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A quantum electrodynamical theory of differential scattering based on a model with two chromophores

II. Differential Raman scattering of circularly polarized light

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The theory of differential scattering described in part I (preceding paper) is applied to the Raman process. Here, a distinction between inequivalent and equivalent chromophores is required. For systems with inequivalent chromophores, the leading contribution to the differential intensity of scattering involves the interference of second- and fourth-order probability amplitudes; in near- and far-zone limits, it depends on the inverse square of the group separation. For systems with equivalent chromophores, the spectrum should, in general, feature a doublet. The dominant contribution to the differential intensity comes from the second-order – second-order interference term and has a different sign for each doublet component. In many cases these contributions cancel and the leading term becomes the second-order – fourth-order interference term as in the case of inequivalent chromophores.

1. Introduction

In part I (Andrews & Thirunamachandran 1978*a*) we discussed the theory of differential Rayleigh scattering of circularly polarized light by optically active systems, and derived expressions for differential scattering intensities using a two-chromophore model. In this paper, the theory is extended to differential Raman scattering, which has been observed in a number of organic compounds (Barron & Buckingham 1975). Raman scattering is an inelastic process where the incident and scattered photons are of unequal energies and the difference is equal to the difference in the energies of the initial and final molecular states. In our present work we confine our attention to a Stokes transition where the final molecular state is vibrationally excited; the theory of the corresponding anti-Stokes transition follows in an analogous manner. In many systems, the nuclear motions of some normal modes are localized within particular functional groups. This feature is the basis for the extensive use of group frequencies in the interpretation of vibrational spectra. In the two-chromophore model, the vibrational excitation may thus be associated with a fundamental transition in one of the chromophores. The chromophores are assumed to be achiral in isolation, but chiral as a pair due to their dissymmetric juxtaposition. It is necessary to distinguish two cases: (*a*) non-identical chromophores, and (*b*) identical chromophores. The distinction is required because for type (*a*) the final state is simply a product of wavefunctions for the

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excited state of one chromophore and the ground state of the other, whereas for (*b*) the final state is a linear combination of product states. Such a distinction was not necessary in our discussion of Rayleigh scattering in part I because both the initial and final states were ground states.

In § 2 we calculate the differential scattering intensities for case (*a*) for an arbitrary scattering geometry and group separation R; the leading contribution is found to involve coupling between the chromophores. It results from the interference between the probability amplitudes for second- and fourth-order graphs, in contrast to Rayleigh differential scattering where a similar contribution appears as a higher-order correction. In both the near- and far-zones, the leading term depends on R^{-2}.

In § 3 we discuss the theory of the equivalent-chromophore model. A near-zone treatment which uses second-order perturbation theory has been given by Barron & Buckingham (1974). In the present work, the calculations are correct to fourth order and apply to arbitrary group separation. In contrast to (*a*) the excitation must be treated as that of the *pair* of chromophores in either a symmetric or an antisymmetric combination of excited states of the individual chromophores. These combinations have frequencies close to the unperturbed frequency, the difference arising from the interaction between the groups. In small molecules, the splitting between the symmetric and antisymmetric modes is seldom more than 40 cm^{-1}. When the chromophores are arranged in a skewed manner, as in chiral systems, the splittings are smaller (Bellamy 1968). For systems of which the spectra show a doublet, the dominant contribution to the differential intensity is the second-order–second-order interference term, the sign being different for each component. When the doublet is unresolved, these contributions cancel and the leading term is that from the interference of second- and fourth-order amplitudes as in the inequivalent chromophore treatment.

2. Non-identical chromophore model

The basic quantum electrodynamical theory is essentially the same as that given in part I, § 2. We again use the Hamiltonian (6) as the starting point for our calculations. We assume that the chromophore A undergoes a vibrational transition during the scattering process. The initial and final states of the system – molecule plus radiation – are $|0^{\mathrm{A}}0^{\mathrm{B}}; \boldsymbol{k}\boldsymbol{e}^{(\mathrm{L/R})}\rangle$ and $|0'^{\mathrm{A}}0^{\mathrm{B}}; \boldsymbol{k}'\boldsymbol{e}'\rangle$. As before, we evaluate the second- and fourth-order matrix elements for the process and use the Fermi rule to calculate the scattering rates.

For the second-order calculation we need to consider only two graphs, fig. 1 *a* and *b* of part I with suitable modifications. The other two graphs 1 *c* and *d* do not contribute because, without coupling between the chromophores, scattering at B cannot lead to the necessary excitation of A. However, for the equivalent chromophore model, all four graphs are admissible because scattering and vibrational excitation can occur simultaneously at either centre. With inequivalent chromophores, the second-order matrix element is

$$M_2(\mathrm{L/R}) = -\left(\frac{2\pi\hbar c}{V}\right)(kk')^{\frac{1}{2}}\,\bar{e}'_i\,e_j^{(\mathrm{L/R})\,\mathrm{A}}\alpha_{ij}^{0'0}(k), \tag{1}$$

where the scattering tensor ${}^{\mathrm{A}}\alpha_{ij}^{0'0}(k)$ is given by

$$ {}^{\mathrm{A}}\alpha_{ij}^{0'0}(k) = \sum_r \left\{ \frac{{}^{\mathrm{A}}\mu_i^{0'r}\,{}^{\mathrm{A}}\mu_j^{r0}}{E_{r0}^{\mathrm{A}} - \hbar ck} + \frac{{}^{\mathrm{A}}\mu_j^{0'r}\,{}^{\mathrm{A}}\mu_i^{r0}}{E_{r0'}^{\mathrm{A}} + \hbar ck} \right\} \tag{2} $$

and the summation is over the intermediate states $|r\rangle$ of A. Expression (2) reduces to the usual frequency-dependent polarizability tensor when $|0'^{\mathrm{A}}\rangle = |0^{\mathrm{A}}\rangle$.

