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# Rayleigh and Raman optical activity: An analysis of the dependence on scattering angle

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The differential scattering of left- and right-handed circularly polarized light by optically active molecules is now well established in both theory and experiment. In this paper the dependence of Rayleigh and Raman differential scattering intensities on the angle of scattering is analyzed. It is demonstrated that an experimental study of this angle-dependence should enable magnetic dipole and electric quadrupole effects to be separately evaluated, and provide a useful method for testing electronic and vibrational wave function calculations. Results for circular differential Raman scattering are given in terms of irreducible tensors, allowing the selection rules for polarized and depolarized Raman bands to be applied in a straightforward way. It is also shown how the validity of the two-group model for chiral systems can be experimentally assessed.

## I. INTRODUCTION

It is now well established that when optically active molecules are irradiated with circularly polarized light, the rate of Rayleigh and Raman scattering is dependent on the handedness of the incident beam. The manifestation of optical activity in the Raman spectrum is of particular interest since it offers information about the chiral environment of functional groups in large molecules, and a number of experimental studies have demonstrated the potential of this method.<sup>1,2</sup>

In general, the difference in scattering intensity when the handedness of the radiation is reversed is measured relative to the absolute scattering intensity in terms of a *circular intensity differential*. As in conventional Raman studies, this can be measured with the scattered light analyzed for plane polarization lying either in, or perpendicular to the scattering plane; early experimental difficulties in determination of the differential ratio in the latter configuration<sup>3</sup> have now been successfully circumvented.<sup>4</sup>

In this paper the dependence of the differential ratios on the angle of scattering is examined. It is shown how the experimental analysis of this dependence should enable contributions resulting from magnetic dipole and electric quadrupole interactions to be separately evaluated, providing a useful method for testing electronic and vibrational wave function calculations. Results for circular differential Raman scattering are given in terms of irreducible tensors, enabling the results for polarized and depolarized Raman bands to be distinguished in a straightforward way. It is also demonstrated that the validity of the two-group model for certain classes of chiral molecule can be directly assessed by a simple experimental method.

Before proceeding further, it is useful to present some basic results applicable to both Rayleigh and Raman differential scattering. First, the circular intensity differential is defined as follows<sup>5</sup>:

$$\Delta_{\mu}(\theta) = \frac{I_{\theta}(R \rightarrow \mu) - I_{\theta}(L \rightarrow \mu)}{I_{\theta}(R \rightarrow \mu) + I_{\theta}(L \rightarrow \mu)} \quad (\mu = \parallel, \perp). \quad (1)$$

Here  $I_{\theta}(L/R \rightarrow \mu)$  denotes the intensity of light scattered from an incident beam with left/right handed circular

polarization,  $\mu = \parallel$  refers to light scattered with polarization vector lying in the scattering plane, and  $\mu = \perp$  refers to light scattered with polarization vector perpendicular to this plane. The angle of scattering is specified by the *convergence angle*  $\theta$ , defined by

$$\cos \theta = -\hat{\mathbf{k}} \cdot \hat{\mathbf{k}}', \quad (2)$$

where  $\hat{\mathbf{k}}$  is the direction of propagation of the incident light, and  $\hat{\mathbf{k}}'$  is that of the scattered light.

Using the methods of quantum electrodynamics,<sup>6</sup> it can be shown that the angle dependence of the differential ratios can be expressed in the following form:

$$\Delta_{\parallel}(\theta) = \frac{\alpha + \beta \cos \theta + \gamma \cos^2 \theta}{\delta + \epsilon \cos^2 \theta}, \quad (3)$$

$$\Delta_{\perp}(\theta) = \frac{\alpha + \gamma + \beta \cos \theta}{\delta + \epsilon}. \quad (4)$$

