3b_i \mu_k + 3\mu_i b_k - 2\delta_{ik} (\mathbf{b} \cdot \boldsymbol{\mu}) + \frac{1}{2} (3b_i b_k - \delta_{ik} b^2) \sum e) \quad (\text{A2.2})$$

$$\mathbf{m}' = \mathbf{m} - \frac{1}{2c} [\mathbf{b} \times \boldsymbol{\mu}] \quad (\text{A2.3})$$

(where our tensor $\hat{\theta}$ is related to the tensor \hat{D} from Ref. 28 by $\hat{D} = 2\hat{\theta}$). However, in contrast to the dipole case, here, the terms $\sim \mu$ have nonzero time derivatives. The well-known expression for the radiation intensity to within terms of the order of $(a/\lambda)^2$, inclusive, [see, for example, Ref. 28-Eq. (71.5); Ref. 29-Eq. (18.5), and Ref. 30-Eq. (12.22)]

$$I = \frac{2}{3c^3} (\ddot{\boldsymbol{\mu}})^2 + \frac{4}{180c^5} (\ddot{\theta}_{ik})^2 + \frac{2}{3c^3} (\ddot{\mathbf{m}})^2 \quad (\text{A2.4})$$

is thus found to acquire an additional term of the order of $(a/\lambda)^2$ when the coordinate frame is shifted if we suppose that $b \sim a$. At the same time, it is clear that the correct expression which takes into account all terms $\sim (a/\lambda)^2$ ought to be modified after this shift only in terms of order $\sim (b/\lambda)^3$ or higher. We have thus obtained the correct expression which turns out to be

$$I = \frac{2}{3c^3} (\ddot{\boldsymbol{\mu}})^2 + \frac{4}{180c^5} (\ddot{\theta}_{ik})^2 + \frac{2}{3c^3} (\ddot{\mathbf{m}})^2 + \frac{2}{15c^5} \ddot{\boldsymbol{\mu}} \cdot \mathbf{L}, \quad (\text{A2.5})$$

where

$$L_i = \frac{d}{dt} \sum e r^2 x_i - \sum e (3x_i x_k - r^2 \delta_{ik}) \dot{x}_k. \quad (\text{A2.6})$$

Thus, to determine the radiation intensity integrated with respect to angles to within terms of order of $\sim (a/\lambda)^2$, inclusive, it is not sufficient to specify the dipole, electric quadrupole, and magnetic dipole terms. A further vector characteristic of the system, namely, \mathbf{L} must also be introduced. Direct substitution of the transformation laws defined by (A2.1)-(A2.3) and the

analogous expression for L into (A2.5) shows that the latter is invariant under small shifts of the origin to within terms of the order of $(a/\lambda)^2$, inclusive. More precisely, the formula given by (A2.5) acquires additional terms of the order of $(a/\lambda)^2$ after a shift $b \sim a$, but these terms take the form of the total time derivative of a bounded function and thus do not contribute over a few periods of oscillation of the wave.

Of course, the new term in (A2.5), which is proportional to L , is important only when the dipole moment of the system is nonzero or, more precisely, when $\ddot{\mu} \neq 0$. Otherwise, (A2.5) reduces to the standard expression given by (A2.4).

The expansion in powers of a/λ was discussed above. All that remains is to decide the meaning of the term $\sim L$ in the language of the multipole expansion, i.e., expansion in terms of the spherical electromagnetic vectors with given parity and angular momentum. Since different spherical vectors in the intensity integrated with respect to the angles cannot interfere because of the orthogonality property, it is clear that the term $\sim L$ corresponds to an odd multipole with $J=1$, i.e., the electric dipole radiation. To within $\sim (a/\lambda)^2$, inclusive, which is the precision in which we are interested, the amplitude of the electric-dipole radiation is determined no longer simply by the vector $\ddot{\mu}$, but by the sum $\ddot{\mu} + (1/10c^2)\ddot{L}$.

In the gauge used in Ref. 13 (Sec. 46), the first term in (A2.6) corresponds to the inclusion of the next term in the expansion of the radial part of the scalar potential ϕ in powers of $(kr)^2$, and the second term corresponds to the inclusion of the vector potential A in the first nonvanishing approximation. We are, of course, concerned here with the electric-dipole photon.