The fourth-order contributions to the matrix elements involve coupling between the two chromophores. As before, the time-ordered graphs may be grouped into two sets, and by means of a canonical transformation each set can be collapsed into four graphs (cf. figures 4 and 5, part I). The calculations using these graphs are straightforward. With chromophore A as the origin, the required matrix elements are

$$ \begin{aligned} M_{4\alpha}(\mathrm{L/R}) = (8\pi^2\hbar c/V)\,(kk')^{\frac{1}{2}}\,\bar{e}_i'\,e_j^{(\mathrm{L/R})}[{}^{\mathrm{A}}\alpha_{im}^{0'0}(k)\,{}^{\mathrm{B}}\alpha_{nj}^{00}(k)\,V_{mn}(k,\boldsymbol{R})\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} \\ + {}^{\mathrm{B}}\alpha_{im}^{00}(k')\,{}^{\mathrm{A}}\alpha_{nj}^{0'0}(k)\,V_{mn}(k',\boldsymbol{R})\,\mathrm{e}^{-\mathrm{i}\boldsymbol{k}'\cdot\boldsymbol{R}}] \end{aligned} \tag{3} $$

and

$$ \begin{aligned} M_{4\beta}(\mathrm{L/R}) = (8\pi^2\hbar c/V)\,(kk')^{\frac{1}{2}}\,\bar{e}_i'\,e_j^{(\mathrm{L/R})}[{}^{\mathrm{A}}\beta_{imj}^{0'0}(k,k')\,{}^{\mathrm{B}}\mu_n^{00}\,V_{mn}(0,\boldsymbol{R}) \\ + {}^{\mathrm{B}}\beta_{imj}^{00}(k,k')\,{}^{\mathrm{A}}\mu_n^{0'0}\,V_{mn}(k-k',\boldsymbol{R})\,\mathrm{e}^{\mathrm{i}(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{R}}]. \end{aligned} \tag{4} $$

The expression for ${}^{\mathrm{A}}\beta_{imj}^{0'0}(k,k')$ in equation (4) is

$$ \begin{aligned} {}^{\mathrm{A}}\beta_{imj}^{0'0}(k,k') = \sum_{r,s} \Bigg\{ & \frac{{}^{\mathrm{A}}\mu_i^{0's}\,{}^{\mathrm{A}}\mu_m^{sr}\,{}^{\mathrm{A}}\mu_j^{r0}}{(E_{s0'}^{\mathrm{A}} - \hbar ck')\,(E_{r0}^{\mathrm{A}} - \hbar ck)} + \frac{{}^{\mathrm{A}}\mu_m^{0's}\,{}^{\mathrm{A}}\mu_i^{sr}\,{}^{\mathrm{A}}\mu_j^{r0}}{(E_{s0}^{\mathrm{A}} + \hbar ck' - \hbar ck)\,(E_{r0}^{\mathrm{A}} - \hbar ck)} \\ & + \frac{{}^{\mathrm{A}}\mu_m^{0's}\,{}^{\mathrm{A}}\mu_j^{sr}\,{}^{\mathrm{A}}\mu_i^{r0}}{(E_{s0}^{\mathrm{A}} + \hbar ck' - \hbar ck)\,(E_{r0}^{\mathrm{A}} + \hbar ck')} + \frac{{}^{\mathrm{A}}\mu_i^{0's}\,{}^{\mathrm{A}}\mu_j^{sr}\,{}^{\mathrm{A}}\mu_m^{r0}}{(E_{s0'}^{\mathrm{A}} - \hbar ck')\,(E_{r0'}^{\mathrm{A}} + \hbar ck - \hbar ck')} \\ & + \frac{{}^{\mathrm{A}}\mu_j^{0's}\,{}^{\mathrm{A}}\mu_i^{sr}\,{}^{\mathrm{A}}\mu_m^{r0}}{(E_{s0'}^{\mathrm{A}} + \hbar ck)\,(E_{r0'}^{\mathrm{A}} + \hbar ck - \hbar ck')} + \frac{{}^{\mathrm{A}}\mu_j^{0's}\,{}^{\mathrm{A}}\mu_m^{sr}\,{}^{\mathrm{A}}\mu_i^{r0}}{(E_{s0'}^{\mathrm{A}} + \hbar ck)\,(E_{r0}^{\mathrm{A}} + \hbar ck')} \Bigg\} \end{aligned} \tag{5} $$

and the corresponding expression for B is obtained from (5) after suitable changes of symbols. It may be noted that (5) reduces to the Rayleigh counterpart by putting $k' = k$ and $|0'^{\mathrm{A}}\rangle = |0^{\mathrm{A}}\rangle$.

Born–Oppenheimer approximation. To proceed further, we adopt the Born–Oppenheimer approximation to describe the molecular states. A molecular wavefunction $|\psi_{rR}(q,Q)\rangle$ is expressed as a product of an electronic wavefunction $|\phi_r(q,Q)\rangle$ and a vibrational wavefunction $|\chi_r^R(Q)\rangle$

$$ |\psi_{rR}(q,Q)\rangle = |\phi_r(q,Q)\rangle\,|\chi_r^R(Q)\rangle, \tag{6} $$

where q represents the electronic coordinates and Q the nuclear coordinates. Usually $|\chi_r^R\rangle$ is a product of wavefunctions for each of the normal modes of the molecule. In our work we concentrate upon one particular mode, taking $|\chi_r^R\rangle$ as the vibrational state with quantum number R. Thus the initial and final states of A are $|{}^{\mathrm{A}}\phi_0\rangle\,|{}^{\mathrm{A}}\chi_0^0\rangle$ and $|{}^{\mathrm{A}}\phi_0\rangle\,|{}^{\mathrm{A}}\chi_0^1\rangle$; for chromophore B the initial and final states are the same and are represented by $|{}^{\mathrm{B}}\phi_0\rangle\,|{}^{\mathrm{B}}\chi_0^0\rangle$.