The values of the parameters  $\alpha - \epsilon$  are generally expressible in terms of the molecular polarizability tensor  $\alpha_{\lambda\mu}$ , the gyration tensor  $G_{\lambda\mu}$  and the quadrupole polarizability tensor  $A_{\lambda\mu\nu}$ . If the incident frequency  $\omega$  is not too close to an electronic absorption band, these can be written as<sup>7</sup>

$$\alpha_{\lambda\mu} = \frac{2}{\hbar} \sum_{r \neq 0} \frac{\omega_{r0}}{\omega_{r0}^2 - \omega^2} \text{Re} \langle 0 | \mu_{\lambda} | r \rangle \langle r | \mu_{\mu} | 0 \rangle, \quad (5)$$

$$G_{\lambda\mu} = -\frac{2}{\hbar} \sum_{r \neq 0} \frac{\omega}{\omega_{r0}^2 - \omega^2} \text{Im} \langle 0 | \mu_{\lambda} | r \rangle \langle r | m_{\mu} | 0 \rangle, \quad (6)$$

$$A_{\lambda\mu\nu} = \frac{2}{\hbar} \sum_{r \neq 0} \frac{\omega_{r0}}{\omega_{r0}^2 - \omega^2} \text{Re} \langle 0 | \mu_{\lambda} | r \rangle \langle r | \Theta_{\mu\nu} | 0 \rangle. \quad (7)$$

Here the electric dipole, magnetic dipole, and electric quadrupole operators are given by

$$\mu_{\lambda} = \sum_i e_i r_{i\lambda}, \quad (8)$$

$$m_{\lambda} = \sum_i \frac{e_i}{2m_i} \epsilon_{\lambda\mu\nu} r_{i\mu} p_{i\nu}, \quad (9)$$

and

$$\Theta_{\lambda\mu} = \frac{1}{2} \sum_i e_i (3r_{i\lambda} r_{i\mu} - r_i^2 \delta_{\lambda\mu}), \quad (10)$$

respectively.<sup>8</sup> The explicit results for Rayleigh and

Raman circular intensity differentials are now given with reference to these expressions in Secs. II and III.

## II. RAYLEIGH CIRCULAR DIFFERENTIAL SCATTERING

The Rayleigh differential ratios are given by Eqs. (3) and (4), with the following expressions for the parameters  $\alpha$ – $\epsilon$ ;

$$\alpha = 4c^{-1} \left( 3\alpha_{\lambda\mu} G_{\lambda\mu} - \alpha_{\lambda\lambda} G_{\mu\mu} - \frac{\omega}{3} \alpha_{\lambda\mu} A_{\lambda\mu} \right), \quad (11)$$

$$\beta = 2c^{-1} (5\alpha_{\lambda\mu} G_{\lambda\mu} - 5\alpha_{\lambda\lambda} G_{\mu\mu} + \omega \alpha_{\lambda\mu} A_{\lambda\mu}), \quad (12)$$

$$\gamma = 2c^{-1} (\alpha_{\lambda\mu} G_{\lambda\mu} + 3\alpha_{\lambda\lambda} G_{\mu\mu} + \omega \alpha_{\lambda\mu} A_{\lambda\mu}), \quad (13)$$

$$\delta = 2(3\alpha_{\lambda\mu} \alpha_{\lambda\mu} - \alpha_{\lambda\lambda} \alpha_{\mu\mu}), \quad (14)$$

$$\epsilon = \alpha_{\lambda\mu} \alpha_{\lambda\mu} + 3\alpha_{\lambda\lambda} \alpha_{\mu\mu}; \quad (15)$$

here

$$A_{\lambda\mu} = \epsilon_{\lambda\sigma\sigma} A_{\rho\sigma\mu}, \quad (16)$$

and the implied summation convention for repeated indices is employed. Note that  $A_{\lambda\mu}$  is traceless, by virtue of the  $\sigma, \mu$  index symmetry of  $A_{\rho\sigma\mu}$ . For right-angled scattering, the formulas for the circular intensity differentials reduce to

$$\Delta_{\parallel} \left( \frac{\pi}{2} \right) = \alpha / \delta, \quad (17)$$

$$\Delta_{\perp} \left( \frac{\pi}{2} \right) = (\alpha + \gamma) / (\delta + \epsilon), \quad (18)$$

giving results in agreement with Barron and Buckingham.<sup>5</sup>

The three molecular parameters which can in principle be obtained from measurement of the Rayleigh differential scattering ratios are  $\alpha_{\lambda\mu} G_{\lambda\mu}$ ,  $\alpha_{\lambda\lambda} G_{\mu\mu}$ , and  $\alpha_{\lambda\mu} A_{\lambda\mu}$ . Clearly, these cannot be obtained from the conventional right-angled scattering measurements, nor from the behavior of  $\Delta_{\perp}(\theta)$  alone. However, if the values of  $\delta$  and  $\epsilon$  are found, analysis of the  $\theta$  dependence of  $\Delta_{\parallel}(\theta)$  does enable these three parameters to be determined from the values of  $\alpha, \beta$ , and  $\gamma$ .

