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Polarisation analysis of bimolecular excitations mediated by energy transfer: A common theoretical framework for fluorescence migration and sequential Raman scattering

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Abstract

When polarised light interacts sequentially with two independently mobile molecules or chromophores, radiation of a longer wavelength and a changed polarisation state is commonly detected. One well-known example is the case where energy migrates from a molecule initially excited by input radiation to another which fluoresces. Another such process is sequential Raman scattering by two separate molecules. In this paper a theoretical framework is developed that formally establishes the link between these two processes. The theory encompasses the most general case; the intermolecular energy transfer can be either radiative or non-radiative, and the transition dipole moments, for the upward and downward processes within each chromophore, can be either parallel or non-parallel. For the Raman processes, resonance features are also accommodated. Results for the fluorescence anisotropy and Raman depolarisation ratio are explicitly presented as well as more general rate equations applicable to arbitrary polarisation conditions.

1. Introduction

The fluorescence anisotropy associated with energy transfer between molecules is a phenomenon that has significant diagnostic applications in many systems, such as photosynthetic complexes, polymers, laser dyes etc. As such it has been the subject of a considerable body of experimental and theoretical work in recent years [1–11]. A process that has received rather less attention, primarily because of the rather lower levels of intensity with which it is associated, is the polarisation anisotropy resulting from bimolecular Raman scattering, generally expressed in terms of depolarisation [12,13]. Although there are a number of significant differences between these processes, principally connected with the timescales over which they operate, they have certain features in common (see Fig. 1). Each involves the sequential interaction of polarised light with two separate molecules or chromophores, both of which acquire some energy of excitation as a result of the process, and as such the term ‘bimolecular excitation’ is an appropriate generalisation. Moreover both fluorescence migration and sequential

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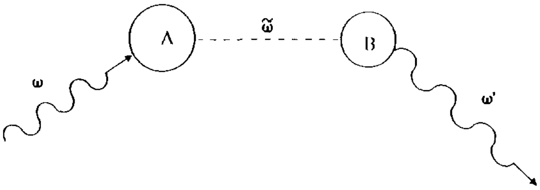

Fig. 1. Features common to both fluorescence migration and sequential Raman scattering. The incident radiation has frequency ω and the emergent radiation a lower frequency ω', with $\tilde{\omega}$ intermediate.

Raman scattering generate doubly Stokes-shifted radiation [1] with a changed polarisation state. These two processes have hitherto always been considered as completely separate types of interaction. It is the purpose of this paper to show that both processes can be accommodated within a common theoretical framework. The individual interactions are shown to be the limiting cases of a single all-embracing theory that can also be applied to processes in which Raman scattering is followed by absorption and fluorescence, or absorption and fluorescence followed by Raman scattering. Results are derived for systems comprising independently mobile (or randomly oriented) chromophores, allowing for the two species involved to be either of the same or of a different type. To save undue repetition, the term 'molecules' in the following may be understood as applying equally to chromophores within independent, orientationally uncorrelated molecular units.

The theory encompasses the most general case, where the intermolecular energy transfer that represents the intermediate stage of the overall process can be either radiative or non-radiative, or even a combination of both. When the intermolecular distance R is less than the reduced wavelength $ƛ = \lambda/2\pi$ (where λ is the wavelength corresponding to the energy being transferred) then the transfer is commonly termed a non-radiative or radiationless process and treated as a longitudinal (Coulombic) interaction [14]; alternatively it may be understood to be mediated by virtual photon coupling [15–24]. From either viewpoint, although it may occur at some interval after initial molecular photoexcitation, each individual transfer of energy is essentially instantaneous, subject to the obvious constraint of causality. In a radiative transfer process, where R is considerably longer than the reduced wavelength $ƛ$, a real photon is emitted by the primary interaction and captured by the second molecule.

The terms of reference for this study allow for the transition dipole moments, for the upward and downward radiative processes within each molecule, to be either parallel or non-parallel. In the case of molecular fluorescence this allows for the possibility of relaxation from a highly excited electronic state, as for example by internal conversion, to occur prior to radiative emission from a lower energy level (see Fig. 2). In the detailed calculations it is assumed that rotational relaxation may be neglected over the fluorescence lifetime – an assumption that is commonly valid for photobiological systems, as well as for certain laser dyes, and for fluorophores in viscous media. Resonance features are accommodated for the sequential Raman process, and it is these which ultimately establish the link with bimolecular fluorescence.

The paper is organised as follows. Section 2 yields results previously established for the fluorescence anisotropy and Raman depolarisation in the common case where signals derive from individual molecules. Irreducible tensors are introduced for the formulation of the Raman scattering process. Although there are no new results presented in this section it provides a background that establishes a framework for the subsequent treatment of bimolecular excitations. Section 3 introduces the virtual photon coupling tensor as the basis for dealing with the sequential processes. Section 4 provides the formal derivation of the fluorescence anisotropy resulting from a single-step energy transfer process between free molecules. A similar treatment of the

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[1] The term 'doubly Stokes-shifted' signifies that the radiation suffers two consecutive shifts in frequency, one at each of the participating molecules.

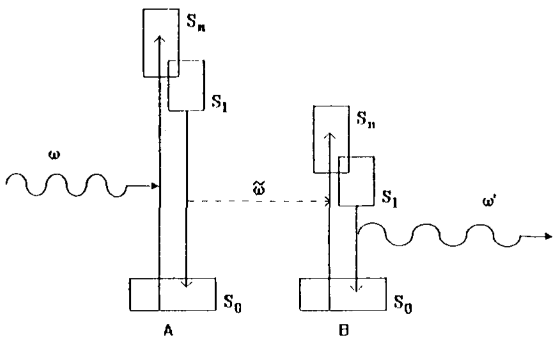

Fig. 2. Modified Jablonski diagram showing the essential energetics of both fluorescence migration and sequential Raman scattering. Here S_0 represents the ground electronic state and its associated manifold; S_1, S_n denote higher electronic states of the same spin multiplicity (normally though not necessarily these are all of singlet designation).

bimolecular Raman process is presented in Section 5. Finally in Section 6 it is shown, by considering the resonance limit of the Raman process, how the results of Sections 4 and 5 fit into one general structure. Thus we reach a position in which it is possible to employ a common theory yielding concise formulae for bimolecular interactions, irrespective of their nature.

2. Common framework for fluorescence and Raman scattering

2.1. Fluorescence

The combined process of absorption and fluorescence for a single molecule A (so labelled with a view to its later distinction from another species B) can be described by a quantum probability amplitude M_{A} whose modulus square will determine the rate. Specifically, M_{A} takes the form

$$M_{\mathrm{A}} \sim \left(\boldsymbol{\mu}_{\mathrm{A}}^{\uparrow} \cdot \boldsymbol{e}_{k}^{\lambda} \right)\left(\boldsymbol{\mu}_{\mathrm{A}}^{\downarrow} \cdot \bar{\boldsymbol{e}}_{k'}^{\lambda'} \right) = e_{k_i}^{\lambda} \bar{e}_{k'_j}^{\lambda'} \mu_{\mathrm{A}_i}^{\uparrow} \mu_{\mathrm{A}_j}^{\downarrow}, \tag{2.1}$$

where $\boldsymbol{\mu}_{\mathrm{A}}^{\uparrow}$ and $\boldsymbol{\mu}_{\mathrm{A}}^{\downarrow}$ respectively represent the transition dipole moments for absorption and emission, with $\boldsymbol{e}_{k}^{\lambda}$ and $\bar{\boldsymbol{e}}_{k'}^{\lambda'}$ the unit polarisation vectors of the incident and fluorescence signal radiation. Although it is eventually intended to focus on the case of plane polarisations, the inclusion of the overbar here to represent a complex conjugate encompasses other possibilities, such as elliptical polarisations [25]. The expression on the right-hand side of equation (2.1) is cast in terms of vector components through use of the convention of implied summation over repeated indices, a utility that we shall find it convenient to exploit in the following. As the indices i and j in Eq. (2.1) are both repeated, the quantity on the left is a scalar. Since we shall ultimately be concerned only with polarisation ratios, the constants of proportionality in such equations need not concern us.

From (2.1) it follows that the rate of signal generation is given by

$$\Gamma \sim e_{k_i}^{\lambda} \bar{e}_{k'_j}^{\lambda'} \bar{e}_{k_k}^{\lambda} e_{k'_l}^{\lambda'} \mu_{\mathrm{A}_i}^{\uparrow} \mu_{\mathrm{A}_j}^{\downarrow} \bar{\mu}_{\mathrm{A}_k}^{\uparrow} \bar{\mu}_{\mathrm{A}_l}^{\downarrow}. \tag{2.2}$$

To consider the common case in which molecules are randomly oriented with respect to the incident radiation, an orientational average has to be performed upon the rate. This involves decoupling the molecular parameters from the laboratory (or radiation) frame, and can be represented as

$$\langle \Gamma \rangle \sim e_{k_i}^{\lambda} \bar{e}_{k'_j}^{\lambda'} \bar{e}_{k_k}^{\lambda} e_{k'_l}^{\lambda'} \mu_{\mathrm{A}_\lambda}^{\uparrow} \mu_{\mathrm{A}_\mu}^{\downarrow} \bar{\mu}_{\mathrm{A}_\nu}^{\uparrow} \bar{\mu}_{\mathrm{A}_o}^{\downarrow} \langle l_{i\lambda} l_{j\mu} l_{k\nu} l_{lo} \rangle \tag{2.3}$$