Using the appropriate wavefunctions, we can now write down expressions for ${}^{\mathrm{A}}\mu_n^{0'0}$, ${}^{\mathrm{A}}\alpha_{ij}^{0'0}(k)$ and ${}^{\mathrm{A}}\beta_{imj}^{0'0}(k,k')$. First we have

$$ {}^{\mathrm{A}}\mu_n^{0'0} = \langle {}^{\mathrm{A}}\chi_0^1|\,{}^{\mathrm{A}}\tilde{\mu}_n^{00}(Q)\,|\,{}^{\mathrm{A}}\chi_0^0\rangle, \tag{7} $$

where $$ {}^{A}\tilde{\mu}_n^{00}(Q) = \langle {}^{A}\phi_0 |\, {}^{A}\mu_n(q, Q)\, | {}^{A}\phi_0 \rangle. \tag{8} $$

The tilde sign indicates that the integration has been performed over the electronic coordinates and the resulting quantity is Q-dependent. Similarly, ${}^{A}\alpha_{ij}^{0'0}(k)$ is given by

$$ {}^{A}\alpha_{ij}^{0'0}(k) = \sum_{r,R} \left\{ \frac{\langle {}^{A}\chi_0^1 | {}^{A}\tilde{\mu}_i^{0r} | {}^{A}\chi_r^R \rangle \langle {}^{A}\chi_r^R | {}^{A}\tilde{\mu}_j^{r0} | {}^{A}\chi_0^0 \rangle}{({}^{A}E_r - {}^{A}E_0) + ({}^{A}E_r^R - {}^{A}E_0^0) - \hbar ck} + \frac{\langle {}^{A}\chi_0^1 | {}^{A}\tilde{\mu}_j^{0r} | {}^{A}\chi_r^R \rangle \langle {}^{A}\chi_r^R | {}^{A}\tilde{\mu}_i^{r0} | {}^{A}\chi_0^0 \rangle}{({}^{A}E_r - {}^{A}E_0) + ({}^{A}E_r^R - {}^{A}E_0^1) + \hbar ck} \right\}. \tag{9} $$

Here the electronic energy $({}^{A}E_r - {}^{A}E_0)$ is taken to be the difference in energy between the states $|{}^{A}\phi_r\rangle$ and $|{}^{A}\phi_0\rangle$ at their equilibrium configurations; $({}^{A}E_r^R - {}^{A}E_0^0)$, $({}^{A}E_r^R - {}^{A}E_0^1)$ are the differences in vibrational energy between the intermediate and the initial, and the intermediate and the final states respectively. Compared with the electronic and photon energies in the denominators of (9), the vibrational energies may be neglected provided the incident frequency is off-resonant with the intermediate states. We may then effect closure over the vibrational states belonging to each electronic state. We thus obtain for the leading contribution to ${}^{A}\alpha_{ij}^{0'0}(k)$

$$ {}^{A}\alpha_{ij}^{0'0}(k) \approx \langle {}^{A}\chi_0^1 |\, {}^{A}\tilde{\alpha}_{ij}^{00}(k; Q) |\, {}^{A}\chi_0^0 \rangle; \tag{10} $$

where ${}^{A}\tilde{\alpha}_{ij}^{00}(k; Q)$ is a generalization of the tensor defined by equation (12) of part I; here the nuclear geometry is not restricted to the equilibrium configuration. Although the tensor ${}^{A}\alpha_{ij}^{0'0}(k)$ given by (2) is not in general symmetric in the indices i and j, the leading term (10) is i,j symmetric; this feature arises only in the off-resonant case (Placzek 1934).

Proceeding in a similar manner, it is readily shown that the tensor ${}^{A}\beta_{imj}^{0'0}(k, k')$ reduces to

$$ {}^{A}\beta_{imj}^{0'0}(k, k') \approx \langle {}^{A}\chi_0^1 |\, {}^{A}\tilde{\beta}_{imj}^{00}(k; Q) |\, {}^{A}\chi_0^0 \rangle \tag{11} $$

with ${}^{A}\tilde{\beta}_{imj}^{00}(k; Q)$ as a generalization of eqn (19) of part I to non-equilibrium geometry. The approximation (11) again implies the neglect of vibrational energy differences and this results in i, j index symmetry of the tensor. Expressions for ${}^{B}\mu_n^{00}$, ${}^{B}\alpha_{ij}^{00}(k)$ and ${}^{B}\beta_{imj}^{00}(k, k')$ now follow from (7), (10) and (11).

