# Collision-Induced Light Scattering and Absorption in Atoms and Symmetric Molecules: a Spherical Tensor Approach

by

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A Thesis submitted to the Faculty of Graduate Studies of

the University of Manitoba

in partial fulfillment of the requirements of the degree of

MASTER OF SCIENCE

Department of Physics and Astronomy

University of Manitoba

Winnipeg

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#### THE UNIVERSITY OF MANITOBA

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# A THESIS SUBMITTED TO THE FACULTY OF GRADUATE STUDIES OF THE UNIVERSITY OF MANITOBA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS OF THE DEGREE OF MASTER OF SCIENCE

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#### Abstract

The theory of collision-induced light scattering in atoms and symmetric molecules is presented using the formalism of spherical tensors. Resulting expressions for the intensity for first and second-order interactions are implemented in the programming language "Mathematica" and results for the depolarization ratio as well as isotropic and anisotropic components to the scattering intensity are presented. Experimental results are shown of the absorption spectrum of water vapour in the far infrared, from 50 to 600 wavenumbers, with a nitrogen perturber. Finally, a novel new formulation of the depolarization ratio based on only tensor ranks is presented.

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#### **CHAPTER 1: Introduction**

#### **1.1 Historical Perspective**

Collision-induced Rayleigh and Raman scattering refers to Rayleigh and Raman spectral features which are forbidden by the symmetry of a free molecule, but which appear in the scattering from dense media through molecular interactions. Though put on a firm theoretical and experimental basis only in the past thirty years, the effect itself was known about for several decades previous [1]. Broad tails on Rayleigh spectra of molecular liquids were observed unexpectedly as far back as the 1930s, and greatly puzzled workers at the time [1]. The invention of the laser in the 1960's lead to improved scattering experiments and accurate studies of weak induced spectra. The work on inert gases by Thibeau et al. and Birnbaum et al. in 1968 led to a renewed interest in the subject which persists up to the present time [1].

This interest is particularily motivated by the fact that collision-induced light scattering is a general effect, appearing in the spectra of isotropic and anisotropic molecules in the gas, liquid and solid phases [1]. Furthermore, it is a source of information about the collision-induced polarizability and, in principle, intermolecular forces. In this case, the inelastic scattering arises from coupling of the radiation field to the translational motion of the molecules by the collision-induced polarizability.

#### **1.2.1 Introductory Theory for Non-Interacting Molecules**

Consider first the scattering by a collection of non-interacting molecules. The polarizability of a pair of widely separated isotropic molecules is the sum of their

individual polarizabilities. The observed scattered radiation will then only have a nonzero intensity component polarized in the same direction as that of the incident radiation due to the properties of a radiating dipole, see figure 1.1.



Figure 1.1: The general features of the interaction of light with a molecule [2]

The relation between the dipole moment  $\mu$ , and the external incident electric field  $\vec{\epsilon}$ , is given by the simple relation:

$$\vec{\mu} = \alpha \vec{\varepsilon} , \qquad (1.1)$$

where  $\alpha$  is the polarizability of the individual molecule [3,4,5]. In general however, molecules are to a greater or lesser degree anisotropic, thus the polarizability is dependent on the orientation of the molecule relative to a coordinate system in the laboratory, (X, Y, Z), say:

$$\mu_{X} = \alpha_{XX}\varepsilon_{X} + \alpha_{XY}\varepsilon_{Y} + \alpha_{XZ}\varepsilon_{Z}$$
  

$$\mu_{Y} = \alpha_{YX}\varepsilon_{X} + \alpha_{YY}\varepsilon_{Y} + \alpha_{YZ}\varepsilon_{Z}.$$
(1.2)  

$$\mu_{Z} = \alpha_{ZX}\varepsilon_{X} + \alpha_{ZY}\varepsilon_{Y} + \alpha_{ZZ}\varepsilon_{Z}$$

Therefore the polarizability of the molecule is, in general, not a scalar quantity, but has a tensorial nature [3,4,5]. This property is fundamental to the subject of this thesis as will be shown later. Expressions for the scattered light intensity of individual radiating dipoles can be obtained once an appropriate polarization/observation geometry is chosen. The standard polarization geometry employed is the following: the light beam is incident along the X-axis and is polarized in either the Y- or Z- directions. The scattered light propagates along the Y-axis [1]. If the scattered beam has a Z-component, the corresponding scattered intensities are referred to as  $I_{zy}$  and  $I_{zz}$ ,

$$I_{ZY} = \frac{16\pi^{4}\nu^{4}}{c^{4}}I_{0}\alpha_{ZY}^{2} \\ I_{ZZ} = \frac{16\pi^{4}\nu^{4}}{c^{4}}I_{0}\alpha_{ZZ}^{2} \end{cases},$$
(1.3)

and if the scattered beam has an X-component, the scattered intensities are  $I_{xy}$  and  $I_{xz}$ 

$$I_{XY} = \frac{16\pi^{4}\nu^{4}}{c^{4}} I_{0}\alpha_{XY}^{2} \\ I_{XZ} = \frac{16\pi^{4}\nu^{4}}{c^{4}} I_{0}\alpha_{XZ}^{2}$$
(1.4)

Here,  $I_0$ , is the intensity of the incident radiation, c is the speed of light in vacuum, and v is the frequency of the radiation. The equations are to be read such that the first subscript denotes the direction of polarization of the scattered beam and the second gives the direction of polarization of the incident beam. The above expressions are appropriate for a single radiator, but in practice we are dealing with a gas whose molecules are free to assume all orientations with respect to the laboratory axes with equal probability [6]. Thus, the intensity equations need to be multiplied by the number of molecules present in the experimental sample and averaged over all orientations of the molecular axes with respect to the laboratory axes [6]. Thus it is of vital importance to be able to transform between these to frames of reference. More will be said on these points as the thesis progresses.

#### **1.2.2 Introductory Theory for Interacting Molecules**

However, the above situation changes when the separation between two molecules is small, on order of the size of the molecules themselves [7,8]. Now the polarizability of the pair, instead of being a simple sum of the individual molecular polarizabilities, will have an additional contribution that arises due to molecular interaction, see figure 1.2. The incident electric field, linearly polarized in one direction, induces a dipole moment in one of the molecules of the pair, labeled 1, as before. But now, to leading order, the total field acting on molecule 2 is the sum of the field of the induced dipole in 1 plus the external field. The resulting dipole induced in molecule 2 manifests itself in an observed non-zero scattered intensity that is depolarized with respect to the incident radiation, and will depend on time through the time dependence of the intermolecular separation and of the orientation of the intermolecular axis [8]. These depolarization ratios are given by [8]:

$$\eta = \frac{\left(\mathbf{I}_{xy} + \mathbf{I}_{zy}\right)}{\left(\mathbf{I}_{zz} + \mathbf{I}_{xz}\right)}.$$
(1.5)





Figure 1.2: The first two induction terms for the dipolar induction interactions, showing the order in polarizability. The solid and dashed arrows represent induced dipole moments due to the external electric field and collisions, respectively. The "bonds" represent the interactions [9].

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However if one chooses to use natural light as a source, or for incident linearly polarized light detected with no analyzer, the depolarization ratio becomes [10]:

$$\eta_n = \frac{2\eta}{1+\eta}.$$
(1.6)

Collision-induced light scattering based on this dipole induced-dipole (DID) model has been well studied, and experimental results show good agreement with theoretical spectra [1,8]. However, experiments on certain isotropic molecules like CF<sub>4</sub> and SF<sub>6</sub> show a spectrum whose intensity in the tails, particularly in the region greater than 100 cm<sup>-1</sup>, is larger than what is accounted for by the DID model alone. Theoretical investigation has shown that this excess intensity is adequately accounted for by including more terms in the description of the induced molecular dipole moment, corresponding to higher order effects. Of particular importance, is the effect of the induced-dipole in 2 resulting from the gradient of the field of the dipole in 1 as well as the dipole in 2 resulting from the second derivative of the field from the dipole in 1. These additional terms are responsible for inducing rotational transitions, through higher order molecular polarizabilities, which extend to high frequencies producing "tails" on the spectra.

Although, the majority of work in collision-induced light scattering has been concerned with the broad depolarized component in Rayleigh scattering, an induced polarized component is also present [11]. Experiments on the inert gases,  $H_2S$ ,  $N_2$ , Hgvapour,  $CF_4$  and liquid Ar have clearly demonstrated its existence, and interest is stimulated due to the fact that it contains, as a component, the purely isotropic (or trace) scattering [11]. The significance is that the contributions to the induced dipole moment coming from higher-order effects in the interaction, in the trace scattering case, are not

negligible. Whereas before we had molecule 1 inducing a dipole in molecule 2, a firstorder effect, we now must consider the effect of the induced-dipole in 2 inducing a dipole back on 1 (DIDID), see figure 2, as well as the field of the dipole induced in molecule 1 inducing a quadrupole in molecule 2 whose field, in turn, induces a dipole back at molecule 1 (DIQID). Such second-order effects have little effect on the depolarized component [11].

#### **1.3 Some Experimental Considerations**

The experimental apparatus required to study the phenomenon of collisioninduced light scattering is similar to that required for laser Raman spectroscopy; in which an example is shown in figure 1.3 [1]. Light generated by a continuous laser is focused on a sample cell, from which light scattered at 90° is collected and brought to a grating double monochromator. The detector is a high gain, low noise photomultiplier tube operated in the photon counting mode [1].



Figure 1.3: An example of the experimental apparatus used in the study of collision-induced light scattering [1].

The major differences from the standard Raman arrangement are the weak focusing of the incident beam (using a lens of focal length 30 cm or larger), and the collection of the scattered light occurs over a small angle (usually less than 4°) [1]. A polarization rotator and prism polarizer in the incident beam and polarization analyzer in the scattered beam allow the selection of polarization geometry [1]. An example of the type of spectrum obtained from this experiment is shown in figure 1.4 for the case of argon.



Figure 1.4: An example of the depolarized component of the light scattering spectrum for Ar. The symbols, ... represent the experimental two-body spectrum data, and \_\_\_\_\_ represents the theoretical first order DID spectrum [12,13].

The overall spectrum decreases approximately exponentially following the relation:  $I(\omega) \cong A \exp(-\Delta \omega/\omega_D)$  where  $\Delta \omega = \omega - \omega_0$  and  $\omega_D \propto 1/\tau$  where  $\tau$  is the characteristic time of the interaction [12]. Of particular significance is the width of the peak, which is approximately 15 cm<sup>-1</sup> at half the intensity. This leads to a value for  $\omega_D$  of about 20 cm<sup>-1</sup> and thus to a characteristic time,  $\tau$ , of 10<sup>-11</sup> seconds. We can contrast this with the result of the non-interacting case, where the spectral width has a value on order of 0.001 cm<sup>-1</sup> [13]. In this case,  $\tau$ , is about  $2\times 10^{-7}$  seconds. We can understand this state of affairs by appealing to the Heisenberg uncertainty principle relating the uncertainty of energy and time. A large spread in energy corresponds to a rapid interaction time, which is what we see in the first case. A very small spread in energy corresponds to a long interaction time as is seen in the second case [9].

#### 1.4 Modeling Collision-Induced Light Scattering (CILS)

The theoretical calculations of CILS parameters have always presented acute challenges. Multipole moments are in general tensor quantities, and resulting theoretical spectral intensities and depolarization ratios are obtained through orientational averaging of tensor products [8]. To this end, the natural language for considering these types of interactions is Cartesian tensor algebra, which gives clear insights into the geometry of the system. However, unless one considers only atoms or highly symmetric molecules in first-order DID interactions, calculations quickly become cumbersome or even intractable when high-order interactions are considered [14].

Fairly recently, there has been an effort to circumvent some of these calculational difficulties by re-expressing the theory of CILS in terms of irreducible spherical tensors.

While this procedure may perhaps obscure some of the interpretational elegance that the Cartesian formalism provides, it makes up for it by providing more general analytic expressions for coupling tensors of arbitrary rank. Utilizing symmetries incorporated in spherical tensor theory that can be exploited through Racah algebra, one can describe the general tensor coupling properties (which appear as "coupling coefficients") once, and then choose particular rank tensors to study [10,14]. In particular, these general coupling coefficients can be programmed into a computer for quick evaluation, thus enabling one to study the interactions of arbitrary-order interactions.

It is in this spirit, that this thesis was conceived: to exploit the convenience of the spherical tensor description of CILS employing the methods of Racah algebra. We intend to argue that this description readily lends itself to calculations of CILS intensities, particularly when high-order interactions are involved. Furthermore it will be shown that the form of the autocorrelation functions obtained is independent of the type of interaction being considered, a useful property that will facilitate computer calculations.

The thesis consists of seven chapters and several appendicies. Chapters 2 and 3 contain the theory of CILS presented in the mathematical language of Cartesian and irreducible spherical tensors respectively. This approach is chosen to illustrate the equality of the two descriptions and to emphasize that while the Cartesian tensor method provides little interpretational difficulties, there are several disadvantages eluded to above. Chapter 4 describes briefly the transformation between Cartesian and spherical tensors illustrating the procedure through a particular example. Chapter 5 discusses the main subject of the thesis, the detailed derivation of the CILS autocorrelation function in first and second-order using Racah algebra. In Chapter 6 the autocorrelation functions

from Chapter 5 and a Mathematica code are used to generate intensities and depolarization ratios for spherical and tetrahedral symmetries. In Chapter 7 we discuss the possible application of this technique to the study of the collision-induced absorption spectrum of water vapour, a molecule that is highly asymmetrical [9]. This is accompanied by preliminary examples of the far-infrared water vapour spectrum, the frequency region of interest for future study.

#### **CHAPTER 2: Collision-Induced Light Scattering – A Cartesian Approach**

In this chapter, we will begin our consideration of collision induced light scattering (CILS). As elaborated in the Introduction, the basic components of a lightscattering experiment consist of a scattering region, with the atoms of interest illuminated by a parallel beam of light, and a detector that measures the scattered intensity at some finite angle to the direction of the incident beam [1]. In terms of the quantum theory of light, the scattering involves the destruction of a photon of energy  $\hbar\omega$  from the incident beam and the creation of a photon of energy  $\hbar\omega_{sc}$  in the scattered beam [2]. Thus light scattering is a two-photon process, with two interactions taking place between the radiation field and the molecular electrons. While scattering occurs at all values of the incident frequency relative to the transition frequencies of the scattering atoms, the intensity of scattering is particularly strong when the incident frequency lies close to that of a atomic transition [1]. However, we will be making several assumptions in constructing our formalism that will restrict the applicability of our theory to all possible situations; and these assumptions will be mentioned at the outset. Despite the photon nature of light being required in a full quantum picture of light scattering, we will be assuming that the incoming exciting light field is classical and represented as a wave of the form,  $\vec{E}(t) = \vec{E} \exp(-i\omega t)$ , that is that the wave changes with time, but not with position over atomic or molecular dimensions. This assumption is valid when we are dealing with light of long wavelength such as that found in the visible and infrared region. Secondly, we will be considering the interactions of atoms (which are spherical)

and highly symmetric molecules, i.e. molecules exhibiting tetrahedral, octahedral and spherical symmetry.

#### 2.1 Molecule in an External Field: The Hamiltonian

Keeping the above in mind, consider a single molecule interacting with an external homogeneous electric field. The total Hamiltonian of this system consists of a sum of the Hamiltonian of the molecule in the absence of the field and the interaction Hamiltonian where the latter is treated as a perturbation to the former

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{int}.$$
(2.1)

The eigenfunctions are  $\psi^{(0)}$ , and eigenvalues of the unperturbed system are  $E^{(0)}$  [15]. The perturbation Hamiltonian is explicitly given as

$$\mathbf{H}^{\mathrm{int}} = -\mu_{\alpha} \mathbf{E}_{\alpha} \tag{2.2}$$

where  $\mu$  is the dipole moment operator for the molecule defined as  $\mu_{\alpha} = \sum_{i} q_{i} r_{i_{\alpha}}$  [9,15].

The energy of the molecule can be obtained by solving the Schrodinger equation for the unperturbed molecule states  $|\psi>$ :

$$\mathbf{H}|\psi\rangle = \mathbf{U}|\psi\rangle \tag{2.3}$$

through the use of time-independent perturbation theory. This approach is valid because we assumed that the interaction between the molecule and field is weak, in the form of a perturbation to the free states [9,15].

$$U = U^{(0)} + \langle 0 | H^{int} | 0 \rangle - \sum_{n>0} \frac{\langle 0 | H^{int} | n \rangle \langle n | H^{int} | 0 \rangle}{\left( U^{(n)} - U^{(0)} \right)} + \emptyset(H^{int^3})...,$$
(2.4)

where the summation occurs over all excited states, including the continuum, which have  $U^{(n)} > U^{(0)}$ .

The first-order perturbed energy is called the electrostatic energy,  $U_{elec}$ ; for the nondegenerate unperturbed states  $|0\rangle$  [9,15],

$$U_{elec} = \langle 0 | H^{int} | 0 \rangle = \langle 0 | -\mu_{\alpha} E_{\alpha} | 0 \rangle = -\langle 0 | \mu_{\alpha} | 0 \rangle E_{\alpha} = -\mu_{\alpha}^{(0)} E_{\alpha}, \qquad (2.5)$$

where  $\langle 0 | \mu_{\alpha} | 0 \rangle$  is the "permanent" dipole moment of the molecule when it is in the unperturbed initial state  $|0\rangle$ . However, since we assumed at the beginning that we would only be considering species that did not have any low order permanent multipoles we can take  $U_{elec} \equiv 0$  in this case. The second-order perturbed energy is called the induction energy, and can be expressed in general as

$$U_{ind} = -\frac{1}{2}\alpha_{\alpha\beta}E_{\alpha}E_{\beta} - \frac{1}{3}A_{\alpha,\beta\gamma}E_{\alpha}E_{\beta\gamma} + \dots, \qquad (2.6)$$

where  $\alpha_{\alpha\beta}$  is the dipole polarizability tensor given by

$$\alpha_{\alpha\beta} = 2\sum_{n>0} \frac{\langle 0|\mu_{\alpha}|n\rangle\langle n|\mu_{\beta}|0\rangle}{\left(U^{(n)} - U^{(0)}\right)}$$
(2.7)

and  $A_{\alpha,\beta\gamma}$  is the dipole-quadrupole polarizability defined as

$$A_{\alpha,\beta\gamma} = \sum_{n>0} \frac{\langle 0|\mu_{\alpha}|n\rangle\langle n|\Theta_{\beta\gamma}|0\rangle}{\left(U^{(n)} - U^{(0)}\right)} + \sum_{n>0} \frac{\langle 0|\Theta_{\alpha\beta}|n\rangle\langle n|\mu_{\gamma}|0\rangle}{\left(U^{(n)} - U^{(0)}\right)}$$
(2.8)

where  $\Theta_{\alpha\beta}$  is the quadrupole moment operator of the molecule, given as

 $\Theta_{\alpha\beta} = \frac{1}{2} \sum_{i} q_i \left( 3r_{i_{\alpha}} r_{i_{\beta}} - r_i^2 \delta_{\alpha\beta} \right).$  Since the external field has no gradient,  $E_{\beta\gamma}$  in the second

term of (2.6) equals zero. Furthermore, the induction energy is negative, since in

equation (2.4) the term  $\langle 0|H^{int}|n\rangle\langle n|H^{int}|0\rangle = |\langle 0|H^{int}|n\rangle|^2$  because  $H^{int}$  is hermitian. Therefore,  $\mu$  is hermitian and so consequently  $\alpha_{\alpha\beta} = \alpha_{\beta\alpha}^*$ .

To understand why the induction energy has the form (2.6), it is useful to consider the following plausibility argument. In a point charge model dipole,  $\mu = qx$ , induced parallel to the external electric field **E**, where x is the separation between charges  $\pm q$ , the work done dW in increasing x to x+dx is dW = (qE) dx = E d\mu. Using the relation, d( $\mu$ E) = d $\mu$ E +  $\mu$ dE, we can write dW as dW = d( $\mu$ E) –  $\mu$  dE. The total work done in creating the dipole is thus W =  $\mu$ E –  $\int \mu$ dE. The energy of interaction U<sub>ind</sub> is therefore the sum of W plus the energy (- $\mu$ E) of the dipole in the field [9]. This gives U<sub>ind</sub> = –  $\int \mu$ dE, but since  $\mu = \alpha$ E, we get U<sub>ind</sub> = –  $\int \alpha$ E dE = – $\frac{1}{2}\alpha$ E<sup>2</sup> as required.

By applying the Hellman-Feynman theorem [9],

$$\partial \langle \psi | \hat{H} | \psi \rangle / \partial E_{\alpha} = \langle \psi | \partial \hat{H} / \partial E_{\alpha} | \psi \rangle, \qquad (2.8)$$

we obtain an expression for the dipole moment of the molecule in the presence of a field,  $\mu_{\alpha}(E_{\alpha})$ :

$$\mu_{\alpha}(\mathbf{E}_{\alpha}) \equiv \langle \psi | \mu_{\alpha} | \psi \rangle = \langle \psi | -\partial \mathbf{H} / \partial \mathbf{E}_{\alpha} | \psi \rangle$$
  
=  $-\partial \langle \psi | \mathbf{H} | \psi \rangle / \partial \mathbf{E}_{\alpha}$   
=  $-\partial \mathbf{U}_{ind} / \partial \mathbf{E}_{\alpha}$   
=  $\alpha_{\alpha\beta} \mathbf{E}_{\beta}$ . (2.9)

Similarly,

$$\Theta_{\alpha\beta}(E_{\alpha\beta}) = \langle \psi | \Theta_{\alpha\beta} | \psi \rangle = \langle \psi | -\partial H / \partial E_{\alpha\beta} | \psi \rangle$$
  
=  $A_{\alpha\beta,\gamma} E_{\gamma}$ . (2.9a)

The preceding arguments hold for a pair of non-interacting molecules in an external electric field as well. If we consider a system of two molecules, denoted 1 and 2, subjected to an external electric field, the dipole moment of the pair is simply the sum of the individual dipole moments

$$\mu_{\alpha}(1,2) = \mu_{\alpha}(1) + \mu_{\alpha}(2) \tag{2.10}$$

#### 2.2 Higher-order Molecular Polarizabilities

For a pair of interacting molecules, equation (2.10) may be expanded in terms of a series of molecular polarizabilities

$$\mu_{\alpha}(1,2) = \alpha_{\alpha\beta}(1)F_{\beta}(1) - \frac{1}{3}A_{\alpha,\beta\gamma}(1)F_{\beta\gamma}(1) + \frac{1}{15}E_{\alpha\beta,\gamma\delta}(1)F_{\beta\gamma\delta}(1)... + \alpha_{\alpha\beta}(2)F_{\beta}(2) + \frac{1}{3}A_{\alpha,\beta\gamma}(2)F_{\beta\gamma}(2) + \frac{1}{15}E_{\alpha\beta,\gamma\delta}(2)F_{\beta\gamma\delta}(2)...$$
(2.11)

where  $F_{\alpha}$ ,  $F_{\alpha\beta}$ , and  $F_{\alpha\beta\gamma}$  are general tensors describing the electric field, field-gradient and second derivative of the field; a field which consists of the sum of the external field and intermolecular fields arising from interactions;  $\alpha_{\alpha\beta}(i)$  is the intrinsic dipole polarizability of molecule i. While the external field is uniform by assumption, the intermolecular fields are in general not because of near-field properties of fields of multipoles. Thus higher multipole moments are induced in the pair, which eventually contribute to the pair dipole moment. Note that,  $A_{\alpha,\beta\gamma}$ , is again the dipole-quadrupole polarizability tensor defined in (2.8). Note that **A** is odd under inversion, unlike  $\alpha$  above; and **A** is non-vanishing only for molecules lacking a centre of inversion [7,8,9,16]. Similarily  $E_{\alpha\beta,\gamma\delta}$ , is the dipole-octopole polarizability tensor, which describes the dipole moment induced by a second derivative of an electric field as well as the octopole induced by a uniform field. This is given by

$$E_{\alpha\beta,\gamma\delta} = \sum_{n>0} \frac{\langle 0|\mu_{\alpha}|n\rangle\langle n|\Omega_{\beta\gamma\delta}|0\rangle}{\left(U^{(n)} - U^{(0)}\right)} + \sum_{n>0} \frac{\langle 0|\Omega_{\beta\gamma\delta}|n\rangle\langle n|\mu_{\alpha}|0\rangle}{\left(U^{(n)} - U^{(0)}\right)}, \qquad (2.12)$$

where  $\Omega_{\alpha\beta\gamma}$  is the octopole moment operator of the molecule.

One should keep in mind that the above treatment of the pair is not completely rigorous as there are dispersion effects that occur as well and should in principle appear in the derivation. These however are small and are usually ignored in study of the collisioninduced light scattering phenomenon; thus the above treatment is sufficient [8,16].