Here the transition moments are referred to a molecular frame (denoted by the greek indices) and the averaging need only be performed on the product of direction cosines $l_{i\lambda}, \ldots$ in the angular brackets. Again summing over repeated indices yields a scalar quantity for the rate (2.3). With the assumption that rotational relaxation can be neglected over the timescale for fluorescence decay, then the appropriate result for the fourth rank rotational average required by Eq. (2.3) is [26]

$$\langle l_{i\lambda} l_{j\mu} l_{k\nu} l_{lo} \rangle = \frac{1}{30} \begin{pmatrix} \delta_{ij}\delta_{kl} \\ \delta_{ik}\delta_{jl} \\ \delta_{il}\delta_{jk} \end{pmatrix}^{\mathrm{T}} \begin{pmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{pmatrix} \begin{pmatrix} \delta_{\lambda\mu}\delta_{\nu o} \\ \delta_{\lambda\nu}\delta_{\mu o} \\ \delta_{\lambda o}\delta_{\mu\nu} \end{pmatrix}, \tag{2.4}$$

where the δ are Kronecker deltas. The rate for the fluorescence process can thus be expressed as below, where in order to accommodate the possibility of non-parallel upward and downward transition dipole moments (since as shown in Fig. 2 these transitions may connect different electronic levels) we introduce an angle θ_{A} to represent their mutual orientation:

$$\langle \Gamma \rangle \sim \frac{|\mu_{\mathrm{A}}^{\uparrow}|^2 |\mu_{\mathrm{A}}^{\downarrow}|^2}{30} \begin{pmatrix} (e \cdot \bar{e}')(\bar{e} \cdot e') \\ 1 \\ (e \cdot e')(\bar{e}' \cdot \bar{e}) \end{pmatrix}^{\mathrm{T}} \begin{pmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{pmatrix} \begin{pmatrix} \cos^2\theta_{\mathrm{A}} \\ 1 \\ \cos^2\theta_{\mathrm{A}} \end{pmatrix}. \tag{2.5}$$

The general result (2.5) can be further reduced for our immediate purposes. If plane (linearly) polarised light is employed, the real and conjugated unit vectors of the incident radiation are equivalent, as are the unit vectors for the emitted radiation denoted by the primes. Consequently each polarisation scalar product can be written in terms of the angle $\phi = \cos^{-1}(e \cdot e')$ between the polarisation vectors for the incident and emitted light. Thus we have

$$\langle \Gamma \rangle \sim \frac{|\mu_{\mathrm{A}}^{\uparrow}|^2 |\mu_{\mathrm{A}}^{\downarrow}|^2}{15} \left[(3\cos^2\phi - 1)\cos^2\theta_{\mathrm{A}} + 2 - \cos^2\phi \right]. \tag{2.6}$$

To determine the fluorescence anisotropy, as commonly defined by

$$r = \frac{\langle \Gamma_{\parallel} \rangle - \langle \Gamma_{\perp} \rangle}{\langle \Gamma_{\parallel} \rangle + 2\langle \Gamma_{\perp} \rangle}, \tag{2.7}$$

we can write down the results for an emergent signal whose polarisation is parallel to the incident radiation, i.e.

$$\langle \Gamma_{\parallel} \rangle \sim \frac{|\mu_{\mathrm{A}}^{\uparrow}|^2 |\mu_{\mathrm{A}}^{\downarrow}|^2}{15} (2\cos^2\theta_{\mathrm{A}} + 1) \tag{2.8}$$

and, in the case of perpendicular incident and signal polarisations

$$\langle \Gamma_{\perp} \rangle \sim \frac{|\mu_{\mathrm{A}}^{\uparrow}|^2 |\mu_{\mathrm{A}}^{\downarrow}|^2}{15} (2 - \cos^2\theta_{\mathrm{A}}). \tag{2.9}$$

Hence for the fluorescence anisotropy of a system comprising freely independent molecules we obtain the well-known Perrin's result:

$$r_0 = \frac{3\cos^2\theta_{\mathrm{A}} - 1}{5}, \tag{2.10}$$

where the subscript on r_0 denotes fluorescence without energy transfer.

2.2. The Raman process

In conventional (i.e. unimolecular) Stokes Raman scattering the radiation field once again experiences the annihilation of one photon and the creation of another with a longer wavelength. For this process a probability amplitude can be derived which shows the explicit dependence upon the unit vectors of the incident and scattered light, $\mathbf{e}_k^{\lambda}$ and $\bar{\mathbf{e}}_{k'}^{\lambda'}$ respectively, and the Raman polarisability $\alpha_{\mathrm{A}_{ij}}$:

$$M_{\mathrm{A}} \sim e_{k_i}^{\lambda} \bar{e}_{k'_j}^{\lambda'} \alpha_{\mathrm{A}_{ij}}. \tag{2.11}$$

The tensor $\alpha_{\mathrm{A}_{ij}} \equiv \alpha_{\mathrm{A}_{ij}}^{nm}(-\omega_{\mathrm{s}}, \omega_0)$ represents a transition $|m\rangle \rightarrow |n\rangle$ associated with annihilation of a photon with frequency ω_0 and emergence of a scattered photon ω_{s}, and is concisely expressible in the following form [27]:

$$\alpha_{\mathrm{A}_{ij}} = \sum_r \left(\frac{\mu_{\mathrm{A}_j}^{nr} \mu_{\mathrm{A}_i}^{rm}}{\left(\omega_{rm} - \omega_0 - \frac{1}{2}\mathrm{i}\gamma_{\mathrm{r}}\right)} + \frac{\mu_{\mathrm{A}_i}^{nr} \mu_{\mathrm{A}_j}^{rm}}{\left(\omega_{rm} + \omega_{\mathrm{s}} + \frac{1}{2}\mathrm{i}\gamma_{\mathrm{r}}\right)} \right), \tag{2.12}$$

in which γ_{r} represents the damping that is necessary in order to accommodate resonance behaviour. The rate is again dependent upon the square of the probability amplitude (2.11), i.e.

$$\Gamma \sim e_{k_i}^{\lambda} \bar{e}_{k'_j}^{\lambda'} \bar{e}_{k_k}^{\lambda} e_{k'_l}^{\lambda'} \alpha_{\mathrm{A}_{ij}} \bar{\alpha}_{\mathrm{A}_{kl}}. \tag{2.15}$$

Upon isotropic rotational averaging, again using the fourth rank rotational result (2.4), we obtain a rate result initially expressible as follows:

$$\begin{aligned} \langle \Gamma \rangle \sim \frac{1}{30} \Big\{ & \left[4(\mathbf{e}\cdot\bar{\mathbf{e}}')(\bar{\mathbf{e}}\cdot\mathbf{e}') - 1 - (\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}'\cdot\bar{\mathbf{e}})\right] \alpha_{\mathrm{A}_{\lambda\lambda}} \bar{\alpha}_{\mathrm{A}_{\mu\mu}} \\ & + \left[-(\mathbf{e}\cdot\bar{\mathbf{e}}')(\bar{\mathbf{e}}\cdot\mathbf{e}') + 4 - (\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}'\cdot\bar{\mathbf{e}})\right] \alpha_{\mathrm{A}_{\lambda\mu}} \bar{\alpha}_{\mathrm{A}_{\lambda\mu}} \\ & + \left[-(\mathbf{e}\cdot\bar{\mathbf{e}}')(\bar{\mathbf{e}}\cdot\mathbf{e}') - 1 + 4(\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}'\cdot\bar{\mathbf{e}})\right] \alpha_{\mathrm{A}_{\lambda\mu}} \bar{\alpha}_{\mathrm{A}_{\mu\lambda}} \Big\}. \end{aligned} \tag{2.16}$$

To facilitate application of the selection rules for the Raman process, it is nonetheless helpful to rewrite the above result in irreducible Cartesian tensor notation [28]. The formal basis for this formulation, together with its relationship to the more familiar Raman parameters, $\bar{\alpha}$, γ and δ [29] is given in Appendix 1. For our present purposes (2.16) can first be rewritten as

$$\begin{aligned} \langle \Gamma \rangle \sim \frac{1}{90} \Big\{ & \left[10(\mathbf{e}\cdot\bar{\mathbf{e}}')(\bar{\mathbf{e}}\cdot\mathbf{e}')\right] \alpha_{\mathrm{A}_{\lambda\lambda}}^{(0)} \bar{\alpha}_{\mathrm{A}_{\mu\mu}}^{(0)} + 3\left[5 - 5(\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}'\cdot\bar{\mathbf{e}})\right] \alpha_{\mathrm{A}_{\lambda\mu}}^{(1)} \bar{\alpha}_{\mathrm{A}_{\lambda\mu}}^{(1)} \\ & + 3\left[-2(\mathbf{e}\cdot\bar{\mathbf{e}}')(\bar{\mathbf{e}}\cdot\mathbf{e}') + 3 + 3(\mathbf{e}\cdot\mathbf{e}')(\bar{\mathbf{e}}'\cdot\bar{\mathbf{e}})\right] \alpha_{\mathrm{A}_{\lambda\mu}}^{(2)} \bar{\alpha}_{\mathrm{A}_{\mu\lambda}}^{(2)} \Big\} \end{aligned} \tag{2.17}$$

and by considering plane polarisations the Raman depolarisation ratio ρ can now be evaluated from its defining equation,

$$\rho_0 = \frac{\langle \Gamma_{\perp \rightarrow \parallel} \rangle}{\langle \Gamma_{\perp \rightarrow \perp} \rangle}, \tag{2.18}$$

where $\perp$ and $\parallel$ denote directions referred to the scattering plane, and the subscript zero again denotes the generation of a signal from individual molecules, i.e. without intermolecular energy transfer. Hence we obtain the result

$$\rho_0 = \frac{3}{2} \left(\frac{5\alpha_{\mathrm{A}_{\lambda\mu}}^{(1)} \bar{\alpha}_{\mathrm{A}_{\lambda\mu}}^{(1)} + 3\alpha_{\mathrm{A}_{\lambda\mu}}^{(2)} \bar{\alpha}_{\mathrm{A}_{\mu\lambda}}^{(2)}}{5\alpha_{\mathrm{A}_{\lambda\lambda}}^{(0)} \bar{\alpha}_{\mathrm{A}_{\mu\mu}}^{(0)} + 6\alpha_{\mathrm{A}_{\lambda\mu}}^{(2)} \bar{\alpha}_{\mathrm{A}_{\mu\lambda}}^{(2)}} \right). \tag{2.19}$$

In non-resonant Raman scattering the weight 1 antisymmetric part of the tensor is equal to zero and hence the depolarisation ratio lies in the range $0 \leqslant \rho_0 \leqslant \frac{3}{4}$; in the resonance case the upper bound of ρ_0 is infinite.

