**Symmetry-based identification and enumeration of independent tensor properties in nonlinear and chiral optics**

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Abstract

For many laser-based methods of material characterisation and analysis, a tensor formulation of theory is necessary, especially in techniques that exploit nonlinear or chiral optics. The fundamental interactions that underpin such methods offer various levels of approach to theory, but the most rigorous often lead to equations of considerable complexity. To compute the values for individual material parameters frequently demands making assumptions of extreme simplicity, overly dependent on calculational method, yet still providing unsatisfactory results.

A pragmatic and entirely rigorous symmetry-based approach to the irreducible tensorial structures circumvents many of these problems, securing reliable results and guiding the pathway to applications. Instead of focusing on individual tensor components, such an approach can rapidly determine the number of linearly independent quantities – and hence the number of operationally different setups necessary for full characterisation. By such means, one can directly ascertain how variations of optical polarisation and beam geometry can reliably capture the response of any material system.

The use of an irreducible tensor method operates independently of any means that might be chosen to calculate material properties. It removes the need for common simplifying assumptions such as the approximation of tensorial structure by a scalar representation, adoption of a two-state model, or disregarding near-resonance damping. It also obviates any dependence on a choice of simulation package, or quantum-calculational software. In this paper, the principles are set down and illustrated by application to experiments of varying degrees of complexity, including interactions of growing significance in the realm of chiral nonlinear optics. Limitations of this approach are also critically assessed.

**Keywords:** nonlinear optics, multiphoton processes, laser spectroscopy, chiral optics, nanophotonics, harmonic generation, quantum electrodynamics, selection rules, angular momentum, irreducible tensors, structured light

1. **Introduction**

In the sphere of chemical and optical physics, it is well known that symmetry properties underpin all quantum selection rules, and as such they exert a powerful influence over most spectroscopic observations. Indeed, they form the basis for the selection rules in every branch and application of optical spectroscopy, beyond free atoms [1]. In the infancy of optical spectroscopy, when nearly all observed transitions could be attributed to single-photon processes involving the lowest order of multipole coupling, the vector electric dipole (E1), studies based on simple absorption demanded no more than a single experimental setup, and analysis of the ensuing results was relatively straightforward. However, with narrow bandwidth and high intensities now routinely available from bench lasers, much more attention focuses on nonlinear optics, multiphoton transitions, and processes involving higher order electric, or magnetic multipoles [2].

In planning and conducting any of these more demanding experiments, one significant consideration is the number of distinct measurements necessary to unambiguously characterise a given sample, and to cast theory in a form that enables correct interpretation of the results. At this level, complications arise due to a common feature of nonlinear and chiral optics: their formulation of material response in terms of tensors. The order of any material response tensor is primarily determined by the number of photons involved in each fundamental, multiphoton interaction: tensors responsible for chirality-dependent signals commonly arise through the interference of quantum amplitudes involving different multipoles [3,4].

Tensor structures carry information that is related, in the case of three-dimensionally isotropic systems, to angular momentum [5,6]; as such, their components are often expressed in terms of spherical tensor algebra, based on spherical polar coordinates [7]. Although most systems of physical interest in chemical and optical physics lack spherical symmetry, undermining a directly bijective (1:1) form of connection between tensor rank and angular momentum, important aspects of the underlying physics remain operative. The relevant tensors can be deconstructed into simple combinations of irreducible forms that carry over the key symmetry information [8]. A study of green fluorescent protein by Bain et al., focusing on orientational order in its two-photon excited state, represents one example of a significant recent application [9] – see also ref. [10].

Nonetheless, for material systems that are structured – whether at the level of individual molecules or of bulk ordered solids – there are often huge advantages to casting theory in terms of tensor components more directly expressed in reference to a Cartesian frame. For molecular or crystalline materials, this expedites immediate connection to intrinsic structural symmetry – see, for example, a powerful recent analysis by Wu and Xiong [11]. But equally, laboratory spectroscopic setups are also most conveniently related to Cartesian space-fixed frame, based on linear directions such as the directions of optical beams or polarisations, applied forces etc. – see, for example, the range of applications in refs [12-19].

The advantages of using a Cartesian frame can be secured by utilizing the explicit connection between irreducible tensors of spherical and Cartesian form [20,21]. This enables selection rules to be directly deduced and, cutting through tiers of calculational analysis, its symmetry principles provide a firm basis to determine the detailed form of independently determinable tensor properties. This not only establishes the number of independent parameters necessary to fully describe each phenomenon: through their enumeration, it equally provides information on the number of optically different setups necessary to fully characterise the physical system. By this procedure, we can therefore ascertain the full extent, and equally the maximum amount of information, that can be derived by experiment. With a variety of illustrative examples, the methodology is comprehensively set out in the following analysis: Sections 2-4 provide the background tensor theory; Sections 5-7 then address applications, before concluding observations are presented in Section 8.

Beginning in Section 2, the general foundations of the approach are succinctly set out, and the linkage to angular momentum properties is established. It is shown how a Cartesian basis can circumvent awkward expression in terms of spherical tensors, while obviating explicit expression in terms of individual Cartesian components. Section 3 pursues the symmetry analysis of irreducible Cartesian tensors that now encompasses cases of index permutational symmetry for tensors of ranks up to and including 5. This lays the ground for a subsequent analysis of tensor coupling, in terms of their irreducible components, in Section 4, proving the basis for a considerable simplification in the subsequent applications.

Section 5 then addresses the enumeration of molecular tensor properties in fluid media, purely on symmetry-based grounds, drawing examples from simple forms of linear and nonlinear optical spectroscopy. Section 6 discusses optimized experimental schemes for the determination of key material characteristics, applied to two-photon absorption and second harmonic (hyper-Rayleigh) scattering. With a view to the burgeoning interest in optically nonlinear forms of chirality, Section 7 introduces the additional tier of complexity that is entailed in addressing enantioselective chiral interactions, as multipolar forms of light-matter coupling are necessarily entertained. An explicit analysis of Raman optical activity paves the way for a detailed consideration of application to second harmonic optical activity, which is the subject of extensive recent experimentation on silver nanohelices, by Valev et al. [22-24]. Application of the method rereported here now affords a swift route to the enumeration of independently measurable characteristics of any such sample.

In Section 8, the paper concludes with a discussion of the strengths of the overall approach, identifying some potential strategies for mitigation of its limitations, and taking a brief look at the promising scope for studies based on structured laser beams, such as optical vortices with a twisted wavefront.

1. **Groundwork formulation**

*2.1 Symmetry and angular momentum*

In the non-relativistic quantum theory of systems with spherical symmetry, such as a hydrogen atom, stationary states have sharp values for both energy and the modulus of orbital angular momentum. This follows from the commutation relation $\left[\hat{H},\hat{L}^{2}\right]=0$, where $\hat{H}$ is the Hamiltonian and $\hat{L}$ the orbital angular operator [25]. Accordingly, the 3D tensor representation of every static property for any such spherical system is isotropic, associated with angular momentum zero, and thereby transforming under rotations and reflections as a scalar – in group theory, the totally symmetric representation S of the symmetry group SO(3) (which is the group of all rotations in 3D space). For each static property, the tensor rank is determined by the phenomenon with which it is associated – for example rank 0 (i.e., a scalar) for charge, and rank 2 for polarisability.