#### 2.3 The Interaction Tensor

At this juncture, we can introduce the "interaction tensor" notation, which will simplify the description of the radial dependence of the molecular interaction terms. Thus, if R is the vector from the origin of molecule 1 to the origin of molecule 2 then:

$$\begin{split} \mathbf{T}(1,2) &= \mathbf{R}^{-1} \\ \mathbf{T}_{\alpha}(1,2) &= \nabla_{\alpha} \mathbf{R}^{-1} = -\mathbf{R}_{\alpha} \mathbf{R}^{-3} \\ \mathbf{T}_{\alpha\beta}(1,2) &= \mathbf{T}_{\beta\alpha}(2) = \nabla_{\alpha} \nabla_{\beta} \mathbf{R}^{-1} = \left( 3\mathbf{R}_{\alpha} \mathbf{R}_{\beta} - \mathbf{R}^{2} \delta_{\alpha\beta} \right) \mathbf{R}^{-5} \\ \mathbf{T}_{\alpha\beta\gamma}(1,2) &= \nabla_{\alpha} \nabla_{\beta} \nabla_{\gamma} \mathbf{R}^{-1} = -3 \left[ 5\mathbf{R}_{\alpha} \mathbf{R}_{\beta} \mathbf{R}_{\gamma} - \mathbf{R}^{2} \left( \mathbf{R}_{\alpha} \delta_{\beta\gamma} + \mathbf{R}_{\beta} \delta_{\gamma\alpha} + \mathbf{R}_{\gamma} \delta_{\alpha\beta} \right) \right] \mathbf{R}^{-7} \\ \cdots \\ \mathbf{T}_{\alpha\beta\gamma\delta\dots}(1,2) &= \nabla_{\alpha} \nabla_{\beta} \nabla_{\gamma} \nabla_{\delta} \dots \mathbf{R}^{-1}. \end{split}$$

$$(2.13)$$

The T tensors are symmetric in all suffixes, and

$$\nabla_{\alpha} \nabla_{\alpha} R^{-1} = \nabla^2 R^{-1} = 0 \tag{2.14}$$

that is, repeated Greek suffixes together with summation reduce any T to zero. Because the vector from 1 to 2 is the negative of the vector from 2 to 1, we also have that

$$T(2,1) = (-1)^{n} T(1,2)$$
(2.15)

where n is the rank of the tensor. Thus we see from (2.13) and (2.14) that the T tensor is proportional to  $R^{-(n+1)}$ ; therefore, the multipole series in the interaction Hamiltonian is really a series in inverse powers of molecular separation, and is rapidly convergent when R is large compared to molecular dimensions [9]. Using this fact, we can write expressions for  $F_{\alpha}$ ,  $F_{\alpha\beta}$ , and  $F_{\alpha\beta\gamma}$  in terms of T tensors:

$$\begin{split} F_{\alpha}(1) &= E_{\alpha} + T_{\alpha\beta}(1,2)\mu_{\beta}(2) + \frac{1}{3}T_{\alpha\beta\gamma}(1,2)\Theta_{\beta\gamma}(2) + ... \\ F_{\alpha\beta}(1) &= T_{\alpha\beta\gamma}(1,2)\mu_{\gamma}(2) + \frac{1}{3}T_{\alpha\beta\gamma\delta}(1,2)\Theta_{\gamma\delta}(2) + ... \\ F_{\alpha\beta\gamma}(1) &= T_{\alpha\beta\gamma\delta}(1,2)\mu_{\delta}(2) + \frac{1}{3}T_{\alpha\beta\gamma\delta\epsilon}(1,2)\Theta_{\delta\epsilon}(2) + ... \\ \text{and} \\ F_{\alpha}(2) &= E_{\alpha} + T_{\alpha\beta}(1,2)\mu_{\beta}(1) - \frac{1}{3}T_{\alpha\beta\gamma}(1,2)\Theta_{\beta\gamma}(1) + ... \\ F_{\alpha\beta\gamma}(2) &= -T_{\alpha\beta\gamma}(1,2)\mu_{\gamma}(1) + \frac{1}{3}T_{\alpha\beta\gamma\delta\epsilon}(1,2)\Theta_{\gamma\delta}(1) + ... \\ F_{\alpha\beta\gamma}(2) &= T_{\alpha\beta\gamma\delta}(1,2)\mu_{\delta}(1) - \frac{1}{3}T_{\alpha\beta\gamma\delta\epsilon}(1,2)\Theta_{\delta\epsilon}(1) + ... \end{split}$$

and thus (2.11) becomes

$$\begin{split} \mu_{\alpha}(1,2) &= \alpha_{\alpha\beta}(1) \Big( E_{\beta} + T_{\beta\gamma}(1,2) \mu_{\gamma}(2) + \frac{1}{3} T_{\beta\gamma\delta}(1,2) \Theta_{\gamma\delta}(2) + ... \Big) \\ &- \frac{1}{3} A_{\alpha,\beta\gamma}(1) \Big( T_{\beta\gamma\delta}(1,2) \mu_{\delta}(2) + \frac{1}{3} T_{\beta\gamma\delta\epsilon}(1,2) \Theta_{\delta\epsilon}(2) + ... \Big) \\ &+ \frac{1}{15} E_{\alpha\beta,\gamma\delta}(1) \Big( T_{\beta\gamma\delta\epsilon}(1,2) \mu_{\epsilon}(2) + \frac{1}{3} T_{\beta\gamma\delta\epsilon\phi}(1,2) \Theta_{\epsilon\phi}(2) + ... \Big) \\ &+ \alpha_{\alpha\beta}(2) \Big( E_{\beta} + T_{\beta\gamma}(1,2) \mu_{\gamma}(1) - \frac{1}{3} T_{\beta\gamma\delta}(1,2) \Theta_{\gamma\delta}(1) + ... \Big) \\ &- \frac{1}{3} A_{\alpha,\beta\gamma}(2) \Big( - T_{\beta\gamma\delta}(1,2) \mu_{\delta}(1) + \frac{1}{3} T_{\beta\gamma\delta\epsilon}(1,2) \Theta_{\delta\epsilon}(1) + ... \Big) \\ &+ \frac{1}{15} E_{\alpha\beta,\gamma\delta}(2) \Big( T_{\beta\gamma\delta\epsilon}(1,2) \mu_{\epsilon}(1) - \frac{1}{3} T_{\beta\gamma\delta\epsilon\phi}(1,2) \Theta_{\epsilon\phi}(1) + ... \Big) ... \end{split}$$
(2.17)

#### 2.4 Pair Dipole Polarizability

The light scattering of a pair of molecules is conveniently described in terms of the pair polarizability tensor  $\pi_{\alpha\beta}$ . From (2.17) we get,

$$\begin{aligned} \pi_{\alpha\beta} &= \frac{\partial \mu_{\alpha}}{\partial E_{\beta}} = \left( \alpha(1) + \alpha(2) \right) \delta_{\alpha\beta} + 2\alpha(1)\alpha(2) T_{\alpha\beta} + \frac{1}{3} T_{\alpha\gamma\delta} \left( \alpha(1) A_{\beta,\gamma\delta}(2) - \alpha(2) A_{\beta,\gamma\delta}(1) \right) \\ &+ \frac{1}{3} T_{\beta\gamma\delta} \left( \alpha(1) A_{\alpha,\gamma\delta}(2) - \alpha(2) A_{\alpha,\gamma\delta}(1) \right) + \dots \\ &= \pi_{\beta\alpha} \end{aligned}$$

Thus, from (2.18) we obtain a general prescription for obtaining the effective polarizability of molecule 1 when it is surrounded by more than one molecule, as [17]:

$$\pi_{\alpha\beta}(1) = \alpha_{\alpha\beta}(1) - \alpha_{\alpha\gamma}(1) \sum_{q(q\neq 1)} T_{\gamma\delta}(1,q) \pi_{\delta\beta}(q)$$
(2.18a)

The above expression is amenable to solution through iteration, thus we have

$$\pi_{\alpha\beta}(1) = \alpha_{\alpha\beta}(1) - \alpha_{\alpha\gamma}(1) \sum_{\substack{q(q\neq 1)\\q(q\neq 1)\\r(r\neq q)}} T_{\gamma\delta}(1,q) \alpha_{\delta\epsilon}(q) T_{\epsilon\eta}(qr) \alpha_{\eta\beta}(r) + \dots$$
(2.18b)  
+ ...

through second-order [17]. This expression only contains contributions due to classical multipolar interactions between the molecules. Effects arising from non-linear polarization in strong fields from the intrinsic multipole moments of neighbouring molecules are too small to be significant [17].

(2.18)

#### 2.5 Time Dependence of the Pair Polarizability

The time dependence of  $\pi_{\alpha\beta}$  comes in through R(t) which is in turn controlled by the intermolecular potential [1,8]. The scattered intensity I( $\omega$ ) is then obtained by taking the Fourier transform of the correlation function of the polarizability:

$$I(\omega) \propto \int \langle \pi_{\alpha\beta} [R(0)] \pi_{\alpha'\beta'} [R(t)] \rangle e^{-i\omega t} dt \qquad (2.19)$$

where  $\langle \pi_{\alpha\beta}[R(0)]\pi_{\alpha'\beta'}[R(t)] \rangle$  is a tensor contraction with the angular brackets denoting an average over all angular orientations of the molecules, signifying a long-time or ensemble average [1,8]. However, the intensity is further governed by the appearance of selection rules, which arise from the symmetry of the particular species of molecule under study. More is said on these points in Appendices A and E.

To compare the contribution of the various terms to the experimental scattered intensity, it is necessary to further average the radial contribution,  $R^{-n}$ , over a pair distribution function, g(R), to obtain  $\overline{R^{-n}}$ . In zeroth-order, the distribution function can be written as

$$g_0(R) = \exp[-V(R)/kT]$$
 (2.20)

where V(R) is the intermolecular potential such as the Leonard-Jones 6-12 potential:

$$V(R) = 4\varepsilon \left[ \left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6} \right].$$
 (2.21)

Thus the expression for the average radial distribution becomes:

$$\overline{R^{-n}} = 4\pi \int R^{-n} g(R) R^2 dR \cong 4\pi \int R^{-n} \exp[-V(R)/kT] R^2 dR.$$
 (2.22)

#### 2.6 Molecules of Tetrahedral and Octahedral Symmetry

When considering scattering from tetrahedral molecules, one usually chooses the origin to be the central atom (tetrahedron center) and the corners of the tetrahedron to be at coordinates: (1,1,1), (1,-1,-1), (-1,1,-1) and (-1,-1,1). In this case, the only non-zero components of A are  $A_{xyz} = A_{xzy} = A_{yzx} = A_{yxz} = A_{zxy} = A_{zyx} = A$ . Thus the tensor A may be specified by a single parameter A, which is independent of the choice of origin:

$$A_{\alpha\beta\gamma} = A \left( i_{\alpha} j_{\beta} k_{\gamma} + i_{\alpha} j_{\gamma} k_{\beta} + i_{\beta} j_{\gamma} k_{\alpha} + i_{\beta} j_{\alpha} k_{\beta} + i_{\gamma} j_{\beta} k_{\alpha} \right)$$
(2.23)

i, j, k are the unit vectors along the x, y, z axes of the tetrahedron [7,8,16]. With the angular average performed on the product of polarizabilities, (ignoring the time dependence), one obtains for tetrahedral molecules:

$$\left\langle \pi_{\alpha\beta}\pi_{\alpha'\beta'} \right\rangle = \left( \alpha(1) + \alpha(2) \right)^2 \delta_{\alpha\beta} \delta_{\alpha'\beta'} + \frac{4}{5} \left( \alpha(1)\alpha(2) \right)^2 R^{-6} \left( -2\delta_{\alpha\beta}\delta_{\alpha'\beta'} + 3\delta_{\alpha\alpha'}\delta_{\beta\beta'} + 3\delta_{\alpha\beta'}\delta_{\alpha'\beta} \right)$$

$$+ \frac{16}{105} \left[ \left( \alpha(1)A(2) \right)^2 + \left( \alpha(2)A(1) \right)^2 \right] R^{-8} \left( 19\delta_{\alpha\beta}\delta_{\alpha'\beta'} + 9\delta_{\alpha\alpha'}\delta_{\beta\beta'} + 9\delta_{\alpha\beta'}\delta_{\alpha'\beta} \right) + \dots$$

$$(2.24)$$

This is essentially the zeroth moment of the correlation function and the total scattered intensity is proportional to it. By now considering specific geometries, we can get specific expressions for the above autocorrelation function. For example, we can consider the incident light beam along the X axis with its electric vector polarized in the Z direction. Observations are made in the Y direction so the relevant terms are  $\langle \pi^2_{ZZ} \rangle$  and  $\langle \pi^2_{XZ} \rangle$ , which can be obtained from (2.24):

$$\left\langle \pi_{ZZ}^{2} \right\rangle = \left( \alpha(1) + \alpha(2) \right)^{2} + \frac{16}{5} \left( \alpha(1)\alpha(2) \right)^{2} R^{-6} + \frac{592}{105} \left[ \left( \alpha(1)A(2) \right)^{2} + \left( \alpha(2)A(1) \right)^{2} \right] R^{-8} + \dots$$
(2.25)

$$\left\langle \pi_{XZ}^{2} \right\rangle = \frac{12}{5} \left( \alpha(1)\alpha(2) \right)^{2} R^{-6} + \frac{48}{35} \left[ \left( \alpha(1)A(2) \right)^{2} + \left( \alpha(2)A(1) \right)^{2} \right] R^{-8} + \dots$$
(2.26)

and the depolarization ratio is

$$\rho = \frac{\left\langle \pi_{XZ}^2 \right\rangle}{\left\langle \pi_{ZZ}^2 \right\rangle}.$$
(2.27)

When considering molecules of higher symmetry, such as octahedral molecules which posses a centre of symmetry, the polarizability A vanishes and contributions from the next polarizability term, E, become important [1,8]. In the molecule fixed reference system, xyz, there are 21 non-zero components and only one origin-independent parameter  $E = \frac{1}{3} (E_{xxxx} + E_{yyyy} + E_{zzzz})$  determining E:

$$E_{\alpha\beta\gamma\delta} = \frac{5}{2} E \Big[ i_{\alpha} i_{\beta} i_{\gamma} i_{\delta} + j_{\alpha} j_{\beta} j_{\gamma} j_{\delta} + k_{\alpha} k_{\beta} k_{\gamma} k_{\delta} - \frac{1}{5} \Big( \delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma} \Big) \Big].$$
(2.28)

From this, the mean-square polarizability contribution due to  ${\bf E}$  can be derived:

$$\left\langle \pi_{\alpha\beta}\pi_{\alpha'\beta'}\right\rangle = \frac{1}{9} \left[ \left( \alpha(1)E(2) \right)^2 + \left( \alpha(2)E(1) \right)^2 \right] \mathbb{R}^{-10} \left( 30\delta_{\alpha\beta}\delta_{\alpha'\beta'} + 11\delta_{\alpha\alpha'}\delta_{\beta\beta'} + 11\delta_{\alpha\beta'}\delta_{\alpha'\beta} \right).$$

$$(2.29)$$

Using the same scattering geometry, we obtain,

$$\left\langle \pi_{ZZ}^{2} \right\rangle = \frac{52}{9} \left[ \left( \alpha(1) E(2) \right)^{2} + \left( \alpha(2) E(1) \right)^{2} \right] \mathbb{R}^{-10}$$
 (2.30)

$$\left\langle \pi_{\rm XZ}^2 \right\rangle = \frac{11}{9} \left[ \left( \alpha(1) E(2) \right)^2 + \left( \alpha(2) E(1) \right)^2 \right] \mathbb{R}^{-10}.$$
 (2.31)

#### 2.7 Second-Order Interactions

As eluded to in the Introduction, in the study of scattering from purely isotropic molecules the consideration of the induced polarized component is of growing importance. This is due to the presence of contributions from second-order induced moments (the first molecule receiving a perturbation from the perturbed second molecule), and up to the time of this writing, only the contributions of the molecular dipole,  $\alpha$ , and quadrupole polarizability **C**, have been investigated [11].

$$\Theta_{\alpha\beta}(n) = C_{\alpha\beta\gamma\delta}(n)F_{\gamma\delta}(n)$$
(2.32)

is the quadrupole moment induced in molecule (n) by the gradient of an electric field and  $C_{\alpha\beta,\gamma\delta}^{(n_1)}$  is the quadrupole polarizability, which describes the quadrupole moment induced by such an electric field gradient.

In spherically symmetric species, the dipole and quadrupole polarizabilities take the forms

$$\alpha_{\alpha\beta} = \alpha \delta_{\alpha\beta} \tag{2.33}$$

$$C_{\alpha\beta\gamma\delta} = C \Big[ \frac{1}{2} \Big( \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma} \Big) - \frac{1}{3} \delta_{\alpha\beta} \delta_{\gamma\delta} \Big]$$
(2.34)

which lead to the pair polarizability [11]:

$$\pi_{\alpha\phi} = \frac{\partial \mu_{\alpha}}{\partial E_{\phi}} = (\alpha(1) + \alpha(2))\delta_{\alpha\phi} + 2\alpha(1)\alpha(2)T_{\alpha\phi} + \alpha(1)\alpha(2)(\alpha(1) + \alpha(2))T_{\alpha\beta}T_{\beta\phi} + \frac{1}{3}\alpha(1)^{2}T_{\alpha\beta\gamma}C(2)T_{\beta\gamma\phi} + \frac{1}{3}\alpha(2)^{2}T_{\alpha\beta\gamma}C(1)T_{\beta\gamma\phi} + \dots$$

(2.35)

The last two terms arise because the gradient of the field of the dipole induced in one molecule by the external field acts through the polarizability **C** to induce a quadrupole in the other molecule, whose field in turn contributes to the induction of a secondary dipole in the first molecule [11].

The mean-square polarizabilities are:

$$\left\langle \pi_{ZZ}^{2} \right\rangle = \frac{2256 \left[ \alpha^{4} C^{2} \right]}{5 R^{16}}$$
 (2.36)

$$\left\langle \pi_{\rm XZ}^2 \right\rangle = \frac{192 \left[ \alpha^4 {\rm C}^2 \right]}{5 {\rm R}^{16}}$$
 (2.37)

with depolarization ratios:

$$\eta = \frac{4}{47}$$
  $\eta_n = \frac{8}{51}$  (2.38)

#### CHAPTER 3: Collision-Induced Light Scattering – A Spherical Tensor Approach

#### 3.1 The Idea of an Irreducible Spherical Tensor

As discussed above, fairly recently there has been a tendency to re-express the interaction in the basis of spherical harmonics [17]. One principal reason for this is that difficulties in using Cartesian tensors in analysis arise because they tend to appear in reducible form; that is products of these tensors form sets of linear combinations of components of a Cartesian tensor, which transform differently [18]. For example, one can form the following from the nine components of a Cartesian tensor of second-rank, Tij: a) a scalar:

$$T = \sum_{i} T_{ii} , \qquad (3.1)$$

that is the trace of the tensor having one component; b) an antisymmetric tensor:

$$A_{k} = \frac{1}{2} (T_{ij} - T_{ji}), \qquad (3.2)$$

having three components where i, j, k are cyclic; c) a symmetric second-rank tensor that has no trace:

$$S_{ij} = \frac{1}{2} (T_{ij} + T_{ji} - \frac{2}{3} T \delta_{ij}), \qquad (3.3)$$

which has five independent components [18-21]. In fact,

$$T_{ij} = \frac{1}{3}T\delta_{ij} + A_k + S_{ij}, \qquad (3.4)$$

and the components of the three quantities T, A, and <u>S</u> transform in the same way as the spherical harmonics of order zero, one, and two respectively [18-20]. Thus, one can define an irreducible tensor of any rank in a way that it must transform like the spherical

harmonic of corresponding rank. Therefore, an irreducible tensor of rank L is defined as a set of 2L+1 functions,  $T_{LM}$  (M = -L, -L+1,...,L), which transform under the 2L+1 dimensional representation of the Rotation Group as [18-20],

$$RT_{LM}R^{-1} = \sum_{M'} D^{L}_{M'M}(\alpha\beta\gamma)T_{LM'}.$$
 (3.5)

Here  $R = \exp(-i\theta n.J)$  is the rotation operator and the  $D_{M'M}^{L}(\alpha\beta\gamma)$  are the Wigner rotation matrix elements in the LM representation.

Let  $T_{L_1M_1}(A_1)$  and  $T_{L_2M_2}(A_2)$  be two such tensors of rank  $L_1$  and  $L_2$ ; the symbols  $A_1$  and  $A_2$  represent all other variables on which the tensors depend: (for instance, in the case of spherical harmonics,  $A_1$  and  $A_2$  are angular coordinates of two points in space). Thus the sum of two spherical tensors of rank L,

$$\Gamma_{\rm LM}(A_1) + T_{\rm LM}(A_2) \tag{3.6}$$

is another tensor of rank L. This follows from the linear nature of the transformation in the definition [18-20].

A tensor of rank L can be constructed from two tensors of ranks L1 and L2 by [18-20]:

$$T_{LM}(A_1, A_2) = \sum_{M_1M_2} \langle L_1M_1, L_2M_2 | LM \rangle T_{L_1M_1}(A_1) T_{L_2M_2}(A_2)$$
(3.7)

where  $\langle L_1M_1, L_2M_2 | LM \rangle$  is a Clebsch-Gordan coefficient if the ranks  $L_1, L_2$  and L obey the triangular condition:

$$\Delta(L_1 L_2 L): |L_1 - L_2| \le L \le L_1 + L_2.$$
(3.8)

That is, the ranks are added vectorially while the projection numbers are added algebraically. The product of  $T_{L_1M_1}(A_1)$  and  $T_{L_2M_2}(A_2)$  may also be written as:
$$T_{LM}(A_1, A_2) = \left[ T_{L_1M_1}(A_1) \otimes T_{L_2M_2}(A_2) \right]_{LM}$$
(3.9)

where the symbol  $\otimes$  denotes the irreducible tensor product. This shows that the direct product of the tensors  $T_{L_1M_1}(A_1)$  and  $T_{L_2M_2}(A_2)$  spans the representation  $D_{L_1} \otimes D_{L_2}$ , which can be decomposed into the representation

$$D_{L_1+L_2} + D_{L_1+L_2-1} + \dots + D_{|L_1+L_2|}.$$
(3.10)

The fact that the particular linear combination of products  $T_{L_1M_1}(A_1)T_{L_2M_2}(A_2)$ , which transform like  $T_{LM}$ , are given through the Clebsch-Gordan coefficients shows that the coupling of spherical tensors is mathematically equivalent to coupling angular momentum eigenvectors with both using only group theoretic properties of operators and states under rotation [18-20].

Of particular importance is the case when the rank of a product of spherical tensors is zero, that being

$$T_{00}(A_1, A_2) = \sum_{M_1M_2} \langle L_1M_1, L_2M_2 | 00 \rangle T_{L_1M_1}(A_1) T_{L_2M_2}(A_2).$$
(3.11)

One can use the properties of Clebsch-Gordan coefficients for a coupled zero-rank state to obtain

$$\begin{split} T_{00}(A_{1},A_{2}) &= \sum_{M_{1}} (-1)^{L_{1}+M_{1}} (2L_{1}+1)^{-1/2} T_{L_{1}M_{1}}(A_{1}) T_{L_{2}M_{2}}(A_{2}) \delta_{M_{1}-M_{2}} \delta_{L_{1}L_{2}} \\ &= (2L_{1}+1)^{-1/2} \sum_{M_{1}} (-1)^{L_{1}+M_{1}} T_{L_{1}M_{1}}(A_{1}) T_{L_{2}-M_{1}}(A_{2}) \delta_{L_{1}L_{2}}. \end{split}$$

$$(3.12)$$

Thus we see that scalars can be built up from tensors of rank L by contracting two tensors of the same rank. By convention, the generalized dot or scalar product is defined to be [20]

$$A_{K} \cdot B_{K} = \sum_{q} (-1)^{q} A_{Kq} B_{K-q}$$
(3.13)

and is related to  $\left[A_{K}\otimes B_{K}\right]_{00}$  by:

$$A_{K} \cdot B_{K} = (-1)^{K} (2K+1)^{1/2} [A_{K} \otimes B_{K}]_{00}$$
(3.14)

#### **3.2 The Description of CILS**

In contrast to chapter 2, we will now treat molecular interactions using spherical tensors, which though conceptually more challenging, simplify calculations due to the fact that many symmetries incorporated in spherical tensor theory can be exploited through Racah algebra [14]. Thus, the interaction portion of the total Hamiltonian describing a pair of molecules in an external electromagnetic field, in spherical tensor form, can be written [14],

$$\begin{aligned} \mathbf{H}_{\text{int}} &= \sqrt{3} \Big[ \Big\{ \hat{\mathbf{M}}_{1}(1) \otimes \mathbf{E}_{1} \Big\}_{00} \cos \omega t + \Big\{ \hat{\mathbf{M}}_{1}(2) \otimes \mathbf{E}_{1} \Big\}_{00} \cos \omega t \Big] \\ &+ \sum_{\mathbf{l}_{1}\mathbf{l}_{2}} (-1)^{\mathbf{l}_{2}} \left( \frac{2^{\mathbf{l}_{1}+\mathbf{l}_{2}}}{(2\mathbf{l}_{1})!(2\mathbf{l}_{2})!} \right)^{1/2} \Big\{ \hat{\mathbf{M}}_{\mathbf{l}_{1}}(1) \otimes \hat{\mathbf{T}}_{\mathbf{N}}(\mathbf{l},2) \Big\}_{\mathbf{l}_{2}} \otimes \hat{\mathbf{M}}_{\mathbf{l}_{2}}(2) \Big\}_{00} \end{aligned}$$
(3.15)

with  $\hat{T}_N$  being the spherical interaction tensor,  $\hat{M}_1$  the irreducible spherical operator of the  $l_{th}$  order multipole moment, and  $E_1$  the external electric field [14].

# 3.2.1 First-Order Interaction

From perturbation theory, to second-order we obtain an expression for the correction to the dipole moment of molecule 1 resulting from the interaction with molecule 2 [14]

$$M_{1}(1) = \sum_{J_{1}J_{2}J_{3}} \sum_{I_{1}I_{2}} \left( \frac{2^{I_{1}+I_{2}}}{(2I_{1})!(2I_{2})!} \right)^{1/2} \frac{(-1)^{I+J_{1}+J_{2}+J_{3}}}{\sqrt{3}} X_{J_{1}J_{2}J_{3}N} \begin{cases} N & I_{1} & I_{2} \\ 1 & J_{3} & J_{1} \end{cases} \\ \times \begin{cases} J_{3} & I_{2} & 1 \\ 1 & J & J_{2} \end{cases} \\ \begin{cases} M_{1}^{(II_{1})}(1) \otimes T_{N}(1,2) \\ J_{3} \otimes B_{J_{2}}^{(II_{2})}(2) \\ \end{bmatrix}_{J} \otimes E_{1} \end{cases}$$
(3.16)

where  $B_{J_1}^{(1l_1)}$  is the irreducible J-rank spherical multipole polarizability tensor defined as above

$$\mathbf{B}_{\mathbf{J}}^{(\mathrm{ln})} = \sum_{\alpha} \frac{1}{\hbar} \left( \frac{\left\{ \langle 0 | \mathbf{M}_{1} | \alpha \rangle \langle \alpha | \mathbf{M}_{n} | 0 \rangle \right\}_{\mathbf{J}}}{\omega_{\alpha 0} - \omega} + \frac{\left\{ \langle 0 | \mathbf{M}_{n} | \alpha \rangle \langle \alpha | \mathbf{M}_{1} | 0 \rangle \right\}_{\mathbf{J}}}{\omega_{\alpha 0} + \omega} \right)$$
(3.17a)

and

$$\begin{cases} A & B & C \\ D & E & F \end{cases}$$
(3.17b)

is the Wigner 6-j symbol.  $T_N$  denotes the spherical multipole interaction tensor. The sum over  $\alpha$  refers to all possible molecular rotational and vibrational states, but not electronic ones.