We now write out the expression for the radiation amplitude in the far zone to within terms $\sim (a/\lambda)^2$, inclusive. Denoting the direction of propagation by $\mathbf{n} = \mathbf{R}/|\mathbf{R}|$, and proceeding by analogy with the treatment given in Ref. 28, we can easily show that

$$\mathbf{H} = \frac{1}{c^2 R_0} \left[\left(\ddot{\mu} + \frac{1}{3c} \ddot{\theta} + [\ddot{\mathbf{m}} \times \mathbf{n}] + \frac{1}{30c^2} \ddot{\mathbf{T}} + \frac{1}{10c^2} \ddot{L} + \frac{1}{3c} \ddot{\mathbf{B}} \right) \cdot \mathbf{n} \right], \quad (\text{A2.7})$$

$$T_i = T_{ijk} n_k n_l, \quad B_j = \epsilon_{jls} B_{lkn} n_s n_k, \quad \theta_i = \theta_{ik} n_k; \quad (\text{A2.8})$$

where T_{ijk} and B_{ijk} are, respectively, the electric octupole and magnetic quadrupole:

$$T_{ikl} = \sum e [5x_l x_k x_i - r^2 (\delta_{ik} x_l + \delta_{il} x_k + \delta_{kl} x_i)], \quad (\text{A2.9})$$

$$B_{ijk} = \frac{1}{2c} \sum e ([\mathbf{r} \cdot \mathbf{r}]_i x_k + x_i [\mathbf{r} \cdot \mathbf{r}]_k). \quad (\text{A2.10})$$

We note that, in contrast to the time-averaged intensity, the instantaneous field amplitude in the far zone (for $r = |\mathbf{r} \cdot \mathbf{n}| \gg \lambda$) should be *covariant* under small shifts of the origin:

$$\mathbf{E}'(\mathbf{n}, t) = \mathbf{E}\left(\mathbf{n}, t - \frac{1}{c}(\mathbf{b} \cdot \mathbf{n})\right). \quad (\text{A2.11})$$

It is readily verified that (A2.7) satisfies (A2.11) to within terms of the order of $\sim (b/\lambda)^2$, inclusive, i.e., exactly with the precision to which it is written down. If we retain only $\ddot{\mu}$, $\ddot{\theta}$ and $\ddot{\mathbf{m}}$, in (A2.7), the corresponding expression will satisfy (A2.11) with linear precision in b/λ . If, on the other hand, we retain only $\ddot{\mu}$ in (A2.7), then (A2.11) will be valid only in zero order

in the small parameter b/λ . The intensity differentiated with respect to the angle contains terms of the following form: $\sim \ddot{\mu}^2$ (zero order in a/λ), $\ddot{\mu} \ddot{\theta}$, $\ddot{\mu} \ddot{\mathbf{m}}$ (first order in a/λ), $\ddot{\mu} \ddot{L}$, $\ddot{\mathbf{m}} \ddot{\theta}$, $\ddot{\mathbf{m}}^2$, $\ddot{\theta}^2$, $\ddot{\mu} \ddot{\mathbf{B}}$, $\ddot{\mu} \ddot{\mathbf{T}}$ (second order in a/λ). However, when the integration with respect to the angles is performed, interference between the different spherical vectors does not take place and, to within $\sim (a/\lambda)^2$, we obtain the expression given by (A2.5).

So far, we have examined the problem of radiation emitted by an arbitrary set of charges. In the molecular light-scattering problem, on the other hand, the expressions for $\hat{\mu}$, $\hat{\mathbf{m}}$, $\hat{\theta}$, \hat{L} , $\hat{\mathbf{T}}$, and B induced by the incident wave, must themselves also be expanded in powers of a/λ . This program was carried out in the first order in a/λ in Sec. 4 [Eqs. (4.2) and (4.8)]. The corresponding expressions including second-order terms in a/λ will not be written out here.

3. New lines in pure rotational Raman scattering by CH_4

We now consider which terms of the tensors ρ_{ijk} and A_{ijkl} in the expansions (A1.2)–(A1.4) are not zero for molecules with the symmetry of methane. We note firstly that all the pseudoquantities, i.e., pseudotensors A_{ijk}^c and ρ_{ijk}^c of rank 2 and the pseudoscalar ρ_0 are equal to zero. Moreover, the symmetry of methane does not admit a vector, so that $A=0$, $\rho=0$. Therefore, the dipole-magnetic-dipole cross polarizability tensor $\hat{\rho}$ is zero, $\rho_{ijk}=0$, and the dipole-quadrupole polarizability tensor A_{ijkl} contains only the representation of rank $l=3$. (These statements refer to the coordinate frame whose origin lies at the carbon atom). If we place the hydrogen atoms at four corners of a cube and direct the coordinate axes at right-angles to the cube faces, the only components A_{ijkl} that are not zero will be those for which all three indices are different. These components are: $A_{xyx} = A_{yxx} = \dots$. For the representation of rank $l=3$, the correlator $\langle \hat{A}\hat{A} \rangle$ has the form