Now in terms of the three *principal components* of the polarizability tensor  $\alpha_{xx}$ ,  $\alpha_{yy}$ , and  $\alpha_{zz}$ , we have

$$\alpha_{\lambda\mu} \alpha_{\lambda\mu} = \alpha_{xx}^2 + \alpha_{yy}^2 + \alpha_{zz}^2 \quad (19)$$

and

$$\alpha_{\lambda\lambda} \alpha_{\mu\mu} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})^2. \quad (20)$$

These three polarizability components can in general be found from measurement of the depolarization ratio, refractive index, and Kerr constant of the sample.<sup>9</sup> However, it is not necessary to determine the Kerr constant to find the quantities in Eqs. (19) and (20). The usual depolarization ratio, measured with the scattered light analyzed for polarization perpendicular to the scattering plane, is given by

$$\rho_{\perp} = \frac{3\alpha_{\lambda\mu} \alpha_{\lambda\mu} - \alpha_{\lambda\lambda} \alpha_{\mu\mu}}{4\alpha_{\lambda\mu} \alpha_{\lambda\mu} + 2\alpha_{\lambda\lambda} \alpha_{\mu\mu}}, \quad (21)$$

and the mean polarizability ( $\frac{1}{3}\alpha_{\lambda\lambda}$ ) can be found from the refractive index by use of the Clausius–Mosotti equa-

tion; hence,  $\alpha_{\lambda\mu} \alpha_{\lambda\mu}$  and  $\alpha_{\lambda\lambda} \alpha_{\mu\mu}$  can be evaluated from these two parameters alone. The values of  $\delta$  and  $\epsilon$  are then provided by Eqs. (14) and (15), respectively.

Values for  $\alpha$ ,  $\beta$ , and  $\gamma$  can thus be found from  $\Delta_{\parallel}(\theta)$ , and the following equations provide the required results for the molecular parameters:

$$\alpha_{\lambda\mu} G_{\lambda\mu} = \frac{c}{40} (3\alpha + 2\gamma), \quad (22)$$

$$\alpha_{\lambda\lambda} G_{\mu\mu} = \frac{c}{80} (3\alpha - 5\beta + 7\gamma), \quad (23)$$

$$\alpha_{\lambda\mu} A_{\lambda\mu} = \frac{3c}{16\omega} (-\alpha + \beta + \gamma). \quad (24)$$

It is worth noting that this method thus provides information about the quadrupole polarizability tensor, which in fluids plays no part in the conventional manifestation of chirality, namely optical rotation. Nevertheless, optical rotation does provide information on the trace of the gyration tensor  $G_{\lambda\lambda}$  through the Rosenfeld–Condon formula, and this together with the trace of the polarizability tensor  $\alpha_{\lambda\lambda}$  can be used as a check upon the result given by Eq. (23).

Useful information can in fact be obtained from the differential scattering ratio and the depolarization ratio alone. Dividing the numerator and denominator of Eq. (3) by  $\alpha_{\lambda\lambda} \alpha_{\mu\mu}$ , we can write

$$\Delta_{\parallel}(\theta) = \frac{\alpha' + \beta' \cos \theta + \gamma' \cos^2 \theta}{\delta' + \epsilon' \cos^2 \theta}, \quad (25)$$

where

$$x' = x / \alpha_{\lambda\lambda} \alpha_{\mu\mu} \quad (x = \alpha, \beta, \gamma, \delta, \epsilon). \quad (26)$$

The denominator of Eq. (25) is now readily obtained since we have

$$\delta' = \frac{20\rho_{\perp}}{3 - 4\rho_{\perp}}, \quad (27)$$

and

$$\epsilon' = \frac{10(1 - \rho_{\perp})}{3 - 4\rho_{\perp}}. \quad (28)$$

From the behavior of  $\Delta_{\parallel}(\theta)$  as a function of  $\theta$  we can thus find  $\alpha'$ ,  $\beta'$  and  $\gamma'$ , and hence determine the values of  $\alpha_{\lambda\mu} G_{\lambda\mu} / \alpha_{\lambda\lambda} \alpha_{\mu\mu}$ ,  $G_{\lambda\lambda} / \alpha_{\lambda\lambda}$ , and  $\alpha_{\lambda\mu} A_{\lambda\mu} / \alpha_{\lambda\lambda} \alpha_{\mu\mu}$  from Eqs. (22) to (24).