To obtain the expression for the pair-polarizability correction, one must apply the derivative with respect to the external electric field in spherical form; i.e. the gradient with respect to field. This is given by [18,20]:

$$\vec{\nabla} \Big[ f(\vec{E}) Y_{lm}(\theta, \phi) \Big] = -\sqrt{\frac{1+1}{2l+1}} \left( \frac{df}{dE} - \frac{l}{E} f \right) Y_{lm}^{l+1}(\theta, \phi) + \sqrt{\frac{1}{2l+1}} \left( \frac{df}{dE} - \frac{l+1}{E} f \right) Y_{lm}^{l-1}(\theta, \phi)$$
(3.18)

where  $Y_{JM}^{L}(\theta, \phi)$  is known as a vector spherical harmonic [18,20]. Rewriting equation (3.16) as:

$$\begin{split} \mathbf{M}_{1}(\mathbf{l}) &= \sum_{\alpha\beta} \left\langle \mathbf{J}\alpha\mathbf{l}\beta \big| \mathbf{1}\mathbf{M} \right\rangle \sum_{\mathbf{J}_{1}\mathbf{J}_{2}\mathbf{J}_{3}} \sum_{\mathbf{l}_{1}\mathbf{l}_{2}} \left( \frac{2^{\mathbf{l}_{1}+\mathbf{l}_{2}}}{(2\mathbf{l}_{1})!(2\mathbf{l}_{2})!} \right)^{1/2} \frac{(-1)^{\mathbf{l}+\mathbf{J}_{1}+\mathbf{J}_{2}+\mathbf{J}_{3}}}{\sqrt{3}} \mathbf{X}_{\mathbf{J}_{1}\mathbf{J}_{2}\mathbf{J}_{3}\mathbf{N}} \begin{cases} \mathbf{N} & \mathbf{l}_{1} & \mathbf{l}_{2} \\ \mathbf{1} & \mathbf{J}_{3} & \mathbf{J}_{1} \end{cases} \\ & \times \begin{cases} \mathbf{J}_{3} & \mathbf{l}_{2} & \mathbf{1} \\ \mathbf{1} & \mathbf{J} & \mathbf{J}_{2} \end{cases} \begin{cases} \mathbf{B}_{\mathbf{J}_{1}}^{(11)}(1) \otimes \mathbf{T}_{\mathbf{N}}(1,2) \\ \mathbf{J}_{3}} \otimes \mathbf{B}_{\mathbf{J}_{2}}^{(112)}(2) \end{cases}_{\mathbf{J}\alpha} \mathbf{E}_{\mathbf{I}\beta} \end{split}$$

(3.19)

we can apply equation (3.18) to (3.19), with L = 0, J = 1, and  $M = \beta$ , to obtain the correction to the molecular pair-polarizability as:

$$\Delta A_{J\alpha}(1) = \sum_{l_1 l_2} \sum_{J_1 J_2 J_3} [1 + P_{12}] \left( \frac{2^N}{(2l_1)!(2l_2)!} \right)^{1/2} X_{J_1 J_2 J_3 N} \begin{cases} J_1 & J_2 & J_3 \\ 1 & 1 & J \\ l_1 & l_2 & N \end{cases}$$
$$\times \left[ T_N(R_{12}) \otimes \left( B_{J_1}^{(1l_1)}(1) \otimes B_{J_2}^{(1l_2)}(2) \right)_{J_3} \right]_{J\alpha}$$
(3.20)

where

$$\begin{cases} a & b & c \\ d & e & f \\ g & h & j \end{cases}$$
(3.21)

is the Wigner 9-j symbol,  $X_{ab...f} = [(2a + 1)(2b + 1)...(2f + 1)]^{1/2}$ ,  $P_{12}$  is a permutation operator that interchanges the molecular labels, and  $N = l_1 + l_2$ .

By considering low-density scattering of incident radiation linearly polarized in the e direction, and detected after passage through a analyzer with pass axis  $\mathbf{n}$ , one has the pair double-differential cross sections for scattered light as:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} = k_i k_s^3 \frac{1}{2\pi} \int \exp(-i\omega t) F(t) dt \qquad (3.22)$$

where

$$F(t) = \sum_{j=0,2} \Phi_{jj} F_{jj}(t)$$
(3.23)

with the geometrical factors equal to  $\Phi_{00} = \frac{1}{3}(\hat{\mathbf{e}}\cdot\hat{\mathbf{n}})^2$  for the isotropic spectrum, and  $\Phi_{22} = \frac{1}{30} [3 + (\hat{\mathbf{e}}\cdot\hat{\mathbf{n}})^2]$  for the anisotropic spectrum [10]. F<sub>ij</sub>(t) is the autocorrelation function of equation (3.20),

$$\mathbf{F}_{JJ}(t) = \left\langle \Delta \mathbf{A}_{J}(0) \cdot \Delta \mathbf{A}_{J}(t) \right\rangle \tag{3.24}$$

where the dot denotes a scalar tensor product, and the angular brackets again denote a canonical average. Thus (3.24) is the general spherical tensor equivalent of equations (2.24) and (2.29). And it is here that we first gain a glimpse of the usefulness of the spherical tensor approach, for in (2.24) and (2.29) we had to initially specify the geometry of the particular molecules under study. In contrast, equation (3.24) using (3.20) is a general result, applicable to all molecular geometries [14]. Due to the fact that the polarizability is symmetric in its indicies (see equation (2.18)), the spherical tensor form contains contributions of rank 0 and rank 2 [10, 17].

## **3.2.2 Second-Order Interaction**

As before in chapter 2, through iteration we can further improve the accuracy of our spherical tensor expression, by considering the case where the perturbed second molecule induces a polarizability perturbation back on the first molecule. We provide details of this general derivation because, to our knowledge, it does not appear anywhere in the literature beyond second-order DID [17]. In this case then the polarizability on the second molecule includes a correction of the type already considered. That is:

$$B_{J_2}^{(1l_2)}(2) = B_{J_2}^{(1l_2)}(2) + \Delta B_{J_2}^{(1l_2)}(2)$$
(3.25)

where the second term is of the form

$$\Delta B_{J_{2}}^{(ll_{2})}(2) = \sum_{n_{2}n_{3}} \sum_{J_{4}J_{5}J_{6}} [1 + P_{21}] \left( \frac{2^{N_{2}}}{(2l_{2})!(2n_{3})!} \right)^{1/2} X_{J_{4}J_{5}J_{6}N_{2}} \begin{cases} J_{4} & J_{5} & J_{6} \\ n_{2} & 1 & J \\ l_{2} & n_{3} & N_{2} \end{cases}$$

$$\times \left[ T_{N_{2}}(R_{21}) \otimes \left( B_{J_{4}}^{(n_{2}l_{2})}(2) \otimes B_{J_{5}}^{(1n_{3})}(1) \right)_{J_{6}} \right]_{J_{2}}$$
(3.26)

Making this substitution in equation (3.20) we obtain

$$\Delta B_{J\alpha}(l) = \sum_{\substack{J_1J_2J_3\\I_1I_2}} \sum_{\substack{J_4J_5J_6\\n_2n_3}} [1+P_{12}][1+P_{21}] \left(\frac{2^{N_1+N_2}}{(2l_1)!(2l_2)!(2n_2)!(2n_3)!}\right)^{1/2} X_{J_1J_2J_3J_4J_5J_6N_1N_2}$$

$$\times \begin{cases} J_1 & J_2 & J_3\\I_1 & I_2 & N \end{cases} \left\{ \begin{matrix} J_4 & J_5 & J_6\\I_2 & I & J\\I_2 & n_3 & N_2 \end{matrix} \right\}$$

$$\times \begin{bmatrix} T_{N_1}(R_{12}) \otimes \left( B_{J_1}^{(1l_1)}(1) \otimes \left\{ T_{N_2}(R_{21}) \otimes \left( B_{J_4}^{(n_2l_2)}(2) \otimes B_{J_5}^{(1n_3)}(1) \right)_{J_6} \right\}_{J_2} \right)_{J_3} \end{bmatrix}_{J\alpha}$$

$$(3.27)$$

Considering only the tensor component (square bracketed term), we can rewrite it as:

$$(-1)^{N_{1}+J_{1}+N_{2}+J_{6}-J}\left[\left(\left\{B_{J_{4}}^{(n_{2}l_{2})}(2)\otimes B_{J_{5}}^{(1n_{3})}(1)\right\}_{J_{6}}\otimes T_{N_{2}}(R_{21})\right\}_{J_{2}}\otimes B_{J_{1}}^{(11)}(1)\right]_{J_{3}}\otimes T_{N_{1}}(R_{12})\right]_{J_{\alpha}}.$$

$$(3.28)$$

And with the help of (C.2) in Appendix C, it can further be rewritten as

$$(-1)^{N_{1}+J_{1}+N_{2}+J_{6}-J+J_{1}+J_{2}+J_{3}}\sum_{a}X_{aJ_{2}}\begin{cases}J_{6} & N_{2} & J_{2}\\J_{3} & J_{1} & a\end{cases}$$

$$\left[\left(T_{N_{2}}(R_{21})\otimes\left\{\!\!\left\{\!B_{J_{4}}^{(n_{2}l_{2})}(2)\otimes B_{J_{5}}^{(1n_{3})}(1)\right\}_{J_{6}}\otimes B_{J_{1}}^{(1l_{1})}(1)\right\}_{a}\right]_{J_{3}}\otimes T_{N_{1}}(R_{12})\right]_{J\alpha}$$
(3.29)

$$= (-1)^{N_{1}+J_{1}+N_{2}+J_{6}-J+2J_{1}+J_{2}+2J_{3}+N_{1}+J} \sum_{a} X_{aJ_{2}} \begin{cases} J_{6} & N_{2} & J_{2} \\ J_{3} & J_{1} & a \end{cases} \sum_{b} X_{bJ_{3}} \begin{cases} N_{2} & a & J_{3} \\ J & N_{1} & b \end{cases}$$
$$\left[ \left\{ B_{J_{4}}^{(n_{2}l_{2})}(2) \otimes B_{J_{5}}^{(1n_{3})}(1) \right\}_{J_{6}} \otimes B_{J_{1}}^{(1l_{1})}(1) \right\}_{a} \otimes \left\{ T_{N_{2}}(R_{21}) \otimes T_{N_{1}}(R_{12}) \right\}_{b} \end{bmatrix}_{J\alpha}$$
(3.30)

$$= (-1)^{N_{1}+2N_{2}+2J_{1}+J_{2}+2J_{3}+J_{4}+J_{5}+J_{6}-J}\sum_{abc} (-1)^{a} X_{aJ_{2}} X_{bJ_{3}} X_{cJ_{6}} \begin{cases} J_{6} & N_{2} & J_{2} \\ J_{3} & J_{1} & a \end{cases} \begin{cases} N_{2} & a & J_{3} \\ J & N_{1} & b \end{cases}$$

$$\begin{cases} J_{4} & J_{5} & J_{6} \\ a & J_{1} & c \end{cases} \begin{bmatrix} T_{N_{2}}(R_{21}) \otimes T_{N_{1}}(R_{12}) \end{bmatrix}_{b} \otimes \left\{ B_{J_{1}}^{(11)}(1) \otimes B_{J_{4}}^{(n_{2}I_{2})}(2) \right\}_{c} \otimes B_{J_{5}}^{(1n_{3})}(1) \end{bmatrix}_{a} \end{bmatrix}_{J\alpha}.$$

$$(3.31)$$

.

Thus, (3.27) becomes:

$$\Delta B_{J\alpha}(l) = \sum_{\substack{J_1J_2J_3\\l_{l_2}\\l_{l_2}\\l_{l_2}\\l_{l_2}\\l_{l_3}$$

Consider now only the coupling part,

$$\sum_{J_{1}J_{2}J_{3}}\sum_{J_{4}J_{5}J_{6}} [1+P_{12}][1+P_{21}]X_{J_{1}J_{2}J_{3}J_{4}J_{5}J_{6}N_{1}N_{2}} \begin{cases} J_{1} & J_{2} & J_{3} \\ 1 & 1 & J \\ l_{1} & l_{2} & N \end{cases} \begin{pmatrix} J_{4} & J_{5} & J_{6} \\ n_{2} & 1 & J \\ l_{2} & n_{3} & N_{2} \end{pmatrix} \\ \times (-1)^{N_{1}+2N_{2}+2J_{1}+J_{2}+2J_{3}+J_{4}+J_{5}+J_{6}-J} \sum_{abc} (-1)^{a} X_{aJ_{2}} X_{bJ_{3}} X_{cJ_{6}} \begin{cases} J_{6} & N_{2} & J_{2} \\ J_{3} & J_{1} & a \end{cases}$$

$$\times \begin{cases} N_{2} & a & J_{3} \\ J & N_{1} & b \end{cases} \begin{cases} J_{4} & J_{5} & J_{6} \\ a & J_{1} & c \end{cases}.$$

$$(3.33)$$

We can rewrite the second 9-j symbol as:

.

$$\begin{cases} J_4 & J_5 & J_6 \\ n_2 & 1 & J \\ l_2 & n_3 & N_2 \end{cases} = \sum_{x} (-1)^{2x} (2x+1) \begin{cases} J_4 & N_2 & x \\ n_3 & n_2 & l_2 \end{cases} \begin{cases} n_3 & n_2 & x \\ J_2 & J_5 & 1 \end{cases} \begin{pmatrix} J_2 & J_5 & x \\ J_4 & N_2 & J_6 \end{cases}.$$
(3.34)

Now we see that there are three 6-j symbols that contain the rank,  $J_6$ . This is one of the ranks that is summed over in (3.33), namely

$$\sum_{\substack{J_{1}J_{2}J_{3}\\J_{4}J_{5}x}} \sum_{\substack{J=1\\J_{4}J_{5}x}} [1+P_{12}][1+P_{21}]X_{J_{1}J_{2}^{2}J_{3}^{2}J_{4}J_{5}x^{2}N_{1}N_{2}abc} \begin{cases} J_{1} & J_{2} & J_{3}\\ 1 & 1 & J\\ l_{1} & l_{2} & N_{1} \end{cases} \\ \times (-1)^{N_{1}+2N_{2}+2J_{1}+J_{2}+2J_{3}+J_{4}+J_{5}+2x+a-J} \\ \times (-1)^{N_{1}+2N_{2}+2J_{1}+J_{2}+2J_{3}+J_{4}+J_{5}+2x+a-J} \\ J_{1} & l_{2} & N_{1} \end{cases}$$

$$\times \begin{cases} N_{2} & a & J_{3}\\ J & N_{1} & b \end{cases} \begin{cases} J_{4} & N_{2} & x\\ n_{3} & n_{2} & l_{2} \end{cases} \begin{cases} n_{3} & n_{2} & x\\ J_{2} & J_{5} & 1 \end{cases} \begin{cases} J_{2} & J_{1} & J_{3}\\ J_{5} & c & a\\ x & J_{4} & N_{2} \end{cases} .$$

$$(3.35)$$

Now we can rearrange the elements in the 9-j symbols so that we can sum over  $J_2$  and  $J_3$ :

~

$$\sum_{\substack{J_{1}J_{2}J_{3} \text{ abc} \\ J_{4}J_{5}x}} \sum_{abc} [1+P_{12}][1+P_{21}] X_{J_{1}J_{2}^{2}J_{3}^{2}J_{4}J_{5}x^{2}N_{1}N_{2}abc} \begin{cases} N_{1} & J & J_{3} \\ l_{2} & 1 & J_{2} \\ l_{1} & 1 & J_{1} \end{cases} \epsilon \begin{cases} N_{2} & a & J_{3} \\ x & J_{5} & J_{2} \\ J_{4} & c & J_{1} \end{cases}$$

$$\times (-1)^{N_{1}+2N_{2}+2J_{1}+J_{2}+2J_{3}+J_{4}+J_{5}+2x+a-J} \begin{cases} N_{2} & a & J_{3} \\ J & N_{1} & b \end{cases} \begin{bmatrix} J_{4} & N_{2} & x \\ n_{3} & n_{2} & l_{2} \end{bmatrix} \begin{bmatrix} n_{3} & n_{2} & x \\ J_{2} & J_{5} & 1 \end{bmatrix}$$

$$(3.36)$$

where  $\varepsilon$  is a phase factor associated with the odd transposition of the rows and columns of the second 9-j symbol:  $\epsilon=(-1)^{a+c+x+N_2+J_1+J_2+J_3+J_4+J_5}$  . Using equality (C.6), from Appendix C, we obtain:

$$\sum_{J_{1}J_{4}J_{5x}} \sum_{abc} [1 + P_{12}] [1 + P_{21}] X_{J_{1}J_{4}J_{5x}^{2}N_{1}N_{2}abc} (-1)^{N_{1} + N_{2} + J_{1} + J_{5} + c - J + b + n_{3} + N_{2} + x + J_{4} - J_{1} - 1 - I - J} \\ \begin{cases} J_{4} & N_{2} & x \\ n_{3} & n_{2} & l_{2} \end{cases} \sum_{y} (-1)^{y} X_{y^{2}} \begin{cases} x & l_{2} & n_{3} \\ N_{2} & N_{1} & b \\ J_{4} & l_{1} & y \end{cases} \begin{cases} J_{a} & a & b \\ 1 & J_{5} & n_{3} \\ 1 & c & y \end{cases} \begin{cases} J_{4} & l_{1} & y \\ 1 & c & J_{1} \end{cases},$$
(3.37)

which can be rearranged to become

$$\sum_{\substack{J_{1}J_{4}J_{5} abc}} \sum_{abc} [1 + P_{12}] [1 + P_{21}] X_{J_{1}J_{4}J_{5}x^{2}y^{2}N_{1}N_{2}abc} (-1)^{N_{1}+J_{4}+J_{5}+x+y+b+c+n_{3}} \\ \times \varepsilon \begin{cases} J_{4} & N_{2} & x \\ l_{1} & N_{1} & l_{2} \\ y & b & n_{3} \end{cases} \begin{cases} J & a & b \\ 1 & J_{5} & n_{3} \\ 1 & c & y \end{cases} \begin{cases} J_{4} & N_{2} & x \\ n_{3} & n_{2} & l_{2} \end{cases} \begin{cases} J_{4} & l_{1} & y \\ 1 & c & J_{1} \end{cases}.$$

$$(3.38)$$

We can insert this into the original expression for the correction to the polarizability (3.27) to obtain:

$$\begin{split} \Delta B_{J\alpha}(1) &= \sum_{\substack{l_{1}l_{2} \\ n_{2}n_{3}abc}} \sum_{xy} [1+P_{12}][1+P_{21}](-1)^{J_{4}+J_{5}+y+c+l_{1}+l_{2}} \left(\frac{2^{N_{1}+N_{2}}}{(2l_{1})!(2l_{2})!(2l_{2})!(2l_{3})!}\right)^{1/2} \\ &\times X_{J_{1}J_{4}J_{5}x^{2}y^{2}N_{1}N_{2}abc} \begin{cases} J_{4} & N_{2} & x \\ l_{1} & N_{1} & l_{2} \\ y & b & n_{3} \end{cases} \begin{cases} J & a & b \\ 1 & J_{5} & n_{3} \\ 1 & c & y \end{cases} \begin{cases} J_{4} & N_{2} & x \\ n_{3} & n_{2} & l_{2} \end{cases} \begin{cases} J_{4} & l_{1} & y \\ 1 & c & J_{1} \end{cases} \\ &\times \left[ \left\{ T_{N_{1}}(R_{12}) \otimes T_{N_{2}}(R_{21}) \right\}_{b} \otimes \left\{ B_{J_{1}}^{(1l_{1})}(1) \otimes B_{J_{4}}^{(n_{2}l_{2})}(2) \right\}_{c} \otimes B_{J_{5}}^{(1n_{3})}(1) \right\}_{a} \right]_{J\alpha}. \end{split}$$

$$(3.39)$$

Now if we perform a change of label on the above, in the form of a = K, b = M, c = L,  $J_4 = J_2$ ,  $J_5 = J_3$ , we obtain the final form of the second order correction to the molecular pair polarizability:

$$\begin{split} \Delta B_{J\alpha}(1) &= \sum_{\substack{l_1l_2 \\ n_2n_3yKML}} \sum_{\substack{J_1J_2J_3x \\ ML}} [[1+P_{12}]](1+P_{21}](-1)^{J_2+J_3+L+l_1+l_2} \left( \frac{2^{N_1+N_2}}{(2l_1)!(2l_2)!(2l_2)!(2l_3)!} \right)^{1/2} \\ &\times X_{J_1J_2J_3x^2y^2N_1N_2KML} \begin{cases} J_2 & N_2 & x \\ l_1 & N_1 & l_2 \\ y & M & n_3 \end{cases} \left| \begin{pmatrix} J & K & M \\ 1 & J_3 & n_3 \\ 1 & L & y \end{pmatrix} \right| \left\{ J_2 & N_2 & x \\ n_3 & n_2 & l_2 \end{pmatrix} \left\{ J_2 & l_1 & y \\ 1 & L & J_1 \right\} \\ &\times \left[ \left\{ T_{N_1}(R_{12}) \otimes T_{N_2}(R_{21}) \right\}_M \otimes \left\{ B_{J_1}^{(1l_1)}(1) \otimes B_{J_4}^{(n_2l_2)}(2) \right\}_K \otimes B_{J_5}^{(1n_3)}(1) \right\}_L \right]_{J\alpha}. \end{split}$$

#### **CHAPTER 4:** Transformation Between Cartesian and Spherical Tensors

As indicated in the previous chapter, depending on the situation, the usefulness of using either a Cartesian tensor or spherical tensor description to solve problems is usually evident. Thus it is also useful to have a self-consistent procedure for transforming from one description to the other, so that properties expressed in one form can readily be expressed in the other [9, 22, 23]. Such a procedure was first introduced by Stone [22,23], and this chapter will basically follow his arguments and include some more explicit Cartesian to spherical tensor transformation calculations. Furthermore it should be noted that only those results that are relevant to the thesis will be stressed. The interested reader should consult the references directly for the complete treatment.

To begin our discussion, we can define a linear transformation T, which describes components of a Cartesian tensor in terms of spherical tensor components. The transformation is invertible, and the inverse describes the spherical tensor components in terms of Cartesian components:

$$A_{\alpha_{1}\alpha_{2}...\alpha_{n}} = \sum_{\eta j;m} T_{\eta j;m}^{\alpha_{1}\alpha_{2}...\alpha_{n}} A_{\eta j;m}$$
(4.1)

and

$$A_{\eta;m} = \sum_{\alpha_1...\alpha_n} T^{\eta;m}_{\alpha_1\alpha_2...\alpha_n} A_{\alpha_1\alpha_2...\alpha_n}$$
(4.2)

where the symbol  $\eta$  is used to distinguish between spherical components of the same rank derived from a given Cartesian tensor, should the need arise [22]. The transformation is unitary, thus

$$T^{\eta;m}_{\alpha_{1}\alpha_{2}...\alpha_{n}} = \left(T^{\alpha_{1}\alpha_{2}...\alpha_{n}}_{\eta;m}\right)^{*}.$$
(4.3)

To explicitly evaluate the transformation, we can make use of the fact that any tensor  $A_{\alpha_1\alpha_2...\alpha_n}$  of rank n transforms under rotation in the same way as the tensor  $A_{\alpha_1}B_{\alpha_2}...Z_{\alpha_n}$ , which is the generalization of the usual vector product [22,23]. Each vector here can be transformed into spherical form using (4.2) above

$$A_{1;m} = \sum_{\alpha} T_{\alpha}^{1;m} A_{\alpha}$$
(4.4)

where the transformation coefficients in matrix form, are

$$\begin{bmatrix} T_x^{1;1} & T_x^{1;0} & T_x^{1;-1} \\ T_y^{1;1} & T_y^{1;0} & T_y^{1;-1} \\ T_z^{1;1} & T_z^{1;0} & T_z^{1;-1} \end{bmatrix} = \begin{bmatrix} -\frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ -\frac{i}{\sqrt{2}} & 0 & -\frac{i}{\sqrt{2}} \\ 0 & 1 & 0 \end{bmatrix}.$$
 (4.5)

These spherical vectors can now be coupled together using (3.7):

$$(AB)_{lj_{2};m} = \sum_{m'm'' \alpha} T_{\alpha}^{l;m'} A_{\alpha} \sum_{\beta} T_{\beta}^{l;m''} B_{\beta} \langle l \, lm'm'' | \, j_{2}m \rangle$$

$$\equiv \sum_{\alpha\beta} T_{\alpha\beta}^{1j_{2};m} A_{\alpha} B_{\beta}$$

$$(4.6)$$

and this procedure can be continued to couple an arbitrary number of vectors,

$$\left(ABC\right)_{1j_2j_3;m} = \sum_{\alpha\beta\gamma} T^{1j_2j_3;m}_{\alpha\beta\gamma} A_{\alpha} B_{\beta} C_{\gamma} .$$
(4.7)

We see that the transformation coefficients take the form

$$T^{1j_{2};m}_{\alpha\beta} = \sum_{m'm'} T^{1;m}_{\alpha} T^{1;m'}_{\beta} \left< 11m'm'' \right| j_{2}m \right>$$
(4.8)

$$T^{1j_{2}j_{3};m}_{\alpha\beta\gamma} = \sum_{m'm'} T^{1j_{2};m'}_{\alpha\beta} T^{1;m'}_{\gamma} \langle j_{2} lm'm'' | j_{3}m \rangle.$$

$$(4.9)$$

The order in which the coupling is made is arbitrary and the particular choice made here is not the only possible one [22]. It is necessary to specify the intermediate quantum numbers because they distinguish different spherical components of a particular  $j_n$ . Here we have explicitly made the substitution  $j_1=1$ , and implicitly assumed that there is also a notational  $j_0=0$  corresponding to a scalar transformation

$$A_{0,0} = T^{0,0} A = A. (4.10)$$

As an application of these ideas, let us consider the second-order DID contribution to the pair polarizability tensor:

$$\alpha_{\alpha\phi} = \alpha_1 \alpha_2 (\alpha_1 + \alpha_2) T_{\alpha\beta} T_{\beta\phi} . \qquad (4.11)$$

Using the definition for the interaction tensors given in (2.13), we find that this contraction of two rank-2 T tensors is itself a rank-2 tensor:

$$T_{\alpha\phi} = \frac{1}{r^8} \left[ 3r_{\alpha}r_{\phi} + r^2\delta_{\alpha\phi} \right]$$
(4.12)

so (4.11) becomes,

$$\alpha_{\alpha\phi} = \alpha_1 \alpha_2 (\alpha_1 + \alpha_2) \frac{1}{r^8} \left[ 3r_\alpha r_\phi + r^2 \delta_{\alpha\phi} \right].$$
(4.13)

In spherical form, this is expressed as

$$\alpha_{m}^{1j_{2}} = \sum_{\alpha\phi} T_{\alpha\phi}^{1j_{2};m} \alpha_{\alpha\phi}$$

$$= \alpha_{1}\alpha_{2}(\alpha_{1} + \alpha_{2})r^{-8} \sum_{\alpha\phi} T_{\alpha\phi}^{1j_{2};m} \left[ 3r_{\alpha}r_{\phi} + r^{2}\delta_{\alpha\phi} \right]$$
(4.14)

and we are now in a position to apply the method outlined above.