The *dynamic* properties of spherically symmetric systems, such as transition dipole moments or transition tensors (including multiphoton absorption, or electronic Raman scattering tensors) transform under the operations of SO(3) according to the symmetry representation generated by a product of the irreducible representations (irreps) of the quantum initial state *i* and final state *f*, i.e. S (*j* = 0), P (*j* = 1), D (*j* = 2) etc. Following the standard rules of angular momentum coupling, such products span irreps whose angular momenta lie in the range |*ji* – *jf*| … *ji* + *jf*, subject to a ceiling value of *n*, the tensor rank [5].

These symmetry principles, both for static and transition properties, hold to no less an extent for systems *lacking* spherical symmetry, as is the case for all molecules and for all real solids. However, such systems commonly possess significant elements of lower symmetry. As such, the intrinsic symmetry elements of anisotropic systems constitute the basis for a point group that is a subgroup of SO(3). In considering physical properties, a key difference in outcome (compared to isotropic systems) emerges from the fact that now the stationary states – eigenstates of the Hamiltonian – are no longer, in general, eigenstates of the operator $\hat{L}^{2}$. In the descent from full spherical symmetry, the representations S, P, D etc. are no longer irreducible; each one decomposes into a linear combination of irreps of the relevant, lower symmetry point group [26]. Dynamic tensor properties, relating to quantum transitions between initial states *i* and final states *f*, now transform under *reducible* representations of the appropriate point group, still spanning irreps with angular momenta in the range |*ji* – *jf*| … *ji* + *jf*, ≤ *n*.

*2.2 Optical interaction observables*

To establish the connection between interactions and measurements let us now, for conciseness, assume the material of interest is a molecule – though the rules that are deduced below nonetheless equally apply to structured matter on a larger, macroscopic scale, such as dielectric crystals. Despite the intricacies of tensor interaction at the microscopic level, any conventional laboratory measurement generating a single numerical value, such as an intensity, process rate, quantum efficiency or photon count, is necessarily a scalar quantity – a tensor of rank zero. To be clear, even the observation of a phenomenon such as optical rotation, which some authors using different terminology may consider a ‘vectorial’ observable [27], still demand the identification of shifted polarization by *scalar* observations of intensity through a rotatable polariser. There is no difference of viewpoint here; the molecular interaction responsible for optical rotation is certainly vectorial, while the direct measurements necessary for its characterization are scalar.

Each observable quantity for an optical interaction process is expressible in terms of a rate of change from one quantum state to another, governed by a Fermi Rule equation [28-31]. Every such direct measurable is thereby cast in terms of the modulus square of what is commonly known as a ‘matrix element’ *MFI*, due to its formally relating any one initial state *I* to any one final state *F* of the interacting system comprising matter plus light. (For example, the matrix element for absorption may link an initial state for a ground level molecule in the presence of resonant radiation, to a final state in which the molecule is excited and there is one less photon present.) To save any confusion with matrix algebra in what follows, the alternative term ‘quantum amplitude’ is used in preference to ‘matrix element’, serving as a reminder that its modulus square represents a transition probability per unit time.

The modulus of the quantum amplitude is necessarily a scalar quantity, whose leading term can be cast in the form of an inner tensor product, denoted by the symbol , of a radiation tensor **S** associated with electromagnetic fields and their derivatives, and a molecular transition or property tensor **T** [32]. The former tensor generally comprises an outer product of radiation field components (such as polarisation and wave-vector components); the latter is a response tensor of the same rank (such as a transition dipole or polarisability), commonly derived from time-dependent perturbation theory [33-39]. In optics applications, the leading term is commonly derived on the basis of electric dipole (E1) coupling between matter and radiation. To avoid any further complications at this stage, this assumption suffices for the primary analysis here and in the Sections that immediately follow. However, to accommodate the significant interest of chiral interactions, the restriction is removed, and the analysis duly extended, in Section 7.

For example, the quantum amplitude for Rayleigh scattering may be cast in terms of  where  denotes an inner tensor product. Expressed in explicit tensor components this may be written as *SijTij*, where . Here, the subscripts *i* and *j* are Cartesian index components of **e**, the input polarization vector, and , the output polarization vector; **a** denotes the molecular polarizability [31]. In the tensor inner product *SijTij* we use the rule, for repeated tensor indices, of implicit summation over all three Cartesian directions – the Einstein convention (as for example in the representation of a simple scalar product of two vectors **a** and **b**: *aibi* = *aibjdij* ≡ **a**.**b**). Note that each polarization and the polarizability are considered as complex quantities, whose conjugates are denoted by an overbar. Complex polarization vectors allow for the consideration of circular or elliptical polarisation states [40], while a complex polarisability accommodates the effects of line-shape and resonance damping.

*2.3 Coherent and incoherent interactions: ordered and disordered media*

In considering observables at the macroscopic level, two significantly distinct cases arise. For *coherent parametric* processes such as SHG (second harmonic generation) – those in which both energy and linear momentum are separately conserved by both the radiation field and the material – the quantum amplitudes from each molecular component have a common phase and, therefore, add together constructively. The net response is a straightforward multiple of the result for any representative molecule. For ordered systems such as regular solids, the macroscopic observable directly arises from the squared modulus of the numerically scaled quantum amplitude. For entirely disordered systems, such as liquids, powdered solids or inhomogeneous samples – systems that are essentially isotropic at the macroscopic level – the corresponding observable emerges from the modulus square of the 3D orientationally averaged quantum amplitude [31,41]. By virtue of the ergodic theorem, this is identical to the long time-averaged result, for any system at equilibrium [42].

For all other, optically *incoherent* processes (such as all kinds of multiphoton absorption, or non-forward scattering), the quantum amplitudes from individual molecules are additive – but since they differ in their position-dependent phase, cross-terms from molecules in different positions disappear through destructive interference. In consequence, the macroscopic observable is linearly proportional to the squared modulus of the quantum amplitude for any representative site. Furthermore, when accounting for the observed response from disordered, macroscopically isotropic systems, the observable arises from an orientational average of the modulus squared amplitude [31,41,43]. Notice the change in the order of squaring and averaging here, compared to the coherent case. Numerous highly significant differences in the character of observations stem from this difference in the correct theoretical representation: an example is the weakness of incoherent second harmonic scattering, compared to the highly efficient process of second harmonic generation.