In using this method, it is clearly important to reduce experimental error to a minimum. While careful experiments with modern instrumentation should produce quite accurate values for the scattering ratios, there are cases where the possibility of error in the measurement of  $\rho_{\perp}$  merits special attention. In particular, for samples where the value of  $\rho_{\perp}$  approaches the upper limit of  $\frac{3}{4}$ , caution must evidently be exercised since the values of  $\delta'$  and  $\epsilon'$  become very large and susceptible to error. In such circumstances the alternative treatment for Raman scattering developed in Sec. III should be much less error prone. The lower limit for the depolarization ratio  $\rho_{\perp} = 0$  only arises for an isotropically polarizable molecule, and hence is unlikely to be relevant for studies on dissymmetric compounds.

We now turn to a consideration of  $\Delta_1(\theta)$ . Although less information is obtainable from  $\Delta_1(\theta)$  than from  $\Delta_0(\theta)$ , the angle dependence is evidently much simpler, and we can write

$$\Delta_1(\theta) = \eta(1 + \xi \cos \theta), \quad (29)$$

where

$$\eta = \frac{\alpha + \gamma}{\delta + \epsilon}, \quad (30)$$

$$\xi = \frac{\beta}{\alpha + \gamma}. \quad (31)$$

It is instructive to compare this result with the corresponding expression for a molecule whose chirality results from a dissymmetric placing of two chromophores A and B; the two-group model for circular differential Rayleigh and Raman scattering was first discussed by Barron and Buckingham.<sup>10</sup> A more recent analysis<sup>11</sup> has shown that in the near-zone limit, where the group separation  $R$  is much less than the wavelength of the incident light, the result takes the form of Eq. (29) with

$$\eta = \frac{8c^{-1}\omega\epsilon_{\nu\tau\tau}R\tau\alpha_{\lambda\nu}^A\alpha_{\lambda\tau}^B}{(\alpha_{\lambda\lambda}^A + \alpha_{\lambda\lambda}^B)^2 + 7(\alpha_{\lambda\mu}^A\alpha_{\lambda\mu}^A + \alpha_{\lambda\mu}^B\alpha_{\lambda\mu}^B + 2\alpha_{\lambda\mu}^A\alpha_{\lambda\mu}^B)}, \quad (32)$$

$$\xi = 1. \quad (33)$$

Since the actual value of  $\xi$  for a given compound should be readily determined by experiment from the angle dependence of  $\Delta_1$ , we therefore have a good method for checking the validity of the two-group result; the usefulness of the model is reflected in the proximity of  $\xi$  to the theoretical value of unity. Since only *relative* measurements of  $\Delta_1(\theta)$  are required for this analysis, it should be possible to obtain a high degree of accuracy.

### III. RAMAN CIRCULAR DIFFERENTIAL SCATTERING

For Raman bands the parameters  $\alpha$ – $\epsilon$  in Eqs. (3) and (4) are expressible in terms of the vibrational transition tensors  $\alpha_{\lambda\mu}^{NM}$ ,  $G_{\lambda\mu}^{NM}$ , and  $A_{\lambda\mu}^{NM}$ . These are given by expressions of the form

$$\alpha_{\lambda\mu}^{NM} = \langle \chi_0^N | \alpha_{\lambda\mu}(Q) | \chi_0^M \rangle, \quad (34)$$

where  $|\chi_0^M\rangle$  and  $|\chi_0^N\rangle$  are the initial and final vibrational states of the molecule, respectively, and  $\alpha_{\lambda\mu}(Q)$  is a generalization of the normal polarizability tensor to a nonequilibrium nuclear configuration; this may be expanded in a Taylor series about the equilibrium position  $Q_e$  in the normal way, giving the leading term

$$\alpha_{\lambda\mu}^{NM} \approx \frac{\partial \alpha_{\lambda\mu}(Q)}{\partial Q} \bigg|_{Q_e} \langle \chi_0^N | Q - Q_e | \chi_0^M \rangle. \quad (35)$$