3. Theoretical framework for bimolecular excitation

As an introduction to the bimolecular processes to be studied in the following sections a formal framework for the intermolecular transfer of energy has to be established. In order to embrace both radiative transfer (long-range, $R \gg \bar{\lambda}$ where $\bar{\lambda} = k^{-1}$) and non-radiative transfer (short-range, $R \ll \bar{\lambda}$) we here adopt a theory that is applicable to both. In this way it is possible to highlight the link between a process in which molecule A emits a real photon that is subsequently captured by a second molecule B, and another process in which apparently radiationless energy transfer in fact proceeds via virtual photon coupling [19]. Such a description of molecular interactions in terms of virtual photons has found extensive applications in other areas of chemical physics. It has, for example, a pivotal role in the description of chiroptical behaviour associated with intermolecular interactions, as in induced circular dichroism [30–32], and it has recently enjoyed extensive application in the theory of intermolecular energy transfer per se [20–25] – areas in which Craig and Thirunamachandran have made a number of important contributions. Such considerations here form the basis for a common representation of bimolecular probability amplitudes in terms of the photophysical interactions of the individual molecules A and B, as will be detailed in Sections 4 and 5. The coupling between molecules, which in the long range may be regarded as mediated by the emitted fluorescence or the Raman-scattered photon, is accommodated within the appropriate probability amplitude expressions by a fully retarded dipole–dipole interaction expressible through the following index-symmetric tensor V_{jk}, [25]:

$$V_{jk}(k, \boldsymbol{R}) = \frac{\exp(\mathrm{i}kR)}{4\pi\varepsilon_0 R^3}\left[(1 - \mathrm{i}kR)\left(\delta_{jk} - 3\hat{R}_j\hat{R}_k\right) - (kR)^2\left(\delta_{jk} - \hat{R}_j\hat{R}_k\right)\right]. \tag{3.1}$$

For the applications in which the above coupling is to be employed, it is expedient to rewrite Eq. (3.1) as a product of two separate functions,

$$V_{jk} = f(k, R)\, g_{jk}(kR, \hat{\boldsymbol{R}}). \tag{3.2}$$

One of these functions, g_{jk}, is dimensionless and alone embodies the tensorial behaviour:

$$g_{jk}(kR, \hat{\boldsymbol{R}}) = \left\{\delta_{jk} + y(kR)\hat{R}_j\hat{R}_k\right\}, \tag{3.3}$$

with the real and imaginary parts of y given by

$$\Re(y) = \frac{-3 + 3k^2R^2 - k^4R^4}{1 - k^2R^2 + k^4R^4}, \qquad \Im(y) = \frac{-2k^3R^3}{1 - k^2R^2 + k^4R^4}. \tag{3.4}$$

For the other function featuring in Eq. (3.2) we have

$$f(k, R) = \frac{z(kR)\exp(\mathrm{i}kR)}{4\pi\varepsilon_0 R^3}, \tag{3.5}$$

likewise with the real and imaginary parts of z given by

$$\Re(z) = (1 - k^2R^2), \qquad \Im(z) = -kR. \tag{3.6}$$

Whilst the above results hold over an unrestricted range of intermolecular distances (beyond the extent of wavefunction overlap), it is easy to see the form that each of the new functions will take in both the short- and long-range limits, $kR \ll 1$ and $kR \gg 1$ respectively.

Short range:

$$f(k, R) = \frac{1}{4\pi\varepsilon_0 R^3}, \quad \Re(y) = -3, \quad \Im(y) = 0, \qquad g_{jk}(kR, \hat{\boldsymbol{R}}) = \left\{\delta_{jk} - 3\hat{R}_j\hat{R}_k\right\}.$$

Long range:

$$f(k, R) = -\frac{k^2\exp(\mathrm{i}kR)}{4\pi\varepsilon_0 R}, \quad \Re(y) = -1, \quad \Im(y) = 0, \qquad g_{jk}(kR, \hat{\boldsymbol{R}}) = \left\{\delta_{jk} - \hat{R}_j\hat{R}_k\right\}.$$

The two limits lead to the well-known short-range R^{-3} dependence of the probability amplitude, as associated with the classical Coulombic interaction of dipole–dipole coupling (cf. the R^{-6} dependence of the Förster energy transfer rate), and a long-range inverse proportionality to R associated with the familiar R^{-2} inverse square radiative transfer rate.

In the rotationally averaged rate equations to be examined in later sections, each term proves to contain a product of components of the coupling tensor with components of its complex conjugate, of the general form $V_{jk}\bar{V}_{no} = f\bar{f} g_{jk}\bar{g}_{no}$. With this in mind, it is instructive to examine the form of each part of the result. Firstly the general result for the scalar $f(k, R)$ multiplied by its complex conjugate can be written as

$$f\bar{f} = \frac{|z|^2}{16\pi^2\varepsilon_0^2 R^6} = \frac{1}{16\pi^2\varepsilon_0^2 R^6}\left(1 - k^2R^2 + k^4R^4\right), \tag{3.7}$$

where the denominator is later to be incorporated in the constant of proportionality. For the tensorial part of the coupling function we can then write the result as

$$g_{jk}\bar{g}_{no} = \left\{\delta_{jk} + y\hat{R}_j\hat{R}_k\right\}\left\{\delta_{no} + \bar{y}\hat{R}_n\hat{R}_o\right\}, \tag{3.8}$$

and three different forms emerge according to the different kinds of index pairing that arise:

$$g_{jk}\bar{g}_{no} = \delta_{jk}\delta_{no} + \delta_{jk}\bar{y}\hat{R}_n\hat{R}_o + \delta_{no}y\hat{R}_j\hat{R}_k + |y|^2\hat{R}_j\hat{R}_k\hat{R}_n\hat{R}_o, \tag{3.9}$$

$$g_{jk}\bar{g}_{nk} = \delta_{jn} + 2\Re(y)\hat{R}_j\hat{R}_n + |y|^2\hat{R}_j\hat{R}_n, \tag{3.10}$$

$$g_{jk}\bar{g}_{jk} = 3 + 2\Re(y) + |y|^2. \tag{3.11}$$

The first of these, (3.9), evidently has terms calling for second and fourth rank rotational averages to be performed to separate the molecular displacement vectors from the laboratory frame; the result (3.10) requires a second rank average and the last, (3.11), is a rotation-invariant scalar.

To summarise, employment of the coupling formalism described above enables both the quantum probability amplitudes and the ensuing rate equations for each entire bimolecular process to be expressed by factorisable expressions. Conceptualisation in terms of two separate processes (as normally considered in the case of radiative energy transfer) will be embraced within each expression and specifically manifest at the limit of large molecular separation.

4. Fluorescence migration

In the specific two-centre case now to be considered, the absorption of light by molecule A is the first step in a process within which a significant part of the excitation energy is exchanged between the two molecules A and B, and it is the fluorescence from molecule B that gives rise to the detected signal. In order for this process to be physically distinguishable from direct fluorescence by A, it may be supposed that A and B are chemically different [2], and that the fluorescence spectrum of B covers a range of appreciably longer wavelengths than A, ideally with no overlap between the two emission spectra. Under such circumstances it may also be assumed that there is no further redistribution of energy between A and B, i.e. energy transfer occurs in one direction only.

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[2] It is also possible to entertain cases where A and B have the same chemical composition, but different electronic states are involved.

The quantum probability amplitude for the process now under consideration is a scalar product of the molecular transition dipole moments, the radiation unit vectors and the virtual photon tensor introduced in Section 3:

$$M \sim e_{k_i}^{\lambda} \bar{e}_{k'_l}^{\lambda'} \mu_{\mathrm{A}_i}^{\uparrow} \mu_{\mathrm{A}_j}^{\downarrow} \mu_{\mathrm{B}_k}^{\uparrow} \mu_{\mathrm{B}_l}^{\downarrow} V_{jk}. \tag{4.1}$$

The rate can be expressed as the square of the probability amplitude as

$$\Gamma \sim e_{k_i}^{\lambda} \bar{e}_{k'_l}^{\lambda'} \bar{e}_{k_m}^{\lambda} e_{k'_p}^{\lambda'} \mu_{\mathrm{A}_i}^{\uparrow} \mu_{\mathrm{A}_j}^{\downarrow} \mu_{\mathrm{B}_k}^{\uparrow} \mu_{\mathrm{B}_l}^{\downarrow} \bar{\mu}_{\mathrm{A}_m}^{\uparrow} \bar{\mu}_{\mathrm{A}_n}^{\uparrow} \bar{\mu}_{\mathrm{B}_o}^{\uparrow} \bar{\mu}_{\mathrm{B}_p}^{\downarrow} V_{jk} \bar{V}_{no}, \tag{4.2}$$

where once again there is implied summation over all Cartesian indices. In allowing for the free rotation of the respective molecules, two independent orientational averages are required to decouple each molecule from the fixed laboratory frame. This procedure again entails two fourth rank isotropic averages of the form given by (2.4)

$$\begin{aligned}\Gamma \sim\ & e_{k_i}^{\lambda} \bar{e}_{k'_l}^{\lambda'} \bar{e}_{k_m}^{\lambda} e_{k'_p}^{\lambda'} \mu_{\mathrm{A}_\lambda}^{\uparrow} \mu_{\mathrm{A}_\mu}^{\downarrow} \mu_{\mathrm{B}_\nu}^{\uparrow} \mu_{\mathrm{B}_o}^{\downarrow} \bar{\mu}_{\mathrm{A}_\pi}^{\uparrow} \bar{\mu}_{\mathrm{A}_\rho}^{\downarrow} \bar{\mu}_{\mathrm{B}_\sigma}^{\downarrow} \bar{\mu}_{\mathrm{B}_\tau}^{\downarrow} V_{jk} \bar{V}_{no} \\ & \times \langle l_{i\lambda} l_{j\mu} l_{m\pi} l_{n\rho} \rangle \langle l_{k\nu} l_{lo} l_{o\sigma} l_{p\tau} \rangle.\end{aligned} \tag{4.3}$$