Considering only the tensorial part

$$\mathfrak{S}_{\mathbf{m}}^{\mathbf{1}\mathbf{j}_{2}} = \sum_{\alpha\phi} \left[ \mathbf{3} \cdot \mathbf{T}_{\alpha\phi}^{\mathbf{1}\mathbf{j}_{2};\mathbf{m}} \mathbf{r}_{\alpha} \mathbf{r}_{\phi} + \mathbf{r}^{2} \cdot \mathbf{T}_{\alpha\phi}^{\mathbf{1}\mathbf{j}_{2};\mathbf{m}} \delta_{\alpha\phi} \right], \tag{4.15}$$

the properties of the Kronecker delta ensure that we may express this as

$$\mathfrak{S}_{m}^{1j_{2}} = \left(\sum_{\alpha\phi} \left[3 \cdot T_{\alpha\phi}^{1j_{2};m} r_{\alpha} r_{\phi}\right]\right) + r^{2} \cdot \left[T_{xx}^{1j_{2};m} \delta_{xx} + T_{yy}^{1j_{2};m} \delta_{yy} + T_{zz}^{1j_{2};m} \delta_{zz}\right]$$
(4.16)

while the other sums must be carried out independently using (4.6). Then

$$\mathfrak{S}_{m}^{1j_{2}} = 3 \left[ \sum_{m'm'} \sum_{\alpha} T_{\alpha}^{1;m'} r_{\alpha} \sum_{\phi} T_{\phi}^{1;m'} r_{\phi} \langle 1 \, 1m'm'' | \, j_{2}m \rangle \right] + r^{2} \left[ T_{xx}^{1j_{2};m} \delta_{xx} + T_{yy}^{1j_{2};m} \delta_{yy} + T_{zz}^{1j_{2};m} \delta_{zz} \right].$$

$$(4.17)$$

Applying the values for the transformation coefficients from (4.5) and calculating the appropriate Clebsch-Gordan coefficients, we can evaluate all the components of  $\mathfrak{S}_m^{1j_2}$ :

$$\begin{aligned} \mathfrak{S}_{0}^{10} &= -\frac{6}{\sqrt{3}r^{6}} \end{aligned} \tag{4.18} \\ \mathfrak{S}_{1}^{11} &= 0 \\ \mathfrak{S}_{0}^{11} &= 0 \\ \mathfrak{S}_{-1}^{11} &= 0 \end{aligned} \tag{4.19} \\ \mathfrak{S}_{-1}^{12} &= \frac{3}{2} \bigg[ \frac{x^{2} - y^{2} + 2ixy}{r^{8}} \bigg] \\ \mathfrak{S}_{1}^{12} &= -3 \bigg[ \frac{xz + iyz}{r^{8}} \bigg] \\ \mathfrak{S}_{0}^{12} &= \sqrt{\frac{3}{2}} \bigg[ \frac{2z^{2} - x^{2} - y^{2}}{r^{8}} \bigg] \\ \mathfrak{S}_{-1}^{12} &= 3 \bigg[ \frac{xz - iyz}{r^{8}} \bigg] \\ \mathfrak{S}_{-2}^{12} &= \frac{3}{2} \bigg[ \frac{x^{2} - y^{2} - 2ixy}{r^{8}} \bigg] \end{aligned} \tag{4.20}$$

These can be put into a more compact form if we recall the definitions of the spherical harmonics [9, 18, 19, 20]. The spherical form of the second-order DID contribution to the pair polarizability tensor thus can be written:

$$\alpha_0^{10} = -\frac{6 \cdot \alpha_1 \alpha_2 (\alpha_1 + \alpha_2)}{r^6} \sqrt{\frac{4\pi}{3}} Y_0^0$$
(4.21)

$$\alpha_1^{11} = 0$$
  
 $\alpha_0^{11} = 0$ 
  
 $\alpha_{-1}^{11} = 0$ 
  
(4.22)

$$\begin{aligned} \alpha_{2}^{12} &= \frac{\alpha_{1}\alpha_{2}(\alpha_{1} + \alpha_{2})}{r^{6}} \sqrt{\frac{24\pi}{5}} Y_{2}^{2} \\ \alpha_{1}^{12} &= \frac{\alpha_{1}\alpha_{2}(\alpha_{1} + \alpha_{2})}{r^{6}} \sqrt{\frac{24\pi}{5}} Y_{1}^{2} \\ \alpha_{0}^{12} &= \frac{\alpha_{1}\alpha_{2}(\alpha_{1} + \alpha_{2})}{r^{6}} \sqrt{\frac{24\pi}{5}} Y_{0}^{2} \\ \alpha_{-1}^{12} &= \frac{\alpha_{1}\alpha_{2}(\alpha_{1} + \alpha_{2})}{r^{6}} \sqrt{\frac{24\pi}{5}} Y_{-1}^{2} \\ \alpha_{-2}^{12} &= \frac{\alpha_{1}\alpha_{2}(\alpha_{1} + \alpha_{2})}{r^{6}} \sqrt{\frac{24\pi}{5}} Y_{-2}^{2}. \end{aligned}$$
(4.23)

As expected, there is no j=1 component due to the symmetry of the dipole polarizability.

## **CHAPTER 5: The Autocorrelation Function**

As discussed above in chapters 2 and 3, the scattered intensities are conveniently expressed in terms of molecular pair polarizabilities, and expressions were derived there for the calculation of the corrections to the pair polarizability for two interacting molecules. In this chapter we will discuss a detailed derivation of the autocorrelation function in spherical tensor form. This will allow us to implement a simple symbolic computer code to evaluate scattering intensities for tetrahedral molecules and atoms which are spherical.

## 5.1 Calculation of the Autocorrelation Function in First-Order

As presented in chapter 3, the  $\alpha$  component of the jth rank dipole-arbitrary order multipole polarizability of a pair of interacting molecules 1 and 2 is given by

$$\Delta A_{J\alpha}(1) = \sum_{l_1 l_2} \sum_{J_1 J_2 J_3} [1 + P_{12}] \left( \frac{2^N}{(2l_1)!(2l_2)!} \right)^{1/2} X_{J_1 J_2 J_3 N} \begin{cases} J_1 & J_2 & J_3 \\ 1 & 1 & J \\ l_1 & l_2 & N \end{cases}$$
$$\times \left[ T_N(R_{12}) \otimes \left( B_{J_1}^{(1l_1)}(1) \otimes B_{J_2}^{(1l_2)}(2) \right)_{J_3} \right]_{J\alpha}.$$
(5.1)

We want to calculate the autocorrelation function  $F_{JJ}(t)$  given by

$$\mathbf{F}_{\mathbf{J}\mathbf{J}}(\mathbf{t}) = \left\langle \Delta \mathbf{A}_{\mathbf{J}}(\mathbf{0}) \cdot \Delta \mathbf{A}_{\mathbf{J}}(\mathbf{t}) \right\rangle \tag{5.2}$$

where the angular brackets denote an angular or ensemble average. Substitution of (5.1) into (5.2) leads to the expression

$$\begin{split} F_{JJ}(t) &= \sum_{\substack{J_1J_2J_3 \\ l_1l_2 \\ m_1m_2}} \sum_{\substack{K_1K_2K_3 \\ m_1m_2}} [1+P_{12}] [1+P_{12}] \left( \frac{2^{N_1+N_2}}{(2l_1)!(2l_2)!(2m_1)!(2m_2)!} \right)^{1/2} X_{J_1J_2J_3K_1K_2K_3N_1N_2} \\ &\times \begin{cases} J_1 & J_2 & J_3 \\ 1 & 1 & J \\ l_1 & l_2 & N_1 \end{cases} \begin{cases} K_1 & K_2 & K_3 \\ 1 & 1 & J \\ m_1 & m_2 & N_2 \end{cases} \left\langle \left[ T_{N_1}(R_{12}(0)) \otimes \left( B_{J_1}^{(1l_1)}(1,0) \otimes B_{J_2}^{(1l_2)}(2,0) \right)_{J_3} \right] \right. \\ & \left. \left[ T_{N_2}(R_{12}(t)) \otimes \left( B_{K_1}^{(1m_1)}(1,t) \otimes B_{K_2}^{(1m_2)}(2,t) \right)_{J_3} \right]_J \right\rangle. \end{split}$$
(5.3)

. .

If we now apply identity (C.7), we can rewrite (5.3) as

$$\begin{split} F_{JJ}(t) &= \sum_{\substack{J_1J_2J_3 \\ I_1I_2 \\ m_1m_2}} \sum_{\substack{K_1K_2K_3 \\ m_1m_2}} [1+P_{12}(0)][1+P_{12}(t)] \left(\frac{2^{N_1+N_2}}{(2l_1)!(2l_2)!(2m_1)!(2m_2)!}\right)^{1/2} \\ &\times X_{J_1J_2J_3K_1K_2K_3N_1N_2} \begin{cases} J_1 & J_2 & J_3 \\ 1 & 1 & J \\ l_1 & l_2 & N_1 \end{cases} \begin{cases} K_1 & K_2 & K_3 \\ 1 & 1 & J \\ m_1 & m_2 & N_2 \end{cases} \\ &\times (-1)^{2N_1+J_3-N_2} \sum_a (2J+1) \begin{cases} N_1 & J_3 & J \\ K_3 & N_2 & a \end{cases} \langle \left[ T_{N_1}(R_{12}(0)) \otimes T_{N_2}(R_{12}(t)) \right]_a \\ &\cdot \left[ \left( B_{J_1}^{(1l_1)}(1,0) \otimes B_{J_2}^{(1l_2)}(2,0) \right)_{J_3} \otimes \left( B_{K_1}^{(1m_1)}(1,t) \otimes B_{K_2}^{(1m_2)}(2,t) \right)_{K_3} \right]_a \rangle. \end{split}$$
(5.4)

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Applying identity (C.4), we obtain

$$\begin{split} F_{JJ}(t) &= \sum_{\substack{J_1J_2J_3 \\ l_1l_2 \\ m_1m_2}} \sum_{\substack{K_1K_2K_3a \\ m_1m_2}} [1+P_{12}(0)][1+P_{12}(t)](2J+1)(-1)^{J_3-N_2} \left( \frac{2^{N_1+N_2}}{(2l_1)!(2l_2)!(2m_1)!(2m_2)!} \right)^{1/2} \\ &\times X_{J_1J_2J_3K_1K_2K_3N_1N_2} \begin{cases} N_1 & J_3 & J \\ K_3 & N_2 & a \end{cases} \begin{bmatrix} J_1 & J_2 & J_3 \\ l_1 & l_2 & N_1 \end{bmatrix} \begin{bmatrix} K_1 & K_2 & K_3 \\ l & 1 & J \\ m_1 & m_2 & N_2 \end{bmatrix} \\ &\times \sum_{\substack{gh}} X_{J_3K_3gh} \begin{cases} J_1 & J_2 & J_3 \\ K_1 & K_2 & K_3 \\ K_1 & K_2 & K_3 \\ g & h & a \end{cases} \langle \left[ T_{N_1} (R_{12}(0)) \otimes T_{N_2} (R_{12}(t)) \right]_a \\ &\cdot \left[ \left( B_{J_1}^{(1l_1)}(1,0) \otimes B_{K_1}^{(1m_1)}(1,t) \right)_g \otimes \left( B_{J_{21}}^{(1l_1)}(2,0) \otimes B_{K_2}^{(1m_2)}(2,t) \right)_h \right]_a \rangle. \end{split}$$
(5.5)

Now, we can consider explicitly the tensor coupling terms in (5.5) above:

$$\sum_{J_{3}K_{3}} (-1)^{J_{3}-N_{2}} (2J_{3}+1)(2K_{3}+1) \begin{cases} N_{1} & J_{3} & J \\ K_{3} & N_{2} & a \end{cases} \begin{cases} J_{1} & J_{2} & J_{3} \\ 1 & 1 & J \\ l_{1} & l_{2} & N_{1} \end{cases} \begin{cases} K_{1} & K_{2} & K_{3} \\ 1 & 1 & J \\ m_{1} & m_{2} & N_{2} \end{cases}$$

$$\times \begin{cases} J_{1} & J_{2} & J_{3} \\ K_{1} & K_{2} & K_{3} \\ g & h & a \end{cases}.$$
(5.6)

Due to the symmetry properties of the Wigner 6-j and 9-j symbols, we can rewrite:

$$\begin{cases} N_1 & J_3 & J \\ K_3 & N_2 & a \end{cases} = \begin{cases} a & K_3 & J_3 \\ J & N_1 & N_2 \end{cases}$$
(5.7)

and

$$\begin{cases} J_1 & J_2 & J_3 \\ 1 & 1 & J \\ l_1 & l_2 & N_1 \end{cases} = \begin{cases} N_1 & J & J_3 \\ l_2 & 1 & J_2 \\ l_1 & 1 & J_1 \end{cases},$$

$$\begin{cases} K_{1} & K_{2} & K_{3} \\ 1 & 1 & J \\ m_{1} & m_{2} & N_{2} \end{cases} = \begin{cases} N_{2} & J & K_{3} \\ m_{2} & 1 & K_{2} \\ m_{1} & 1 & K_{1} \end{cases},$$
$$\begin{cases} J_{1} & J_{2} & J_{3} \\ K_{1} & K_{2} & K_{3} \\ g & h & a \end{cases} = \begin{cases} a & K_{3} & J_{3} \\ h & K_{2} & J_{2} \\ g & K_{1} & J_{1} \end{cases}.$$
(5.8)

Combining these we obtain the definition of the 18-j symbol,

 $\begin{cases} h & K_{2} & 1 & J & 1 & J_{1} & g \\ J_{2} & m_{2} & & l_{1} & K_{1} \\ 1 & l_{2} & N_{1} & a & N_{2} & m_{1} & 1 \end{cases} = \sum_{K_{3}J_{3}} (-1)^{h+g+N_{1}+N_{2}+J_{1}+J_{2}+l+l-m_{1}-l_{1}} \\ \times \begin{cases} a & K_{3} & J_{3} \\ J & N_{1} & N_{2} \end{cases} \begin{cases} a & K_{3} & J_{3} \\ h & K_{2} & J_{2} \\ g & K_{1} & J_{1} \end{cases} \begin{cases} N_{2} & J & K_{3} \\ m_{2} & 1 & K_{2} \\ m_{1} & 1 & K_{1} \end{cases} \begin{cases} N_{1} & J & J_{3} \\ l_{2} & 1 & J_{2} \\ l_{1} & 1 & J_{1} \end{cases}$ (5.9)

and a re-expression of (5.5), consistent with Bancewicz [10]:

$$F_{JJ}(t) = \sum_{\substack{J_1J_2 \\ l_1l_2 \\ m_1m_2}} \sum_{\substack{K_1K_2gha \\ m_1m_2}} [1 + P_{12}(0)][1 + P_{12}(t)](2J + 1)(-1)^{J_1 + J_2 - N_2} \left(\frac{2^{N_1 + N_2}}{(2l_1)!(2l_2)!(2m_1)!(2m_2)!}\right)^{1/2}$$

$$\times X_{J_{1}J_{2}K_{1}K_{2}N_{1}N_{2}gh}(-1)^{m_{1}+l_{1}-h-g-N_{1}-J_{2}} \begin{cases} h & K_{2} & 1 & J & 1 & J_{1} & g \\ J_{2} & m_{2} & & l_{1} & K_{1} \\ 1 & l_{2} & N_{1} & a & N_{2} & m_{1} & 1 \end{cases}$$
  
$$\langle \left[ T_{N_{1}}(R_{12}(0)) \otimes T_{N_{2}}(R_{12}(t)) \right]_{a} \cdot \left[ \left( B_{J_{1}}^{(1l_{1})}(1,0) \otimes B_{K_{1}}^{(1m_{1})}(1,t) \right)_{g} \otimes \left( B_{J_{21}}^{(1l_{1})}(2,0) \otimes B_{K_{2}}^{(1m_{2})}(2,t) \right)_{h} \right]_{a} \rangle.$$
  
$$(5.10)$$

At this juncture, we make a common approximation in the theory of Collision-

Induced Rotational Raman (CIRR); that is we assume that the molecules of the scattering volume are correlated radially but not orientationally [10]. The physical basis of this assumption is that the anisotropy of the intermolecular potential is often small. Therefore, we assume that the tensors of ranks a, g, h are isotropic and hence scalar. The appropriate substitutions are, a = g = h = 0. Equation (5.10) is reduced to

$$\begin{split} F_{JJ}(t) &= \sum_{\substack{J,J_2 \ K_1K_2 \ l_1l_2 \ m_1m_2}} \left[ 1 + P_{12}(0) \right] [1 + P_{12}(t)] (2J+1) (-1)^{m_1 + l_1 - N_1 - N_2} \left( \frac{2^{N_1 + N_2}}{(2l_1)!(2l_2)!(2m_1)!(2m_2)!} \right)^{1/2} \\ &\times X_{J_1J_2K_1K_2N_1N_2} \sum_{K_3J_3} (-1)^{N_1 + N_2 + J_1 + J_2 + l + l - m_1 - l_1} (2J_3 + 1)(2K_3 + 1) \begin{cases} 0 & K_3 & J_3 \\ J & N_1 & N_2 \end{cases} \right] \begin{cases} 0 & K_3 & J_3 \\ 0 & K_2 & J_2 \\ 0 & K_1 & J_1 \end{cases} \\ \begin{cases} N_2 & J & K_3 \\ m_2 & 1 & K_2 \\ m_1 & 1 & K_1 \end{cases} \left\{ N_1 & J & J_3 \\ l_2 & 1 & J_2 \\ l_1 & 1 & J_1 \end{cases} \left\langle \left[ T_{N_1}(R_{12}(0)) \otimes T_{N_2}(R_{12}(t)) \right]_0 \right. \right. \end{cases} \\ &\cdot \left[ \left( B_{J_1}^{(l_1)}(l,0) \otimes B_{K_1}^{(lm_1)}(l,t) \right)_0 \otimes \left( B_{J_{21}}^{(l_1)}(2,0) \otimes B_{K_2}^{(lm_2)}(2,t) \right)_0 \right]_0 \right\rangle. \end{split}$$
(5.11)

With the spherical tensor relationship (3.14), the following Wigner 6-j and 9-j symbol properties,

$$\begin{cases} 0 & K_3 & J_3 \\ J & N_1 & N_2 \end{cases} = (-1)^{K_3 + N_1 + J} \frac{\delta_{K_3 J_3} \delta_{N_1 N_2}}{\sqrt{(2K_3 + 1)(2N_1 + 1)}}$$
(5.12)

$$\begin{cases} 0 & K_{3} & J_{3} \\ 0 & K_{2} & J_{2} \\ 0 & K_{1} & J_{1} \end{cases} = \frac{\delta_{J_{1}K_{1}} \delta_{J_{2}K_{2}} \delta_{J_{3}K_{3}}}{\sqrt{(2J_{1}+1)(2J_{2}+1)(2J_{3}+1)}},$$
(5.13)

as well as the explicit form of the spherical interaction tensor,

$$T_{N} = (-1)^{N} \left(\frac{(2N)!}{2^{N}}\right)^{1/2} \sqrt{\frac{4\pi}{2N+1}} R^{-(N+1)} Y_{N}(\theta, \phi), \qquad (5.14)$$

we obtain a reduced form of (5.11):

$$F_{JJ}(t) = \frac{8\pi}{2N_1 + 1} \sum_{J_1J_2} \sum_{\substack{I,I_2 \\ m_1m_2}} [1 + P_{12}(0)] [1 + P_{12}(t)] (2J + 1)(-1)^{J_1 + J_2} \left( \frac{(2N_1)!^2}{(2I_1)!(2I_2)!(2m_1)!(2m_2)!} \right)^{1/2}$$

$$\times \sum_{J_3} (2J_3 + 1)^2 \begin{cases} N_1 & J & J_3 \\ m_2 & 1 & J_2 \\ m_1 & 1 & J_1 \end{cases} \begin{cases} N_1 & J & J_3 \\ I_2 & 1 & J_2 \\ I_1 & 1 & J_1 \end{cases} \begin{cases} N_1 & J & J_3 \\ I_2 & 1 & J_2 \\ I_1 & 1 & J_1 \end{cases} \begin{cases} (R_{12}^{-(N_1 + 1)}(0)Y_{N_1}(R_{12}(0)) \cdot R_{12}^{-(N_1 + 1)}(t)Y_{N_1}(R_{12}(t))) \end{cases}$$

$$\times \left( B_{J_{1}}^{(1l_{1})}(1,0) \cdot B_{J_{1}}^{(1m_{1})}(1,t) \right) \left( B_{J_{2}}^{(1l_{1})}(2,0) \cdot B_{J_{2}}^{(1m_{2})}(2,t) \right) \right).$$
(5.15)

In the static limit (t = 0), we make use of the relation [10]:

$$\frac{4\pi}{2N_1 + 1} \left\langle R_{12}^{-(N_1 + 1)}(0) Y_{N_1}(R_{12}(0)) \cdot R_{12}^{-(N_1 + 1)}(t = 0) Y_{N_1}(R_{12}(t = 0)) \right\rangle = \left\langle R_{12}^{-2(N_1 + 1)} \right\rangle \quad (5.16)$$

to reach the final form for the first-order autocorrelation function

$$\begin{split} F_{JJ}(t) &= 2 \sum_{J_1 J_2} \sum_{\substack{l_1 l_2 \\ m_1 m_2}} [1 + P_{12}(0)] [1 + P_{12}(t)] (2J + 1) (-1)^{J_1 + J_2} \left( \frac{(2N_1)!^2}{(2l_1)! (2l_2)! (2m_1)! (2m_2)!} \right)^{1/2} \\ &\times \sum_{J_3} (2J_3 + 1)^2 \begin{cases} N_1 & J & J_3 \\ m_2 & 1 & J_2 \\ m_1 & 1 & J_1 \end{cases} \begin{cases} N_1 & J & J_3 \\ l_2 & 1 & J_2 \\ l_1 & 1 & J_1 \end{cases} \begin{cases} N_1 & J & J_3 \\ l_2 & 1 & J_2 \\ l_1 & 1 & J_1 \end{cases} \langle R_{12}^{-2(N_1 + 1)} \rangle \langle B_{J_1}^{(1l_1)}(1, 0) \cdot B_{J_1}^{(1m_1)}(1, t) \rangle \\ &\times \langle B_{J_2}^{(1l_1)}(2, 0) \cdot B_{J_2}^{(1m_2)}(2, t) \rangle \end{split}$$

.