It is now convenient to make the usual Taylor expansion of the electric dipole transition moment $\tilde{\boldsymbol{\mu}}^{rs}$, in terms of vibrational mode coordinates Q', about the ground state equilibrium position Q'_e;

$$ \tilde{\boldsymbol{\mu}}^{rs}(Q') = \tilde{\boldsymbol{\mu}}^{rs}(Q'_e) + (\partial \tilde{\boldsymbol{\mu}}^{rs}/\partial Q')_{Q'_e}(Q' - Q'_e) + \ldots. \tag{12} $$

For the present calculations it is sufficient to retain only the first two terms in the expansion. This approximation is satisfactory if the equilibrium positions for the various electronic states of a given chromophore are not appreciably different. In other cases, it is essential to include higher-order terms of the Taylor series. By (12), the leading terms for each of the chromophore parameters discussed above are as follows:

$$ {}^{A}\mu_n^{0'0} \approx \left[\frac{\partial}{\partial Q'_\alpha} {}^{A}\tilde{\mu}_n^{00}(Q') \right]_{Q'_e} \langle {}^{A}\chi_0^1 |\, Q'_\alpha - Q'_e \,| {}^{A}\chi_0^0 \rangle, \tag{13} $$

$$ {}^{B}\mu_n^{00} \approx {}^{B}\tilde{\mu}_n^{00}(Q'_e), \tag{14} $$

$$^{\mathrm{A}}\alpha_{ij}^{0'0}(k) \approx \left[\frac{\partial}{\partial Q'_\alpha}\,^{\mathrm{A}}\tilde{\alpha}_{ij}^{00}(k;Q')\right]_{Q'_e} \langle^{\mathrm{A}}\chi_0^1|Q'_\alpha - Q'_e|\,^{\mathrm{A}}\chi_0^0\rangle, \tag{15}$$

$$^{\mathrm{B}}\alpha_{ij}^{00}(k) \approx {}^{\mathrm{B}}\tilde{\alpha}_{ij}^{00}(k;Q'_e), \tag{16}$$

$$^{\mathrm{A}}\beta_{imj}^{0'0}(k,k') \approx \left[\frac{\partial}{\partial Q'_\alpha}\,^{\mathrm{A}}\tilde{\beta}_{imj}^{00}(k;Q')\right]_{Q'_e} \langle^{\mathrm{A}}\chi_0^1|\,Q'_\alpha - Q'_e\,|^{\mathrm{A}}\chi_0^0\rangle, \tag{17}$$

$$^{\mathrm{B}}\beta_{imj}^{00}(k,k') \approx {}^{\mathrm{B}}\tilde{\beta}_{imj}^{00}(k;Q'_e). \tag{18}$$

In equations (13)–(18), Q'_α is the vibrational coordinate in chromophore A corresponding to the mode involved in the Raman transition. If this is associated with a circular frequency ω, and force constant κ, then the integrals in equations (13), (15) and (17) expressed by the angular brackets may be replaced by $(\hbar\omega/2\kappa)^{\frac{1}{2}}$. For simplicity, we write $\tilde{\mu}_n^{00}(Q'_e)$, $[\partial\tilde{\mu}_n^{00}(Q')/\partial Q'_\alpha]_{Q'_e}$, etc., as μ_n, μ'_n, etc., in the results we derive below.

We introduce two more approximations in the matrix element expressions. The first is

$$^{\mathrm{B}}\alpha_{ij}^{00}(k') \approx {}^{\mathrm{B}}\alpha_{ij}^{00}(k), \tag{19}$$

which is consistent with the neglect of the vibrational energy differences in the denominators of the tensors. Secondly, we write

$$V_{mn}(k',\boldsymbol{R}) \approx V_{mn}(k,\boldsymbol{R}), \tag{20}$$

although for the present we do not put $V_{mn}(k-k',\boldsymbol{R})$ equal to $V_{mn}(0,\boldsymbol{R})$ in view of the rather different behaviour of these functions in the long range limit. We return to this point later.

Differential scattering intensities. With the approximate expressions given in the previous subsection, the differential scattering intensities can be calculated in the same manner as for Rayleigh scattering. An important difference is that there are no contributions from the square of the second-order matrix element (1). We recall that for Rayleigh scattering such a second-order contribution does exist. It arises from the interference of the amplitudes for graphs 1 *a* and 1 *b* with 1 *c* and 1 *d* (figure 1 part I). However, for Raman scattering with non-identical chromophores, only one pair of graphs is permissible and no such interference is possible. The leading contributions to the differential intensities now come from the interference of the second- and fourth-order matrix elements and the results are

$$\begin{aligned}\Delta I^{\parallel}_{2,\,4\alpha} = &-8\pi I_0 k'^4 \left(\frac{\hbar\omega}{2\kappa}\right) V_{\rho\sigma}(k,\boldsymbol{R})\,\epsilon_{\nu\pi\tau}\,\hat{R}_\tau[4(\mathscr{I}_1(b)-\mathscr{I}_2(b))\\ &\times\{\cos\theta(\delta_{\lambda\mu}-\hat{R}_\lambda\hat{R}_\mu)(^{\mathrm{A}}\alpha'_{\lambda\nu}\,^{\mathrm{B}}\alpha_{\mu\rho}\,^{\mathrm{A}}\alpha'_{\sigma\pi}-\cos\theta\,^{\mathrm{A}}\alpha'_{\lambda\nu}\,^{\mathrm{B}}\alpha_{\pi\rho}\,^{\mathrm{A}}\alpha'_{\sigma\mu})\\ &+2(\cos^2\theta-1)\hat{R}_\lambda\hat{R}_\mu\,^{\mathrm{A}}\alpha'_{\lambda\nu}\,^{\mathrm{B}}\alpha_{\pi\rho}\,^{\mathrm{A}}\alpha'_{\sigma\mu}\}\\ &+\mathscr{I}_2(b)\{(3\cos^2\theta+\cos\theta-2)\,^{\mathrm{A}}\alpha'_{\lambda\lambda}\,^{\mathrm{B}}\alpha_{\nu\rho}\,^{\mathrm{A}}\alpha'_{\sigma\pi}\\ &-(3\cos^2\theta-3\cos\theta-2)\,^{\mathrm{A}}\alpha'_{\lambda\nu}\,^{\mathrm{B}}\alpha_{\lambda\rho}\,^{\mathrm{A}}\alpha'_{\sigma\pi}\\ &+(\cos^2\theta+\cos\theta-4)\,^{\mathrm{A}}\alpha'_{\lambda\nu}\,^{\mathrm{B}}\alpha_{\pi\rho}\,^{\mathrm{A}}\alpha'_{\sigma\lambda}\}];\end{aligned} \tag{21}$$