There are, therefore, four different system scenarios (i.e., possible combinations of coherent/incoherent interaction with solid/fluid media) with potentially very different signal characteristics. These are exemplified for the process of frequency doubling in Table 1, which assumes the usual leading-order electric-dipole mechanism for each of the three photons engaged in the  process. These cases illustrate more general rules for securing observables from derived quantum amplitudes, as discussed in more detail elsewhere – see, for example, p.72 in ref. [31].

|  |  |  |
| --- | --- | --- |
| Process | Coherent | Incoherent |
| Solid | Second harmonic generationStrong forward-emission Non-centrosymmetric bulk medium | Second harmonic elastic scatteringWeak non-forward scattering Non-centrosymmetric bulk medium |
| Fluid | Forbidden | Second harmonic elastic scatteringWeak non-forward scattering Non-centrosymmetric molecules |

**Table 1**. Different outcomes and constraints in optical frequency doubling, i.e., for the three-photon nonlinear optical process *w* + *w* → 2*w*. The represented characteristics apply to the dominant, all-electric dipole (E13) mechanism.

In all cases where an orientational average is involved, the implementational principle is that the radiation tensor **S** is cast against axes in 3D space that are fixed with respect to the external environment, while the molecular tensor **T** is cast on axes internally fixed by the molecular internal structure. The three Euler angles that relate either of these frames of reference to the other [44] are each subjected to a free rotational average.

A well-used method to accomplish this average, circumventing explicit angular integration, is described in ref. [45]; it delivers results in the form of linear combinations of products of isotropic tensors in each reference frame. The physically dimensionless Cartesian structure of isotropic tensors is determined by the tensor rank *n*, comprising products of (*n*/2) Kronecker deltas for even ranks, and products of  Kronecker deltas with one Levi-Civita antisymmetric tensor for odd ranks [46,47]. For all tensor ranks *n* > 3, there is more than one isotropic tensor [48]: the relevant multiplicity is given by , a specific instance of a general formula to be discussed in the next section. In the following, this should be borne in mind: all that is necessary is to recognise the number and form of these isotropic tensors: the complicated arrays of numerical coefficient that multiply their products will not be required.

1. **Transformation and symmetry properties of Cartesian tensors**

*3.1 Irreducible Cartesian tensors*

To proceed further, we need to establish in more detail the transformation and symmetry properties of a general Cartesian tensor. In 3D space, a tensor of rank *n* has in principle= 3*n* distinct components, (the superscript of *N* here signifying the generic standard), representable in Cartesian form by referring each index to one of the axes *x*, *y* and *z*. Linear dependence amongst the 3*n* components may arise from the geometrical symmetry of the material, or the properties of the optical field, as will be discussed later. If the represented property tensor is completely symmetric with respect to any permutation of its *n* indices, (as for example in single-beam *n*-photon absorption, where all *n* absorbed photons are identical), the number of independent tensor components reduces dramatically to the binomial coefficient  = $\_{2}$. However, this number is lowered further for any tensor with the specific transformation properties of angular momentum equal to its rank, sometimes termed a *natural tensor*; it then has only  = (2*n* + 1) non-zero, independent components. This form is fully symmetric with respect to interchange of any index pair, and it is also traceless with respect to each index pair [49]. An example is the traceless electric quadrupole [50], whose components are expressible as;

 ,

where the sum is taken over all charges labelled *z* at positions **r**(*z* ) relative to the centre of charge, and *dij* is again the Kronecker delta. The subscript indices *i* and *j* represent components in 3D space, and brackets around subscript indices, as on the left, signify permutational symmetry amongst its contents; their overbar on subscripts denotes a vanishing trace. Equation represents a rank-2 tensor expressed in terms of its components; it is clearly traceless and symmetric in its indices (recall *dii* = 3). It has five linearly independent components; three off-diagonal elements mirroring their diagonal counterparts, and two diagonal elements (any third one being minus the sum of the other two).

The values of , , and  for the first few orders *n* are given in Table 2.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| *n* | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|  | 3 | 9 | 27 | 81 | 243 | 729 | 2187 | 6561 |
|  | 3 | 6 | 10 | 15 | 21 | 28 | 36 | 45 |
|  | 3 | 5 | 7 | 9 | 11 | 13 | 15 | 17 |

**Table 2**. Number of independent elements of tensors of rank *n* in 3D space,  in general, reduced by full index symmetry to , and further reduced to  for the natural, irreducible form.

*3.2 Reducible Cartesian tensors and weights*

In systems of less than spherical symmetry, tensors describing a physical property or stimulus response will have more than the irreducible minimum number of (2*n* + 1) linearly independent components. These more generic tensors, termed *reducible*, can be expressed as a sum of irreducible tensors of weights *j*, where *j* is an integer in the interval (0, *n*) [51]. Again, by way of example, for a general rank-2 tensor **A**(2) we have, a decomposition into three weights, *j* = 0, 1, 2, expressible as follows in explicit component form;

 ;

 ;

 ;

 .

The first equality in each of equations , and is cast as a projection onto the tensor *Akl*, and the contents of the square brackets represent tensors of rank 0, 1 and 2 respectively, as is evident from the number of free, unpaired indices in the terms they encompass. On the right of each of these expressions is the simplified result – making use, in equation , of the product rule *eijmeklm = dikdjl – dildjk*. Notice, here, that the number of independent components of each weight *j* is (2*j* + 1), so that the sum in equation accounts for 1 + 3 + 5 = 9 independent components, as befits a rank-2 tensor in 3D space.

*3.3 Independent tensor elements, multiplicities, and index symmetry*

In general, a Cartesian tensor of rank *n* and weight *j* represents a natural tensor of rank *j*, embedded in rank *n* tensor space [52,53]. Within its *n* Cartesian indices, a subset of *j* indices has the same traceless and exchange symmetry as the rank *j* natural tensor. It is important to recognise that, for all cases *n* > 2, weights *j* will commonly be represented with a multiplicity  ≥ 1, the individual terms within the multiplet being known as branches [54]. Numerical values for are given by the following formula;

 ,

in which the index *k* is limited to the integer range , where, for the upper limit,  signifies the floor function (i.e., the highest integer below its argument).

Equation owes its origin to an inductive analysis of spin-coupling by Mikhailov [55] – as also applies, for example, to the theory of quantum states in multielectron atoms [56]. The coupling of two integer angular momenta *j*1 and *j*2 produces results in the integer range from *j*1 + *j*2 down to either 0 or |*j*1 – *j*2|, whichever is the larger [6]. Here, the relevant case (corresponding to a coupling of *n* equivalent P states, each of unit orbital angular momentum) is illustrated in Table 3 for tensor ranks *n* = 1 – 5. Thus, starting with one P state, the first coupling with a second generates S + P + D, as indicated by the uppermost set of downward arrows between rows 1 and 3 in the Table. Coupling with another P state, using the rules given above, generates S, P, D, and F states with multiplicities 1, 3, 2 1 respectively (observe where the arrows lead).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| *j* | 0 (S) | 1 (P) | 2 (D) | 3 (F) | 4 (G) | 5 (H) |
|  |  | 1 |  |  |  |  |
| ⊗P↓ |   | ↓ |  |  |  |  |
|  | 1 | 1 | 1 |  |  |  |
| ⊗P↓ |   | ↓ | ↓ |  |  |  |
|  | 1 | 3 | 2 | 1 |  |  |
| ⊗P↓ |   | ↓ | ↓ | ↓ |  |  |
|  | 3 | 6 | 6 | 3 | 1 |  |
| ⊗P↓ |   | ↓ | ↓ | ↓ | ↓ |  |
|  | 9 | 15 | 15 | 10 | 4 | 1 |

**Table 3**. Successive coupling of *n* inequivalent P states, generating the degeneracy of each ensuing angular momentum component *j*, and hence . Starting (top row) with one P state, progressive coupling with additional P states follows as indicated by the successive rows of downward arrows.