For the Raman selection rules to be most clearly evident, it is desirable to express results in terms of irreducible components of the transition tensors, using the general reduction formulas

$$X_{\lambda\mu}^{NM} = X_{\lambda\mu}^{(0)} + X_{\lambda\mu}^{(2)}, \quad (36)$$

$$X_{\lambda\mu}^{(0)} = \frac{1}{3} X_{\nu\nu}^{NM} \delta_{\lambda\mu}, \quad (37)$$

$$X_{\lambda\mu}^{(2)} = X_{\lambda\mu}^{NM} - \frac{1}{3} X_{\nu\nu}^{NM} \delta_{\lambda\mu}, \quad (38)$$

for an arbitrary index-symmetric tensor  $X_{\lambda\mu}^{NM}$ . We then have

$$\alpha = \frac{4c^{-1}}{3} (9\alpha_{\lambda\mu}^{(2)} G_{\lambda\mu}^{(2)} - \omega \alpha_{\lambda\mu}^{(2)} A_{\lambda\mu}^{(2)}), \quad (39)$$

$$\beta = \frac{2c^{-1}}{3} (-10\alpha_{\lambda\lambda}^{(0)} G_{\mu\mu}^{(0)} + 15\alpha_{\lambda\mu}^{(2)} G_{\lambda\mu}^{(2)} + 3\omega \alpha_{\lambda\mu}^{(2)} A_{\lambda\mu}^{(2)}), \quad (40)$$

$$\gamma = \frac{2c^{-1}}{3} (10\alpha_{\lambda\lambda}^{(0)} G_{\mu\mu}^{(0)} + 3\alpha_{\lambda\mu}^{(2)} G_{\lambda\mu}^{(2)} + 3\omega \alpha_{\lambda\mu}^{(2)} A_{\lambda\mu}^{(2)}), \quad (41)$$

$$\delta = 6\alpha_{\lambda\mu}^{(2)} \alpha_{\lambda\mu}^{(2)}, \quad (42)$$

$$\epsilon = \frac{1}{3} (10\alpha_{\lambda\lambda}^{(0)} \alpha_{\mu\mu}^{(0)} + 3\alpha_{\lambda\mu}^{(2)} \alpha_{\lambda\mu}^{(2)}). \quad (43)$$

There are no weight-0 contributions from the tensor  $A_{\lambda\mu}$  since it is traceless. For totally symmetric modes, corresponding to polarized Raman bands, both the weight-0 and weight-2 contributions are finite; for non-totally symmetric modes (where  $\rho_1 = \frac{3}{4}$ ), only the weight-2 contributions are nonzero.

Again, most information can be obtained from  $\Delta_0(\theta)$  if the values of  $\delta$  and  $\epsilon$  are found. In principle, these can be determined from absolute scattering intensities and depolarization ratios.<sup>12</sup> Then from  $\alpha$ ,  $\beta$ , and  $\gamma$  we can find values for the following tensor products:

$$\alpha_{\lambda\lambda}^{(0)} G_{\mu\mu}^{(0)} = \frac{c}{80} (3\alpha - 5\beta + 7\gamma), \quad (44)$$

$$\alpha_{\lambda\mu}^{(2)} G_{\lambda\mu}^{(2)} = \frac{c}{48} (3\alpha + \beta + \gamma), \quad (45)$$

$$\alpha_{\lambda\mu}^{(2)} A_{\lambda\mu}^{(2)} = \frac{3c}{16\omega} (-\alpha + \beta + \gamma). \quad (46)$$

For depolarized bands,  $\alpha_{\lambda\lambda}^{(0)} G_{\mu\mu}^{(0)}$  will be zero.