$$\langle A_{ijk}^c A_{lmn}^c \rangle = C_6 \left[\delta_{jp} \delta_{ik} \delta_{il} + \delta_{jk} \delta_{il} \delta_{ip} + \delta_{ji} \delta_{ip} \delta_{ik} + \delta_{jp} \delta_{il} \delta_{ik} + \delta_{jk} \delta_{ip} \delta_{il} + \delta_{ji} \delta_{ik} \delta_{ip} \right. \\ \left. - \frac{2}{5} (\delta_{ij} \delta_{ip} \delta_{kt} + \delta_{il} \delta_{jp} \delta_{kt} + \delta_{jl} \delta_{ip} \delta_{kt} + \delta_{ji} \delta_{pt} \delta_{ik} + \delta_{jk} \delta_{il} \delta_{pt} + \delta_{ij} \delta_{kt} \delta_{pt} \right. \\ \left. + \delta_{ij} \delta_{it} \delta_{kp} + \delta_{jt} \delta_{il} \delta_{kp} + \delta_{ji} \delta_{it} \delta_{kp} \right]. \quad (\text{A3.1})$$

The constant C_6 which is the coefficient of the part of the correlator $\langle \hat{A}\hat{A} \rangle$ with $l=3$ for an arbitrary A_{ijkl} is

$$C_6 = \frac{1}{3} \left(\langle A_{jil} A_{jil} \rangle + \langle A_{jli} A_{jli} \rangle + \langle A_{jli} A_{jli} \rangle - \frac{4}{5} \langle A_{jil} A_{jil} \rangle \right). \quad (\text{A3.2})$$

Specifically, for a molecule with the symmetry of methane,

$$C_6 = 6A_{xyx}^2. \quad (\text{A3.3})$$

The differential cross section for pure rotational Raman scattering is

$$\frac{d\sigma}{d\Omega} = \left(\frac{\omega}{c} \right)^6 \frac{A_{xyx}^2}{6} \left\{ 2 [1 - (\mathbf{n}_1 \mathbf{n}_2)] + \frac{3}{5} |\mathbf{e}_1 \mathbf{n}_2|^2 + \frac{3}{5} |\mathbf{e}_2 \mathbf{n}_1|^2 + 2 |\mathbf{e}_1 \mathbf{e}_2|^2 [1 - (\mathbf{n}_1 \mathbf{n}_2)] \right. \\ \left. - \frac{4}{5} |\mathbf{e}_1 \mathbf{e}_2|^2 [1 - (\mathbf{n}_1 \mathbf{n}_2)] - 2 \text{Re} (\mathbf{e}_1 \mathbf{e}_2) (\mathbf{e}_1^* \mathbf{n}_2) (\mathbf{e}_2^* \mathbf{n}_1) \right. \\ \left. + \frac{4}{5} \text{Re} (\mathbf{e}_1 \mathbf{e}_2) (\mathbf{e}_1^* \mathbf{n}_2) (\mathbf{e}_2 \mathbf{n}_1) + \frac{2}{5} \text{Re} (\mathbf{e}_1 \mathbf{e}_2) (\mathbf{e}_1^* \mathbf{n}_2) (\mathbf{e}_2^* \mathbf{n}_1) \right\}. \quad (\text{A3.4})$$

This cross section is distributed over the scattered

lines with $\Delta J = -3$, $\Delta J = -1$, $\Delta J = +1$ and $\Delta J = +3$. The expression for the distribution over these components is rather complicated because of the identity of the hydrogen nuclei in CH_4 (compare this with the discussion in Ref. 19 or 31).

4. New lines in pure rotational Raman scattering by the isotope-substituted hydrogen molecule HD

We denote the principal values of the polarizability tensor of H_2 and HD molecules by α_{\parallel} (along the axis) and α_{\perp} (perpendicular to the axis). For the wavelength $\lambda \approx 6328 \mu$, we then have $\alpha_{\parallel} \approx 1.028 \times 10^{-24} \text{ cm}^3$, $\alpha_{\perp} \approx 0.714 \times 10^{-24} \text{ cm}^3$ (Ref. 25). In the coordinate frame with the origin at the center of gravity of the HD molecule, the tensors $\hat{\rho}$ and \hat{A} then have the form