Since each occurrence of weight *j* accounts for (2*j* + 1) independent parameters, it now follows that we have;

 ,



duly accounting for the complete, linearly independent set of tensor components in the general case. For totally index-symmetric tensors, the multiplicity factor is simply unity for non-negative values , and hence:

 .

Trivially, for the case of natural tensors, only the highest weight, *n =* *j*, arises and hence we have

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By iterative use of the rules for angular momentum coupling, it is a straightforward matter to identify  values for tensors of the ranks most prominent in optical applications. For *n* > 2, we need to account for the possible incomplete extent of index symmetry. For example, in frequency doubling, the tensor indices corresponding to the pair of input photons may be freely permuted, but not together with the index for the distinct emitted photon. The restricted symmetry amongst components of the associated hyperpolarizability tensor may accordingly be expressed as *bi*(*jk*), whose irreducible structure is discernible by coupling the results for tensors of the form *ai* and *b*(*jk*), i.e.: . Hence, we obtain the *Q* factors shown in the *bi*(*jk*) row in Table 4, which also shows the number *N* of independent components; here, 3 × 6 ≡ (2 × 3) + 5 + 7. The Table, based on the logic of Table 3 and duly taking into account the weight multiplicities, shows newly extended results for this, and all other index partitions originating from index symmetry, again for tensors of ranks 1–5.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | *N* |  |  |  |  |  |  |
| *Ti* | 3 |  | 1 |  |  |  |  |
| *Tij* | 9 | 1 | 1 | 1 |  |  |  |
| *T*(*ij*) | 6 | 1 |  | 1 |  |  |  |
| *Tijk* | 27 | 1 | 3 | 2 | 1 |  |  |
| *Ti*(*jk*) | 18 |  | 2 | 1 | 1 |  |  |
| *T*(*ijk*) | 10 |  | 1 |  | 1 |  |  |
| *Tijkl* | 81 | 3 | 6 | 6 | 3 | 1 |  |
| *Tij*(*kl*) | 54 | 2 | 3 | 4 | 2 | 1 |  |
| *T*(*ij*)(*kl*) | 36 | 2 | 1 | 3 | 1 | 1 |  |
| *Ti*(*jkl*) | 30 | 1 | 1 | 2 | 1 | 1 |  |
| *T*((*ij*)(*kl*)) | 21 | 2 |  | 2 |  | 1 |  |
| *T*(*ijkl*) | 15 | 1 |  | 1 |  | 1 |  |
| *Tijklm* | 243 | 9 | 15 | 15 | 10 | 4 | 1 |
| *Tijk*(*lm*) | 162 | 3 | 9 | 9 | 7 | 3 | 1 |
| *Ti*(*jk*)(*lm*) | 108 | 1 | 6 | 5 | 5 | 2 | 1 |
| *Tij*(*klm*) | 90 | 1 | 4 | 4 | 4 | 2 | 1 |
| *Ti*((*jk*)(*lm*)) | 63 |  | 4 | 2 | 3 | 1 | 1 |
| *T*(*ij*)(*klm*) | 60 |  | 3 | 2 | 3 | 1 | 1 |
| *Ti*(*jklm*) | 45 |  | 2 | 1 | 2 | 1 | 1 |
| *T*(*ijklm*) | 21 |  | 1 |  | 1 |  | 1 |

**Table 4**. Number of independent components, *N*, and multiplicities , for each weight *j* in the reduction of tensor ranks 1–5. Each permissible form of index symmetry is indicated by indices enclosed within brackets; outer brackets indicate permutational symmetry between the inner index pairs. In cases where the multiplicity >1, explicit components are conventionally distinguished with labels A, B, C…, as for example 1A and 1B for the weight-1 branches in the reduction of *Ti*(*jk*).

As noted earlier, expressing tensor components in terms of a Cartesian reference frame directly manifests the connection between structural symmetry of materials and their tensor response. It yields an especially clear connection to selection rules, since the imposition of structural symmetry frequently simplifies rate or signal formulae, as forbidden terms drop out of the rate equations – see, for example, the analysis of three-photon absorption in refs [12,57]. A recent, powerful analysis recently published by Wu and Xiong [11], useful for 2D and high-order forms of spectroscopy of *achiral* molecules, sets out the general principles for determining the equivalence of tensor elements resulting from structural symmetry, with several illustrative applications.

Studies by Zyss et al. have exploited the congruence in mathematical structure between natural tensors and multipoles, adopting the descriptors ‘quadrupole’, ‘octupole’ etc. to denote natural tensors of rank 2, 3 etc. Notwithstanding a potential ambiguity (allowing possible confusion with electric or magnetic multipoles) it has become commonplace in certain quarters – see, for example, ref. [58]. Nonetheless, Zyss et al. make very clear the connectivity between molecular structure and tensor selection rules, and they also showcase the oversimplifying effects of assuming full index symmetry in optical response tensors (Kleinman symmetry [59]) where the assumption may not always be warranted [60] – see also ref. [61].

A detailed analysis of exact connection between these irreducible tensors in Cartesian form, and their alternative, spherical harmonic counterparts, is to be found in papers by Stone [20,62]: recent work by Grinter and Jones illustrates the application of the latter formalism in energy transfer processes [63].

1. **Angular momentum constraints in tensor coupling**

*4.1 Achieving simplification in tensor products*

The principles that are now to be elicited are consequences of the general rule for tensor coupling. Since more than one such application arises in the following analysis, let us introduce the principles by considering a coupling of two arbitrary, reducible tensors **A** and **B**, specifically of the *same* rank *n*. Each individual tensor generally comprises a sum of irreducible tensors of weights *j* in the range . As noted above, the rules of angular momentum coupling decree that arbitrary tensor products of **A** and **B** will generally deliver a sum of terms with weights in the interval between the difference and the sum of the coupled components, and in the present case the *product* therefore has weights . However, the specific cases that primarily concern us specifically involve the *inner* product. If we break both tensors **A** and **B** into their irreducible parts, we have the following key result:

 .

Here, the indices *p*, *p'* designate individual terms within the multiplicity  associated with the weights *j*, *j'.* In the above inner product, the sets of tensor indices of the two tensors (representing their Cartesian components, not shown in the equation above) are identical, so that each such index implicitly appears twice: an example of such an inner product of third rank tensors could be written as *Aijk* *Bijk*, whose evaluation is known as an index *contraction*. In the explicit coordinate representation, we again use the rule for repeated tensor indices, of implicit summation over all three Cartesian directions. Thus, the second equality in equation follows from the fact that the result of any such an inner product is a scalar, i.e. a tensor of rank 0. Since the upper bound on the weight of non-vanishing irreducible terms is invariably the tensor rank – here zero – the inner product of **A** and **B** contains only terms in which their *j* values exactly match. Hence, the inner tensor product emerges as a simple sum of all the terms  for all identical-weight components of the two tensors. This is a key principle: *all terms that couple unequal weights vanish*.