The result of performing these averages carries expressions of the form (3.7)–(3.11), and at this stage relates to a system in which the intermolecular displacement vector ***R*** still has a fixed orientation relative to the laboratory frame. To complete the rate calculation, further rotational averages have to be taken to decouple the radiation vectors ***e*** and ***e***′ from the ***R***-dependent virtual photon coupling tensor, since the vector displacement of molecule B relative to A can also assume an arbitrary orientation. This calculation will nonetheless allow for any (fixed) angle between the absorption and emission transition moments within each molecule. Where no constraint is placed on either the incident or emergent polarisation, the derivation produces a lengthy expression, although for the purposes of obtaining the fluorescence anisotropy a substantially simpler expression will emerge. Nonetheless, dealing first with the most general case, the fully averaged rate can be expressed in the following compact form, taking out a common factor of $\frac{1}{900}|\boldsymbol{\mu}_{\mathrm{A}}^{\uparrow}|^2 |\boldsymbol{\mu}_{\mathrm{A}}^{\downarrow}|^2 |\boldsymbol{\mu}_{\mathrm{B}}^{\uparrow}|^2 |\boldsymbol{\mu}_{\mathrm{B}}^{\downarrow}|^2$:

$$\langle \Gamma \rangle \sim \sum_{n=1}^{9} \langle \Gamma_n \rangle, \tag{4.4}$$

and five distinct kinds of rate contribution can be identified:

$$\langle \Gamma_n \rangle \sim \frac{|z|^2}{15}(3\cos^2\theta_{\mathrm{A}} - 1)(3\cos^2\theta_{\mathrm{B}} - 1)\left[15p_1 + 10\Re(y)p_1 + |y|^2(1 + p_1 + p_2)\right], \quad n = 1, 9, \tag{4.5}$$

$$\langle \Gamma_n \rangle \sim \frac{|z|^2}{15}(3\cos^2\theta_{\mathrm{A}} - 1)(3\cos^2\theta_{\mathrm{B}} - 1)\left[15p_2 + 10\Re(y)p_2 + |y|^2(1 + p_1 + p_2)\right], \quad n = 3, 7, \tag{4.6}$$

$$\langle \Gamma_n \rangle \sim \frac{|z|^2}{3}(4 - 2\cos^2\theta_{\mathrm{A}})(3\cos^2\theta_{\mathrm{B}} - 1)\left[3 + 2\Re(y) + |y|^2\right], \quad n = 2, 8, \tag{4.7}$$

$$\langle \Gamma_n \rangle \sim \frac{|z|^2}{3}(3\cos^2\theta_{\mathrm{A}} - 1)(4 - 2\cos^2\theta_{\mathrm{B}})\left[3 + 2\Re(y) + |y|^2\right], \quad n = 4, 6, \tag{4.8}$$

$$\langle \Gamma_n \rangle \sim |z|^2(4 - 2\cos^2\theta_{\mathrm{A}})(4 - 2\cos^2\theta_{\mathrm{B}})\left[3 + 2\Re(y) + |y|^2\right], \quad n = 5. \tag{4.9}$$

The polarisation parameters, p_1 and p_2, introduced for convenience in the preceding equations, are here defined as

$$p_1 = (\boldsymbol{e}\cdot\bar{\boldsymbol{e}}')(\bar{\boldsymbol{e}}\cdot\boldsymbol{e}'), \tag{4.10}$$

$$p_2 = (\bar{\boldsymbol{e}}\cdot\bar{\boldsymbol{e}}')(\boldsymbol{e}\cdot\boldsymbol{e}'), \tag{4.11}$$

and y, z are as given in Section 3.

In calculating the concomitant fluorescence anisotropy only plane polarisations are of interest, and the polarisation vectors of the incident and emergent radiation are real. In this case the above rate contributions simplify considerably, and can again be written in terms of the angle ϕ between these vectors. Hence we obtain:

$$\begin{aligned}\langle\Gamma\rangle \sim \frac{|z|^2}{15}\Big[&4\Big(\big\{|y|^2+\big[15+10\Re(y)+2|y|^2\big](\cos^2\phi)\big\}(3\cos^2\theta_A-1)(3\cos^2\theta_B-1)\Big)\\&+5\big[3+2\Re(y)+|y|^2\big]\big[2(4-2\cos^2\theta_A)(3\cos^2\theta_B-1)\\&+2(3\cos^2\theta_A-1)(4-2\cos^2\theta_B)+3(4-2\cos^2\theta_A)(4-2\cos^2\theta_B)\big]\Big].\end{aligned} \tag{4.12}$$

From the above perfectly general result it is possible to derive explicit expressions for the fluorescence anisotropy, $r_1=(1-\xi)/(1+2\xi)$ where $\xi=\langle\Gamma_\perp\rangle/\langle\Gamma_\parallel\rangle$, the subscript on r_1 denoting single-step energy transfer. The result is as follows:

$$\begin{aligned}r_1 = {}&\tfrac{4}{5}(3\cos^2\theta_A-1)(3\cos^2\theta_B-1)\big[15+10\Re(y)+2|y|^2\big]\big[3+2\Re(y)+|y|^2\big]^{-1}\\&\times\big[4(3\cos^2\theta_A-1)(3\cos^2\theta_B-1)+6(4-2\cos^2\theta_A)(3\cos^2\theta_B-1)\\&+6(3\cos^2\theta_A-1)(4-2\cos^2\theta_B)+9(4-2\cos^2\theta_A)(4-2\cos^2\theta_B)\big]^{-1}\end{aligned} \tag{4.13}$$

and the short- and long-range behaviour follows from the limits of y as given in Section 3. It is readily shown that, in the case where the absorption and emission transition moments within each molecule are parallel, i.e. $\theta_A=\theta_B=0$, the resulting anisotropy has precisely the range dependence found previously [3]; however the present result accommodates the case of non-parallel moments. Again, with $\theta_A=\theta_B=0$ the specific results for the short- and long-range anisotropy are:

Short range

$$\langle\Gamma\rangle \sim 4\cos^2\phi+82, \tag{4.14}$$

giving the following relation between the anisotropy associated with single-step transfer and transfer-free fluorescence:

$$r_1=\frac{1-\xi}{1+2\xi}=\frac{2}{125}=\frac{r_0}{25},\quad \theta_A=\theta_B=0, \tag{4.15}$$

consistent with the non-radiative result of Galanin [33].

Long range

$$\langle\Gamma\rangle \sim 14\cos^2\phi+37, \tag{4.16}$$

from which the following result ensues in accordance with a relation previously reported [3]:

$$r_1=\frac{14}{125}=\frac{7r_0}{25},\quad \theta_A=\theta_B=0. \tag{4.17}$$

5. Sequential two-molecule Raman scattering

The theory of bimolecular Raman scattering can be developed in a similar manner to the two-molecule fluorescence process examined in Section 4. This process involves a double Stokes shift in frequency, associated with the sequential Raman excitation of molecules A and B. In the current context, and with a view to establishing in Section 6 a relationship with bimolecular fluorescence, we shall here restrict consideration to the case where excitation of A precedes that of B – a more general theory allowing for the reciprocal process has been presented previously [12,13]. As developed here, the theory can address cases where both molecules are of the same chemical type. Experimentally, the appearance in the Raman spectrum of a single-component system of frequency shifts attributable to pairwise vibrational excitations ought, as a result of their different degrees of anharmonicity, to be distinguishable from the slightly lower frequency corresponding overtones. As we shall observe, such bimolecular scattering events can also be characterised by unusual depolarisation behaviour.

The quantum probability amplitude for the entire process can again be cast as a single factorisable expression in terms of the virtual photon tensor. The probability amplitude involves the transition polarisability tensors for the individual molecules and the incident and scattered radiation vectors (cf. Section 2)

$$M \sim e^{\lambda}_{k_i}\bar{e}^{\lambda'}_{k'_l}\alpha_{\mathrm{A}_{ij}}\alpha_{\mathrm{B}_{kl}}V_{jk}, \tag{5.1}$$

and the rate is once more obtained through multiplication by the complex conjugate

$$\Gamma \sim e^{\lambda}_{k_i}\bar{e}^{\lambda'}_{k'_l}\bar{e}^{\lambda}_{k_m}e^{\lambda'}_{k'_p}\alpha_{\mathrm{A}_{ij}}\alpha_{\mathrm{B}_{kl}}\bar{\alpha}_{\mathrm{A}_{mn}}\bar{\alpha}_{\mathrm{B}_{op}}V_{jk}\bar{V}_{no}, \tag{5.2}$$

giving a rotationally averaged result:

$$\Gamma \sim e^{\lambda}_{k_i}\bar{e}^{\lambda'}_{k'_l}\bar{e}^{\lambda}_{k_m}e^{\lambda'}_{k'_p}\alpha_{\mathrm{A}_{\lambda\mu}}\alpha_{\mathrm{B}_{\nu o}}\bar{\alpha}_{\mathrm{A}_{\pi\rho}}\bar{\alpha}_{\mathrm{B}_{\sigma\tau}}V_{jk}\bar{V}_{no}\langle l_{i\lambda}l_{j\mu}l_{m\pi}l_{n\rho}\rangle\langle l_{k\nu}l_{lo}l_{o\sigma}l_{p\tau}\rangle. \tag{5.3}$$