$$\Delta I^{\perp}_{2,4\alpha} = -8\pi I_0 k'^4 \left(\frac{\hbar\omega}{2\kappa}\right) V_{\rho\sigma}(k, \boldsymbol{R})\, \epsilon_{\nu\pi\tau} \hat{R}_\tau [4(\mathscr{I}_1(b) - \mathscr{I}_2(b))$$
$$\times (\delta_{\lambda\mu} - \hat{R}_\lambda \hat{R}_\mu)(\cos\theta\, {}^{\mathrm{A}}\alpha'_{\lambda\nu}\, {}^{\mathrm{B}}\alpha_{\mu\rho}\, {}^{\mathrm{A}}\alpha'_{\sigma\pi} - {}^{\mathrm{A}}\alpha'_{\lambda\nu}\, {}^{\mathrm{B}}\alpha_{\pi\rho}\, {}^{\mathrm{A}}\alpha'_{\sigma\mu})$$
$$+ \mathscr{I}_2(b)\{(\cos\theta + 1)\, {}^{\mathrm{A}}\alpha'_{\lambda\lambda}\, {}^{\mathrm{B}}\alpha_{\nu\rho}\, {}^{\mathrm{A}}\alpha'_{\sigma\pi} + (3\cos\theta - 1)\, {}^{\mathrm{A}}\alpha'_{\lambda\nu}\, {}^{\mathrm{B}}\alpha_{\lambda\rho}\, {}^{\mathrm{A}}\alpha'_{\sigma\pi}$$
$$+ (\cos\theta - 3)\, {}^{\mathrm{A}}\alpha'_{\lambda\nu}\, {}^{\mathrm{B}}\alpha_{\pi\rho}\, {}^{\mathrm{A}}\alpha'_{\sigma\lambda}\}]; \tag{22}$$

$$\Delta I^{\parallel}_{2,4\beta} = 8\sqrt{2}\pi I_0 k'^4 \left(\frac{\hbar\omega}{2\kappa}\right) V_{\rho\sigma}(k - k', \boldsymbol{R})\, \epsilon_{\nu\pi\tau} \hat{R}_\tau (1 - \cos\theta)^{\frac{3}{2}}$$
$$\times [(\delta_{\lambda\mu} - \hat{R}_\lambda \hat{R}_\mu)\mathscr{I}_1(a) + \hat{R}_\lambda \hat{R}_\mu \mathscr{I}_2(a)]\, {}^{\mathrm{A}}\alpha'_{\lambda\nu}\, {}^{\mathrm{B}}\beta_{\mu\rho\pi}\, {}^{\mathrm{A}}\mu'_\sigma, \tag{23}$$

$$\Delta I^{\perp}_{2,4\beta} = 2(1 - \cos\theta)^{-1} \Delta I^{\parallel}_{2,4\beta}. \tag{24}$$

In equations (21)–(23), $\mathscr{I}_1$ and $\mathscr{I}_2$ are given by (31) and (32) of part I, with $a = |\boldsymbol{k} - \boldsymbol{k}'|\, R$ and $b = kR$; also we have made the approximation $k' \approx k$ where appropriate. For each polarization, the circular intensity differential ratios again follow from (41) of part I. The numerators are given by $\Delta I'_{2,4\alpha} + \Delta I'_{2,4\beta}$, and the approximate expressions for the denominators are

$$I^{\parallel}(\mathrm{R}) + I^{\parallel}(\mathrm{L}) \approx \frac{I_0 k'^4}{30} \left(\frac{\hbar\omega}{2\kappa}\right) [(3\cos^2\theta - 2)\, {}^{\mathrm{A}}\alpha'_{\lambda\lambda}\, {}^{\mathrm{A}}\alpha'_{\mu\mu} + (\cos^2\theta + 6)\, {}^{\mathrm{A}}\alpha'_{\lambda\mu}\, {}^{\mathrm{A}}\alpha'_{\lambda\mu}] \tag{25}$$

and
$$I^{\perp}(\mathrm{R}) + I^{\perp}(\mathrm{L}) \approx \frac{I_0 k'^4}{30} \left(\frac{\hbar\omega}{2\kappa}\right) [{}^{\mathrm{A}}\alpha'_{\lambda\lambda}\, {}^{\mathrm{A}}\alpha'_{\mu\mu} + 7\, {}^{\mathrm{A}}\alpha'_{\lambda\mu}\, {}^{\mathrm{A}}\alpha'_{\lambda\mu}]. \tag{26}$$

Whilst the only scattering tensor for chromophore A which appears in most of the intensity contributions is the usual polarizability derivative ${}^{\mathrm{A}}\alpha'_{\lambda\mu}$, it is to be noted that the $\Delta I'_{2,4\beta}$ terms involve products of components of this tensor with components of the electric dipole moment derivative ${}^{\mathrm{A}}\boldsymbol{\mu}'$. Consequently, a given vibrational mode must be both Raman- and IR-active, and hence the group must be non-centrosymmetric for these terms to be non-vanishing. The derivative tensor ${}^{\mathrm{A}}\beta'_{\mu\rho\pi}$ does not appear in the $\Delta I'_{2,4\beta}$ expressions. This may be ascribed to the lack of retardation in the product of M_2 with the term in $M_{4\beta}$ which involves this tensor.