(5.17)

# 5.2 Calculation of the Autocorrelation Function in Second-Order

Up to this point we have been giving results, which though detailed, are contributions made by others [10,14]. We will now consider the detailed derivation of the second-order autocorrelation function, which is an analogous extension of the first order case. To our knowledge, this is an original contribution. To begin, let us consider the second-order correction to the molecular pair polarizability as derived in (3.40) of chapter 3

$$\begin{split} \Delta B_{J\alpha}(1) &= \sum_{\substack{l_{l_2} \\ n_2 n_3 y KML}} \sum_{\substack{J_1 J_2 J_3 x \\ n_2 n_3 y KML}} [1 + P_{12}][1 + P_{21}](-1)^{J_2 + J_3 + L + l_1 + l_2} \left( \frac{2^{N_1 + N_2}}{(2l_1)!(2l_2)!(2l_2)!(2l_3)!} \right)^{1/2} \\ &\times X_{J_1 J_2 J_3 x^2 y^2 N_1 N_2 KML} \begin{cases} J_2 & N_2 & x \\ l_1 & N_1 & l_2 \\ y & M & n_3 \end{cases} \left\{ \begin{matrix} J & K & M \\ 1 & J_3 & n_3 \\ l & L & y \end{matrix} \right\} \left\{ \begin{matrix} J_2 & N_2 & x \\ n_3 & n_2 & l_2 \end{matrix} \right\} \left\{ \begin{matrix} J_2 & l_1 & y \\ l & L & J_1 \end{matrix} \right\} \\ &\times \left[ \left\{ T_{N_1}(R_{12}) \otimes T_{N_2}(R_{21}) \right\}_M \otimes \left\{ \begin{matrix} B_{J_1}^{(11)}(1) \otimes B_{J_4}^{(n_2 l_2)}(2) \right\}_L \otimes B_{J_5}^{(1n_3)}(1) \right\}_K \right]_{J\alpha}. \end{split}$$

$$(5.18)$$

where  $N_1 = l_1 + l_2$  and  $N_2 = l_2 + n_3$ . We will now calculate the function

$$F_{JJ}(t) = \left\langle {}^{(2)}\Delta B_{J}(0) \cdot {}^{(2)}\Delta B_{J}(t) \right\rangle$$
(5.19)

Making the appropriate substitutions, we obtain the lengthy expression:

$$\begin{split} F_{JJ}(t) &= \sum_{\substack{l_{12} \\ l_{12} \\$$

First we will consider only the tensorial part of (5.20), which we can recouple using (C.7) as

and then using identity (C.4) three times, the tensor products on both sides of the direct product can be re-expressed as

$$= (-1)^{2M+K-M'} \sum_{\substack{abcd \\ egh}} X_{JJMM'LL'KK'bc\,degh} \begin{cases} M & K & J \\ K' & M' & a \end{cases} \begin{cases} N_1 & N_2 & M \\ N'_1 & N'_2 & M' \\ b & c & a \end{cases} \begin{cases} L & J_3 & K \\ L' & J'_3 & K' \\ d & e & a \end{cases} \begin{cases} J_1 & J_2 & L \\ J'_1 & J'_2 & L' \\ g & h & d \end{cases}$$
$$\left\langle \left[ \left( T_{N_1} (12,0) \otimes T_{N'_1} (12,t) \right)_b \otimes \left( T_{N_2} (21,0) \otimes T_{N'_2} (21,t) \right)_c \right]_a \cdot \left[ \left\{ B_{J_1}^{(11)} (1,0) \otimes B_{J'_1}^{(11'_1)} (1,t) \right)_g \otimes \left( B_{J_2}^{(n_2l_2)} (2,0) \otimes B_{J'_2}^{(n'_2l'_2)} (2,t) \right)_h \right\}_d \otimes \left\{ B_{J_3}^{(1n_3)} (1,0) \otimes B_{J'_3}^{(1n'_3)} (1,t) \right\}_e \right]_a \right\rangle$$
(5.22)

Now, let us consider the "T" portion only. To be able to average the tensors over all orientations, we must first reduce the product of four T's (in reality four spherical harmonics) to a product of only two. To accomplish this, we make use of identity (C.5) and obtain:

$$\begin{split} & \left[ \left( T_{N_{1}} (12,0) \otimes T_{N_{1}'} (12,t) \right)_{b} \otimes \left( T_{N_{2}} (21,0) \otimes T_{N_{2}'} (21,t) \right)_{c} \right]_{a} \\ &= (-1)^{N_{2}+N_{2}'} \sum_{\beta \gamma} \left\langle bc, \beta \gamma \right| a\alpha \right\rangle \left( T_{N_{1}} (12,0) \otimes T_{N_{1}'} (12,t) \right)_{b}^{\beta} \left( T_{N_{2}} (12,0) \otimes T_{N_{2}'} (12,t) \right)_{c}^{\gamma} \\ &= (-1)^{N_{2}+N_{2}'} \sum_{\beta \gamma} \sum_{n_{V}} \sum_{N_{3}N_{3}'} \left\langle bc, \beta \gamma \right| a\alpha \right\rangle \left\langle bc, \beta \gamma \right| nv \right\rangle \frac{X_{N_{1}N_{1}'N_{2}N_{2}'bc}}{4\pi} \left\langle N_{1}N_{2},00 \right| N_{3}0 \right\rangle \left\langle N_{1}'N_{2}',00 \right| N_{3}'0 \right\rangle \\ &\times \left\{ \begin{matrix} N_{1} & N_{2} & N_{3} \\ N_{1}' & N_{2}' & N_{3}' \\ b & c & n \end{matrix} \right\} \left\{ Y_{N_{3}} (12,0) \otimes Y_{N_{3}'} (12,t) \right\}_{n}^{\nu} (-1)^{N_{1}+N_{1}'+N_{2}+N_{2}'} \left[ \frac{(2N_{1})!(2N_{1}')!(2N_{2})!(2N_{2}')!}{2^{N_{2}+N_{2}'+N_{1}+N_{1}'}} \right]^{1/2} \\ &\times \frac{(4\pi)^{2}}{X_{N_{1}N_{1}'N_{2}N_{2}'}} R_{12}^{-(N_{2}+N_{2}'+N_{1}+N'+4)} \end{split}$$

$$(5.23)$$

This lengthy expression reduces to

$$= 4\pi (-1)^{N_{1}+N_{1}'} \sum_{\beta\gamma} \sum_{n\nu} \sum_{N_{3}N_{3}'} \langle bc, \beta\gamma | a\alpha \rangle \langle bc, \beta\gamma | n\nu \rangle \langle N_{1}N_{2}, 00 | N_{3}0 \rangle \langle N_{1}'N_{2}', 00 | N_{3}'0 \rangle \prod_{bc} \langle N_{1}' N_{2}' N_{3}' N_{1}' N_{2}' N_{3}' N_{1}' N_{2}' N_{3}' N_{3}' N_{3}' N_{3}' N_{3}' N_{1}' N_{2}' N_{3}' N_{3}'$$

(5.24)

This can then be substituted back into equation (5.22) to give:

$$\begin{split} \langle'\rangle &= (-1)^{2M+K-M'} 4\pi (2J+1) \sum_{\substack{abc \\ deg}} \sum_{\beta\gamma\nu} \sum_{\substack{hnN_3 \\ N'_3}} (-1)^{N_1+N'_1} \begin{cases} N_1 & N_2 & M \\ N'_1 & N'_2 & M' \\ b & c & a \end{cases} \begin{cases} L & J_3 & K \\ L' & J'_3 & K' \\ d & e & a \end{cases} \begin{cases} J_1 & J_2 & L \\ J'_1 & J'_2 & L' \\ g & h & d \end{cases} \\ \\ \begin{cases} N_1 & N_2 & N_3 \\ N'_1 & N'_2 & N'_3 \\ b & c & n \end{cases} \begin{cases} M & K & J \\ K' & M' & a \end{cases} \langle bc, \beta\gamma | a\alpha \rangle \langle bc, \beta\gamma | n\nu \rangle \langle N_1N_2, 00 | N_30 \rangle \langle N'_1N'_2, 00 | N'_30 \rangle \\ \\ \\ \frac{(2N_1)!(2N'_1)!(2N_2)!(2N'_2)!}{2^{N_2+N'_2+N_1+N'_1}} \end{bmatrix}^{1/2} X_{MM'LL'KK'b^2c^2 degh} \langle \left\{ R_{12}^{-(N_3+2)}Y_{N_3} (12,0) \otimes R_{12}^{-(N'_3+2)}Y_{N'_3} (12,t) \right\}_n^{\nu} \\ \\ \cdot \left[ \left( B_{J_1}^{(11)} (1,0) \otimes B_{J'_1}^{(11')} (1,t) \right)_g \otimes \left( B_{J_2}^{(n_2l_2)} (2,0) \otimes B_{J'_2}^{(n'_2l'_2)} (2,t) \right)_h \right]_d \otimes \left\{ B_{J_3}^{(1n_3)} (1,0) \otimes B_{J'_3}^{(1n'_3)} (1,t) \right\}_e \right]_a \rangle. \end{aligned}$$
(5.25)

Now if we make use of the relation [20]:

$$\sum_{\beta\gamma} \langle bc, \beta\gamma | a\alpha \rangle \langle bc, \beta\gamma | n\nu \rangle = \delta_{an} \delta_{\alpha\nu}$$
(5.26)

we obtain from equation (5.25) the expression

$$\begin{split} &\langle ' \rangle = (-1)^{2M+K-M'} 4\pi (2J+1) \sum_{\substack{abc \\ deg}} \sum_{\alpha} \sum_{\substack{hN_{3}N'_{3} \\ deg}} (-1)^{N_{1}+N'_{1}} \begin{cases} N_{1} & N_{2} & M \\ N'_{1} & N'_{2} & M' \\ b & c & a \end{cases} \begin{cases} L & J_{3} & K \\ L' & J'_{3} & K' \\ d & e & a \end{cases} \begin{cases} J_{1} & J_{2} & L \\ J'_{1} & J'_{2} & L' \\ g & h & d \end{cases} \\ \\ \begin{cases} N_{1} & N_{2} & N_{3} \\ N'_{1} & N'_{2} & N'_{3} \\ b & c & n \end{cases} \begin{cases} M & K & J \\ K' & M' & a \end{cases} \langle N_{1}N_{2}, 00 | N_{3}0 \rangle \langle N'_{1}N'_{2}, 00 | N'_{3}0 \rangle \left[ \frac{(2N_{1})!(2N'_{1})!(2N'_{1})!(2N_{2})!(2N'_{2})!}{2^{N_{2}+N'_{2}+N_{1}+N'_{1}}} \right]^{1/2} \\ \\ \end{cases} \\ \\ \qquad X_{MM'LL'KK'b^{2}c^{2}degh} \left\langle \left\{ R_{12}^{-(N_{3}+2)}Y_{N_{3}}(12,0) \otimes R_{12}^{-(N'_{3}+2)}Y_{N'_{3}}(12,t) \right\}_{a}^{\alpha} \\ \\ \end{cases} \\ \\ \begin{cases} \left[ \left( B_{J_{1}}^{(II_{1})}(1,0) \otimes B_{J'_{1}}^{(II'_{1})}(1,t) \right)_{g} \otimes \left( B_{J_{2}}^{(n_{2}l_{2})}(2,0) \otimes B_{J'_{2}}^{(n'_{2}l'_{2})}(2,t) \right)_{h} \right\}_{d} \otimes \left\{ B_{J_{3}}^{(In_{3})}(1,0) \otimes B_{J'_{3}}^{(In'_{3})}(1,t) \right\}_{c} \right]_{a}^{\alpha} \\ \end{cases}$$

(5.27)

At this point we can once again make the CIRR approximation; thus a=g=h=e=0and equation (5.27) reduces to

.

$$\begin{split} \langle " \rangle &= (-1)^{2M+K-M'} (-1)^{N_{1}+N'_{1}} 4\pi (2J+1) \sum_{\substack{bcd\\N_{3}N'_{3}}} \begin{cases} M & K & J \\ K' & M' & 0 \end{cases} \begin{cases} N_{1} & N_{2} & M \\ N'_{1} & N'_{2} & M' \\ b & c & 0 \end{cases} \begin{cases} L & J_{3} & K \\ L' & J'_{3} & K' \\ d & 0 & 0 \end{cases} \begin{cases} J_{1} & J_{2} & L \\ J'_{1} & J'_{2} & L' \\ 0 & 0 & d \end{cases} \\ \\ \begin{cases} N_{1} & N'_{2} & N'_{3} \\ b & c & 0 \end{cases} \\ \langle N_{1}N_{2}, 00 | N_{3}0 \rangle \langle N'_{1}N'_{2}, 00 | N'_{3}0 \rangle \left[ \frac{(2N_{1})!(2N'_{1})!(2N_{2})!(2N'_{2})!}{2^{N_{2}+N'_{2}+N_{1}+N'_{1}}} \right]^{1/2} \\ \\ \\ X_{MMTLL'KKb^{2}c^{2}d} \langle \left\{ R_{12}^{-(N_{3}+2)}Y_{N_{3}}(12,0) \otimes R_{12}^{-(N'_{3}+2)}Y_{N'_{3}}(12,t) \right\}_{0}^{0} \\ \left[ \left( B_{J_{1}}^{(1l_{1})}(1,0) \otimes B_{J_{1}}^{(l'_{1})}(1,t) \right)_{g} \otimes \left( B_{J_{2}}^{(n_{2}l_{2})}(2,0) \otimes B_{J_{2}}^{(n'_{2}l'_{2})}(2,t) \right)_{h} \right\}_{d} \otimes \left\{ B_{J_{3}}^{(1n_{3})}(1,0) \otimes B_{J_{3}}^{(1n'_{3})}(1,t) \right\}_{c} \left[ 0 \\ \rangle \\ \end{cases} \\ (5.28) \end{split}$$

Evaluation of the 6-j and 9-j symbols in equation (5.28) leads to the expression

$$\frac{(-1)^{L+M+J}}{X_{M^{2}L^{2}b^{2}K^{2}J_{1}J_{2}J_{3}N_{3}}} \begin{cases} N_{1} & N_{2} & M \\ N'_{2} & N'_{1} & b \end{cases} \begin{cases} N_{1} & N_{2} & N_{3} \\ N'_{2} & N'_{1} & b \end{cases} \delta_{LL'} \delta_{MM'} \delta_{KK'} \delta_{d0} \delta_{N_{3}N'_{3}} \delta_{J_{1}J'_{1}} \delta_{J_{2}J'_{2}} \delta_{J_{3}J'_{3}} \end{cases}$$
(5.29)

and so (5.28) becomes,

$$\langle "\rangle = (-1)^{N_{1}+N_{1}'+J} 4\pi (2J+1) \sum_{bN_{3}} \frac{X_{M^{2}L^{2}K^{2}b^{4}}}{X_{M^{2}L^{2}K^{2}b^{2}J_{1}J_{2}J_{3}}} \begin{cases} N_{1} & N_{2} & M \\ N_{2}' & N_{1}' & b \end{cases} \begin{cases} N_{1} & N_{2} & N_{3} \\ N_{2}' & N_{1}' & b \end{cases} \langle N_{1}N_{2},00 | N_{3},0 \rangle \\ \langle N_{1}'N_{2}',00 | N_{3}'0 \rangle \left[ \frac{(2N_{1})!(2N_{1}')!(2N_{2})!(2N_{2}')!}{2^{N_{2}+N_{2}'+N_{1}+N_{1}'}} \right]^{1/2} \langle \frac{(-1)^{N_{3}}}{X_{N_{3}^{2}}} \{ R_{12}^{-(N_{3}+2)}Y_{N_{3}}(12,0) \cdot R_{12}^{-(N_{3}+2)}Y_{N_{3}}(12,t) \} \\ \frac{(-1)^{J_{1}+J_{2}+J_{2}}}{X_{J_{1}^{2}J_{2}^{2}J_{3}^{2}}} \langle B_{J_{1}}^{(1I_{1})}(1,0) \cdot B_{J_{1}}^{(1I_{1}')}(1,t) \rangle \langle B_{J_{2}}^{(n_{2}I_{2})}(2,0) \cdot B_{J_{2}}^{(n_{2}'L_{2}')}(2,t) \rangle \langle B_{J_{3}}^{(1n_{3})}(1,0) \cdot B_{J_{3}}^{(1n_{3}')}(1,t) \rangle \rangle \\ \times \delta_{LL'}\delta_{MM'}\delta_{KK'}\delta_{d0}\delta_{N_{3}N_{3}'}\delta_{J_{1}J_{1}'}}\delta_{J_{2}J_{2}'}\delta_{J_{3}J_{3}'}. \end{cases}$$

$$(5.30)$$

We can now substitute this back into the original expression for the autocorrelation function, equation (5.20):

.

Now, if we explicitly consider the sum:

$$\sum_{b} X_{b^{2}} \begin{cases} N_{1} & N_{2} & M \\ N'_{2} & N'_{1} & b \end{cases} \begin{cases} N_{1} & N_{2} & N_{3} \\ N'_{2} & N'_{1} & b \end{cases} \begin{cases} N'_{2} & N'_{1} & b \end{cases}$$
(5.32)

with the symmetries of the 6-j symbols [20], this can be written as

.

$$\sum_{b} X_{b^{2}} \begin{cases} N_{1} & N_{1}' & b \\ N_{2}' & N_{2} & M \end{cases} \begin{cases} N_{1} & N_{1}' & b \\ N_{2}' & N_{2} & M \end{cases} \begin{cases} N_{1} & N_{1}' & b \\ N_{2}' & N_{2} & N_{3} \end{cases},$$
(5.33)

which is equivalent to [20]:

$$\sum_{b} X_{b^{2}} \begin{cases} N_{1} & N_{1}' & b \\ N_{2}' & N_{2} & M \end{cases} \begin{cases} N_{1} & N_{1}' & b \\ N_{2}' & N_{2} & N_{3} \end{cases} = \delta_{MN_{3}} \frac{\{N_{1}N_{2}M\}\{N_{1}'N_{2}'M\}}{(2M+1)}$$
(5.34)

where  $\{a \ b \ c\} = 1$  if a, b, c satisfy the triangular condition, and  $\{a \ b \ c\} = 0$  otherwise. Making this substitution into equation (5.31), and after some algebraic simplification, we obtain for the second-order autocorrelation function:

$$\begin{split} F_{JJ}(t) &= (2J+I) \sum_{l_{1}^{J}} \sum_{l_{1}^{J_{1}^{J}}} \sum_{J_{2}^{J}} \sum_{J_{2}^{J}} \sum_{J_{2}^{J}} [1+P_{12}][1+P_{12}](-I)^{l_{1}+l_{2}+l_{1}^{J}+l_{2}^{J}+J_{1}+J_{2}+J_{3}} \\ &\times \left( \frac{(2N_{1})!(2N_{1}^{\prime})!(2N_{2})!(2N_{2}^{\prime})!}{(2l_{1})!(2l_{2})!(2l_{2})!(2l_{2}^{\prime})!(2l_{2}^{\prime})!} \right)^{1/2} \frac{X_{x^{2}y^{2}N_{1}N_{2}K^{2}L^{2}x^{2}y^{2}N_{1}N_{2}}{X_{M}} \\ &\times \begin{cases} J_{2} \quad N_{2} \quad x \\ l_{1} \quad N_{1} \quad l_{2} \\ y \quad M \quad n_{3} \end{cases} \left| \begin{array}{c} J \quad K \quad M \\ 1 \quad J_{3} \quad n_{3} \\ 1 \quad L \quad y \end{array} \right| \left\{ J_{2} \quad N_{2} \quad x' \\ n_{3} \quad n_{2} \quad l_{2} \end{array} \right) \left\{ \begin{array}{c} J_{2} \quad l_{1} \quad y \\ 1 \quad L \quad J_{1} \end{array} \right\} \\ &\times \begin{cases} J_{2} \quad N_{2} \quad x' \\ l_{1} \quad N_{1} \quad l_{2} \\ y' \quad M \quad n_{3} \end{array} \right| \left\{ \begin{array}{c} J \quad K \quad M \\ 1 \quad J_{3} \quad n_{3} \\ 1 \quad L \quad y' \end{array} \right| \left\{ J_{2} \quad N_{2} \quad x' \\ n_{3} \quad n_{2} \quad l_{2} \end{array} \right) \left\{ \begin{array}{c} J_{2} \quad l_{1} \quad y \\ 1 \quad L \quad J_{1} \end{array} \right\} \\ &\times \begin{cases} N_{1} \quad N_{1} \quad l_{2} \\ l_{1} \quad N_{1} \quad l_{2} \\ y' \quad M \quad n_{3} \end{array} \right) \left\{ \begin{array}{c} J \quad K \quad M \\ 1 \quad J_{3} \quad n_{3}' \\ 1 \quad L \quad y' \end{array} \right) \left\{ \begin{array}{c} J_{2} \quad N_{2} \quad x' \\ n_{3} \quad n_{2} \quad l_{2} \end{array} \right) \left\{ \begin{array}{c} J_{2} \quad l_{1} \quad y' \\ 1 \quad L \quad J_{1} \end{array} \right\} \\ &\times \begin{cases} N_{1} \quad N_{2} \quad M \\ N_{1} \quad N_{2} \quad M \\ N_{1} \quad N_{2} \quad M \\ N_{1} \quad N_{2} \quad N'_{3} \quad N'_{3} \end{array} \right\} \left\{ \begin{array}{c} J_{2} \quad N'_{2} \quad x' \\ n_{3} \quad n_{2} \quad l_{2} \end{array} \right) \left\{ \begin{array}{c} J_{2} \quad l_{1} \quad y' \\ 1 \quad L \quad J_{1} \end{array} \right\} \\ &\times \begin{cases} N_{1} \quad N_{2} \quad M \\ N_{1} \quad N_{2} \quad M \\ N_{1} \quad N_{2} \quad M \\ N_{1} \quad N_{2} \quad N'_{2} \quad N'_{2} \quad N'_{2} \quad N'_{2} \quad N'_{2} \end{array} \right\} \left\{ \begin{array}{c} J_{2} \quad l_{1} \quad L \quad J_{1} \end{array} \right\} \\ &\times \begin{cases} N_{1} \quad N_{2} \quad M \\ N_{1} \quad N_{2} \quad N'_{2} \quad N'_{$$

Again we have made use of the identity, that if t=0, the average becomes explicit only over the radial distance R between the two molecules.

Equations (5.17) and (5.35) can be directly applied and evaluated with symbolic mathematical software such as Mathematica [10]. Before the autocorrelation function can be evaluated, the rank of the induced multipole needs to be specified, as well as the rank of the pair polarizability tensors and the rank of the interaction tensors. These details will be demonstrated in the next chapter.

#### **CHAPTER 6:** The Computer Program and its Results

This chapter will discuss the implementation of the computer program and the results that the program gives. The language that was chosen was Mathematica, primarily because the many vector-coupling coefficients are already precompiled in the language. Thus Clebsch-Gordon and Wigner 6-j symbols are already defined, see Appendix B. From these, one can define higher-order Wigner symbols as shown in Appendix D. Thus we can define a Mathematica function to calculate the Wigner 9-j symbol as

$$\begin{aligned} &\text{NineJSymbolA}[\{a_{, f_{, r_{, }}, \{d_{, q_{, e_{, }}, \{p_{, c_{, }}, b_{, }\}\} := \\ &\text{Sum}[(-1)^{2T} (2T+1) \text{SixJSymbol}[\{a, b, T\}, \{c, d, p\}] \\ & \times \text{SixJSymbol}[\{c, d, T\}, \{e, f, q\}] \\ & \times \text{SixJSymbol}[\{e, f, T\}, \{a, b, r\}], \{T, 0, \text{NI} + j1\}]; \end{aligned}$$

$$(6.1)$$

using equation (3.34), and a function that checks for the triangular condition of the ranks as

Triangular[
$$a_{b_{c_{1}}}$$
]:=If [Abs[ $a - b$ ]  $\leq c \leq a + b, 1, 0$ ]; (6.2)

With the use of these functions, equations (5.17) and (5.35) were directly written in Mathematica; thus one obtains:

Fjj=(2 j+1) 2 (-1)^(l1+m1) (2N1)!/Sqrt[(2 l1)! (2 (N1-l1))! (2 m1)! (2 (N1-m1))!] R^(-2 (N1+1)) (1+(-1)^(j1+N1+j2+j)) Sum[(2 x+1) SixJSymbol[{1,1,x},{1,1,j}] SixJSymbol[{1,1,x},{N1-l1,N1-m1,j2}] SixJSymbol[{N1-l1,N1-m1,x},{m1,l1,N1}] SixJSymbol[{m1,l1,x},{1,1,j1}],{x,0,2}] (Sum[(-1)^m A[1,j1,l1,m] A[1,j1,m1,-m],{m,-j1,j1}] Sum[(-1)^m A[2,j2,(N1-l1),m] A[2,j2,(N1-m1),-m],{m,-j2,j2}])

which calculates the first-order correction to the pair polarizability, and,

H[j\_] := (2j+1)422+n3 Sum[ Sm Sm[ Sum Sum  $Sum[Sum[(-1)^{(B+C+\Delta+j1+j2+j3+j)}]$ (Sqrt[(2NI) ! (2N2) ! (2N1) ! (2N2) !] / Sqrt[(211) ! (212) ! (212) ! (213) ! (2a1) ! (2a2) ! (2a2) ! (2b3) !]) $\mathbb{R}^{(-2(N_1+N_2+2))}$  (2N1+1) (2N2+1) (2X+1) (2C+1) (2 $\triangle$ +1) (2K+1) (2F+1) (2G+1) (ClebschGordan[{NI, 0}, {N2, 0}, {B, 0}])<sup>2</sup> Triangular[NI, N2, B] Triangular[j2, j3, G] Triangular[j1, X, G] CompSum[NL, N2, Diff]  $SixISymbol[{G, N2, C}, {K, j1, X}] SixISymbol[{G, N2, <math>\Delta$ }, {F, j1, X}] SixISymbol[{N2, X, K}, {j, N1, B}] SixJSymbol[{N2, X, F}, {j, N1, B}] NineJSymbolA[{j1, C, K}, {1, 1, j}, {11, 12, N1}] NineJSymbolA[{j1, 4, F}, {1, 1, j}, {a1, a2, Nl}] NineJSymbolB[{j2, j3, G}, {12, 1, C}, {12, n3, N2}] NineJSymbolB[ $\{j2, j3, G\}, \{a2, 1, \Delta\}, \{a2, b3, N2\}$ ]  $\left(\sum_{a=-j1}^{j1} (-1)^{a} A[1, j1, 1, 11, a] A[1, j1, 1, a1, -a]\right) \left(\sum_{b=-j2}^{j2} (-1)^{b} A[2, j2, n2, 12, b] A[2, j2, b2, a2, -b]\right)$  $\left(\sum_{c=-i3}^{j3} (-1)^{c} A[1, j3, 1, n3, c] A[1, j3, 1, b3, -c]\right), \{X, Abs[j1+12+1-N2], j1+12+1+N2\}], \{B, Abs[N1-N2], N1+N2\}],$  $\{C,Abs[12-1], 12+1\}, \{\Delta,Abs[a2-1], a2+1\}, \{K,Abs[j1-12-1], j1+12+1\}, \{F,Abs[j1-a2-1], j1+a2+1\}, \{F,Abs[j1-a2-1], j1+a2+1], \{F,Abs[j1-a2-1], j1+a2+1\}, \{F,Abs[j1-a2-1], j1+a2+1\}, \{F,Abs[j1-a2-1], j1+a2+1\}, \{F,Abs[j1-a2-1], j1+a2+1], j1+a2+1\}, j1+a2+1\}, j2+a2+1\}, j2+a2+$  $\{G, Abs[j2-j3], j2+j3\}$ F[j\_] := (2j+1)4Sm[ Sum Sum Sum Sum  $Sum[Sum[(-1)^{(B+C+\Delta+j1+j2+j3+j)}]$ (Sqrt[(2N1)!(2N2)!(2N2)!(2N2)!)/Sqrt[(211)!(212)!(212)!(2n3)!(2n3)!(2n2)!(2n2)!(2n3)!(2n3)!(2n2)!(2n2)!(2n3)!) $\mathbb{R}^{(-2(NL+N2+2))}(2NL+1)(2N2+1)(2X+1)(2C+1)(2\Delta+1)(2K+1)(2F+1)(2G+1)$ (ClebschGordan[{Nl, 0}, {N2, 0}, {B, 0}])<sup>2</sup> Triangular[Nl, N2, B] Triangular[j2, j3, G] Triangular[j1, X, G] SixTSymbol[(G, N2, C}, {K, j1, X}] SixTSymbol[(G, N2, A}, {F, j1, X}] SixTSymbol[(N2, X, K}, {j, N1, B}] SixUSymbol[{N2, X, F}, {j, N1, B}] NineUSymbolA[{j1, C, K}, {1, 1, j}, {11, 12, N1}]  $\label{eq:linearized_linearized$ NineJSynbolB[ $\{j2, j3, G\}, \{a2, 1, \Delta\}, \{a2, b3, N2\}$ ]

$$\left( \sum_{a=-j1}^{j1} (-1)^{a} A[1, j1, 1, 11, a] A[1, j1, 1, a1, -a] \right) \left( \sum_{b=-j2}^{j2} (-1)^{b} A[2, j2, n2, 12, b] A[2, j2, b2, a2, -b] \right)$$

$$\left( \sum_{c=-j3}^{j3} (-1)^{c} A[1, j3, 1, n3, c] A[1, j3, 1, b3, -c] \right)$$

,  $\{X, Abs[j1+12+1-N2], j1+12+1+N2\}$ ,  $\{B, Abs[N1-N2], N1+N2\}$ ,  $\{C, Abs[12-1], 12+1\}$ ,  $\{\Delta, Abs[a2-1], a2+1\}$ ,  $\{K, Abs[j1-12-1], j1+12+1\}$ ,  $\{F, Abs[j1-a2-1], j1+a2+1\}$ ,  $\{G, Abs[j2-j3], j2+j3\}$ ;

which calculate the second-order correction to the pair polarizability. Before running the above programs, one needs to specify J, which is the rank of the pair polarizability (either 0 or 2), the ranks of the interaction tensors, N, N<sub>1</sub>, N<sub>2</sub>, as well as the ranks of the multipole moments, 11, 12, n2, n3, and the polarizability tensors, J1, J2, and J3. An example of this is shown in Appendix D for both the first and second-order cases.