Here the result is not directly factorisable in terms of transition dipole moments as in the case of fluorescence, essentially because non-resonant intermediate states (incorporated within the structure of the transition tensors) are included in the quantum amplitudes for transition from the initial to the final state of each molecule. After implementing the full orientational average procedure as described in Section 4, and extracting from each term the common factor of $\frac{1}{900}$, we then have for arbitrary polarisation conditions a result expressible as

$$\langle\Gamma\rangle \sim \sum_{n=1}^{9}\langle\Gamma_n\rangle, \tag{5.4}$$

whose contributions are explicitly as follows:

$$\begin{aligned}\langle\Gamma_1\rangle \sim \frac{|z|^2}{15}\Big\{&17\big[15p_1 + 10p_1\Re(y) + |y|^2(1+p_1+p_2)\big]\\ &-8\big[15p_2 + 10p_2\Re(y) + |y|^2(1+p_1+p_2)\big]\\ &-15\big[3 + 2\Re(y) + |y|^2\big]\Big\}\big(\alpha_{\mathrm{A}_{\lambda\lambda}}\bar{\alpha}_{\mathrm{A}_{\mu\mu}}\big)\big(\alpha_{\mathrm{B}_{\nu\nu}}\bar{\alpha}_{\mathrm{B}_{oo}}\big),\end{aligned} \tag{5.5}$$

$$\begin{aligned}\langle\Gamma_2\rangle \sim \frac{|z|^2}{15}\Big\{&-3\big[15p_1 + 10p_1\Re(y) + |y|^2(1+p_1+p_2)\big]\\ &-3\big[15p_2 + 10p_2\Re(y) + |y|^2(1+p_1+p_2)\big]\\ &+10\big[3 + 2\Re(y) + |y|^2\big]\Big\}\big(\alpha_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}_{\mathrm{A}_{\lambda\mu}}\big)\big(\alpha_{\mathrm{B}_{\nu\nu}}\bar{\alpha}_{\mathrm{B}_{oo}}\big),\end{aligned} \tag{5.6}$$

$$\begin{aligned}\langle \Gamma_3 \rangle \sim \frac{|z|^2}{15}\Big\{&-8\big[15p_1+10p_1\Re(y)+|y|^2(1+p_1+p_2)\big]\\&+17\big[15p_2+10p_2\Re(y)+|y|^2(1+p_1+p_2)\big]\\&-15\big[3+2\Re(y)+|y|^2\big]\Big\}\big(\alpha_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}_{\mathrm{A}_{\mu\lambda}}\big)\big(\alpha_{\mathrm{B}_{\nu\nu}}\bar{\alpha}_{\mathrm{B}_{oo}}\big),\end{aligned} \tag{5.7}$$

$$\begin{aligned}\langle \Gamma_5 \rangle \sim \frac{|z|^2}{15}\Big\{&2\big[15p_1+10p_1\Re(y)+|y|^2(1+p_1+p_2)\big]\\&+2\big[15p_2+10p_2\Re(y)+|y|^2(1+p_1+p_2)\big]\\&+160\big[3+2\Re(y)+|y|^2\big]\Big\}\big(\alpha_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}_{\mathrm{A}_{\lambda\mu}}\big)\big(\alpha_{\mathrm{B}_{\nu o}}\bar{\alpha}_{\mathrm{B}_{\nu o}}\big).\end{aligned} \tag{5.8}$$

For $n = 9$ an expression of similar structure to the $n = 1$ result arises, the only difference being the form of the transition tensor products; the corresponding result is expressed by the right-hand side of Eq. (5.5) but with tensor product $(\alpha_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}_{\mathrm{A}_{\mu\lambda}})(\alpha_{\mathrm{B}_{\nu o}}\bar{\alpha}_{\mathrm{B}_{o\nu}})$. For $n = 4$, 6 and 8 the results are as given by Eq. (5.6), but with corresponding product tensors $(\alpha_{\mathrm{A}_{\lambda\lambda}}\bar{\alpha}_{\mathrm{A}_{\mu\mu}})(\alpha_{\mathrm{B}_{\nu o}}\bar{\alpha}_{\mathrm{B}_{\nu o}})$, $(\alpha_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}_{\mathrm{A}_{\mu\lambda}})(\alpha_{\mathrm{B}_{\nu o}}\bar{\alpha}_{\mathrm{B}_{\nu o}})$ and $(\alpha_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}_{\mathrm{A}_{\lambda\mu}})(\alpha_{\mathrm{B}_{\nu o}}\bar{\alpha}_{\mathrm{B}_{o\nu}})$ respectively. Finally, the $n = 7$ result has the form of (5.7), with a tensor product $(\alpha_{\mathrm{A}_{\lambda\lambda}}\bar{\alpha}_{\mathrm{A}_{\mu\mu}})(\alpha_{\mathrm{B}_{\nu o}}\bar{\alpha}_{\mathrm{B}_{o\nu}})$.

In order to facilitate application of the Raman selection rules it is more convenient to recast the rate in a form, similar in structure to (5.4), expressed in terms of irreducible tensors (see Appendix 1). This representation necessarily yields another nine terms; though not *individually* identifiable with those given above, their sum is of course the same in either representation. Here we can write

$$\langle \Gamma \rangle = \sum_{j,j'=0}^{2} \langle \Gamma_{jj'} \rangle, \tag{5.9}$$

with

$$\langle \Gamma_{00} \rangle \sim \frac{|z|^2}{135}\Big\{100\big[15p_1+10p_1\Re(y)+|y|^2(1+p_1+p_2)\big]\Big\}\big(\alpha^{(0)}_{\mathrm{A}_{\lambda\lambda}}\bar{\alpha}^{(0)}_{\mathrm{A}_{\mu\mu}}\big)\big(\alpha^{(0)}_{\mathrm{B}_{\nu\nu}}\bar{\alpha}^{(0)}_{\mathrm{B}_{oo}}\big), \tag{5.10}$$

$$\begin{aligned}\langle \Gamma_{11} \rangle \sim \frac{|z|^2}{15}\Big\{&25\big[15p_1+10p_1\Re(y)+|y|^2(1+p_1+p_2)\big]\\&+125\big[3+2\Re(y)+|y|^2\big]\Big\}\big(\alpha^{(1)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(1)}_{\mathrm{A}_{\lambda\mu}}\big)\big(\alpha^{(1)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(1)}_{\mathrm{B}_{\nu o}}\big),\end{aligned} \tag{5.11}$$

$$\begin{aligned}\langle \Gamma_{22} \rangle \sim \frac{|z|^2}{15}\Big\{&13\big[15p_1+10p_1\Re(y)+|y|^2(1+p_1+p_2)\big]\\&-12\big[15p_2+10p_2\Re(y)+|y|^2(1+p_1+p_2)\big]\\&+165\big[3+2\Re(y)+|y|^2\big]\Big\}\big(\alpha^{(2)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(2)}_{\mathrm{A}_{\mu\lambda}}\big)\big(\alpha^{(2)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(2)}_{\mathrm{B}_{o\nu}}\big),\end{aligned} \tag{5.12}$$

$$\begin{aligned}\langle \Gamma_{01} \rangle \sim \frac{|z|^2}{45}\Big\{&-50\big[15p_2+10p_2\Re(y)+|y|^2(1+p_1+p_2)\big]\\&+250\big[3+2\Re(y)+|y|^2\big]\Big\}\big(\alpha^{(0)}_{\mathrm{A}_{\lambda\lambda}}\bar{\alpha}^{(0)}_{\mathrm{A}_{\mu\mu}}\big)\big(\alpha^{(1)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(1)}_{\mathrm{B}_{\nu o}}\big),\end{aligned} \tag{5.13}$$

$$\begin{aligned}\langle \Gamma_{02}\rangle \sim \frac{|z|^2}{45}\Big\{&-20\big[15p_1+10p_1\Re(y)+|y|^2(1+p_1+p_2)\big]\\&+30\big[15p_2+10p_2\Re(y)+|y|^2(1+p_1+p_2)\big]\\&+150\big[3+2\Re(y)+|y|^2\big]\Big\}\Big(\alpha^{(0)}_{\mathrm{A}_{\lambda\lambda}}\overline{\alpha}^{(0)}_{\mathrm{A}_{\mu\mu}}\Big)\Big(\alpha^{(2)}_{\mathrm{B}_{\nu o}}\overline{\alpha}^{(2)}_{\mathrm{B}_{o\nu}}\Big),\end{aligned}\tag{5.14}$$

$$\begin{aligned}\langle \Gamma_{12}\rangle \sim \frac{|z|^2}{15}\Big\{&-15\big[15p_1+10p_1\Re(y)+|y|^2(1+p_1+p_2)\big]\\&+10\big[15p_2+10p_2\Re(y)+|y|^2(1+p_1+p_2)\big]\\&+175\big[3+2\Re(y)+|y|^2\big]\Big\}\Big(\alpha^{(1)}_{\mathrm{A}_{\lambda\mu}}\overline{\alpha}^{(1)}_{\mathrm{A}_{\lambda\mu}}\Big)\Big(\alpha^{(2)}_{\mathrm{B}_{\nu o}}\overline{\alpha}^{(2)}_{\mathrm{B}_{o\nu}}\Big).\end{aligned}\tag{5.15}$$

For $\langle \Gamma_{10}\rangle$, Eq. (5.13) is applicable upon reversal of the molecular tensor products, i.e. $(\alpha^{(1)}_{\mathrm{A}_{\lambda\mu}}\overline{\alpha}^{(1)}_{\mathrm{A}_{\lambda\mu}})(\alpha^{(0)}_{\mathrm{B}_{\nu\nu}}\overline{\alpha}^{(0)}_{\mathrm{B}_{oo}})$. Similarly for $\langle \Gamma_{20}\rangle$ we can employ (5.14) with $(\alpha^{(2)}_{\mathrm{A}_{\lambda\mu}}\overline{\alpha}^{(2)}_{\mathrm{A}_{\mu\lambda}})(\alpha^{(0)}_{\mathrm{B}_{\nu\nu}}\overline{\alpha}^{(0)}_{\mathrm{B}_{oo}})$, and for $\langle \Gamma_{21}\rangle$ Eq. (5.15) applies with $(\alpha^{(2)}_{\mathrm{A}_{\lambda\mu}}\overline{\alpha}^{(2)}_{\mathrm{A}_{\mu\lambda}})(\alpha^{(1)}_{\mathrm{B}_{\nu o}}\overline{\alpha}^{(1)}_{\mathrm{B}_{\nu o}})$.