$$\left. \begin{aligned} \rho_{ik} &= \frac{1}{2} a \alpha_{\perp} \epsilon_{ijk} n_j, \\ A_{ik}^{(1)} &= -\frac{9}{10} a \left(\alpha_{\perp} + \frac{2}{3} \alpha_{\parallel} \right) \left(n_k \delta_{il} + n_l \delta_{ik} - \frac{2}{3} n_i \delta_{kl} \right), \\ A_{ik}^{(2)} &= -3a (\alpha_{\parallel} - \alpha_{\perp}) \left[n_i n_k n_l - \frac{1}{5} (n_i \delta_{kl} + n_k \delta_{il} + n_l \delta_{ik}) \right]; \end{aligned} \right\} \quad (\text{A4.1})$$

where $a \approx 0.748 \times 10^{-8} \text{ cm}$ is the equilibrium separation between the nuclei for the vibrational ground state of the HD molecule, and \mathbf{n} is the unit vector along the molecular axis (from H to D). The tensor $\hat{\beta}$ is expressed in terms of $\hat{\rho}$ and \hat{A} by (4.11).

The presence of only the odd powers of the vector \mathbf{n} in $\hat{\rho}$ and \hat{A} indicates that the selection rules for $D \rightarrow M$ and $D \rightarrow Q$ scattering are: $\Delta J = \pm 1, \pm 3$. Since the expression for the differential cross section with respect to the angle and the polarizations is very complicated, we reproduce only the angle-integrated cross section:

$$\sigma(\Delta J = \pm 1, \pm 3) = 8\pi \left(\frac{\omega}{c} \right)^6 \left(\frac{2}{3} \rho^2 + \frac{8}{9} A_1^2 + \frac{4}{675} A_3^2 \right); \quad (\text{A4.2})$$

where

$$\rho = \frac{a\alpha_{\perp}}{12}, \quad A_1 = \frac{a}{20} \left(\alpha_{\perp} + \frac{2\alpha_{\parallel}}{3} \right), \quad (\text{A4.3})$$

$$A_3 = \frac{a}{2} (\alpha_{\parallel} - \alpha_{\perp}). \quad (\text{A4.3}')$$

The cross section $\sigma(J \rightarrow J+1)$ is given by

$$\sigma(J \rightarrow J+1) = 8\pi \left(\frac{\omega}{c} \right)^6 \left[\frac{J+1}{2J+1} \left(\frac{2}{3} \rho^2 + \frac{8}{9} A_1^2 \right) + \frac{J(J+1)(J+2)}{(2J+5)(2J+1)(2J-1)} \cdot \frac{2}{225} A_3^2 \right], \quad (\text{A4.4})$$

whereas the cross section for the $J \rightarrow J+3$ transition is

$$\sigma(J \rightarrow J+3) = 8\pi \left(\frac{\omega}{c} \right)^6 \frac{(J+1)(J+2)(J+3)}{(2J+4)(2J+3)(2J+5)} \cdot \frac{2}{135} A_3^2. \quad (\text{A4.5})$$

The cross sections for transitions with negative ΔJ can be obtained with the aid of the relationships

$$\sigma(J \rightarrow J')(2J+1) = \sigma(J' \rightarrow J)(2J'+1). \quad (\text{A4.6})$$

The formula given by (A4.2) yields $\sigma \approx 10^{-35} \text{ cm}^2$ for $\lambda = 632.8 \text{ nm}$, where $\Delta J = \pm 3$ transitions account for approximately 1% of the total cross section.

Finally, we want to mention a number of further publications. Left-right asymmetry in Raman scattering is discussed in detail by Barron,³² who gives a review of the experimental results and an account of the theory which, in our terminology, corresponds to the

LMA approach. The polarization fine structure in the Raman spectrum due to a gas is examined by Baranova *et al.*³³ within the framework of the DDA approach. This paper also contains a more detailed account of the material given above in Sec. 3. Scattering by isotropic liquids in the neighborhood of the point of phase transition to nematic or cholesteric liquid crystals is discussed theoretically within the framework of the DDA approach (in our terminology) in Refs. 34–37. In particular, Zel'dovich and Tabiryan³⁷ note that the correlator M_7 of the longitudinal-transverse components of the tensor $\delta\epsilon_{ijk}$ can be measured by coherent active spectroscopy (these methods are reviewed in Ref. 38). Natural optical activity, i.e., left-right asymmetry in the refraction of light (in contrast to the effects seen in scattered radiation, as reviewed above) due to the spatial correlation between the fluctuations $\delta\epsilon_{ijk}$ is discussed within the framework of the DDA approach (in our terminology) in Refs. 27, 39, and 40.

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Translated by S. Chomet