*4.2 Example: two-photon absorption*

This form of analysis, based on the symmetry and trace properties of each weight, greatly expedites the analysis of high-rank tensor products. Consider, by way of simple illustration, the tensor inner product between an index-symmetric tensor *S*(*ij*) and a tensor lacking index symmetry, *Tij*. Single-beam two-photon absorption provides one such example, where the former represents the input optical polarization tensor and the latter the molecular transition tensor – as delivered in non-index symmetric form by the single time-ordering. From the right-hand sides of the generic equations , , and , the weight-1 part of *S*(*ij*) clearly vanishes, and in principle there remain just six terms in the product: **S(**0)**T(**0); **S(**0)**T(**1); **S(**0)**T(**2); **S(**2)**T(**0); **S(**2)**T(**1); **S(**2)**T(**2). Inspection of the index symmetry and trace properties of each case in turn delivers the result that only **S(**0)**T(**0) and **S(**2)**T(**2) are in fact non-zero – but that conclusion could immediately be drawn from the conclusion of the previous paragraph.

Using this identical-weight principle can circumvent a great deal of arduous analysis when dealing with tensors of significantly higher rank. At this stage, we can also draw the conclusion that two-photon allowed *transitions* from the ground state can only be supported to states whose irreducible representations span those of weight 0 and/or 2 – i.e., one of three symmetry classes: . The first of these, designated {0}, signifies a class of two-photon transition that arises only for molecules belonging to one of the cubic symmetry groups, where it applies to symmetry-preserving transitions alone. For molecules of any *other* symmetry type, transitions associated with totally symmetric representations fall into class {0,2}, since that representation spans both weight 0 and weight 2. For *all* molecular symmetry types, every other two-photon allowed transition naturally falls into the class {2}. While such symmetry classes may seem almost superfluous for two-photon transitions, they establish a form of categorization that proves immensely useful for higher order processes. (Of course, any *static property* value must transform under the corresponding totally symmetric representation, necessarily spanned by weight 0: only cases  then arise.)

*4.3 Generalization*

In applying the above method, a significant difference arises between coherent and incoherent processes, for the reasons alluded to in Section 2. Whereas for any coherent process the observable G emerges directly from evaluation of the quantum amplitude, for incoherent processes we find the observable originates from the modulus square. The difference proves especially significant in the case of fluid media, where a rotational average has to be performed to identify the result, as we saw in Section 2. Before we explore the details in the next Section, we may observe that in the coherent case a rank-*n* orientational average will serve to detach the molecular and laboratory frames of reference. However, for the *incoherent* case a rank-2*n* average is required since;

 ,

where each bracket contains an outer product denoted by the symbol  between terms. There is no commonality between the sets of (implicit) tensor indices: accordingly, the net contents of each bracket constitute a tensor of rank 2*n*.

Here we also notice that, defining , the structure of equation (11) submits to exactly the same form of analysis as equation (10). Individually, however, each of these outer product tensors takes the generic form , whose decomposition into irreducible parts is as follows;

 ,

where, the product spans unrestricted weights *j* in the range (0, 2*n*). Assuming the tensors **S** and **T** have complex components, there need be no intrinsic index symmetry amongst the 2*n* indices of either  or .

With the above background, we are now able to appreciate how symmetry-based factors precisely determine the maximum number of independent molecular parameters that can characterise any particular form of optical interaction, informing strategies for those parameters to be elucidated in measurements. Generally, it will be apparent that as the order of optical nonlinearity increases, the explicit equations for experimental observables acquire a progressively more complex form, being cast in an increasing number of terms. However, with appropriate experimental methodology, this same feature has a virtue in potentially extending the amount of information that can be derived, on the material system.

Developing the earlier analysis in Section 2, we can now delineate the specific tensor structures for different application scenarios. Thus far we can summarize as follows:

Static property *values*:  ;

Coherent process *amplitudes*: ;

Incoherent process *rates*:  .

The result of each of the above expressions (13) – (15) is a scalar, and hence the weight-0 part in any explicit decomposition based on equation (10). For orientable solids, it is in principle possible to derive all elements of a molecular response or property tensor by conducting a series of experiments with a judiciously controlled stimulus or detector. For example, varying the polarization of optical input and resolving the polarization of throughput light in the case of Rayleigh scattering enables elements of the polarizability to be determined. However, tackling fluids introduces an important additional tier of analysis and, moreover, in the evaluation of process rates for fluids, isotropic averages are required; this is the subject of the next Section.

1. **Symmetry-based enumeration of tensor properties in fluids**

*5.1 Rotationally averaging rate equations for fluids*

Randomly oriented systems, and isotropic fluids (e.g., liquids, solutions, and suspensions) represent a remarkably broad range of condensed phase media. Here, the maximum amount of information that can be secured by experiment arises in the form of linearly independent molecular parameters known as *invariants* (since they are intrinsic scalars and, therefore, invariant of molecular orientation). For any specific process these invariants together represent a complete set of material parameters, in terms of which all equations for observables can be cast. Of course, there is flexibility in the choice of basis for the invariants: any complete, linearly independent set can be employed. As described below, one such set is directly delivered by the procedure for rotational averaging; the other exploits the irreducible tensor forms that facilitate selection rule elucidation. Both sets necessarily comprise the same number of independent terms, representing an upper bound on experimentally determinable information.

Denoting a 3D rotational average by angular brackets, < …. >, the explicitly different construction for coherent and incoherent processes can readily be seen from the following:

Coherent process rates:  ;

Incoherent process rates:  .

For coherent processes in fluid media, implementation of the orientational averaging procedure delivers an observable cast in terms of a linear combination of products between molecular and radiation invariants. For the molecule, the radiation invariants result from the inner products (i.e., index contractions) of the **S** tensors with isotropic tensors of the same rank, both referred to a laboratory-fixed Cartesian frame. Equally, the molecular invariants result from the contractions of **T** with isotropic tensors of the same rank, expressed in the molecular frame.  As observed above, for all ranks *n* > 3, there is more than one independent isotropic tensor, the number being given by with *j* = 0, as delivered by equation . It is interesting to note that we may equally use the following expression, which remarkably provides the same result:



where . Equation emerges from an identification of the number of S states in the vector coupling of *n* inequivalent P states – see for example ref. [64]. In general, for a process entailing a rank *n* tensor response, (**T** for the coherent case and **W** for the incoherent case), is therefore the number of molecular parameters featuring in general expressions for the observable – and, hence, the maximum number of independent quantities that can be experimentally determined in characterising the material response.