If absolute scattering intensities are not amenable to experimental determination, it is useful to rewrite Eq. (3) as

$$\Delta_0(\theta) = \frac{\tilde{\alpha} + \tilde{\beta} \cos \theta + \tilde{\gamma} \cos^2 \theta}{\tilde{\delta} + \tilde{\epsilon} \cos^2 \theta}, \quad (47)$$

with

$$\tilde{x} = x / \alpha_{\lambda\mu}^{(2)} \alpha_{\lambda\mu}^{(2)} \quad (x = \alpha, \beta, \gamma, \delta, \epsilon). \quad (48)$$

Then the denominator of Eq. (47) can be found from the depolarization ratio, since we have<sup>13</sup>

$$\rho_1 = \frac{9\alpha_{\lambda\mu}^{(2)} \alpha_{\lambda\mu}^{(2)}}{10\alpha_{\lambda\lambda}^{(0)} \alpha_{\mu\mu}^{(0)} + 12\alpha_{\lambda\mu}^{(2)} \alpha_{\lambda\mu}^{(2)}}, \quad (49)$$

Hence,

$$\tilde{\delta} = 6, \quad (50)$$

and

$$\tilde{\epsilon} = 3 \left( \frac{1 - \rho_1}{\rho_1} \right). \quad (51)$$

The behavior of  $\Delta_0(\theta)$  thus enables the values of  $\tilde{\alpha}$ ,  $\tilde{\beta}$ , and  $\tilde{\gamma}$  to be found, and hence the results for  $\alpha_{\lambda\lambda}^{(0)} \alpha_{\mu\mu}^{(0)} / \alpha_{\lambda\mu}^{(2)} \alpha_{\lambda\mu}^{(2)}$ ,  $\alpha_{\lambda\mu}^{(2)} G_{\lambda\mu}^{(2)} / \alpha_{\lambda\mu}^{(2)} \alpha_{\lambda\mu}^{(2)}$ , and  $\alpha_{\lambda\mu}^{(2)} A_{\lambda\mu}^{(2)} / \alpha_{\lambda\mu}^{(2)} \alpha_{\lambda\mu}^{(2)}$ .

Again, attention should be given to the effect of errors inherent in the measurements of scattering ratios. The depolarization ratio lies in the range  $0 \leq \rho_1 \leq \frac{3}{4}$ , and the lower limit corresponds to totally symmetric vibrations in molecules of cubic or icosahedral symmetry. Although this yields an infinite value for  $\tilde{\epsilon}$  which is obviously very susceptible to error, the case is clearly

not likely to occur for chiral molecules. On the other hand, for any non-totally symmetric vibration we have  $\rho_1 = \frac{3}{4}$  and hence  $\bar{\epsilon} = 1$ . Since in this case the precise values for  $\bar{\delta}$  and  $\bar{\epsilon}$  are known, the only source of error lies in measurement of the circular intensity differential. As mentioned earlier, this analysis in terms of irreducible tensor components is also applicable to Rayleigh scattering, and in cases where the Rayleigh depolarization ratio  $\rho_1$  approaches  $\frac{3}{4}$  it is certainly preferable to use Eq. (47) rather than Eq. (25).

Finally, we note that the result for  $\Delta_1(\theta)$  can once again be written in the form  $\eta(1 + \xi \cos\theta)$ , as in Eq. (29). The value of  $\xi$ , which should be readily determined with some accuracy, is

$$\xi = \frac{-10\alpha_{\lambda\lambda}^{(0)} G_{\mu\mu}^{(0)} + 15\alpha_{\lambda\mu}^{(2)} G_{\lambda\mu}^{(2)} + 3\omega\alpha_{\lambda\mu}^{(2)} A_{\lambda\mu}^{(2)}}{10\alpha_{\lambda\lambda}^{(0)} G_{\mu\mu}^{(0)} + 21\alpha_{\lambda\mu}^{(2)} G_{\lambda\mu}^{(2)} + \omega\alpha_{\lambda\mu}^{(2)} A_{\lambda\mu}^{(2)}}. \quad (52)$$

For non-totally symmetric modes, the weight-0 contributions disappear and hence the value of  $\xi$  is restricted to the range  $\frac{1}{3} \leq \xi \leq 3$ . The lower limit is reached in cases where the  $\alpha A$  terms are negligible compared to the  $\alpha G$  terms; the upper limit is reached when the converse is true.