The polarisation parameter most of interest for bimolecular Raman scattering is the depolarisation ratio as given by (2.18), here denoted by ρ_1 to signify the involvement of energy transfer. For the evaluation of this ratio we again need only consider plane polarisations, and a result applicable for all intermolecular distances is directly obtainable from the above. In view of its complexity we report the general result in Appendix 2 and concentrate here on the limiting short- and long-range behaviour.

Short range

Here the complete bimolecular Raman depolarisation ratio, to be denoted below by ρ_1, may be expressed as

$$\begin{aligned}\rho_1 = 3\Big\{&100\Big(\alpha^{(0)}_{\mathrm{A}_{\lambda\lambda}}\overline{\alpha}^{(0)}_{\mathrm{A}_{\mu\mu}}\Big)\Big(\alpha^{(0)}_{\mathrm{B}_{\nu\nu}}\overline{\alpha}^{(0)}_{\mathrm{B}_{oo}}\Big)+975\Big(\alpha^{(1)}_{\mathrm{A}_{\lambda\mu}}\overline{\alpha}^{(1)}_{\mathrm{A}_{\lambda\mu}}\Big)\Big(\alpha^{(1)}_{\mathrm{B}_{\nu o}}\overline{\alpha}^{(1)}_{\mathrm{B}_{\nu o}}\Big)+999\Big(\alpha^{(2)}_{\mathrm{A}_{\lambda\mu}}\overline{\alpha}^{(2)}_{\mathrm{A}_{\mu\lambda}}\Big)\Big(\alpha^{(2)}_{\mathrm{B}_{\nu o}}\overline{\alpha}^{(2)}_{\mathrm{B}_{o\nu}}\Big)\\&+350\Big(\alpha^{(0)}_{\mathrm{A}_{\lambda\lambda}}\overline{\alpha}^{(0)}_{\mathrm{A}_{\mu\mu}}\Big)\Big(\alpha^{(1)}_{\mathrm{B}_{\nu o}}\overline{\alpha}^{(1)}_{\mathrm{B}_{\nu o}}\Big)+350\Big(\alpha^{(1)}_{\mathrm{A}_{\lambda\mu}}\overline{\alpha}^{(1)}_{\mathrm{A}_{\lambda\mu}}\Big)\Big(\alpha^{(0)}_{\mathrm{B}_{\nu\nu}}\overline{\alpha}^{(0)}_{\mathrm{B}_{oo}}\Big)+330\Big(\alpha^{(0)}_{\mathrm{A}_{\lambda\lambda}}\overline{\alpha}^{(0)}_{\mathrm{A}_{\mu\mu}}\Big)\Big(\alpha^{(2)}_{\mathrm{B}_{\nu o}}\overline{\alpha}^{(2)}_{\mathrm{B}_{o\nu}}\Big)\\&+330\Big(\alpha^{(2)}_{\mathrm{A}_{\lambda\mu}}\overline{\alpha}^{(2)}_{\mathrm{A}_{\mu\lambda}}\Big)\Big(\alpha^{(0)}_{\mathrm{B}_{\nu\nu}}\overline{\alpha}^{(0)}_{\mathrm{B}_{oo}}\Big)+1005\Big(\alpha^{(1)}_{\mathrm{A}_{\lambda\mu}}\overline{\alpha}^{(1)}_{\mathrm{A}_{\lambda\mu}}\Big)\Big(\alpha^{(2)}_{\mathrm{B}_{\nu o}}\overline{\alpha}^{(2)}_{\mathrm{B}_{o\nu}}\Big)+1005\Big(\alpha^{(2)}_{\mathrm{A}_{\lambda\mu}}\overline{\alpha}^{(2)}_{\mathrm{A}_{\mu\lambda}}\Big)\Big(\alpha^{(1)}_{\mathrm{B}_{\nu o}}\overline{\alpha}^{(1)}_{\mathrm{B}_{\nu o}}\Big)\Big\}\\\times\Big\{&400\Big(\alpha^{(0)}_{\mathrm{A}_{\lambda\lambda}}\overline{\alpha}^{(0)}_{\mathrm{A}_{\mu\mu}}\Big)\Big(\alpha^{(0)}_{\mathrm{B}_{\nu\nu}}\overline{\alpha}^{(0)}_{\mathrm{B}_{oo}}\Big)+3150\Big(\alpha^{(1)}_{\mathrm{A}_{\lambda\mu}}\overline{\alpha}^{(1)}_{\mathrm{A}_{\lambda\mu}}\Big)\Big(\alpha^{(1)}_{\mathrm{B}_{\nu o}}\overline{\alpha}^{(1)}_{\mathrm{B}_{\nu o}}\Big)+3006\Big(\alpha^{(2)}_{\mathrm{A}_{\lambda\mu}}\overline{\alpha}^{(2)}_{\mathrm{A}_{\mu\lambda}}\Big)\Big(\alpha^{(2)}_{\mathrm{B}_{\nu o}}\overline{\alpha}^{(2)}_{\mathrm{B}_{o\nu}}\Big)\\&+900\Big(\alpha^{(0)}_{\mathrm{A}_{\lambda\lambda}}\overline{\alpha}^{(0)}_{\mathrm{A}_{\mu\mu}}\Big)\Big(\alpha^{(1)}_{\mathrm{B}_{\nu o}}\overline{\alpha}^{(1)}_{\mathrm{B}_{\nu o}}\Big)+900\Big(\alpha^{(1)}_{\mathrm{A}_{\lambda\mu}}\overline{\alpha}^{(1)}_{\mathrm{A}_{\lambda\mu}}\Big)\Big(\alpha^{(0)}_{\mathrm{B}_{\nu\nu}}\overline{\alpha}^{(0)}_{\mathrm{B}_{oo}}\Big)+1020\Big(\alpha^{(0)}_{\mathrm{A}_{\lambda\lambda}}\overline{\alpha}^{(0)}_{\mathrm{A}_{\mu\mu}}\Big)\Big(\alpha^{(2)}_{\mathrm{B}_{\nu o}}\overline{\alpha}^{(2)}_{\mathrm{B}_{o\nu}}\Big)\\&+1020\Big(\alpha^{(2)}_{\mathrm{A}_{\lambda\mu}}\overline{\alpha}^{(2)}_{\mathrm{A}_{\mu\lambda}}\Big)\Big(\alpha^{(0)}_{\mathrm{B}_{\nu\nu}}\overline{\alpha}^{(0)}_{\mathrm{B}_{oo}}\Big)+2970\Big(\alpha^{(1)}_{\mathrm{A}_{\lambda\mu}}\overline{\alpha}^{(1)}_{\mathrm{A}_{\lambda\mu}}\Big)\Big(\alpha^{(2)}_{\mathrm{B}_{\nu o}}\overline{\alpha}^{(2)}_{\mathrm{B}_{o\nu}}\Big)+2970\Big(\alpha^{(2)}_{\mathrm{A}_{\lambda\mu}}\overline{\alpha}^{(2)}_{\mathrm{A}_{\mu\lambda}}\Big)\Big(\alpha^{(1)}_{\mathrm{B}_{\nu o}}\overline{\alpha}^{(1)}_{\mathrm{B}_{\nu o}}\Big)\Big\}^{-1}.\end{aligned}\tag{5.16}$$

In off-resonance applications all terms involving weight 1 effectively disappear and the result simplifies further. Here we find that for excitation of 'polarised', i.e. totally symmetric, bands in each molecule, ρ_1 values must lie in the interval $(\frac{3}{4}, \frac{333}{334})$. If both A and B undergo vibrational transitions involving non-totally symmetric 'depolarised' bands, the upper limit on ρ_1 applies, reflecting almost completely unpolarised scattering [3]. The result is noteworthy in establishing a possible mechanism for the appearance of depolarisation values above the normal $(0, \frac{3}{4})$ range *without* necessary involvement of resonance.

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[3] The short-range result $\rho_1 = \frac{3}{4}$ which applies for polarised transitions in both A and B reflects the overall weight 2 character of the pair response tensor $\boldsymbol{\alpha}\cdot\mathbf{V}\cdot\boldsymbol{\alpha}$, since $\mathbf{V}$ is weight 2 and both $\boldsymbol{\alpha}$ tensors weight 0. For this reason the result is the same as applies for a pure weight 2 transition in conventional Raman scattering.

Long range
In the long range limit ρ_1 is as follows;