As an aside, note that implementing the rotational averages in equations (16) and (17) casts each result in terms of a linear combination of the isotropic rotation invariants of the radiation tensor and those of the material tensor, i.e. the weight-0 parts of  and  in equation (16), or those of  and  in equation (17). Note that for odd *n* > 3, and even *n* > 6, this number is less than the number of distinct permutations of the indices. A suitably complete, linearly independent set can be identified by the use of Young’s tableaux [44,65]. The numerical coefficients of those linear combinations can be secured by a matrix inversion method detailed in ref. [45] for tensors of all ranks up to *n* = 7; the result for *n* = 8 is given in ref. [66], and for *n* = 9 in ref. [67]. Friese et al. have used similar methods for even-rank averages, for specific application to high-order multiphoton absorption [68]. (Any inclusion of weak correction terms, such as may result from the incorporation of higher forms of electric or magnetic multipole coupling, requires additional scrutiny – see Section 6.) Again, however, it is to be emphasized that the present symmetry analysis requires no such evaluation or knowledge of the numerical coefficients.

*5.2 Example: Four-wave mixing*

Let us first consider, as a simple illustration, a *coherent* process that entails a fourth rank result, such as non-degenerate four-wave mixing in a fluid (an example of which is CARS – Coherent Anti-Stokes Raman Scattering), where the material response is associated with the rank-4 tensor nonlinear susceptibility tensor **c**. There are three linearly independent irreducible contributions of weight-0 (see the entry for  with *j* = 0 in Table 3) that are also known as *isomers*, since they comprise index permutations of a common formulation. To identify the general form of these independent terms, we explicitly effect index contractions of *cijkl* with the corresponding rank-4 isotropic tensors *dijdkl*, *dikdjl* and *dildjk*, delivering the three independent elements *ciijj*, *cijij* and *cijji*. Effecting the Einstein summation over repeated indices means, for example, that *ciijj* denotes the linear combination *cxxxx + cxxyy + cxxzz + cyyxx + cyyyy + cyyzz + czzxx + czzyy + czzzz*. However, this is a level of detail that is not required for the present development.

*5.3 Example: Rayleigh and Raman scattering*

Now let us examine an *incoherent* process – one that again calls for a fourth rank rotational average. A good example here is the case of Rayleigh scattering, previously cited in Section 2. Here, the molecular response is cast in terms of the fourth rank tensor . For clarity of the general approach, let us here assume a dispersion character that treats the polarizability tensor as complex, i.e., . Contracting  with the rank-4 isotropic tensors *dijdkl*, *dikdjl* and *dildjk*. gives ,  and : these are three molecular invariants that together determine the Rayleigh signal observable from a fluid.

However, it is clearly possible to express results in terms of any other complete and linearly independent set. For example, using the results of equations (2) – (5) we have;

 ;

 ;

 ,

and conversely;

 ;

 ;

 ,

(see for example equation 5.9 in ref. [69], which delivers rotational averages directly in terms of irreducible tensor components). The use of equations (22) – (24) enables all rate equations to be recast in terms of the irreducible parts of the polarizability tensor. While this alternative has no particular attraction in the case of Rayleigh scattering, significant advantages arise in the case of spectroscopic processes involving molecular transitions. For example, in resonance Raman scattering the material response tensor is not index-symmetric and, therefore, has contributions from all three weights – 0, 1, and 2, whereas off-resonance conditions result in a vanishing weight-1 contribution – see the entry for *T*(*ij*) in Table 3. In the latter, more common case, the rate equations can thus be cast in terms of just the two invariants  and , and a clear distinction can be drawn between two types of Raman-allowed transitions: those for which the vibrations transform under the totally symmetric representation of the molecular point group, and those of a different symmetry class. This is the origin of classification in terms of depolarisation ratios – see, for example, ref. [40]. A similar analysis can be performed for multiphoton absorption [57].

*5.4 Example: three-photon absorption with two different wavelengths*

The benefits of casting results in terms of irreducible components are more striking for higher order processes. For example, consider double-beam three photon absorption, for which the rank-3 response tensor *Ti*(*jk*) admits components of weights 1, 2 and 3. Here, the analysis affords a categorization of each allowed transition into one of six classes, determined by symmetry constraints imposed by the molecule and that of each allowed transition. These six classes are those in which the following weights alone are non-zero:  (a combination of weights 1 and 2, without representation of weight 3, does not arise for any common molecular point group [8]). Details and examples of how to experimentally identify the class for each band in the spectrum are given in refs. [12,70]; *ab initio* calculations performed on this basis are exemplified in studies of hydrogen chalcogenides by Galasso [71-73].

1. **Optimised strategies for experimental characterization**

*6.1 Complete polarization studies*

Now we approach the heart of this method. Numerous studies have developed from principles first enunciated by McClain [74-76] (see also ref. [77]), whose analysis of multiphoton absorption adopted the approach of identifying non-zero molecular invariants by means of *complete polarization studies*. The basis for this method is that, since a generic rate equation is expressible as a linear combination of molecular invariants, it is in principle possible to extract the values of those invariants from an equal number of experiments in which the corresponding radiation invariants are themselves linearly independent. This entails performing a series of experiments with a suitably complete set of distinct optical field setups: the key to testing different optical setups is to have prior knowledge of the number required.

The adoption of such a strategy entirely displaces any dependence on the suitability of electrodynamics simulation packages, or on the reliability or choice of basis for high-power quantum calculations. It also removes the need for simplifying assumptions such as an approximation of tensorial structure by a scalar representation, the use of a limited basis set of wavefunctions, or an unrealistically simplified treatment of dispersion. Moreover, as an entirely pragmatic tactic it also removes the possibility of attempting a multiparameter fit with variables that prove to be not entirely independent. As will emerge, certain difficulties nonetheless emerge when higher-order processes are considered. Essentially, the parameter space accessible to experimentation becomes insufficiently large to enable complete and absolute system characterization.

*6.2 Application: two-photon absorption*

As a very simple example, we can return to the case of single-beam two-photon absorption, first introduced in Section 4, where our analysis revealed that the molecular invariants can involve only weights 0 and 2. For example, two-photon transitions in tetrahedral (Td) molecules, from the ground state to excited states of symmetries A1, E, and F2, span tensor weights {0}, {2} and {0, 2} respectively [78]. The determination of vanishing or non-vanishing values for each weight, thus provides for unambiguous resolution between these three possibilities – these being the only states accessible by two-photon absorption in molecules of Td symmetry. Here, we have *S*(*ij*) = *eiej* where **e** is the input polarisation vector; once again only the tensor weights 0 and 2 can arise.

Experimental control is thus effected by using two different polarization conditions, ideally plane and circular; for the former, (**e.e**) = 1, while for the latter, (**e.e**) = 0. Thus, the radiation tensor  has isotropic parts  whose values are respectively 1, 1 and 1 for plane-polarised light; 0, 1 and 1 for circular input. The combined results reveal that it is indeed easily possible to discriminate between totally symmetric and other transitions – see, for instance, the ground-breaking experimental results on inert gas excimers in ref. [79].