Recently, Prasad and Burow have computed the relative contributions of the  $\alpha G$  and  $\alpha A$  terms in the circular intensity differentials for HCB<sub>2</sub>ClF and DCB<sub>2</sub>ClF, using an atom-dipole interaction model.<sup>14</sup> Clearly, the derivation of experimental values using the methods described above could provide a valuable way of checking and if necessary improving upon such calculations.

#### IV. CONCLUSION

The theory developed in this paper has been formulated specifically for a single component fluid, in other words a pure gas or liquid. Because of the low scattering intensity associated with gases, most experimental work on circular differential scattering has involved liquids, generally pure organic compounds. The theory given above should be directly applicable to all such cases. The theory is also valid for solutions, provided solvent contributions to the depolarization ratio, refractive index, etc. are taken into account. Here, however, the possible formation of a solvation shell needs to be given careful consideration. In comparing results with computer calculations it is obviously important to take into account the local environment of the molecules, since this will modify the polarizability and other properties to some extent.

In conclusion, it has been demonstrated that experi-

mental analysis of the angle dependence of Rayleigh and Raman optical activity offers a great deal more information than the standard measurements for right-angled scattering alone. Raman studies in particular should provide a very accurate way of testing vibrational wave function calculations for simple chiral molecules, possibly in conjunction with vibrational circular dichroism measurements.

For more complex compounds, the data available from the angle dependence of Rayleigh differential scattering provides a reliable indication of the usefulness of a two-chromophore model. More generally, the results can be used for testing electronic wave function calculations. This method may have interesting implications in view of the growing number of calculations on biological and pharmaceutical compounds.

<sup>1</sup>L. D. Barron and A. D. Buckingham, *Annu. Rev. Phys. Chem.* **26**, 381 (1975).

<sup>2</sup>L. D. Barron, *Advances in Infrared and Raman Spectroscopy*, edited by R. J. H. Clark and R. E. Hester (Heyden, London, 1978), Vol. 4, p. 271.

<sup>3</sup>See, for example, H. Boucher, T. R. Brocki, M. Moskovits, and B. Bosnich, *J. Am. Chem. Soc.* **99**, 6870 (1977).

<sup>4</sup>W. Hug and H. Surbeck, *Chem. Phys. Lett.* **60**, 186 (1979).

<sup>5</sup>L. D. Barron and A. D. Buckingham, *Mol. Phys.* **20**, 1111 (1971).

<sup>6</sup>The approach used in these calculations is identical to that adopted for recent studies of hyper-Raman scattering; for details refer to D. L. Andrews and T. Thirunamachandran, *J. Chem. Phys.* **68**, 2941 (1978); **70**, 1027 (1979).

<sup>7</sup>For the sake of conformity with previous work, the definitions of these tensors correspond to those given by Barron and Buckingham<sup>1</sup> (where the gyration tensor  $G$  is denoted by  $G'$ ).

<sup>8</sup>Note that the magnetic dipole and electric quadrupole moments so defined are greater by factors of  $c$  and 3, respectively, than those commonly used in quantum electrodynamics, as for example in Ref. 6.

<sup>9</sup>I. L. Fabelinskii, *Molecular Scattering of Light* (Plenum, New York, 1968).

<sup>10</sup>L. D. Barron and A. D. Buckingham, *J. Am. Chem. Soc.* **96**, 4769 (1974).

<sup>11</sup>D. L. Andrews and T. Thirunamachandran, *Proc. R. Soc. (London) Ser. A* **358**, 297 (1978). Here results are given in terms of the scattering angle ( $\pi$ -convergence angle).

<sup>12</sup>W. F. Murphy, W. Holzer, and H. J. Bernstein, *Appl. Spectrosc.* **23**, 211 (1969).

<sup>13</sup>The parameters  $\bar{\alpha}^2$  and  $\gamma^2$ , in terms of which Raman scattering results are frequently expressed, are related to the irreducible tensors by  $\bar{\alpha}^2 = \frac{1}{3} \alpha_{\lambda\lambda}^{(0)} \alpha_{\mu\mu}^{(0)}$  and  $\gamma^2 = \frac{3}{2} \alpha_{\lambda\mu}^{(2)} \alpha_{\lambda\mu}^{(2)}$ .

<sup>14</sup>P. L. Prasad and D. F. Burow, *J. Am. Chem. Soc.* **101**, 800 (1979); **101**, 806 (1979).