$$\begin{aligned}
\rho_1 = \Big\{ & 100\left(\alpha^{(0)}_{\mathrm{A}_{\lambda\lambda}}\bar{\alpha}^{(0)}_{\mathrm{A}_{\mu\mu}}\right)\left(\alpha^{(0)}_{\mathrm{B}_{\nu\nu}}\bar{\alpha}^{(0)}_{\mathrm{B}_{oo}}\right) + 2475\left(\alpha^{(1)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(1)}_{\mathrm{A}_{\lambda\mu}}\right)\left(\alpha^{(1)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(1)}_{\mathrm{B}_{\nu o}}\right) + 2979\left(\alpha^{(2)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(2)}_{\mathrm{A}_{\mu\lambda}}\right)\left(\alpha^{(2)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(2)}_{\mathrm{B}_{o\nu}}\right) \\
& + 1350\left(\alpha^{(0)}_{\mathrm{A}_{\lambda\lambda}}\bar{\alpha}^{(0)}_{\mathrm{A}_{\mu\mu}}\right)\left(\alpha^{(1)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(1)}_{\mathrm{B}_{\nu o}}\right) + 1350\left(\alpha^{(1)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(1)}_{\mathrm{A}_{\lambda\mu}}\right)\left(\alpha^{(0)}_{\mathrm{B}_{\nu\nu}}\bar{\alpha}^{(0)}_{\mathrm{B}_{oo}}\right) + 930\left(\alpha^{(0)}_{\mathrm{A}_{\lambda\lambda}}\bar{\alpha}^{(0)}_{\mathrm{A}_{\mu\mu}}\right)\left(\alpha^{(2)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(2)}_{\mathrm{B}_{o\nu}}\right) \\
& + 930\left(\alpha^{(2)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(2)}_{\mathrm{A}_{\mu\lambda}}\right)\left(\alpha^{(0)}_{\mathrm{B}_{\nu\nu}}\bar{\alpha}^{(0)}_{\mathrm{B}_{oo}}\right) + 3105\left(\alpha^{(1)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(1)}_{\mathrm{A}_{\lambda\mu}}\right)\left(\alpha^{(2)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(2)}_{\mathrm{B}_{o\nu}}\right) + 3105\left(\alpha^{(2)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(2)}_{\mathrm{A}_{\mu\lambda}}\right)\left(\alpha^{(1)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(1)}_{\mathrm{B}_{\nu o}}\right)\Big\} \\
\times \Big\{ & 800\left(\alpha^{(0)}_{\mathrm{A}_{\lambda\lambda}}\bar{\alpha}^{(0)}_{\mathrm{A}_{\mu\mu}}\right)\left(\alpha^{(0)}_{\mathrm{B}_{\nu\nu}}\bar{\alpha}^{(0)}_{\mathrm{B}_{oo}}\right) + 4050\left(\alpha^{(1)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(1)}_{\mathrm{A}_{\lambda\mu}}\right)\left(\alpha^{(1)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(1)}_{\mathrm{B}_{\nu o}}\right) + 3042\left(\alpha^{(2)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(2)}_{\mathrm{A}_{\mu\lambda}}\right)\left(\alpha^{(2)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(2)}_{\mathrm{B}_{o\nu}}\right) \\
& + 300\left(\alpha^{(0)}_{\mathrm{A}_{\lambda\lambda}}\bar{\alpha}^{(0)}_{\mathrm{A}_{\mu\mu}}\right)\left(\alpha^{(1)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(1)}_{\mathrm{B}_{\nu o}}\right) + 300\left(\alpha^{(1)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(1)}_{\mathrm{A}_{\lambda\mu}}\right)\left(\alpha^{(0)}_{\mathrm{B}_{\nu\nu}}\bar{\alpha}^{(0)}_{\mathrm{B}_{oo}}\right) + 1140\left(\alpha^{(0)}_{\mathrm{A}_{\lambda\lambda}}\bar{\alpha}^{(0)}_{\mathrm{A}_{\mu\mu}}\right)\left(\alpha^{(2)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(2)}_{\mathrm{B}_{o\nu}}\right) \\
& + 1140\left(\alpha^{(2)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(2)}_{\mathrm{A}_{\mu\lambda}}\right)\left(\alpha^{(0)}_{\mathrm{B}_{\nu\nu}}\bar{\alpha}^{(0)}_{\mathrm{B}_{oo}}\right) + 2790\left(\alpha^{(1)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(1)}_{\mathrm{A}_{\lambda\mu}}\right)\left(\alpha^{(2)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(2)}_{\mathrm{B}_{o\nu}}\right) + 2790\left(\alpha^{(2)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(2)}_{\mathrm{A}_{\mu\lambda}}\right)\left(\alpha^{(1)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(1)}_{\mathrm{B}_{\nu o}}\right)\Big\}^{-1}.
\end{aligned} \tag{5.17}$$

Again where terms involving weight 1 disappear in off-resonance studies we have for pairwise excitation of polarised bands ρ_1 values in the interval $(\frac{1}{8}, \frac{331}{338})$, the upper limit obtaining for excitation of depolarised bands.

6. Unified formulation

A unification of theory for the two bimolecular processes studied in the previous sections can be established by reference to the limiting behaviour of the Raman process in the case where both molecules exhibit resonance scattering. This invokes Raman polarisability tensors dominated by the 'classical' time-ordering in which absorption precedes emission [4], and in which the intervening state is physically realisable in the sense that it can persist over measurable times [5]. Although anywhere near resonance the Raman tensors must be regarded as complex, their imaginary parts arise from the damping in the energy denominators (see 2.12), and the transition dipole moments may still be assumed real. Each tensor product can thus be expressed as follows:

$$\alpha_{\mathrm{A}_{\lambda\lambda}}\bar{\alpha}_{\mathrm{A}_{\mu\mu}} \sim |\boldsymbol{\mu}_{\mathrm{A}}^{\downarrow}\cdot\boldsymbol{\mu}_{\mathrm{A}}^{\uparrow}|^2 = |\mu_{\mathrm{A}}^{\downarrow}|^2|\mu_{\mathrm{A}}^{\uparrow}|^2\cos^2\theta_{\mathrm{A}}, \tag{6.1}$$

$$\alpha_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}_{\mathrm{A}_{\lambda\mu}} \sim |\boldsymbol{\mu}_{\mathrm{A}}^{\downarrow}\cdot\boldsymbol{\mu}_{\mathrm{A}}^{\downarrow}|\times|\boldsymbol{\mu}_{\mathrm{A}_\mu}^{\uparrow}\cdot\boldsymbol{\mu}_{\mathrm{A}_\mu}^{\uparrow}| = |\mu_{\mathrm{A}}^{\downarrow}|^2|\mu_{\mathrm{A}}^{\uparrow}|^2, \tag{6.2}$$

$$\alpha_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}_{\mathrm{A}_{\mu\lambda}} \sim |\boldsymbol{\mu}_{\mathrm{A}}^{\downarrow}\cdot\boldsymbol{\mu}_{\mathrm{A}}^{\uparrow}|^2 = |\mu_{\mathrm{A}}^{\downarrow}|^2|\mu_{\mathrm{A}}^{\uparrow}|^2\cos^2\theta_{\mathrm{A}}. \tag{6.3}$$

Equally, for the irreducible form of the results of Section 5 we can express the individual product weights, using the results of Appendix 1, as

$$\alpha^{(0)}_{\mathrm{A}_{\lambda\lambda}}\bar{\alpha}^{(0)}_{\mathrm{A}_{\mu\mu}} \sim |\mu_{\mathrm{A}}^{\downarrow}|^2|\mu_{\mathrm{A}}^{\uparrow}|^2\cos^2\theta_{\mathrm{A}}, \tag{6.4}$$

$$\alpha^{(1)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(1)}_{\mathrm{A}_{\lambda\mu}} \sim |\mu_{\mathrm{A}}^{\downarrow}|^2|\mu_{\mathrm{A}}^{\uparrow}|^2\tfrac{1}{2}\left(1-\cos^2\theta_{\mathrm{A}}\right), \tag{6.5}$$

$$\alpha^{(2)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(2)}_{\mathrm{A}_{\mu\lambda}} \sim |\mu_{\mathrm{A}}^{\downarrow}|^2|\mu_{\mathrm{A}}^{\uparrow}|^2\tfrac{1}{2}\left(1+\tfrac{1}{3}\cos^2\theta_{\mathrm{A}}\right). \tag{6.6}$$

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[4] It is to be understood that even under resonance conditions there is a small contribution from the 'anti-resonant' second term in Eq. (2.12), as discussed in a more general context elsewhere [27,34].

[5] For detailed discussions of the relationship between resonance Raman scattering and resonance fluorescence, both from theoretical and experimental viewpoints, see Refs. [35,36].

The final results can now be calculated using either the reducible form, (5.4), or the irreducible form, (5.9), of the Raman result. By either route the following result is obtained:

$$\begin{aligned}\tilde{\Gamma} \sim \frac{|z|^2}{15}\Big[&\Big(36\Big\{|y|^2+\big[15+10\mathfrak{R}(y)+2|y|^2\big](\cos^2\phi)\Big\}-60\big[3+2\mathfrak{R}(y)+|y|^2\big]\Big)(\cos^2\theta_A)(\cos^2\theta_B)\\ &+\Big(-12\Big\{|y|^2+\big[15+10\mathfrak{R}(y)+2|y|^2\big](\cos^2\phi)\Big\}+20\big[3+2\mathfrak{R}(y)+|y|^2\big]\Big)(\cos^2\theta_B)\\ &+\Big(-12\Big\{|y|^2+\big[15+10\mathfrak{R}(y)+2|y|^2\big](\cos^2\phi)\Big\}+20\big[3+2\mathfrak{R}(y)+|y|^2\big]\Big)(\cos^2\theta_A)\\ &+\Big(4\Big\{|y|^2+\big[15+10\mathfrak{R}(y)+2|y|^2\big](\cos^2\phi)\Big\}+160\big[3+2\mathfrak{R}(y)+|y|^2\big]\Big)\Big],\end{aligned} \tag{6.7}$$

which, by simple regrouping of the terms, can be seen to be identical to the two-molecule fluorescence result as given by Eq. (4.12). Therefore it is proven that in the exact resonance limit the result for the bimolecular Raman process fully embraces the case of two-molecule fluorescence. Thus it transpires that, by re-interpreting the polarisation ratio $\xi = \langle \Gamma_\perp \rangle / \langle \Gamma_\parallel \rangle = (1 - r_1)/(1 + 2r_1)$ as the depolarisation ρ_1, we obtain from (4.15) and (4.17) the results:

Short range

$$\rho_1^{\text{res}} = \frac{41}{43}, \quad kR \ll 1. \tag{6.8}$$

Long range

$$\rho_1^{\text{res}} = \frac{37}{51}, \quad kR \gg 1. \tag{6.9}$$

The former result reveals a possible contributory role for bimolecular scattering, under resonance conditions, in producing a depolarisation ratio exceeding the off-resonance limit of $\frac{3}{4}$.

7. Conclusion

A theoretical framework has been developed to formally establish the link between two bimolecular processes hitherto always regarded as completely separate types of interaction. The theory encompasses energy transfer between independently mobile chromophores across arbitrary distances, accommodating resonance features, and allowing for the transition dipoles for the upward and downward processes within each moiety to be either parallel or non-parallel. Explicit results for the degree of fluorescence anisotropy and Raman depolarisation ratio have been presented, as well as more general rate equations applicable to arbitrary polarisation conditions. Both at and away from resonance a Raman depolarisation ratio exceeding the normal off-resonance limit of $\frac{3}{4}$ is shown to be a possible consequence of bimolecular scattering. Although the foci of attention in our theory have been processes in which either both molecules undergo Raman transitions or both absorb and fluoresce, the results can also accommodate processes in which Raman scattering is followed by absorption and fluorescence, or vice versa.