Many features of the asymptotic behaviour of the intensity differentials are similar to those discussed in part I in connection with Rayleigh scattering, the obvious exception being the absence of $\Delta I'_{2,2}$ contributions. However, we now have to examine the behaviour of $V_{mn}(k - k', \boldsymbol{R})$ which only assumes its long-range form when $(k - k')R \gg 1$. Since $(\hbar ck - \hbar ck')$ is the energy of the vibrational transition, it is readily seen that this would imply a value of R which is large compared with infra-red wavelengths. In actual applications, it is far more likely that the magnitude of R would be in the region where $V_{mn}(k - k', \boldsymbol{R})$ assumes its short-range behaviour, i.e. where $(k - k')R \ll 1$; as shown previously, the tensor tends to $V_{mn}(0, \boldsymbol{R})$ in this region. Thus for the near-zone, $kR \ll 1$, we find the same R^{-2} dependence of both $\Delta I'_{2,4\alpha}$ and $\Delta I'_{2,4\beta}$ as in Rayleigh scattering, and in the region $(k - k')R \ll 1 \ll kR$ the $\Delta I'_{2,4\alpha}$ and $\Delta I'_{2,4\beta}$ results again depend on R^{-2} and R^{-4} apart from modulating factors.

3. Identical chromophore model

We assume as before that wavefunction overlap and electron exchange between chromophores can be neglected. Since the chromophores are identical, the states $|0'^{A}0^{B}\rangle$ and $|0^{A}0'^{B}\rangle$ are degenerate in contrast to the case discussed previously. The final state is therefore represented by one of the linear combinations

$$2^{-\frac{1}{2}}\{|0'^{A}0^{B}\rangle \pm |0^{A}0'^{B}\rangle\}. \tag{27}$$

If the symmetric and antisymmetric combinations have sufficiently different energies, the spectrum should, in general, feature a doublet. In this section we compute the differential scattering intensities for the components. The relevant matrix element is

$$M(\pm) = 2^{-\frac{1}{2}}[\langle \boldsymbol{k}'\boldsymbol{e}';\, 0^{B}0'^{A}|\, \hat{M}\, |0^{A}0^{B};\, \boldsymbol{k}\boldsymbol{e}^{(L/R)}\rangle \pm \langle \boldsymbol{k}'\boldsymbol{e}';\, 0'^{B}0^{A}|\, \hat{M}\, |0^{A}0^{B};\, \boldsymbol{k}\boldsymbol{e}^{(L/R)}\rangle], \tag{28}$$

where $\hat{M}$ is given by (10) of part I. The calculation of each term of (28) is carried out in exactly the same way as for the non-identical chromophore model described in the previous section. It may be noted that, for the calculation of the second-order matrix element, the first term in (28) requires graphs of the type 1*a* and 1*b* of part I, figure 1, whereas the second term needs 1*c* and 1*d*. This may be contrasted with the non-identical chromophore calculation where the chromophore B remained unchanged, and graphs 1*c* and 1*d* were not required. Thus the scattering intensities now include interference terms from the second-order graphs in a manner similar to that in Rayleigh scattering. However, we should point out that the second-order interference terms arise in Rayleigh scattering irrespective of whether the two chromophores are identical or not because all four graphs are allowed in either case.

As in the case of Rayleigh scattering, the dominant contributions to the differential intensities result from interference of second-order amplitudes. For parallel and perpendicular polarizations they are given by

$$\Delta I^{\parallel}_{2,2}(\pm) = \mp\sqrt{2}\, I_0 k'^4 \left(\frac{\hbar\omega}{2\kappa}\right) \epsilon_{\nu\pi\tau} \hat{R}_\tau (1-\cos\theta)^{\frac{3}{2}} \times [(\delta_{\lambda\mu} - \hat{R}_\lambda \hat{R}_\mu)\, \mathscr{I}_1(a) + \hat{R}_\lambda \hat{R}_\mu \mathscr{I}_2(a)]\, {}^{A}\alpha'_{\lambda\nu}\, {}^{B}\alpha'_{\mu\pi} \tag{29}$$

and

$$\Delta I^{\perp}_{2,2}(\pm) = 2(1-\cos\theta)^{-1}\, \Delta I^{\parallel}_{2,2}. \tag{30}$$

The leading corrections to the differential intensities arise from interference of second-order amplitudes with fourth-order amplitudes. These are