*6.3 Application: hyper-Rayleigh scattering*

By the extension of such methods we can, for example, readily ascertain the number of invariants for second harmonic light scattering in fluids. Taking information from the entry for *Ti*(*jk*) in Table 4, coupling only the components of  and  with identical weights, as shown in Section 4, and noting the two weight-1 components (distinguished below by appending labels A and B) we can list the following six independent material invariants: . Then, on assuming the process is sufficiently off-resonance that the tensor can be treated as real,  becomes identical to and the number of independent quantities thus reduces to five – see refs. [80,81]. (Earlier studies [82,83] cast equations in terms of a invariants comprising linear combinations of the irreducible forms discussed here). Purely on symmetry grounds, we immediately deduce that second harmonic scattering may be characterized as fully as possible by just five measurements, conducted under appropriately different experimental conditions. In practice, a complete analysis can be achieved by judiciously varying the input polarization, the angle of signal collection, and resolving specific components of polarization in the harmonic signal. A detailed protocol scription for such an investigation is described in chapter 8 of ref. [84]. While absolute scattering intensities may be difficult to secure, one such measurement may be taken to serve as a standard, the other four then representing ratioed values (just as two intensity measurements in Raman spectroscopy are reported in terms of a single ‘depolarization’ ratio).

1. **Optical chirality**

*7.1 Higher multipole contributions*

Interesting and highly important complications arise when we entertain the possibility of multipole contributions. As observed earlier, for example, the tensors responsible for enantioselective (chirality-dependent) signals commonly arise through the interference of quantum amplitudes involving different multipoles. Despite the additional complication, the methods described above retain a power to deliver experimentally useful information. To introduce the necessary extension of theory by way of illustration, let us focus on two cases; the helicity-sensitive signals generated by chiral materials in conventional light scattering, and then their optically nonlinear counterparts.

*7.2 Application: Raman optical activity*

First we consider the dependence of incoherent Rayleigh or Raman scattering on the helicity of circularly polarised input light, in the case of a chiral fluid (the latter often termed ‘Raman optical activity’ [85,86]). Section 2 already introduced the leading term in the quantum amplitude for Rayleigh scattering, cast as , where the explicit tensor components are .The polarization vectors are as defined previously, the prime denoting the scattered output, while the brackets introduced around the component indices of the tensor **a** reflect the effective index symmetry that holds under the usual off-resonant conditions. For Rayleigh scattering, **a** is the electronic polarizability; for vibrational Raman scattering, it is to be interpreted as a Raman transition tensor (directly related to , where *Q*vib is the vibrational mode coordinate [87,88].)

For Rayleigh and Raman optical activity, it is well known that the leading terms in the rate equation, that discriminate between the two kinds of handedness of either the input or the medium itself, originate from the interference of the term involving the molecular polarizability, **a**, with two other distinct elements in the quantum amplitude, represented as tensors **G** and **A** [3]. The quantum amplitude  directly accommodates only electric dipole (E1) material interactions, one with each input and output photon. The leading correction terms of interest, each of broadly comparable levels of significance, may be cast as  and  with explicit components  and . Here,  is the unit wave-vector of the input radiation (i.e., the direction of beam input): **G** is a tensor that accommodates magnetic dipole (M1) interactions with the optical input, while **A** involves electric quadrupole (E2) coupling with the input [89]; accordingly, the two corresponding indices are enclosed in brackets, and once again the overbar denotes their tracelessness – see equation (1).

In all cases, the exiting photon emerges through E1 coupling, so that in shorthand notation we may represent **a**, **G** and **A** as (E1E1), (E1M1) and (E1E2) tensors, respectively. To this (sufficient) level of approximation, the quantum amplitude may thus be cast as . Hence, for the observable, we may write:

 .

Effecting the rotational average for a fluid, the leading terms in this product take the form – to be compared with equation (17);

 .

The explicitly expressed components of each tensor featured above are as follows:

 ;

 ;

 ;

 ;

 ;

 .

Note that, since off-resonance conditions are now assumed for the polarizability, its components may be taken as real. As such, the two pairs of indices in  are also freely permutable, as indicated by the outer brackets around its subscript indices.

Exploiting the above analysis, a major simplification now occurs for a fluid system, since only the weight-0, isotropic parts of each of the tensors in equations (27) – (32) contribute to the observed signal. These result from the following specific contractions between equal weights of **a** and each of **a**, **G**, and **A**. We therefore find three distinct sets of invariants contributing to observations: the scalar (i.e. weight 0) part of has contributions from the inner products of **a** with itself, comprising its weights 0 and 2; the scalar part of  comprises the corresponding products of **a** with **G**, while has just one inner product, of the weight 2 parts of **a** and **A**. Succinctly, we can write;

 ;

 ;

 .

Significantly,  does not arise, since the index structure of **A** means that it has no weight 0 – see the relevant *Ti*(*jk*) entry in Table 4. (Incidentally, the tracelessness in the indices *j*, *k* also means that the multiplicity of weight 1 is only singular.) So, the tensor **A** has only weights 1, 2, and 3 and, using the key principle enunciated in Section 4, we therefore find that only weight 2 survives in the result, since it alone matches a non-zero weight of **a**. From the above analysis, we may conclude that there are just five independent quantities that contribute to the absolute scattering signal – so that for their relative values, four intensity ratio measurements suffice.

We now rapidly home in on a conclusion on the full characterisation of differential scattering. As we saw at the end of Section 6, one measurement may be taken to serve as a standard, and as such the relative values of  and  in equation (33) may be resolved from a determination of the traditional depolarisation ratio. For a *chirally sensitive* response, we look to the interference terms in equations (34) and (35); since the spatial parity of **a** is the opposite of both **G** and **A**, their interference terms in are only supported by chiral molecules [4]. (Equally, for their counterpart radiation tensors, the interference terms are only supported by chiral radiation – ideally a circular polarization). Hence, only the three terms in equations (34) and (35) are chirally sensitive and these are indeed the three other quantities that explicitly feature in the analytic result – see equation (52) of ref. [90] – hence, experimental measurements at angles other than the usual right-angle geometry enable full characterization [91,92].

The above successes exploit the fact that experiments can be performed with variable polarization: for scattering processes the output can also be resolved for polarized components and, in addition, the scattering angle can be varied. Each polarization might in general be represented by a pair of values, corresponding for example to coordinates on the Poincaré sphere. We can nonetheless anticipate more difficulty arising when we move to processes involving more photons in each elementary interaction.

*7.3 Application: second harmonic optical activity*

Let us, therefore, consider in detail a more intricate, second example of chiral response. Optical activity in hyper-Rayleigh (or hyper-Raman) scattering is a phenomenon that has recently been verified in several experiments on suspensions of Ag and Au nanohelices, and also on molecular helices formed by the self-organization of aromatic oligoamides [22,23,93]. Noting that, for the generation of terms sensitive to the handedness of the optical input, magnetic dipole and electric quadrupole interactions must again be photon annihilation processes, we can directly write down the counterparts to equations (25) – (35), as follows:

;  ;

 ;

 ;

 ;

 ;

 ;

 .

Explicit expressions for the **J** and **K** tensors, though not required here, are deployed in the calculations reported in refs [94] and [95]. With regard to the parameter space for polarization studies, we can already appreciate there are limitations imposed by the degeneracy in the two photon annihilation processes, and also a degree of interdependence of the **P** tensors. For example, . Relationships of this kind between **S** tensors, and also between **P** tensors, may arise through their defining constitution as polyadics, i.e., outer products of vector components. No such reductions arise in the material tensors **T** or **W**, as for example is evident from any conventional sum-over-states formulation of material response tensors [40].