Acknowledgement

It is a pleasure to have the opportunity here again to acknowledge the seminal influence of David Craig on the theoretical formulations we employ, most notably set forth in the *Molecular quantum electrodynamics* text

[25] which serves as a model of clarity in chemical physics. We are also pleased to acknowledge many helpful discussions with A.A. Demidov, and one of us (PA) also acknowledges financial support from the Engineering and Physical Sciences Research Council.

Appendix A. Second rank irreducible Cartesian tensors

It is possible to reduce any tensor into a sum of parts (weights) transforming under irreducible representations of the full rotation group. Using the methods of Coope et al. [28] it can be shown that second rank tensors, such as the Raman tensors used throughout this paper, can be expressed in this form as a sum of three separate weights expressed as

$$\alpha_{ij}^{(0)} = \tfrac{1}{3}\alpha_{kk}\delta_{ij}, \tag{A.1}$$

$$\alpha_{ij}^{(1)} = \tfrac{1}{2}(\alpha_{ij} - \alpha_{ji}), \tag{A.2}$$

$$\alpha_{ij}^{(2)} = \tfrac{1}{2}(\alpha_{ij} + \alpha_{ji}) - \tfrac{1}{3}\alpha_{kk}\delta_{ij}. \tag{A.3}$$

The properties of these irreducible forms are as follows. The weight-zero term (A.1) acts like a scalar and gives a non-zero trace, whereas both the weight-one (A.2) and the weight-two (A.3) terms are traceless. The weight-one term transforms like a pseudo-vector and the weight-two as a deviator (i.e. a symmetric traceless second rank tensor), carrying three and five individual components respectively; as in angular momentum theory the number of terms for weight j is $(2j + 1)$. Although working directly in terms of irreducible weights offers a certain advantage of clarity [37], much existent Raman theory is expressed in terms of parameters which are directly related to the products of the above irreducible tensors; the relationships necessary to express our results in such terms are the following:

$$\left[\alpha_{ij}^{(0)} : \alpha_{ij}^{(0)}\right] = 3\bar{\alpha}^2, \tag{A.4}$$

$$\left[\alpha_{ij}^{(1)} : \alpha_{ij}^{(1)}\right] = \tfrac{2}{3}\delta^2, \tag{A.5}$$

$$\left[\alpha_{ij}^{(2)} : \alpha_{ij}^{(2)}\right] = \tfrac{2}{3}\gamma^2. \tag{A.6}$$

Appendix B. General depolarisation ratio for sequential Raman scattering

The general result for the depolarisation ratio associated with sequential Raman scattering, from which the limiting long- and short-range results given in Section 5 are obtained, is as follows:

$$\begin{aligned}
\rho_1 = \Big\{ & \left[100\,|y|^2\right]\left(\alpha^{(0)}_{\mathrm{A}_{\lambda\lambda}}\bar{\alpha}^{(0)}_{\mathrm{A}_{\mu\mu}}\right)\left(\alpha^{(0)}_{\mathrm{B}_{\nu\nu}}\bar{\alpha}^{(0)}_{\mathrm{B}_{oo}}\right) \\
& + 225\left[|y|^2 + 5\left(3 + 2\Re(y) + |y|^2\right)\right]\left(\alpha^{(1)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(1)}_{\mathrm{A}_{\lambda\mu}}\right)\left(\bar{\alpha}^{(1)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(1)}_{\mathrm{B}_{\nu o}}\right) \\
& + 9\left[|y|^2 + 165\left(3 + 2\Re(y) + |y|^2\right)\right]\left(\alpha^{(2)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(2)}_{\mathrm{A}_{\mu\lambda}}\right)\left(\alpha^{(2)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(2)}_{\mathrm{B}_{o\nu}}\right) \\
& + 150\left[-|y|^2 + 5\left(3 + 2\Re(y) + |y|^2\right)\right]\left(\alpha^{(0)}_{\mathrm{A}_{\lambda\lambda}}\bar{\alpha}^{(0)}_{\mathrm{A}_{\mu\mu}}\right)\left(\alpha^{(1)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(1)}_{\mathrm{B}_{\nu o}}\right) \\
& + 150\left[-|y|^2 + 5\left(3 + 2\Re(y) + |y|^2\right)\right]\left(\alpha^{(1)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(1)}_{\mathrm{A}_{\lambda\mu}}\right)\left(\alpha^{(0)}_{\mathrm{B}_{\nu\nu}}\bar{\alpha}^{(0)}_{\mathrm{B}_{oo}}\right) \\
& + 30\left[|y|^2 + 15\left(3 + 2\Re(y) + |y|^2\right)\right]\left(\alpha^{(0)}_{\mathrm{A}_{\lambda\lambda}}\bar{\alpha}^{(0)}_{\mathrm{A}_{\mu\mu}}\right)\left(\alpha^{(2)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(2)}_{\mathrm{B}_{o\nu}}\right)
\end{aligned}$$

$$
\begin{aligned}
&+30\left[|y|^2+15\left(3+2\mathfrak{R}(y)+|y|^2\right)\right]\left(\alpha^{(2)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(2)}_{\mathrm{A}_{\mu\lambda}}\right)\left(\alpha^{(0)}_{\mathrm{B}_{\nu\nu}}\bar{\alpha}^{(0)}_{\mathrm{B}_{oo}}\right)\\
&+45\left[-|y|^2+35\left(3+2\mathfrak{R}(y)+|y|^2\right)\right]\left(\alpha^{(1)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(1)}_{\mathrm{A}_{\lambda\mu}}\right)\left(\alpha^{(2)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(2)}_{\mathrm{B}_{o\nu}}\right)\\
&+45\left[-|y|^2+35\left(3+2\mathfrak{R}(y)+|y|^2\right)\right]\left(\alpha^{(2)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(2)}_{\mathrm{A}_{\mu\lambda}}\right)\left(\alpha^{(1)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(1)}_{\mathrm{B}_{\nu o}}\right)\Big\}\\
&\times\Big\{\left[100\left(15+10\mathfrak{R}(y)+3|y|^2\right)\right]\left(\alpha^{(0)}_{\mathrm{A}_{\lambda\lambda}}\bar{\alpha}^{(0)}_{\mathrm{A}_{\mu\mu}}\right)\left(\alpha^{(0)}_{\mathrm{B}_{\nu\nu}}\bar{\alpha}^{(0)}_{\mathrm{B}_{oo}}\right)\\
&+225\left[\left(15+10\mathfrak{R}(y)+3|y|^2\right)+5\left(3+2\mathfrak{R}(y)+|y|^2\right)\right]\left(\alpha^{(1)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(1)}_{\mathrm{A}_{\lambda\mu}}\right)\left(\bar{\alpha}^{(1)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(1)}_{\mathrm{B}_{\nu o}}\right)\\
&+9\left[\left(15+10\mathfrak{R}(y)+3|y|^2\right)+165\left(3+2\mathfrak{R}(y)+|y|^2\right)\right]\left(\alpha^{(2)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(2)}_{\mathrm{A}_{\mu\lambda}}\right)\left(\alpha^{(2)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(2)}_{\mathrm{B}_{o\nu}}\right)\\
&+150\left[-\left(15+10\mathfrak{R}(y)+3|y|^2\right)+5\left(3+2\mathfrak{R}(y)+|y|^2\right)\right]\left(\alpha^{(0)}_{\mathrm{A}_{\lambda\lambda}}\bar{\alpha}^{(0)}_{\mathrm{A}_{\mu\mu}}\right)\left(\alpha^{(1)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(1)}_{\mathrm{B}_{\nu o}}\right)\\
&+150\left[-\left(15+10\mathfrak{R}(y)+3|y|^2\right)+5\left(3+2\mathfrak{R}(y)+|y|^2\right)\right]\left(\alpha^{(1)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(1)}_{\mathrm{A}_{\lambda\mu}}\right)\left(\alpha^{(0)}_{\mathrm{B}_{\nu\nu}}\bar{\alpha}^{(0)}_{\mathrm{B}_{oo}}\right)\\
&+30\left[\left(15+10\mathfrak{R}(y)+3|y|^2\right)+15\left(3+2\mathfrak{R}(y)+|y|^2\right)\right]\left(\alpha^{(0)}_{\mathrm{A}_{\lambda\lambda}}\bar{\alpha}^{(0)}_{\mathrm{A}_{\mu\mu}}\right)\left(\alpha^{(2)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(2)}_{\mathrm{B}_{o\nu}}\right)\\
&+30\left[\left(15+10\mathfrak{R}(y)+3|y|^2\right)+15\left(3+2\mathfrak{R}(y)+|y|^2\right)\right]\left(\alpha^{(2)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(2)}_{\mathrm{A}_{\mu\lambda}}\right)\left(\alpha^{(0)}_{\mathrm{B}_{\nu\nu}}\bar{\alpha}^{(0)}_{\mathrm{B}_{oo}}\right)\\
&+45\left[-\left(15+10\mathfrak{R}(y)+3|y|^2\right)+35\left(3+2\mathfrak{R}(y)+|y|^2\right)\right]\left(\alpha^{(1)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(1)}_{\mathrm{A}_{\lambda\mu}}\right)\left(\alpha^{(2)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(2)}_{\mathrm{B}_{o\nu}}\right)\\
&+45\left[-\left(15+10\mathfrak{R}(y)+3|y|^2\right)+35\left(3+2\mathfrak{R}(y)+|y|^2\right)\right]\left(\alpha^{(2)}_{\mathrm{A}_{\lambda\mu}}\bar{\alpha}^{(2)}_{\mathrm{A}_{\mu\lambda}}\right)\left(\alpha^{(1)}_{\mathrm{B}_{\nu o}}\bar{\alpha}^{(1)}_{\mathrm{B}_{\nu o}}\right)\Big\}^{-1},
\end{aligned}
\tag{B.1}
$$

with the appropriate y values as given in Section 3.

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