$$\begin{aligned}
\Delta I^{\parallel}_{2,4\alpha}(\pm) = {} & -4\pi I_0 k'^4 \left(\frac{\hbar\omega}{2\kappa}\right) V_{\rho\sigma}(k, \boldsymbol{R})\, \epsilon_{\nu\pi\tau} \hat{R}_\tau [[4(\mathscr{I}_1(b) - \mathscr{I}_2(b)) \\
& \times \{\cos\theta(\delta_{\lambda\mu} - \hat{R}_\lambda \hat{R}_\mu)\, ({}^{A}\alpha'_{\lambda\nu}\, {}^{B}\alpha_{\mu\rho}\, {}^{A}\alpha'_{\sigma\pi} - \cos\theta\, {}^{A}\alpha'_{\lambda\nu}\, {}^{B}\alpha_{\pi\rho}\, {}^{A}\alpha'_{\sigma\mu} \\
& \pm {}^{A}\alpha'_{\lambda\nu}\, {}^{B}\alpha'_{\mu\rho}\, {}^{A}\alpha_{\sigma\pi} \mp \cos\theta\, {}^{A}\alpha'_{\lambda\nu}\, {}^{B}\alpha'_{\pi\rho}\, {}^{A}\alpha_{\sigma\mu}) \\
& + 2\hat{R}_\lambda \hat{R}_\mu (\cos^2\theta - 1)\, ({}^{A}\alpha'_{\lambda\nu}\, {}^{B}\alpha_{\pi\rho}\, {}^{A}\alpha'_{\sigma\mu} \pm {}^{A}\alpha'_{\lambda\nu}\, {}^{B}\alpha'_{\pi\rho}\, {}^{A}\alpha_{\sigma\mu})\} \\
& + \mathscr{I}_2(b)\, \{(3\cos^2\theta + \cos\theta - 2)\, ({}^{A}\alpha'_{\lambda\lambda}\, {}^{B}\alpha_{\nu\rho}\, {}^{A}\alpha'_{\sigma\pi} \pm {}^{A}\alpha'_{\lambda\lambda}\, {}^{B}\alpha'_{\nu\rho}\, {}^{A}\alpha_{\sigma\pi}) \\
& + (3\cos^2\theta - 3\cos\theta - 2)\, ({}^{A}\alpha'_{\lambda\nu}\, {}^{B}\alpha_{\lambda\rho}\, {}^{A}\alpha'_{\sigma\pi} \pm {}^{A}\alpha'_{\lambda\nu}\, {}^{B}\alpha'_{\lambda\rho}\, {}^{A}\alpha_{\sigma\pi}) \\
& + (\cos^2\theta + \cos\theta - 4)\, ({}^{A}\alpha'_{\lambda\nu}\, {}^{B}\alpha_{\pi\rho}\, {}^{A}\alpha'_{\sigma\lambda} \pm {}^{A}\alpha'_{\lambda\nu}\, {}^{B}\alpha'_{\pi\rho}\, {}^{A}\alpha_{\sigma\lambda})\}] \\
& - \text{terms obtained by interchanging A and B}],
\end{aligned} \tag{31}$$

$$\Delta I^{\perp}_{2,4\alpha}(\pm) = -4\pi I_0 k'^4 \left(\frac{\hbar\omega}{2\kappa}\right) V_{\rho\sigma}(k, \boldsymbol{R})\, \epsilon_{\nu\pi\tau}\, \hat{R}_\tau [[4(\mathscr{I}_1(b) - \mathscr{I}_2(b))$$
$$\times (\delta_{\lambda\mu} - \hat{R}_\lambda \hat{R}_\mu)(\cos\theta\, {}^{\mathrm{A}}\alpha'_{\lambda\nu}\, {}^{\mathrm{B}}\alpha_{\mu\rho}\, {}^{\mathrm{A}}\alpha'_{\sigma\pi} - {}^{\mathrm{A}}\alpha'_{\lambda\nu}\, {}^{\mathrm{B}}\alpha_{\pi\rho}\, {}^{\mathrm{A}}\alpha'_{\sigma\mu}$$
$$\pm \cos\theta\, {}^{\mathrm{A}}\alpha'_{\lambda\nu}\, {}^{\mathrm{B}}\alpha'_{\mu\rho}\, {}^{\mathrm{A}}\alpha_{\sigma\pi} \mp {}^{\mathrm{A}}\alpha'_{\lambda\nu}\, {}^{\mathrm{B}}\alpha'_{\pi\rho}\, {}^{\mathrm{A}}\alpha_{\sigma\mu})$$
$$+ \mathscr{I}_2(b)\{(\cos\theta + 1)({}^{\mathrm{A}}\alpha'_{\lambda\lambda}\, {}^{\mathrm{B}}\alpha_{\nu\rho}\, {}^{\mathrm{A}}\alpha'_{\sigma\pi} \pm {}^{\mathrm{A}}\alpha'_{\lambda\lambda}\, {}^{\mathrm{B}}\alpha'_{\nu\rho}\, {}^{\mathrm{A}}\alpha_{\sigma\pi})$$
$$+ (3\cos\theta - 1)({}^{\mathrm{A}}\alpha'_{\lambda\nu}\, {}^{\mathrm{B}}\alpha_{\lambda\rho}\, {}^{\mathrm{A}}\alpha'_{\sigma\pi} \pm {}^{\mathrm{A}}\alpha'_{\lambda\nu}\, {}^{\mathrm{B}}\alpha'_{\lambda\rho}\, {}^{\mathrm{A}}\alpha_{\sigma\pi})$$
$$+ (\cos\theta - 3)({}^{\mathrm{A}}\alpha'_{\lambda\nu}\, {}^{\mathrm{B}}\alpha_{\pi\rho}\, {}^{\mathrm{A}}\alpha'_{\sigma\lambda} \pm {}^{\mathrm{A}}\alpha'_{\lambda\nu}\, {}^{\mathrm{B}}\alpha'_{\pi\rho}\, {}^{\mathrm{A}}\alpha_{\sigma\lambda})\}]$$
$$- \text{terms obtained by interchanging A and B}], \tag{32}$$

$$\Delta I^{\parallel}_{2,4\beta}(\pm) = 4\sqrt{2}\pi I_0 k'^4 \left(\frac{\hbar\omega}{2\kappa}\right) \epsilon_{\nu\pi\tau}\, \hat{R}_\tau (1 - \cos\theta)^{\frac{3}{2}}$$
$$\times [(\delta_{\lambda\mu} - \hat{R}_\lambda \hat{R}_\mu)\mathscr{I}_1(a) + \hat{R}_\lambda \hat{R}_\mu \mathscr{I}_2(a)]$$
$$\times [[{}^{\mathrm{A}}\alpha'_{\lambda\nu}\, {}^{\mathrm{B}}\beta_{\mu\rho\pi}\, {}^{\mathrm{A}}\mu'_\sigma V_{\rho\sigma}(k - k', \boldsymbol{R}) \pm {}^{\mathrm{A}}\alpha'_{\lambda\nu}\, {}^{\mathrm{B}}\beta'_{\mu\rho\pi}\, {}^{\mathrm{A}}\mu_\sigma V_{\rho\sigma}(0, \boldsymbol{R})]$$
$$- \text{terms obtained by interchanging A and B}], \tag{33}$$

$$\Delta I^{\perp}_{2,4\beta}(\pm) = 2(1 - \cos\theta)^{-1} \Delta I^{\parallel}_{2,4\beta}(\pm). \tag{34}$$