The question arises why two functions are required to calculate the second-order correction. The answer can be found in the nature of the molecular polarizability of molecule 2. As explained in Chapter 2 of this thesis, the polarizabilities, A and E, contribute to the induction of two different molecular moments. In the case of A, an electric field acts to induce a quadrupole moment and the gradient of the field acts to induce a dipole moment in the molecule. For E, a field induces an octupole and a second-derivative of the field induces a dipole moment. Both of these contributions must be taken into account when calculating the intensities and depolarization ratios.

To get a clearer sense of the above argument, consider the situation in diagram 6.1. In (a)-(c) we have a graphical depiction of the two molecules with the interaction proceeding from left to right for convenience. If we recall our experimental assumptions that the incoming field is free of derivatives and that the final radiation due to the interaction is dipolar in nature, we see that the number of contributions for any particular case depends on which polarizability we are considering in molecule 2. For simplicity we depict only the dipole polarizability ( $\alpha$ ) in molecule 1 and the dipole ( $\alpha$ ), dipole - quadrupole (A) and the dipole-octupole (E) polarizabilites in molecule 2 from (a) to (c) respectively. The greek letters at the



Figure 6.1: A graphical representation of the contributions leading to a particular multipolar intensity.

end of the line segments at each molecule represent the moments that are induced in that particular molecule via the labelled polarizability. The "branches" between the molecules, with their respective negative labels, represent the radial dependence of the electromagnetic interaction where the label designates the exponent on R. Thus "–3" means R<sup>-3</sup>, the electric field due to a dipole, while "-4" means R<sup>-4</sup>, the field of a quadrupole and the field-gradient of a dipole. Finally, "-5" means R<sup>-5</sup>, the electric field of a of an octupole moment and the gradient of the gradient of a dipole field.

Thus when the particular interaction involves only one branch, in the sense given in diagram 6.1, the function  $F[J_]$  is used. If two branches are involved, the function  $H[J_]$  is used whereby the two branches are evaluated and then summed.

The results of the program are displayed in table form below. Table 1 gives the first-order depolarization ratios for molecules of tetrahedral geometry. Table 2 gives the second-order depolarization ratios, and table 3 gives the second-order depolarization ratios for atoms for isotropic scattering.

Induction operator	$J_1$	J <sub>2</sub>	I <sub>1</sub>	m <sub>1</sub>	$\eta_n$	η
αΤ2α*	0	0	1	1	$\frac{6}{7}$	$\frac{3}{4}$
αT <sub>3</sub> A*	0	3	1	1	$\frac{9}{23}$	$\frac{9}{37}$
AT <sub>3</sub> α*	3	0	2	2	$\frac{9}{23}$	$\frac{9}{37}$
αT₄E*	0	4	1	1	$\frac{22}{63}$	$\frac{11}{52}$
ET₄α*	4	0	3	3	$\frac{22}{63}$	$\frac{11}{52}$
AT <sub>4</sub> A	3	3	2	2	<u>1966</u> 2477	<u>938</u> 1494
AT5E	3	4	2	2	$\frac{29}{36}$	$\frac{29}{43}$

Table 1: Depolarization ratios and successive first-order multipolar mechanisms for two interacting tetrahedral molecules. The \* symbol indicates that the particular interaction occurs also between an atom and a molecule.

ET <sub>5</sub> A	4	3	3	3	29	29
					36	43
ET6E	4	4	3	3	103	103
					126	149
					120	149

Table 2: Depolarization ratios and successive second-order multipolar mechanisms for two interacting tetrahedral molecules. The \* symbol indicates that the particular interaction occurs also between an atom and a molecule.

Induction	$J_1$	$J_2$	$J_3$	$l_1$	n <sub>2</sub>	<b>l</b> <sub>2</sub>	n <sub>3</sub>	η <sub>n</sub>	η
operator									
$\alpha T_2 \alpha T_2 \alpha^*$	0	0	0	1	1	1	1	$\frac{2}{9}$	$\frac{1}{8}$
αΤ3ΑΤ3α*	0	3	0	1	1	2	1	2538 4961	<u>1269</u> 3692
$AT_3 \alpha T_2 \alpha^*$	3	0	0	2	1	1	1	738 941	<u>369</u> 572
αΤ2αΤ3Α*	0	0	3	1	1	1	2	$\frac{342}{719}$	$\frac{171}{548}$
αT4ET4α*	0	4	0	1	1	3	1	<u>1574318</u> 2359371	787159 1572212
$ET_4 \alpha T_2 \alpha^*$	4	0	0	3	1	1	1	7058 8901	<u>3529</u> 5372
$\alpha T_2 \alpha T_4 E^*$	0	0	4	1	1	1	3	<u>598</u> 1231	<u>299</u> 932
αT <sub>3</sub> AT <sub>4</sub> A	0	3	3	1	1	2	2	<u>369324</u> 2346763	848577 1498186

ΑΤ <sub>3</sub> αΤ <sub>3</sub> Α*	3	0	3	2	1	1	2 12410 6205		6205
								25853	19648
						-			
$AT_4AT_3\alpha$	3	3	0	2	1	2	1	369324	184662
								505753	321091
$\alpha T_4 E T_5 E$	0	4	4	1	1	3	3	1312064070	656032035
	_							1584530087	928498052
$ET_4 \alpha T_4 E^*$	4	0	4	3	1	1	3	1413262	706631
								3082187	2375556
$ET_5ET_4\alpha$	4	4	0	3	1	3	1	203483970042	101741985021
								386682535957	284940550936
αT <sub>3</sub> AT <sub>5</sub> E	0	3	4	1	1	2	3	674166	337083
								908027	570944
αT <sub>4</sub> ET <sub>5</sub> A	0	4	3	1	1	3	2	3946594	1973297
								4938213	2964916
AT <sub>3</sub> αT <sub>4</sub> E*	3	0	4	2	1	1	3	1718	859
								3615	2756
$AT_5ET_4\alpha$	3	4	0	2	1	3	1	55442751226	27721375613
								96335891897	68614516284
ET <sub>4</sub> αT <sub>3</sub> A*	4	0	3	3	1	1	2	257142	128571
								553529	424958
ET <sub>5</sub> AT <sub>3</sub> α	4	3	0	3	1	2	1	17188934	8594467
								24418203	15823736
AT <sub>4</sub> AT <sub>4</sub> A	3	3	3	2	1	2	2	81116778	40558389
								180359281	139800892
AT5ET5A	3	4	3	2	1	3	2	2734251466	1367125733
								4769436049	3402310316
ET5AT4A	4	3	3	3	1	2	2	114116348946	57058174473
								179882860987	122824686514

AT <sub>4</sub> AT <sub>5</sub> E	3	3	4	2	1	2	3	46194222	23097111
								99802679	76705568
AT5ET6E	3	4	4	2	1	3	3	62639016888858	31319508444429
								103746032796217	72426524351788
e									
ET5AT5E	4	3	4	3	1	2	3	116081946	58040973
								258529561	200488588
ET6ET5A	4	4	3	3	1	3	2	500479852914	250239926457
								2448311155733	2198071229276
ET6ET6E	4	4	4	3	1	1	3	8491458945654	4245729472827
								16541830751663	12296101278836

Table 3: Depolarization ratios and successive second-order multipolar mechanisms for two interacting atoms

Induction	$J_1$	J <sub>2</sub>	J <sub>3</sub>	l <sub>1</sub>	l <sub>2</sub>	<b>n</b> <sub>2</sub>	• <b>n</b> <sub>3</sub>	ղո	η
operator									
$\alpha T_2 \alpha T_2 \alpha$	0	0	0	1	1	1	1	$\frac{2}{9}$	$\frac{1}{8}$
αT <sub>3</sub> CT <sub>3</sub> α	0	0	0	1	2	2	1	$\frac{8}{51}$	$\frac{4}{47}$
In the cases that were considered the anisotropic and isotropic intensities differ only in numerical factors. Thus the depolarization ratios for linearly polarized light detected with no analyzer (natural light):

$$\eta_{\rm n} = \frac{6F_{22}}{7F_{22} + 10F_{00}}$$

And, for linearly polarized light with analyzer:

$$\eta = \frac{\eta_n}{2 - \eta_n}$$

depend only on the ratio of the anisotropic and isotropic intensities, and so are constants [10]. Thus they can be calculated without a detailed knowledge of the multipole polarizability tensor terms, but as before, the ranks of the respective tensors must be specified. This feature is further explored in Appendix F.

When calculating explicit expressions for light scattered intensities, a detailed knowledge of the form of the irreducible spherical components of the multipole polarizability tensors is necessary. For molecules of tetrahedral symmetry, the nonzero Cartesian multipole polarizability components are well known [7, 24]. We can then use the procedures discussed in chapter 4 to calculate the nonzero irreducible spherical components of the dipole-dipole, dipole-quadrupole and dipole-octopole molecular polarizabilities for tetrahedral molecules. Thus one obtains:

$$A_{00}^{(1,1)} = -\sqrt{3}\alpha, \qquad \text{dipole} - \text{dipole}$$

$$A_{3\pm2}^{(1,2)} = \pm i\sqrt{2}A, \qquad \text{dipole} - \text{quadrupole}$$

$$A_{40}^{(1,3)} = \frac{1}{2}\sqrt{7}E,$$

$$A_{4+4}^{(1,3)} = \frac{1}{4}\sqrt{10}E. \qquad \text{dipole} - \text{octopole}$$
(6.3)

Table 4: Anisotropic and isotropic intensit	es for first-order multipolar	mechanisms for two	interacting
tetrahedral molecules	-		C C

Induction	$<\alpha_{xz}^2>$	$<\alpha_{zz}^{2}>$
operator		
$\alpha T_2 \alpha$	$12 \alpha^4$	$16 \alpha^4$
	5 R <sup>6</sup>	5 R <sup>6</sup>
αT <sub>3</sub> A	$48 \operatorname{A2}^2 \alpha^2$	$592 \text{ A}2^2 \alpha^2$
	35 R <sup>8</sup>	105 R <sup>8</sup>
AT <sub>3</sub> α	$48 \operatorname{A1}^2 \alpha^2$	$592 \operatorname{A2}^2 \alpha^2$
	35 R <sup>8</sup>	105 R <sup>8</sup>
αT <sub>4</sub> E	$11 \text{ E}2^2 \alpha^2$	$52 \text{ E}2^2 \alpha^2$
	9 R <sup>10</sup>	9 R <sup>10</sup>
ET <sub>4</sub> α	$11 \text{ E2}^2 \alpha^2$	$52 \text{ E}2^2 \alpha^2$
	9 R <sup>10</sup>	9 R <sup>10</sup>
AT <sub>4</sub> A	$62912 \text{ A1}^2 \text{ A2}^2$	$10624 \text{ A1}^2 \text{ A2}^2$
	$4725 R^{10}$	525 R <sup>10</sup>
AT <sub>5</sub> E	$464 \operatorname{Al}^2 \mathrm{E2}^2$	$688  \text{A1}^2  \text{E2}^2$
	21 R <sup>12</sup>	21 R <sup>12</sup>
ET <sub>5</sub> A	$464 \text{ A1}^2 \text{ E2}^2$	688 A1 <sup>2</sup> E2 <sup>2</sup>
	21 R <sup>12</sup>	21 R <sup>12</sup>
ET6E	$1133 \text{ E1}^2 \text{ E2}^2$	1639 E1 <sup>2</sup> E2 <sup>2</sup>
	21 R <sup>14</sup>	$21  \mathrm{R}^{14}$

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Induction	$<\alpha_{xz}^2>$	$<\alpha_{zz}^{2}>$
operator		
-		
$\alpha T_2 \alpha T_2 \alpha$	$12 \alpha 1^4 \alpha 2^2$	$96 \alpha 1^4 \alpha 2^2$
	5 R <sup>12</sup>	5 R <sup>12</sup>
$\alpha T_3 A T_3 \alpha$	$846 \operatorname{A2}^2 lpha 1^4$	7384 A2 <sup>2</sup> $\alpha$ 1 <sup>4</sup>
	$4375 R^{14}$	13125 R <sup>14</sup>
$AT_3\alpha T_2\alpha$	$1968 \operatorname{A1}^2 \alpha 1^2 \alpha 2^2$	9152 A1 $^{2} \alpha 1^{2} \alpha 2^{2}$
	175 R <sup>14</sup>	525 R <sup>14</sup>
$\alpha T_2 \alpha T_3 A$	$228 \operatorname{Al}^2 lpha 1^2 lpha 2^2$	$2192 \operatorname{A1}^2 lpha 1^2 lpha 2^2$
	$175  R^{14}$	525 R <sup>14</sup>
$\alpha T_4 E T_4 \alpha$	787159 $E2^2 \alpha 1^4$	393053 $E2^2 \alpha 1^4$
	190159200 R <sup>16</sup>	47539800 R <sup>16</sup>
$ET_4 \alpha T_2 \alpha$	3529 $E1^2 \alpha 1^2 \alpha 2^2$	$5372 \text{ E1}^2 \alpha 1^2 \alpha 2^2$
	315 R <sup>16</sup>	315 R <sup>16</sup>
$\alpha T_2 \alpha T_4 E$	$299 \operatorname{E1}^2 \alpha 1^2 \alpha 2^2$	$233 \text{ E1}^2 \alpha 1^2 \alpha 2^2$
	252 R <sup>16</sup>	63 R <sup>16</sup>
αT <sub>3</sub> AT <sub>4</sub> A	$1131436 \text{ A1}^2 \text{ A2}^2 \alpha 1^2$	$5992744 \text{ A1}^2 \text{ A2}^2 \alpha 1^2$
	1378125 R <sup>16</sup>	4134375 R <sup>16</sup>
ΑΤ3αΤ3Α	$39712 \operatorname{Al}^4 \alpha 2^2$	$628736 \operatorname{Al}^4 \alpha 2^2$
	5145 R <sup>16</sup>	25725 R <sup>16</sup>
AT <sub>4</sub> AT <sub>3</sub> α	$164144 \text{ A1}^2 \text{ A2}^2 \alpha 1^2$	$2568728 \text{ A1}^2 \text{ A2}^2 \alpha 1^2$
	128625 R <sup>16</sup>	1157625 R <sup>16</sup>
αT4ET5E	$43735469 \text{ E1}^2 \text{ E2}^2 \alpha 1^2$	232124513 $E1^2 E2^2 \alpha 1^2$
	892480512 R <sup>20</sup>	3346801920 R <sup>20</sup>
ET <sub>4</sub> αT <sub>4</sub> E	$706631  \text{E1}^4  \alpha 2^2$	$197963 \text{ E1}^4 \alpha 2^2$
	95256 R <sup>20</sup>	7938 R <sup>20</sup>

Table 5: Anisotropic and isotropic intensities for second-order multipolar mechanisms for two interacting tetrahedral molecules

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ET5ET4α	$33913995007 \text{ E1}^2 \text{ E2}^2 \alpha 1^2$	$35617568867  \text{E1}^2  \text{E2}^2  \alpha 1^2$				
	$461500079040 R^{20}$	173062529640 R <sup>20</sup>				
αT <sub>3</sub> AT <sub>5</sub> E	$112361 \text{ A2}^2 \text{ E1}^2 \alpha 1^2$	$570944 \text{ A2}^2 \text{ E1}^2 \alpha 1^2$				
	91875 R <sup>18</sup>	275625 R <sup>18</sup>				
αT4ET5A	$1973297  \text{A1}^2  \text{E}2^2 lpha 1^2$	$1482458 \text{ A1}^2 \text{ E2}^2 \alpha 1^2$				
	83194650 R <sup>18</sup>	$41597325  \mathbb{R}^{18}$				
AT <sub>3</sub> αT <sub>4</sub> E	3436 Al <sup>2</sup> El <sup>2</sup> $\alpha 2^2$	$11024 \text{ A1}^2 \text{ E1}^2 \alpha 2^2$				
	441 R <sup>18</sup>	441 R <sup>18</sup>				
$AT_5ET_4\alpha$	$27721375613 \text{ A1}^2 \text{ E2}^2 \alpha 1^2$	$5717876357  \text{A1}^2  \text{E2}^2  \alpha 1^2$				
	$635369427000 R^{18}$	52947452250 R <sup>18</sup>				
ΕΤ4αΤ3Α	$342856 \text{ A1}^2 \text{ E1}^2 \alpha 2^2$	3399664 A1 <sup>2</sup> E1 <sup>2</sup> $\alpha$ 2 <sup>2</sup>				
-	46305 R <sup>18</sup>	138915 R <sup>18</sup>				
ET <sub>5</sub> AT <sub>3</sub> α	$1227781 \text{ A2}^2 \text{ E1}^2 \alpha 1^2$	7911868 A2 $^2$ E1 $^2$ $\alpha$ 1 $^2$				
	727650 R <sup>18</sup>	2546775 R <sup>18</sup>				
AT <sub>4</sub> AT <sub>4</sub> A	216311408 A1 $^4$ A2 $^2$	$29049536{ m A1}^4{ m A2}^2$				
	$1489863375 R^{18}$	58046625 R <sup>18</sup>				
AT5ET5A	$1367125733  \mathrm{A1}^4  \mathrm{E2}^2$	$850577579{ m A1}^4{ m E2}^2$				
	39332393100 R <sup>20</sup>	9833098275 R <sup>20</sup>				
ET <sub>5</sub> AT <sub>4</sub> A	$76077565964 \mathrm{A1}^2 \mathrm{A2}^2 \mathrm{E1}^2$	$491298746056 \mathrm{A1}^2 \mathrm{A2}^2 \mathrm{E1}^2$				
	$17381739375  R^{20}$	$52145218125 R^{20}$				
AT <sub>4</sub> AT <sub>5</sub> E	$61592296 \operatorname{A1}^2 \operatorname{A2}^2 \operatorname{E1}^2$	$613644544 \text{ A1}^2 \text{ A2}^2 \text{ E1}^2$				
	$386260875  \mathbb{R}^{20}$	$1158782625 R^{20}$				
AT5ET6E	$10439836148143 \text{ A1}^2 \text{ E1}^2 \text{ E2}^2$	$18106631087947 \mathrm{A1}^2 \mathrm{E1}^2 \mathrm{E2}^2$				
	$48457508299200 R^{22}$	36343131224400 R <sup>22</sup>				
ET <sub>5</sub> AT <sub>5</sub> E	$6448997  \mathrm{A2}^2  \mathrm{E1}^4$	$50122147 \text{ A2}^2 \text{ E1}^4$				
	52972920 R <sup>22</sup>	119189070 R <sup>22</sup>				
ET6ET5A	$27804436273 \text{ A1}^2 \text{ E1}^2 \text{ E2}^2$	$42270600563 \text{ A1}^2 \text{ E1}^2 \text{ E2}^2$				
	$3461250592800 R^{22}$	599062602600 R <sup>22</sup>				

ET6ET6E	$471747719203 \text{ E1}^4 \text{ E2}^2$					
	26151671145600 R <sup>24</sup>					

Table 6: Anisotropic and isotropic intensities for second-order multipolar mechanisms for two interacting atoms

Induction	$<\alpha_{xz}^{2}>$	$<\alpha_{zz}^{2}>$			
operator					
$\alpha T_2 \alpha T_2 \alpha$	$12 \alpha 1^4 \alpha 2^2$	96 $\alpha 1^4 \alpha 2^2$			
	5 R <sup>12</sup>	5 R <sup>12</sup>			
$\alpha T_3 C T_3 \alpha$	$192 C2^2 \alpha 1^4$	$2256 C2^2 \alpha 1^4$			
	5 R <sup>16</sup>	5 R <sup>16</sup>			

CHAPTER 7: Possible Implications for the Collision-Induced Absorption (CIA) Spectrum of Water Vapour

In this chapter, the most speculative, we outline some of the possible implications that the discussions in the previous chapters have on the analysis of the collision-induced rotational spectrum of water vapour. This is motivated in part by the study of the continuum absorption in the far-infrared region by water molecules in the Earth's atmosphere. This phenomenon was recognized more than sixty years ago [26,27]. Through numerous experiments since that time, nearly unanimous agreement has been reached concerning the density dependence of this absorption, which is quadratic, and the temperature dependence, which is strongly negative [26]. However there is still considerable disagreement as to the source of this absorption, but three proposed theoretical mechanisms have come to the forefront of investigation: collision broadened far-wings of allowed water transitions [26,27] (free-free transitions arising from the allowed dipole moments of isolated molecules), diamers [26,27] (bound-bound and bound-free transitions involving the dipole moments of the pairs), and collision-induced absorption [26,27] (arising from transient dipoles induced during collisions). In the framework of this thesis, the third mechanism is of particular interest, it is here that the methods developed hitherto could be of benefit. But the exact role played by CIA in the continuum problem remains an open question.

## 7.1 The Water Molecule

The water molecule is composed of one oxygen atom and two hydrogen atoms, arranged in a structure depicted in the Figure 7.1.



Figure 7.1: The structure of the water molecule [28]

The angle between the two H-O bonds is  $104^0$  36'. The hydrogen atoms are identical, thus the water molecule has the following symmetry properties: one two-fold axis, and two planes going through this axis at right angles to each other. These symmetries indicate that the water molecule belongs to the point group C<sub>2v</sub> [3, 28].



Figure 7.2: The symmetry properties of the water molecule [28]

In the gas phase, the water molecule rotates freely about an instantaneous axis, thus acting like a rigid rotor. The moment of inertia of a rigid body about an axis is defined to be

$$I = \sum_{i} m_{i} r_{i}^{2}$$
(7.1)

where  $r_i$  is the distance perpendicular to the axis of the mass element  $m_i$ . The water molecule has no three-fold or higher axis [28], thus the three principal moments of inertia,  $I_x$ ,  $I_y$ , and  $I_z$ , are not equal. Therefore the water molecule behaves as an asymmetric top [28]. In calculating the structure of the rotational energy levels, one must use a different procedure than one employed for the case of the symmetric top. Wang [28] in 1929, put forward a theory in which the rotational energy of asymmetric top has the form

$$E_{J\sigma} = \frac{\hbar}{2} \left[ SJ(J+1) + W_{\sigma} \right]$$
(7.2)

where J and  $\sigma$  are the angular momentum quantum numbers. J takes on the values: 0, 1, 2, ..., and for each J, there are 2J + 1 sublevels labelled by  $\sigma$ ,  $\sigma = -J$ , -J + 1, ..., J - 1, J. The constant, S, can be determined from the three principal moments of inertia, while  $W_{\sigma}$  can be obtained through solving the secular equation:

where

$$f(J,\sigma) = -\frac{1}{2} [(J-\sigma)(J-\sigma+1)(J+\sigma)(J+\sigma+1)]^{1/2}$$
(7.4)

For each value of J, the determinant can be expressed by four algebraic equations, with a total of 2J + 1 roots of  $W_{\sigma}$ . The lowest value corresponds to  $W_{-J}$ , and the highest, to  $W_{J}$ . This results in the energy level scheme depicted in Figure 7.3.



Figure 7.3: The structure of rotational energy levels of the water molecule [28]

The water molecule has a permanent dipole moment [3,28]. The selection rule for J is

$$\Delta \mathbf{J} = \mathbf{0}, \pm \mathbf{1}. \tag{7.5}$$

The selection rule for the quantum number  $\sigma$  is more difficult to obtain. Consideration of the rotational eigenfunction probability with respect to changes of orientation of the ellipsoid formed by the three moments of inertia must be made [28].

#### 7.2 Measurements of the Water Vapour Spectrum

Preliminary measurements were made of the water vapour spectrum in a nitrogen perturber bath using the methods of Fourier Transform Spectroscopy. A Nexus 870 FT-IR E.S.P. Michelson interferometer together with a 10 m multipass gas cell both manufactured by Nicolet were used to take the spectra. A simple gas transfer vacuum system was used to transfer sample into the cell. The region of interest was the far infrared; thus the multipass cell had to be fitted with polyethylene windows, which are transparent in this region. On the transfer system, primary vacuum was achieved using a mechanical pump, while a lower vacuum pressure was achieved using an oil diffusion pump. Pressure was measured directly in the multi-pass cell using a piezo transducer accurate to 0.1 Torr. Illustrations of the interferometer and multi-pass cell are shown below.



Figure 7.4a: External view of the Nexus 870 FT-IR E.S.P. Michelson interferometer [taken from Nicolet Nexus 870 instruction manual]



Figure 7.4b: Internal view of the Nexus 870 FT-IR E.S.P. Michelson interferometer [taken from Nicolet Nexus 870 instruction manual]



Figure 7.5: The 10 m multi-pass cell

The general procedure followed was the following: the multi-pass cell was purged with the mechanical pump and then the diffusion pump was engaged to evacuate the cell for 24 hours. A small sample of water vapour was then added in the range of pressure from 1 Torr to 100 Torr. Water was transferred to the multi-pass cell via a small sample cell, which was attached to the vacuum system. Then  $N_2$  was let into the multi-pass cell. To ensure a minimum escape of water vapour, the pressure of the nitrogen was kept higher, from 250 to 700 Torr, than the pressure in the water vapour inside the multi-pass cell. Upon completion of its filling, the cell was transferred to the interferometer where the background and sample interferograms were taken. Before each scan, the intensity of the source in proportion to the aperture size was adjusted as well as the gain of the

detector. The source used was a ceramic "Globar" and the detector was "DTGS Polyethylene" and the beam-splitter was "Solid Substrate". The interferograms were reprocessed into absorbance spectra at a resolution of 0.125 cm<sup>-1</sup> using the Fast Fourier Transform algorithm, with Happ-Genzel apodization, Mertz phase correction, and no zero-filling.

Two representative spectra are shown in figures 7.6 and 7.7 below. The first is the spectrum of water vapour only, at a pressure of 2.5 +/- 0.1 Torr and a resolution of 0.125 cm<sup>-1</sup>. It was compiled with 128 passes of the mirror moving at 0.1581 cm/s. The second spectrum is of the same sample of water-vapour at 2.5 Torr with the addition of 530 Torr of nitrogen gas. Again 128 scans of the mirror were made at a velocity of 0.1581 cm/s. The region of interest for both spectra was the absorption of far infrared radiation by the water molecule. Thus the spectral range from 50 to 450 cm<sup>-1</sup> was sampled. Immediately we see that the spectrum of pure water-vapour is very complicated in the low wavenumber region. This is adequately explained by the presence of many rotational energy levels present in the water molecule, as seen in Figure 7.3. If we compare the two graphs, however, we see a curious feature. In the second graph with the presence of N<sub>2</sub>, the absorbance does not fall off to zero away from the spectral lines, particularly in the region between 100 and 200 cm<sup>-1</sup>.