It is instructive to note that, in contrast to the inequivalent chromophore results, the above expressions contain the first derivative tensors ${}^{\mathrm{A/B}}\beta'_{\mu\rho\pi}$. The selection rules associated with these tensors are the same as those for the hyper-Raman effect (Andrews & Thirunamachandran 1978*b*). The above expressions may be used to obtain the circular intensity differential ratios according to (41) of part I with the following results for the denominators:

$$I^{\parallel}_{\pm}(\mathrm{R}) + I^{\parallel}_{\pm}(\mathrm{L}) = \left(\frac{I_0 k'^4}{60}\right)\left(\frac{\hbar\omega}{2\kappa}\right)[(3\cos^2\theta - 2)({}^{\mathrm{A}}\alpha'_{\lambda\lambda} \pm {}^{\mathrm{B}}\alpha'_{\lambda\lambda})^2$$
$$+ (\cos^2\theta + 6)({}^{\mathrm{A}}\alpha'_{\lambda\mu}\, {}^{\mathrm{A}}\alpha'_{\lambda\mu} + {}^{\mathrm{B}}\alpha'_{\lambda\mu}\, {}^{\mathrm{B}}\alpha'_{\lambda\mu} \pm 2\, {}^{\mathrm{A}}\alpha'_{\lambda\mu}\, {}^{\mathrm{B}}\alpha'_{\lambda\mu})], \tag{35}$$

$$I^{\perp}_{\pm}(\mathrm{R}) + I^{\perp}_{\pm}(\mathrm{L}) = \left(\frac{I_0 k'^4}{60}\right)\left(\frac{\hbar\omega}{2\kappa}\right)[({}^{\mathrm{A}}\alpha'_{\lambda\lambda} \pm {}^{\mathrm{B}}\alpha'_{\lambda\lambda})^2 + 7({}^{\mathrm{A}}\alpha'_{\lambda\mu}\, {}^{\mathrm{A}}\alpha'_{\lambda\mu} + {}^{\mathrm{B}}\alpha'_{\lambda\mu}\, {}^{\mathrm{B}}\alpha'_{\lambda\mu} \pm 2\, {}^{\mathrm{A}}\alpha'_{\lambda\mu}\, {}^{\mathrm{B}}\alpha'_{\lambda\mu})]. \tag{36}$$

In equations (29)–(36) the upper signs refer to the symmetric combination state and the lower signs to the antisymmetric state as given by (27). When these states have appreciably different energies a doublet should be observed in the circular differential Raman spectrum with a splitting equal to the energy difference between the two states. The dominant contributions are given by (29) and (30), and their signs are opposite for the two components of the doublet.

4. Discussion

From our calculations in previous sections, it is clear that the largest differential intensity effects are likely to be observed in molecules containing equivalent groups, provided the components of the doublet are resolvable. (Molecules with inequivalent groups can also show large effects when the vibrational frequencies are accidentally

degenerate or nearly degenerate.) In the short range limit, the dominant contributions are

$$\Delta I^{\parallel}_{2,2}(\pm) \simeq \pm(\tfrac{1}{15}) I_0 k'^5 R \left(\frac{\hbar\omega}{2\kappa}\right) \epsilon_{\nu\pi\tau} \hat{R}_\tau (1-\cos\theta)^2 \, {}^{\mathrm{A}}\alpha'_{\lambda\nu} {}^{\mathrm{B}}\alpha'_{\lambda\pi}, \tag{37}$$

$$\Delta I^{\perp}_{2,2}(\pm) = 2(1-\cos\theta)^{-1} \Delta I^{\parallel}_{2,2}. \tag{38}$$

An interesting feature is once again the linear R-dependence of these terms (cf. Barron & Buckingham 1974). In this region, the magnitude of kR provides an estimate of the size of the circular intensity differential ratio.

In molecules with small group separation as in 1,3-diketones, coplanar carbonyl groups give rise to symmetric and antisymmetric bands separated by 30–40 cm^{-1}. However, molecules such as acetylacetone with non-coplanar carbonyl groups show smaller splitting (Mecke & Funck 1956; Bellamy 1968). The doublet splitting in chiral molecules is likely to be small even in the near-zone region. When the two states are nearly degenerate, the total differential intensity is obtained by adding the contributions for the symmetric and antisymmetric states. Since the dominant terms (37) and (38) have opposite signs for the two components they cancel, and the leading contributions are then those from the interference of second- and fourth-order amplitudes as in the inequivalent-chromophore treatment. In the region $(k-k')R \ll 1 \ll kR$, the differential intensities have the same limiting behaviour as for the inequivalent-chromophore model.

Finally, for chemically equivalent groups, it is important to draw a distinction between isotopic equivalence and inequivalence. In the latter case, the group vibrational frequencies differ appreciably and the results are given by the non-identical chromophore model. Thus, with systems which show a doublet, isotopic substitution of one group should lead to a marked decrease in the differential intensities. Further, isotopic labelling of a chromophore can be used to monitor the presence of the same isotope in the other chromophore. Experiments of this kind should also give an indication of the relative importance of coupling.

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