Figure 7.6: Absorption spectrum of water vapour only, at a pressure of 2.5 +/- 0.1 Torr and a resolution of 0.125 cm<sup>-1</sup>.



Figure 7.7: Spectrum is of the same sample of water-vapour at 2.5 Torr with the addition of 530 Torr of nitrogen gas at a resolution of 0.125 cm<sup>-1</sup>. Water vapour continuum is beginning to form at low frequencies.

This anomalous excess absorption has been known for some time now and has been given the name "The far-infrared water vapour continuum" [27]. As mentioned above, the exact mechanisms leading to an explanation of the continuum are in some dispute and are a topic of intensive research [26,27].

# 7.3 Implications for the Collision-Induced Absorption Spectrum

As a direct possible application of the general ideas of this thesis and a motivation for future work in this area, one can consider the collision-induced absorption (CIA) behaviour of the water molecule with a nitrogen perturber. CIA, unlike CILS involves only the interaction of the permanent molecular multipole moments in the sample under study [7]. One is interested in the attenuation of the incident radiation due to the collision-induced dipole moment of a pair of molecules in the sample. This is portrayed schematically in figure 7.8:





The probability of absorption of a light wave by a pair of molecules is proportional to the square of the matrix element involving the pair collision-induced dipole moment [7]

$$Abs_{1\to 2} \propto \left| \left\langle \phi_1 \left| \mu_{CIA} \right| \phi_2 \right\rangle \right|^2 \tag{7.6}$$

where  $\phi_1$  and  $\phi_2$  are molecular rotational states and  $\mu_{CIA}$  is the collision-induced dipole moment of the pair. But from figure 7.8 together with the formalism developed in this thesis we know that the collision-induced dipole moment is in reality the tensor product of the permanent dipole-moment of water, the permanent quadrupole moment of nitrogen and the **T** tensor describing their electro-magnetic interaction. That is,  $\mu_{CIA}$  is of the form

$$\mu_{\text{CIA}} = \alpha_{\text{L}}^{(\text{H}_2\text{O})} \otimes \text{T}_{\text{N}} \otimes \Theta_{\text{Q}}^{(\text{N}_2)}$$
(7.7)

from which (7.6) may be expressed as

$$Abs_{1\to 2} \propto \left| \left\langle \phi_1 \left| \alpha_L^{(H_2O)} \otimes T_N \otimes \Theta_Q^{(N_2)} \right| \phi_2 \right\rangle \right|^2$$
(7.8)

Unlike the molecules that have been considered up to now in the thesis, water has the symmetry properties of an asymmetric top; leading to the explicit presence of more than one polarizability tensor component. For the case of the dipole polarizability  $\alpha$ ,  $\alpha_{xx}$ ,  $\alpha_{yy}$  and  $\alpha_{zz}$  all differ [7,9]. Whereas, N<sub>2</sub> is a homoatomic-linear molecule, belonging to the group C<sub>evv</sub>. Being axially symmetric, it does not posses a permanent dipole moment but does posses a permanent quadrupole moment,  $\Theta$  [7,8]. Thus the spherical components of the of the dipole polarizability,  $\alpha_{LM}$  are:

$$\alpha_{00} = \frac{-\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right)}{\sqrt{3}}$$

$$\alpha_{11} = 0$$

$$\alpha_{10} = 0$$

$$\alpha_{1-1} = 0$$

$$\alpha_{22} = \frac{\alpha_{xx} - \alpha_{yy}}{2}$$

$$\alpha_{21} = 0$$

$$\alpha_{20} = \frac{-\left(\alpha_{xx} + \alpha_{yy} - 2\alpha_{zz}\right)}{\sqrt{6}}$$

$$\alpha_{2-1} = 0$$

$$\alpha_{2-2} = \frac{\alpha_{xx} - \alpha_{yy}}{2}.$$

(7.9)

For molecules in the group  $C_{wv}$ , the quadrupole moment tensor is specified by only a single constant [7,9], thus the spherical component of the of the quadrupole polarizability,  $\Theta_{QR}$  is:

$$\Theta_{20} = \Theta_{ZZ} \tag{7.10}$$

Values for these components have been calculated using quantum mechanical methods and are shown in Gray and Gubbins [9]. With these components in hand, one can utilize the mathematical principles described, developed and exploited in the previous calculation of the characteristics of induced light scattering to calculate the CIA of the water molecule.

## **CHAPTER 8: Summarizing Discussion**

In this thesis, we have outlined a method for calculating CILS intensities and depolarization ratios using a formalism based on irreducible spherical tensors. In chapter 2, we saw that the polarizability of a pair of widely separated molecules is the sum of their isotropic polarizabilities, and that observed scattered radiation will only have a non-zero intensity component polarized in the direction of the incident radiation due to the properties of a radiating dipole. However, when the separation between the two molecules is small enough, the polarizability will have a correction, which arises due to their interaction, and occurs to arbitrary order. This results in an observed non-zero intensity that is depolarized with respect to the incident radiation.

Furthermore, it was explained that the polarizability is in general a tensor quantity depending on multiple spatial directions simultaneously, and initially the theory of CILS was worked out in the Cartesian basis. Although this has an advantage in being conceptually very simple, it holds a disadvantage in that unless the tensors being considered are of low rank (<3), the number of components needed to specify them becomes very large. In an attempt to try to circumvent some of these issues, a parallel formulation using spherical tensors has been developed but its use has been more limited because it is conceptually more difficult to interpret. Thus, up to this writing it had only been applied to investigate the first-order correction of the pair polarizability.

Therefore, one of the main thrusts of the thesis was to extend the spherical tensor CILS formalism so that the contribution to the pair polarizability from the second-order correction could be investigated. In chapters 4 and 5, it was shown how this could be

achieved in a consistent manner and in chapter 6, how the resulting intensities and depolarization ratios could be calculated using symbolic programming techniques. The results of the programming show a general increase in the size of the numerator and denominator in the depolarization ratio in both first and second-order cases, even though the ratio itself always remains less than unity. Specifically in the second-order case, the depolarization ratio ranges from:

$$\eta = \frac{1}{8}$$
, corresponding to the interaction:  $\alpha T_2 \alpha T_2 \alpha$   
to  
 $\eta = \frac{31319508444429}{72426524351788}$ , corresponding to the interaction:  $AT_5ET_6E$ 

This trend reflects the general increase in complexity of the polarizabilities acting in a particular interaction. However, this rule does not appear to hold absolutely as there also appears to be a strong dependence on the order of the polarizabilities for each molecule, which is not manifest in the first-order case. As an example, consider the case,

 $\alpha T_3 A T_3 \alpha$ , which has three possible configurations:

1	$\alpha T_3 A T_3 \alpha$	$\eta = \frac{1269}{3692}$
2	$AT_3 \alpha T_2 \alpha$	$\eta = \frac{369}{572}$
3	$\alpha T_2 \alpha T_3 A$	$\eta = \frac{171}{548}$

We see that configuration 1 has a depolarization ratio composed of factors far larger than the either of the other two cases, whose factors are comparable to each other. A possible explanation for this state of affairs is that because molecule 2 is not treated as a radiator in the interaction, it is in some sense in a virtual state. It is not known which multipole is being induced in molecule 2 if the polarizability considered has more than one type of multipole associated with it, and all the possible contributions associated with that polarizability must be accounted for. Thus configuration 1 above involves both dipolar and quadrupolar contributions from molecule 2, and so the depolarization ratio is more complicated than for configurations 2 and 3 which only involve dipolar contributions from molecule 2.

In figures 7.5 and 7.6 we show far-infrared spectra, from 50 to 600 wavenumbers, of water vapor-nitrogen mixtures obtained using the technique of Fourier Transform spectroscopy. The measurements were made at a resolution of 0.125 wavenumbers and at mixture pressures ranging from several tenths of a Torr to about 530 Torr. The most significant feature of these spectra are their i) complexity, indicating that water is a very strong absorber in this region of the electromagnetic spectrum, and ii) the presence of the water vapour continuum, which is clearly seen in figure 7.6.

As a way of concluding this thesis, a few comments can be made about possible directions for further research. As a direct extension of the work presented here, the intensities for collision-induced absorption in water vapour can be calculated. In addition the analytic form for the depolarization ratio presented in Appendix F is for the case of the first-order interaction only. However, the procedure presented is general and so one should be able to extend it to obtain an analogous expression for the second-order case. In fact, such an endeavour could act as an appropriate consistency check for the results obtained by calculating the entire autocorrelation function.

## **APPENDIX A: Selection Rules**

When discussing the spectrum of CILS it is important to consider the selection rules, which govern the allowed rotational transitions. Our discussion mirrors that found in Buckingham and Tabisz [8], and Shelton [12].

The calculation of the spectral distribution is analogous to the quantum mechanical calculation of the spectrum for a diatomic rotor, however now one must consider the rotational states of both molecules in the pair [8,12]. Therefore, the quantities that will be of interest are of the form:  $|\langle J'_1 J'_2 | \alpha_{\alpha\beta} | J_1 J_2 \rangle|$  where J<sub>i</sub> and J'<sub>i</sub> are initial and final rotational states of molecule i, and  $\alpha_{\alpha\beta}$  is the pair polarizability [8,12]. As wavefunctions, one uses the normalized symmetric-top wavefunction for a molecule in rotational state J, given as  $[(2J+1)/8\pi^2]^{1/2}D_{mk}^{J*}(\Omega)$ , m is the quantum number associated with the projection of the angular momentum J on the space-fixed Z axis and k is the quantum number associated with the projection of J on the molecule-fixed z axis.  $D_{mk}^{J*}(\Omega)$  is the Wigner rotation matrix where both k and m have (2J+1) components, and each rotational state J is  $(2J+1)^2$  degenerate which is the rigid-rotor approximation [8].

As a specific example of the technique, we can consider the tensor **A**, and it must be noted that the terms which are only dependent on isotropic polarizabilities,  $\alpha_i$  (rank of  $\alpha_i = 0$ ) do not give rise to a rotational spectrum [8,12]. As an example, consider pair polarizability contribution:

$$\frac{1}{3}T_{\alpha\gamma\delta}\left(\alpha(1)A_{\beta,\gamma\delta}(2) - \alpha(2)A_{\beta,\gamma\delta}(1)\right) + \frac{1}{3}T_{\beta\gamma\delta}\left(\alpha(1)A_{\alpha,\gamma\delta}(2) - \alpha(2)A_{\alpha,\gamma\delta}(1)\right). \quad (A.1)$$

This can be rewritten in spherical form; in the molecule-fixed frame there are only two non-zero components to the spherical tensor A in  $T_d$  symmetry. Thus in the space-fixed coordinate system, A is given as

$$A_{m}^{3} = i\sqrt{3}A \Big( D_{m2}^{3*}(\Omega) - D_{m-2}^{3*}(\Omega) \Big),$$
(A.2)

in the Wigner rotation matrix notation [8]. Here,  $\Omega$ , represents the Euler angles between the space-fixed and molecule-fixed frames [8]. The matrix elements  $|\langle J'_1 J'_2 | \alpha_{\alpha\beta} | J_1 J_2 \rangle|$ reduce to

$$\left| \left\langle J_{1}' J_{2}' \left| D_{m2}^{3*}(\Omega) - D_{m-2}^{3*}(\Omega) \right| J_{1} J_{2} \right\rangle \right|,$$
 (A.3)

from which the selection rules on  $\Delta J$  can be obtained as,

$$\Delta J_{i} = 0; \Delta J_{j} = 0, \pm 1, \pm 2, \pm 3, (J_{j} + J'_{j} \ge 3).$$
(A.4)

The subscripts i and j represent either a 1, 2 or a 2, 1 molecular pair [8].

Applying a similar analysis for the terms of type,  $\alpha_i E_i$ , gives the selection rules as:

$$\Delta J_{i} = 0; \Delta J_{j} = 0, \pm 1, \pm 2, \pm 3, \pm 4 \ (J_{j} + J'_{j} \ge 4).$$
(A.5)

Contributions to the pair polarizability involving  $A_1A_2$  result from the gradient of the field of the induced quadrupole and lead to double rotational transitions;

$$\Delta J_{i} = 0 \pm 1, \pm 2, \pm 3, \quad (J_{i} + J'_{i} \ge 3)$$

$$\Delta J_{j} = 0, \pm 1, \pm 2, \pm 3, \quad (J_{j} + J'_{j} \ge 3).$$
(A.6)

This results because A tensors are involved for both molecules [8].

The Stokes spectral intensity resulting from the rotational transitions

 $J_{i}J_{j} \rightarrow J'_{i}\,J'_{j}$  is proportional to

$$\Gamma(J'_{i}, J'_{j}, J_{i}, J_{j}) = \omega_{R}^{4} (2J'_{1}+1)(2J'_{2}+1)(2J_{1}+1)(2J_{2}+1) \times \exp\{-[J_{1}(J_{1}+1)B_{1}+J_{2}(J_{2}+1)B_{2}]hc/kT\}$$
(A.7)

where,

$$\omega_{\mathsf{R}} = \omega_0 - [J'_1(J'_1+1) - J_1(J_1+1)]B_1 - [J'_2(J'_2+1) - J_2(J_2+1)]B_2. \tag{A.8}$$

Here,  $\omega_0$  is the incident light frequency and  $B_i$  is the rotational constant of molecule i [8,12].

.

## **APPENDIX B: Useful MATHEMATICA Functions**

In this appendix, we will list some explicit Mathematica functions that were used in the implementation of the ideas of this thesis. All of these have been explicitly taken from reference [30], and are gathered here for the convenience of the reader.

Sqrt[A]: Calculates the square root of A

ClebschGordan[{j1,m1}, {j2,m2}, {j,m}]: Calculates the Clebsch-Gordan coefficient of the arguments

SixJSymbol [{a,b,c}, {d,e,f}]: Calculates the Wigner 6j symbol of the arguments

 $Sum[F[x], \{x, -n, n\}]$ : Calculates the sum of F[x] with x ranging from -n to n

# **APPENDIX C: Useful Spherical Tensor Relationships**

In this appendix, we will list some explicit spherical tensor identities that greatly simplify the operations of spherical tensor algebra. All of these have been explicitly taken from reference [20], and are gathered here for the convienience of the reader.

$$\left\{\left\{P_{a}\otimes Q_{b}\right\}_{c}\otimes R_{d}\right\}_{f}=\left(-1\right)^{a+b+f+d}\sum_{h}X_{hc}\begin{cases}a&b&c\\d&f&h\end{cases}\left\{P_{a}\otimes\left\{Q_{b}\otimes R_{d}\right\}_{h}\right\}_{f}$$
(C.1)

$$\left\{\left\{P_{a}\otimes Q_{b}\right\}_{c}\otimes R_{d}\right\}_{f}=\left(-1\right)^{c+d+f}\sum_{h}X_{ch}\left\{\begin{matrix}a&b&c\\f&d&h\end{matrix}\right\}\left\{Q_{b}\otimes\left\{P_{a}\otimes R_{d}\right\}_{h}\right\}_{f}$$
(C.2)

$$\left(\left\{\mathbf{P}_{a}\otimes\mathbf{Q}_{b}\right\}_{c}\cdot\mathbf{R}_{c}\right)=\left(-1\right)^{-a}\frac{X_{c}}{X_{b}}\left(\mathbf{Q}_{b}\cdot\left\{\mathbf{P}_{a}\otimes\mathbf{R}_{c}\right\}_{b}\right)$$
(C.3)

$$\left\{\left\{P_{a}\otimes Q_{b}\right\}_{c}\otimes\left\{R_{d}\otimes S_{e}\right\}_{f}\right\}_{k}=\sum_{gh}X_{cfgh}\begin{cases}a & b & c\\d & e & f\\g & h & k\end{cases}\left\{\left\{P_{a}\otimes R_{d}\right\}_{g}\otimes\left\{Q_{b}\otimes S_{e}\right\}_{h}\right\}_{k}\qquad(C.4)$$

$$\begin{cases} Y_{l_{1}'}(\Omega_{1}) \otimes Y_{l_{2}'}(\Omega_{2})_{L_{1}'}^{M'} \cdot \left\{ Y_{l_{1}'}(\Omega_{1}) \otimes Y_{l_{2}'}(\Omega_{2})_{L_{2}'}^{M'} = \sum_{LM} \sum_{l_{1}l_{2}} \left\langle L'L'', M'M'' \middle| LM \right\rangle \frac{X_{l_{1}'l_{2}'l_{1}''_{2}L'L'}}{4\pi} \\ \times \left\langle l_{1}'l_{1}'', 00 \middle| l_{1}0 \right\rangle \left\langle l_{2}'l_{2}'', 00 \middle| l_{2}0 \right\rangle \begin{cases} l_{1}' & l_{1}'' & l_{1} \\ l_{2}' & l_{2}'' & l_{2} \\ L' & L''' & L \end{cases} \begin{cases} Y_{l_{1}}(\Omega_{1}) \otimes Y_{l_{2}}(\Omega_{2})_{L}^{M'} \end{cases}$$
(C.5)

$$\sum_{xy} (-1)^{x+y} X_{x^2y^2} \begin{cases} a & b & x \\ c & d & y \\ p & q & s \end{cases} \begin{cases} e & f & x \\ g & h & y \\ r & t & s \end{cases} \begin{cases} a & b & x \\ g & h & y \\ f & e & k \end{cases} \begin{cases} c & d & y \\ h & g & m \end{cases}$$

$$= (-1)^{k+m+a+c+p-s-h-t-f} \sum_{z} (-1)^{z} X_{z^2} \begin{cases} c & g & m \\ a & e & k \\ p & r & z \end{cases} \begin{cases} f & b & k \\ h & d & m \\ t & q & z \end{cases} \begin{cases} p & r & z \\ t & q & s \end{cases}$$
(C.6)

.

$$\left(\left\{P_{a}\otimes Q_{b}\right\}_{c}\cdot\left\{R_{d}\otimes S_{e}\right\}_{c}\right)=\left(-1\right)^{2a+b-d}\sum_{g}X_{cc}\left\{\begin{matrix}a&b&c\\e&d&g\end{matrix}\right\}\left(\left\{P_{a}\otimes R_{d}\right\}_{g}\cdot\left\{Q_{b}\otimes S_{e}\right\}_{g}\right)\right) (C.7)$$

## **APPENDIX D: Sample Input**

Below is an example of the first order correction being calculated for the case of  $\alpha T \alpha$ :

```
N1=2;
             <- rank of interaction tensor
j1=0;
             <- rank of polarizability of molecule 1
j2=0;
             <- rank of polarizability of molecule 2
11=1;
             <- rank of multipole moment operator of molecule 1
m1=1;
A[1,0,1,0] := -Sqrt[3] * \alpha;
                                <- components of dipole polarizability
A[2,0,1,0] := -Sqrt[3] * \alpha;
j=0;
             <- rank of pair polarizability
F00=(2 j+1) 2(-1)^(11+m1) (2N1)!/Sqrt[(2 11)! (2 (N1-11))! (2 m1)! (2
(N1-m1))! R<sup>(-2</sup> (N1+1)) (1+(-1)<sup>(j1+N1+j2+j)</sup>) Sum[(2 x+1)]
SixJSymbol[{1,1,x}, {1,1,j}] SixJSymbol[{1,1,x}, {N1-11,N1-m1,j2}]
```

SixJSymbol[{N1-11,N1-m1,x}, {m1,11,N1}] SixJSymbol[{m1,11,x}, {1,1,j1}], {x,0,2}] (Sum[(-1)^m A[1,j1,11,m]

```
A[1,j1,m1,-m],{m,-j1,j1}] Sum[(-1)^m A[2,j2,(N1-11),m] A[2,j2,(N1-m1),-
m],{m,-j2,j2}]);
```

```
Clear[j];
```

```
j=2; <- rank of pair polarizability
F22=(2 j+1) 2(-1)^(l1+m1) (2N1)!/Sqrt[(2 l1)! (2 (N1-l1))! (2 m1)! (2
(N1-m1))!] R^(-2 (N1+1)) (1+(-1)^(j1+N1+j2+j)) Sum[(2 x+1)
SixJSymbol[{1,1,x},{1,1,j}] SixJSymbol[{1,1,x},{N1-l1,N1-m1,j2}]
SixJSymbol[{N1-l1,N1-m1,x},{m1,l1,N1}]
SixJSymbol[{N1-l1,N1-m1,x},{m1,l1,N1}]
SixJSymbol[{m1,l1,x},{1,1,j1}],{x,0,2}] (Sum[(-1)^m A[1,j1,l1,m]
A[1,j1,m1,-m],{m,-j1,j1}] Sum[(-1)^m A[2,j2,(N1-l1),m] A[2,j2,(N1-m1),-m],{m,-j2,j2}]);
Clear[N1,j1,j2,l1,m1,j];</pre>
```

```
alphaXZ=F22/10

alphaZZ=F00/3 + (2 F22)/15

Iso = alphaZZ-4/3 (F22/10)

\etan=6 F22/(7 F22+10 F00) <- calculation of depolarization ratio \eta_n

\eta=\etan/(2-\etan) <- calculation of depolarization ratio \eta
```

$12 \alpha^4$	
5 R <sup>6</sup>	<- output for intensity $\langle \alpha_{xz}^2 \rangle$
$16 \alpha^4$	
5 R <sup>6</sup>	<- output for intensity $\langle \alpha_{zz}^2 \rangle$
0	
6	
7	<- output for depolarization ratio $\eta_n$
3	
4	<- output for depolarization ratio $\boldsymbol{\eta}$

Here is an example of the second-order correction being calculated for the case of  $\alpha T_2 \alpha T_2 \alpha$ , the meanings of the functions are the same as in the first order case except where indicated:

•

11 = 1;	<- rank of multipole moment operator of molecule 1
n2 = 1; 12 = 1;	<- ranks of multipole moment operators of molecule 2
n3 = 1;	<- rank of multipole moment operator of molecule 1
j1 = 0; j2 = 0; j3 = 0;	<- rank of polarizability of molecule 1 - <- rank of polarizability of molecule 2 <- rank of second-order polarizability of molecule 1
a1 = 11; a2 = 12; b2 = n2; b3 = n3;	
Diff=1;	<- user specified difference for the interaction tensors
N1 = 11 + 12; N2 = 12 + n3;	<- rank of interaction tensor
NineJSymbol Sum[(-1) <sup>2</sup> *SixJSy	[{a_, f_, r_}, {d_, q_, e_}, {p_, c_, b_}] := <sup>T</sup> (2 T + 1) SixJSymbol[{a, b, T}, {c, d, p}] * SixJSymbol[{c, d, T}, {e, f, q}] mbol[{e, f, T}, {a, b, r}], {T, 0, N1}]; <- Wigner 9j symbol function
Triangular[	a_, b_, c_] := If[Abs[a - b] ≤ c ≤ a + b, 1, 0]; <pre>&lt;-checks triangular inequality</pre>
CompSum[N1_	, N2_, Q_] := If[N1 ≠ N2 && Abs[N1 - N2] == Q, 1, 0]; <- Compares the ranks of the interaction tensors with a user specified difference

# H[j]:= (2j+1)4Sun

<- intensity calculating function when molecule 2 polarizability has multiple contributions

Sum Sun

Sun

Sum

Sun

 $Sun[Sun[(-1)^{(B+C+\lambda+j1+j2+j3+j)} (Sqrt[(2N1)!(2N2)!(2N1)!(2N2)!]/Sqrt[$ 

(211) ! (212) ! (212) ! (2n3) ! (2a1) ! (2a2) ! (2a2) ! (2b3) !]) R^(-2 (H+N2+2)) (2H1+1) (2H2+1)

(2X+1) (2C+1) (2A+1) (2K+1) (2F+1) (2G+1) (ClebschGardan [{N1, 0}, {N2, 0}, {B, 0}])<sup>2</sup> Triangular [N1, N2, B] Triangular [j2, j3, G] Triangular [j1, X, G] CompSum[NL, N2, Diff]

Six/Symbol [{G, N2, C}, {K, j1, X}]Six/Symbol [{G, N2, A}, {F, j1, X}] Six/Symbol [{N2, X, K}, {j, N1, B}]

Six/Synbol [{N2, X, F}, {j, N1, B}] Nine/Synbol [{j1, C, K}, {1, 1, j}, {11, 12, N1}]

NinelSymbol [{j1, A, F}, {1, 1, j}, {a1, a2, N1}] NinelSymbol [{j2, j3, G}, {12, 1, C}, {12, n3, N2}]

NinelSymbol [{j2, j3, G}, {a2, 1, A}, {a2, b3, N2}]

(Sm[(-1) ^m A[1, j1, 1, 11, m] A[1, j1, 1, a1, -m], {m, -j1, j1}]Sm[(-1) ^m A[2, j2, n2, 12, m] A[2, j2, h2, a2, -m], {m, -j2, j2}]Sm[(-1) ^mA[1, j3, 1, n3, m] A[1, j3, 1, h3, -m], {m, -j3, j3}])

, {X, Abs[j1+12+1-N2], j1+12+1+N2}], {B, Abs[N1-N2], N1+N2}], {C, Abs[12-1], 12+1}], {A, Abs[a2-1], a2+1}], {K, #ks[j1-l2-1], j1+l2+l}], {F, #ks[j1-a2-1], j1+a2+l}], {G, #ks[j2-j3], j2+j3}], {N1, (L1+l2) - Diff, 11+l2}],  $\{12, (12+n3) - Diff, 12+n3\}$ ;

F[j] := (2j+1)4

> 9m Sum Sum[

Sum

Sum

9m

 $\mathbf{Sun}[((-1)^{(B+C+\Delta+j1+j2+j3+j)} (\mathbf{Surt}[(2N1)!(2N2)!(2N1)!(2N2)!)] /$ 

 $\mathbf{Spt}[(211)!(212)!(212)!(213)!(2n3)!(2a1)!(2a2)!(2a2)!(2b3)!]) \mathbb{R}^{(-2(\mathbf{N}_{1}+\mathbf{N}_{2}+2))}(2\mathbf{N}_{1}+1)(2\mathbf{N}_{2}+1)$  $(2X+1)(2C+1)(2\Delta+1)(2K+1)(2F+1)(2G+1)(ClebschGordan[{NL, 0}, {N2, 0}, {B, 0}])^2$ Triangular[NL, N2, B] Triangular[j2, j3, G] Triangular[j1, X, G] SixJSymbol[{G, N2, C}, {K, j1, X}] SixJSymbol[{G, N2, △}, {F, j1, X}]

SixEyabol[{N2, X, K}, (j, N1, B}] SixEyabol[{N2, X, F}, (j, N1, B}]

 $\label{eq:linear} NinearSymbol[{j1, C, K}, {1, 1, j}, {11, 12, M}] \\ NinearSymbol[{j1, \Delta, F}, {1, 1, j}, {a1, a2, M}] \\$ 

 $\label{eq:linearized_linearized$ 

(Sum[(-1) ^mA[1, j1, 1, 11, m] A[1, j1, 1, a1, -m], {m, -j1, j1}]

Sum[ (-1) ^mA[2, j2, n2, 12, m] A[2, j2, b2, a2, -m], {m, -j2, j2}]

 $Sum[(-1) ^mA[1, j3, 1, n3, m] A[1, j3, 1, b3, -m], \{m, -j3, j3\}])$ 

,  $\{X, Abs[j1+12+1-N2], j1+12+1+N2\}$ ,  $\{B, Abs[N1-N2], N1+N2\}$ ,  $\{C, Abs[12-1], 12+1\}$ ,  $\{\Delta, Abs[a2-1], a2+1\}$ ,  $\{ \texttt{K}, \texttt{Abs}[\texttt{j}\texttt{1}-\texttt{1}\texttt{2}-\texttt{1}], \texttt{j}\texttt{1}+\texttt{1}\texttt{2}+\texttt{1} \} \big], \ \{ \texttt{F}, \texttt{Abs}[\texttt{j}\texttt{1}-\texttt{a}\texttt{2}-\texttt{1}], \texttt{j}\texttt{1}+\texttt{a}\texttt{2}+\texttt{1} \} \big], \ \{ \texttt{G}, \texttt{Abs}[\texttt{j}\texttt{2}-\texttt{j}\texttt{3}], \texttt{j}\texttt{2}+\texttt{j}\texttt{3} \} \big];$ 

```
A[1,0,1,1,0]:= - Sqrt[3]*α1;
A[2,0,1,1,0]:= - Sqrt[3]*α2;
```

```
A[1,3,1,2,3]:=0; <- components of dipole-quadrupole polarizability
A[1,3,1,2,2]:= i*Sqrt[2]*A1;
A[1,3,1,2,1]:=0;
A[1,3,1,2,-1]:=0;
A[1,3,1,2,-2]:= - i*Sqrt[2]*A1;
A[1,3,1,2,-3]:=0;
A[2,3,1,2,3]:=0;
A[2,3,1,2,1]:=0;
A[2,3,1,2,1]:=0;
A[2,3,1,2,0]:=0;
A[2,3,1,2,-1]:=0;
A[2,3,1,2,-1]:=0;
A[2,3,1,2,-3]:=0;
A[2,3,1,2,-3]:=0;</pre>
```

```
A[1,4,1,3,4]:=Sqrt[10]/4E1;
A[1,4,1,3,3]:=0; <- components of dipole-octopole polarizability
A[1,4,1,3,2] := 0;
A[1,4,1,3,1]:=0;
A[1,4,1,3,0]:=Sqrt[7]/2E1;
A[1,4,1,3,-1]:=0
A[1,4,1,3,-2]:= 0;
A[1,4,1,3,-3]:=0;
A[1,4,1,3,-4]:=Sqrt[10]/4E1;
A[2,4,1,3,4]:=Sqrt[10]/4E2;
A[2,4,1,3,3]:=0;
A[2,4,1,3,2] := 0;
A[2,4,1,3,1]:=0;
A[2,4,1,3,0]:=Sqrt[7]/2E2;
A[2,4,1,3,-1]:=0
A[2,4,1,3,-2]:= 0;
A[2,4,1,3,-3]:=0;
A[2,4,1,3,-4]:=Sqrt[10]/4E2;
```

```
A[1, 4, 2, 2, -4] := 0;
A[1, 4, 2, 2, -3] := 0;
A[1, 4, 2, 2, -2]:= 3C/Sqct[7];
A[1, 4, 2, 2, -1] := 0;
A[1, 4, 2, 2, 0] :=4Sqct[2/35]C;
A[1, 4, 2, 2, 1] := 0;
A[1, 4, 2, 2, 2] := 3C/Sqrt[7];
A[1, 4, 2, 2, 3] := 0;
A[1, 4, 2, 2, 4] := 0;
A[2, 4, 2, 2, -4]:= 0;
A[2, 4, 2, 2, -3] := 0;
A[2, 4, 2, 2, -2]:= 3C/Sqct[7];
A[2, 4, 2, 2, -1] := 0;
A[2, 4, 2, 2, 0] :=4Sqct[2/35]C;
R[2, 4, 2, 2, 1] := 0;
A[2, 4, 2, 2, 2] := 3C/Sqct[7];
A[2, 4, 2, 2, 3] := 0;
A[2, 4, 2, 2, 4] := 0;
```

- calculates the second-order intensity

 $If [n2 == 1 & l2 \neq 1, (alpha Z = H[2] / 10; alpha Z = H[0] / 3 + 20 \\ alpha Z / 15; ), (alpha Z = F[2] / 10; alpha Z = F[0] / 3 + 2F[2] / 15; )];$ 

 $\begin{aligned} &\operatorname{Print}[`` < & \alpha_{ss}^2 > = ", \operatorname{Simplify}[alpha%Z]]\operatorname{Print}[`` < & \alpha_{ss}^2 > = ", \operatorname{Simplify}[alpha%Z]]\\ & \eta_1 = 2 \operatorname{alpha%Z}/(alpha%Z + alpha%Z);\\ & \eta_1 = \eta_1/(2 - \eta_1);\\ & \operatorname{Print}[`` & \eta_1 = ", \eta_1] \end{aligned}$ 

ClebschGordan	::tri	:	SixJSymbol	[{0, 2,	0},	{2,	0,0}]	is	not	triangular	•	More
ClebschGordan	::tri	:	SixJSymbol	[{0, 2,	0},	{2,	0,0}]	is	not	triangular		More
ClebschGordan	::tri	:	SixJSymbol	[{2, 0,	2},	{2,	2, 0]	is	not	triangular		More



# **APPENDIX E: Time-Correlation Functions and Rotational Averaging**

Whenever two systems are weakly coupled to one another (such as in the case of radiation weakly coupled to matter), it is only necessary to know how both systems behave in the absence of the coupling in order to describe the way in which one system responds to the other. This description is the goal of linear response theory, which shows that the response of one system to the other is completely describable by time-correlation functions of the dynamical variables of the systems [6]. Correlation functions provide a concise method for expressing the degree to which two dynamical properties are correlated over some average time interval.

Suppose we are concerned with a property A, which depends on the positions and momenta of all the particles in the system. Due to thermal motion, the particles are constantly jostling about thus the momenta and positions of each particle are constantly changing. Therefore, A is also constantly changing. Although the motion of the individual particle is described by Schrödinger's equation, the large number of them makes their motion appear random, so generally the time dependence of property A, A(t), resembles a noise pattern. Thus the (measured) bulk property of an equilibrium system is, in actuality, a time average:

$$\overline{A}(t_0, T) = \frac{1}{T} \int_{t_0}^{t_0+T} A(t) dt$$
(E.1)

where  $t_0$  is the time at which measurement was initiated and T is the averaging time [6]. Averages of this type are only meaningful if T>> $\Delta t$  where  $\Delta t$  is the period of the fluctuation, thus ideally

$$\overline{A}(t_0) = \lim_{T \to \infty} \frac{1}{T} \int_{t_0}^{t_0 + T} A(t) dt$$
(E.2)

If the average of the property under consideration is in general independent of  $t_0$ , it is referred to as a stationary property [6],

$$\langle A \rangle = \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} A(t) dt$$
 (E.3)

Considering A(t) more closely, we note that at two different times, t and t +  $\tau$ , A(t) can take on two different values such that A(t +  $\tau$ )  $\neq$  A(t), or A(t +  $\tau$ ) – A(t)  $\cong$  0. As  $\tau$  approaches  $\Delta t$ , A(t +  $\tau$ ) – A(t)  $\neq$  0 so A(t +  $\tau$ ) is correlated with A(t) if  $\tau \ll \Delta t$ , and this correlation is measured by the autocorrelation function [6]:

$$\langle A(0)A(\tau) \rangle = \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} A(t)A(t+\tau)dt$$
 (E.4)

An autocorrelation function is a measure of the similarity between two noise signals A(t)and  $A(t + \tau)$  [6]. When  $\tau = 0$ , the two signals are completely in phase and  $\langle A(0)A(\tau) \rangle$  is large; as t increases A(t) and  $A(t + \tau)$  become out of phase and  $\langle A(0)A(\tau) \rangle$  is small [6].

Using these results we can define the spectral density  $I_A(\omega)$  of the a time-correlation function as

$$I_{A}(\omega) \equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle A^{*}(0)A(\tau) \rangle e^{-i\omega t} dt$$
(E.5)

This quantity plays an important role in light scattering where sometimes one measures the spectral density of the electric field of the scattered light [6]. If we apply an inverse Fourier Transform to (E5) we obtain
$$\left\langle \mathbf{A}^{*}(0)\mathbf{A}(t)\right\rangle = \int_{-\infty}^{\infty} \mathbf{I}_{\mathbf{A}}(\omega)e^{-i\omega t}d\omega$$
 (E.6)

Thus we see that experimental determination of one is sufficient for determination of the other, with  $I_A(\omega)$  being the quantity that is usually measured. If we set t = 0, we get the mean-square value of property A, so that

$$\left\langle \left| A \right|^{2} \right\rangle = \left\langle \left| A(0) \right|^{2} \right\rangle = \int_{-\infty}^{\infty} I_{A}(\omega) d\omega$$
 (E.7)

In effect,  $I_A(\omega)d\omega$  is the "amount" of  $|A|^2$  in frequency interval ( $\omega$ ,  $\omega + d\omega$ ).

However, in dealing with the theory of light scattering the theoretical value of the autocorrelation function describing scattering from collections of molecules is required, and since the autocorrelation function frequently involves products of tensors, this amounts to evaluating isotropic averages to tensor components [16,29]. An expression for an observable, such as a polarization change in our case, is first written in terms of molecular property tensor components specified in space fixed axes. Because we want to relate the observable to intrinsic molecular properties, we must then transform to a set of axes fixed in the molecule's frame. Then if the molecule is tumbling freely, the expressions must be averaged over all orientations [16]. This problem reduces to the evaluation of products of direction cosines, averaged over all possible relative orientations of the two coordinate systems [16].

Thus, if we let the components of an nth rank tensor A with respect to a spacefixed frame be  $A_{i_1...i_n}$ , and if A refers to a molecular property, it can be expressed with respect to a molecule-fixed frame through the relation

$$A_{i_1...i_n} = c_{i_1\lambda_1}...c_{i_n\lambda_n}A_{\lambda_1...\lambda_n}$$
(E.8)

where  $c_{i_p\lambda_p}$  is the cosine of the angle between the space-fixed axis  $i_p$  and the moleculefixed axis  $\lambda_p$  [16,29]. The rotational average of  $A_{i_1...i_n}$  requires the rotational average of the direct cosine product  $c_{i_1\lambda_1}...c_{i_n\lambda_n}$ , which can be obtained if the direction cosines are expressed in terms of Euler angles. This leads to the following

$$\left\langle c_{i_{1}\lambda_{1}}...c_{i_{n}\lambda_{n}}\right\rangle = \frac{1}{8\pi^{2}} \int_{0}^{\pi} \int_{0}^{2\pi 2\pi} c_{i_{1}\lambda_{1}}...c_{i_{n}\lambda_{n}} \sin\theta d\theta d\phi d\psi$$
(E.9)

where  $\phi$ ,  $\theta$ ,  $\psi$  are the Euler angles relating the two frames [16,29]. The averaging procedure, though simple to use for tensors of low rank, becomes very tedious for high rank. Included in this are products of low rank tensors leading to high rank tensors. Therefore, techniques that re-express the property tensors in a form that allows one to circumvent some of this tediousness are of great practical importance. Exploring one such technique is of course the thrust of this thesis.

## **APPENDIX F: The Depolarization Ratio**

The purpose of this appendix is to act as a bit of an Afterward, and to report some interesting results derived concerning the depolarization ratio for first-order interactions. To our knowledge, this type of derivation does not appear anywhere in the literature. From chapter 6 we saw that the depolarization ratio is expressible in spherical form as

$$\eta = \frac{3F_{22}}{4F_{22} + 10F_{00}},\tag{F.1}$$

which can be rearranged to the simplified form

$$\eta = \frac{3}{4 + 10(F_{00}/F_{22})}.$$
 (F.2)

From chapter 5, we saw that the separation of the tensor components from the rank components means that the quotient inside the brackets reduces to

$$\frac{F_{00}}{F_{22}} = \frac{1}{5} \frac{\left[\sum_{x=0}^{2} (2x+1)^2 \begin{cases} N_1 & J & x \\ m_2 & 1 & J_2 \\ m_1 & 1 & J_1 \end{cases} \left[ N_1 & J & x \\ l_2 & 1 & J_2 \\ l_1 & 1 & J_1 \end{cases} \right]}{\left[\sum_{y=0}^{2} (2y+1)^2 \begin{cases} N_1 & J & y \\ m_2 & 1 & J_2 \\ m_1 & 1 & J_1 \end{cases} \left[ N_1 & J & y \\ l_2 & 1 & J_2 \\ l_1 & 1 & J_1 \end{cases} \right]},$$
(F.3)

or equivalently

$$\frac{F_{00}}{F_{22}} = \frac{1}{5} \frac{\left[\sum_{x=0}^{2} (2x+1)^{2} \begin{cases} 1 & 1 & x \\ 1 & 1 & 0 \end{cases} \begin{pmatrix} 1 & 1 & x \\ 1 & 1 & 0 \end{cases} \begin{pmatrix} 1 & 1 & x \\ 1_{2} & m_{2} & J_{2} \end{cases} \begin{pmatrix} 1_{2} & m_{2} & x \\ m_{1} & l_{1} & N \end{pmatrix} \begin{pmatrix} m_{1} & l_{1} & x \\ 1 & 1 & J_{1} \end{pmatrix} \right]}{\left[\sum_{y=0}^{2} (2y+1)^{2} \begin{pmatrix} 1 & 1 & y \\ 1 & 1 & 2 \end{pmatrix} \begin{pmatrix} 1 & 1 & y \\ l_{2} & m_{2} & J_{2} \end{pmatrix} \begin{pmatrix} 1_{2} & m_{2} & y \\ m_{1} & l_{1} & N \end{pmatrix} \begin{pmatrix} m_{1} & l_{1} & y \\ 1 & 1 & J_{1} \end{pmatrix} \right]}.$$
 (F.4)

To evaluate (F.4), the challenge remaining is to carry out the above sums. This may be accomplished using computer software like that employed in the thesis, or to analytically reduce the sums into polynomial expressions. This second method will be elucidated here.

It is advantageous to break up the sum into individual terms and deal with each, one at a time. Thus the numerator:

$$\sum_{x=0}^{2} (2x+1)^{2} \begin{cases} 1 & 1 & x \\ 1 & 1 & 0 \end{cases} \begin{cases} 1 & 1 & x \\ l_{2} & m_{2} & J_{2} \end{cases} \begin{cases} l_{2} & m_{2} & x \\ m_{1} & l_{1} & N \end{cases} \begin{cases} m_{1} & l_{1} & x \\ 1 & 1 & J_{1} \end{cases}$$
(F.5)

is the sum of three terms corresponding to x = 0, 1, 2; that is,  $S_0 + S_1 + S_2$ . The term with x = 0 can be evaluated using the relations for the 6j symbols shown in chapter 5, particularly (5.42). This leads to the first term in the sum (S<sub>0</sub>) being

$$S_{0} = \frac{(-1)^{N+J_{1}+J_{2}}}{9(2l_{2}+1)(2m_{1}+1)}.$$
 (F.6)

To simplify the expressions somewhat, the substitutions: l1 = m1 = a and l2 = m2 = b, can be made. Thus S<sub>0</sub> becomes,

$$S_0 = \frac{(-1)^{N+J_1+J_2}}{9(2b+1)(2a+1)}.$$
 (F.7)

 $S_1$  is obtained if we make the substitutions:

$$\begin{cases} 1 & 1 & 1 \\ 1 & 1 & 0 \end{cases} = -\frac{1}{3}$$
 (F.8a)

$$\begin{cases} 1 & 1 & 1 \\ b & b & J_2 \end{cases} = (-1)^{b+J_2} \left[ \frac{(2b-1)!}{4!(2b+2)!} \right]^{1/2} V_1(1, J_2, b)$$
(F.8b)

where  $V_1(1, J_2, b) = -2(J_2(J_2+1) - 2 - b(b+1))$ 

$$\begin{cases} b & b & 1 \\ a & a & N \end{cases} = (-1)^{b+a+1+N} \left[ \frac{(2b-1)!(2a-1)!}{(2b+2)!(2a+2)!} \right]^{1/2} V_1(b, N, a)$$
(F.8c)

where  $V_1(b, N, a) = -2(N(N+1) - b(b+1) - a(a+1))$ 

$$\begin{cases} a & a & 1 \\ 1 & 1 & J_1 \end{cases} = (-1)^{a+J_1} \left[ \frac{(2a-1)!}{(2a+2)!4!} \right]^{1/2} V_1(a, J_1, l)$$
(F.8d)

where  $V_1(a, J_1, 1) = -2(J_1(J_1 + 1) - a(a + 1) - 2)$ 

Combining these we get:

$$S_{1} = \frac{(-1)^{J_{1}+J_{2}+N}}{9} \frac{(2b-1)!(2a-1)!}{(2b+2)!(2a+2)!} (J_{2}(J_{2}+1) - 2 - b(b+1)) (N(N+1) - b(b+1) - a(a+1)) \times (J_{1}(J_{1}+1) - a(a+1) - 2).$$
(F9)

A similar analysis leads to a result for x = 2,

$$\begin{split} S_2 &= \frac{(-1)^{J_1+J_2+N}}{3\cdot 5!} \frac{(2a-2)!(2b-2)!}{(2a+3)!(2b+3)!} \\ &\times \Big\{ 6 \big( J_1(J_1+1) - a(a+1) - 2 \big)^2 + 6 \big( J_1(J_1+1) - a(a+1) - 2 \big) - 16a(a+1) \Big\} \\ &\times \Big\{ 6 \big( N(N+1) - b(b+1) - a(a+1) \big)^2 + 6 \big( N(N+1) - b(b+1) - a(a+1) \big) - 8ab(a+1)(b+1) \Big\} \\ &\times \Big\{ 6 \big( J_2(J_2+1) - 2 - b(b+1) \big)^2 + 6 \big( J_2(J_2+1) - 2 - b(b+1) \big) - 16b(b+1) \Big\} \\ \text{or} \end{split}$$

$$S_{2} = \frac{(-1)^{J_{1}+J_{2}+N}}{3 \cdot 5!} \frac{(2a-2)!(2b-2)!}{(2a+3)!(2b+3)!} V_{2}(a, J_{1}, 1) V_{2}(b, N, a) V_{2}(1, J_{2}, b).$$
(F.10)

Therefore, taking the sum  $S_0+S_1+S_2$  explicitly, leads to the lengthy expression for  $F_{00}$ 

.

$$F_{00} = \frac{(-1)^{N+J_1+J_2}}{9(2b+1)(2a+1)} - \frac{(-1)^{J_1+J_2+N}}{4!} \frac{(2b-1)!(2a-1)!}{(2b+2)!(2a+2)!} V_1(1,J_2,b) V_1(b,N,a) V_1(a,J_1,l) + \frac{(-1)^{J_1+J_2+N}}{3\cdot 5!} \frac{(2a-2)!(2b-2)!}{(2a+3)!(2b+3)!} V_2(a,J_1,l) V_2(b,N,a) V_2(l,J_2,b).$$

(F.11)

We now repeat the same procedure for the case of J = 2. Thus we need to evaluate the sum,

$$F_{22} = 5\sum_{x=0}^{2} (2x+1)^{2} \begin{cases} 1 & 1 & x \\ 1 & 1 & 2 \end{cases} \begin{cases} 1 & 1 & x \\ b & b & J_{2} \end{cases} \begin{cases} b & b & x \\ a & a & N \end{cases} \begin{cases} a & a & x \\ 1 & 1 & J_{1} \end{cases}.$$
 (F.12)

Analogous procedures to those above lead to the following three terms in this sum. For the term corresponding to x = 0 we get

$$S_0 = \frac{(-1)^{N+J_1+J_2}}{9(2a+1)(2b+1)},$$
 (F.13)

the identical term to the J = 0 case. For x = 1 we obtain

$$S_{1} = -\frac{12(-1)^{J_{1}+J_{2}+N}}{(4!)^{2}} \frac{(2b-1)!(2a-1)!}{(2b+2)!(2a+2)!} V_{1}(1, J_{2}, b) V_{1}(b, N, a) V_{1}(a, J_{1}, 1), \quad (F.14)$$

differing from the J = 0 case by only a numerical factor. Finally for the x = 2 case we get

$$S_{2} = \frac{20(-1)^{J_{1}+J_{2}+N}}{(5!)^{2}} \frac{(2a-2)!(2b-2)!}{(2a+3)!(2b+3)!} V_{2}(a, J_{1}, 1) V_{2}(b, N, a) V_{2}(1, J_{2}, b), \quad (F.15)$$

again differing by a numerical factor from the J = 0 case. Summing these three terms leads to the expression

$$F_{22} = 5 \left( \frac{(-1)^{N+J_1+J_2}}{9(2b+1)(2a+1)} - \frac{12(-1)^{J_1+J_2+N}}{(4!)^2} \frac{(2b-1)!(2a-1)!}{(2b+2)!(2a+2)!} V_1(1, J_2, b) V_1(b, N, a) V_1(a, J_1, 1) \right. \\ \left. + \frac{20(-1)^{J_1+J_2+N}}{(5!)^2} \frac{(2a-2)!(2b-2)!}{(2a+3)!(2b+3)!} V_2(a, J_1, 1) V_2(b, N, a) V_2(1, J_2, b) \right).$$
(F16)

Taking the quotient of  $F_{00}$  and  $F_{22}$  leads to the following after some simplification

$$\frac{F_{00}}{F_{22}} = \frac{\left(\frac{1}{9(2b+1)(2a+1)} - \frac{(2b-1)!(2a-1)!}{24(2b+2)!(2a+2)!}V_1(1,J_2,b)V_1(b,N,a)V_1(a,J_1,1)\right)}{+ \frac{(2a-2)!(2b-2)!}{72(2a+3)!(2b+3)!}V_2(a,J_1,1)V_2(b,N,a)V_2(1,J_2,b)}\right)}{5\left(\frac{1}{9(2b+1)(2a+1)} - \frac{12}{576}\frac{(2b-1)!(2a-1)!}{(2b+2)!(2a+2)!}V_1(1,J_2,b)V_1(b,N,a)V_1(a,J_1,1)\right)}{+ \frac{20}{14400}\frac{(2a-2)!(2b-2)!}{(2a+3)!(2b+3)!}V_2(a,J_1,1)V_2(b,N,a)V_2(1,J_2,b)}\right)}.$$
(F.17)

This expression can further be simplified if we rewrite the factorial expressions as

$$\frac{(2b-1)!(2a-1)!}{(2b+2)!(2a+2)!} = \frac{1}{4ab(2a+2)(2a+1)(2b+2)(2b+1)},$$
(F.18a)

and

$$\frac{(2a-2)!(2b-2)!}{(2a+3)!(2b+3)!} = \frac{1}{(2a+3)(2a+2)(2a+1)(2a+1)(2a+3)(2b+3)(2b+2)(2b+1)(2b+1)(2b-1)}$$
(F.18b)

Making these substitutions, we get

.

$$\frac{F_{00}}{F_{22}} = \frac{1}{5} \frac{\left(1 - \frac{9V_1(1, J_2, b)V_1(b, N, a)V_1(a, J_1, 1)}{96ab(2a+2)(2a+1)(2b+2)(2b+1)} + \frac{V_2(a, J_1, 1)V_2(b, N, a)V_2(1, J_2, b)}{32ab(2a+3)(2a+2)(2a+1)(2a-1)(2b+3)(2b+2)(2b+1)(2b-1)}\right)}{\left(1 - \frac{9V_1(1, J_2, b)V_1(b, N, a)V_1(a, J_1, 1)}{192ab(2a+2)(2a+1)(2b+2)(2b+1)} + \frac{V_2(a, J_1, 1)V_2(b, N, a)V_2(1, J_2, b)}{320ab(2a+3)(2a+2)(2a+1)(2a-1)(2b+3)(2b+2)(2b+1)(2b-1)}\right)}.$$
 (F.19)

Substituting equation (F19) into (F2) leads to an analytic expression for the depolarization ratio:

$$\eta = 3 \left[ 4 + 2 \left[ \frac{\left(1 - \frac{9V_1(1, J_2, b)V_1(b, N, a)V_1(a, J_1, 1)}{96ab(2a + 2)(2a + 1)(2b + 2)(2b + 1)} + \frac{V_2(a, J_1, 1)V_2(b, N, a)V_2(1, J_2, b)}{32ab(2a + 3)(2a + 2)(2a + 1)(2a - 1)(2b + 3)(2b + 2)(2b + 1)(2b - 1))} \right] \right]^{-1} + \frac{9V_1(1, J_2, b)V_1(b, N, a)V_1(a, J_1, 1)}{192ab(2a + 2)(2a + 1)(2b + 2)(2b + 1)} + \frac{V_2(a, J_1, 1)V_2(b, N, a)V_2(1, J_2, b)}{320ab(2a + 3)(2a + 2)(2a + 1)(2a - 1)(2b + 3)(2b + 2)(2b + 1)(2b - 1))} \right] \right]^{-1}$$
(F. 20)

With (F.20)  $\eta$  can be calculated by simple arithmetic. As an example, consider the case of the interaction  $\alpha T_4 E$ . In Chapter 6 we saw that  $\eta$  was calculated to be 11/52, now applying (F.20):

$$\eta = 3 \left[ 4 + 2 \left( \frac{1/81}{11/4536} \right) \right]^{-1} = \frac{11}{52}.$$

To our knowledge such a general expression for the depolarization ratio of two interacting molecules in terms simply of tensor ranks does not appear in the literature.

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