The tensor decomposition of **b**, which has the index structure *Ti*(*jk*), can be directly read off from the appropriate entry in Table 4 and, following its caption, written as ; similarly for **J** with non-symmetric index structure *Tijk*, we have . The **K** tensor requires additional scrutiny since it introduces another factor, namely its tracelessness as well as index symmetry in one index pair. We deduce its decomposition from a tensor outer coupling with the form , whose tensor reduction into irreducible parts therefore takes the form  which we write as . Hence, we can immediately secure the following, key information on the extent of the parameter space for the molecular invariants:

 ;





The large number of terms in the last of these results largely reflects the complexity of reduction in the tensors **J** and **K**.

From equations (45) and (46), we learn that rigorous results for chirally differential hyper-Rayleigh response are, in general, cast in terms of eighteen linearly independent quantities. Clearly, the usual parameter space for experiments with different **P** tensor values is too limited to provide a conventional basis to identify this number of invariants. Scattering experiments usually afford no more than five degrees of freedom: two for the input polarisation, two for the output polarisation, plus one for the scattering angle. It is possible that, in certain cases, physical structure symmetry in the material might reduce the number of **W** invariants. However, the condition of chirality excludes all elements of structural symmetry save for rotations – and pure rotational symmetry is rare in chiral substances [96]. The initial conclusion has to be that no experimental protocol could uniquely identify any complete and suitably independent set of material characteristics for hyper-Rayleigh optical activity in a fluid.

One means to circumvent the scale of this problem might be to entirely dispense with the **K** terms. This can be argued on the basis of the lesser significance of quadrupole coupling for long-wavelength input radiation – as has been suggested for the third harmonic case [19]. Still, the nine chirally sensitive **b** **J** terms in equation (45) remain. On the other hand, there can be different, equally persuasive reasons to focus on the **b** **K** terms alone, if structured light with high topological charge is used as input – since this kind of beam structure accentuates terms dependent on the phase gradient to which quadrupoles couple [97,98]. Once again, nine independent invariants govern the response, as indicated in equation (46). Indeed, using matrix algebra, a recent analysis by Forbes has identified exactly nine independent parameters – labelled A – I in Table 1 of ref. [95]. The invariants listed there, directly delivered by a lengthy procedure for rotational averaging, equally constitute a complete, linearly independent set, necessarily expressible as linear combinations of the irreducible tensor invariants in the present equation (46). (The supplementary parameters A'' – E'' in Table 1 of ref. [95] relate to quadrupole interactions with the emitted light, which are not sensitive to sense of circular polarisation in the optical input). In this crucial test, the applicability of the symmetry analysis reported here is therefore explicitly verified, in even this spectroscopically most complex case.

There is an alternative basis for a still more simplified approach, if a gross assumption of complete index symmetry (a Kleinman approximation) is made for each of the tensors **b**, **J**, and **K**. Then, all nine of the **b**  **K** invariants in equation (46) identically vanish, since there is no match between their non-vanishing weights – compare the entries for *T*(*ijk*) and *T*(*ijkl*) in Table 4. All that survive from equations (44) and (45) are terms of weight 1 and 3, namely , ,  and . An analysis of experiments on this approximate basis, through variation of the optical measurement conditions, therefore represents a residually symmetry-based rationale for system characterisation.

1. **Discussion**

In their wide applications to optical spectroscopy, nonlinear spectroscopy, and nanoscale photonics, an irreducible tensor framework of analysis provides a powerful means for readily enumerating the number of fundamentally independent quantities that characterize any specific level of photon-matter interaction. In the preceding account, numerous examples have exemplified the strengths of such an approach, providing strategic direction for experimental characterization. Several features are worth emphasizing: (a) explicit expression in terms of specific Cartesian components has not been necessary; (b) the analysis of experiments on the basis of these principles facilitates characterization without the risk of a multi-parameter fit that may entail hidden degrees of interdependence; (c) despite its rigorous foundation, the approach is essentially pragmatic, without reliance on software-based computations of optical properties or electromagnetic fields; (d) the analysis of fluid systems provides for a significant simplification of the analysis. For partially ordered systems, irreducible Cartesian methods remain applicable, analytically expressed in terms of moments of the corresponding angular distributions [99].

The analysis of optically active second harmonic scattering has illustrated both the power of such an approach, and the constraints it reveals on the ultimate limitations of experimental measurement. For example, this case has highlighted the facility to quickly and precisely enumerate the number of independent invariant parameters that can fully characterizes enantioselective, chirally differential response, contrasting with the lengthy calculations required to deliver the same result from a full electrodynamic analysis (the latter being a task that itself involves manipulations with a non-sparse, non-symmetric 36 × 36 matrix of tensor products). Limitations arising from the interference of multipoles have been identified and possible mitigations identified. Attention has been drawn to the fact that the limited parameter space, for the study of fluids, undermines an ideally complete degree of characterization. In principle, more could be achieved through the study of isolated molecules – but most systems of interest would display quite different properties when removed from the dielectric and solvation effects of the medium in which their applications are intended.

Part of the difficulty introduced by focusing on chiral interactions is that such materials do not lead to the substantial simplifications that arise when the samples of interest possess inversion or mirror symmetry elements, which can lead to simplifications nicely shown in recent work by Wu and Xiong [11]. However, as intimated above, a newly promising approach is to explore the use of wavefront-structured and polarization-structured vortex beam sources [100-102]. Work newly published by Bégin et al. shows that helicity-dependent nonlinear absorption occurs even in achiral molecules such as propanone and methanol, and also that it can be experimentally controlled [103]. The emerging science of optical interactions with structured optical modes has instigated the introduction of generalized Poincaré spheres for their representation and led to detailed prescriptions for their laboratory production – see for example refs [104-108]. Indeed, work in progress is now examining the scope for using these principles for the complete characterization of Raman optical activity using the additional degree of experimental control afforded by optical vortex radiation [109,110]. The broad significance of such an approach is that it expands the parameter space accessible to experimental control – essentially by recasting the basis for optical mode expansions to accommodate a variable topological charge [111]. The attention that is now being focused on chiral effects in second harmonic scattering has also led to the use of vortex light being recently addressed for the first time [95]. As ever, the increasing sophistication of experimental techniques opens up new grounds for studies with enhanced precision for robust data acquisition.

To conclude, it is interesting to observe the relevance of the present work to the burgeoning range of nonlinear optical and plasmonic methods for detecting chirally sensitive interactions between circularly polarised (CP) light and chiral molecules. In this connection, experimental work on nanoparticle-enhanced chirality, by Valev et al. [22,23,112,113], exemplifies a range of new, enhanced laser-based methods of product characterization, readily applicable to mL volumes of sample. As has recently observed by Greenfield et al. [114], such techniques now play a central role in a range of areas, from spectroscopy and imaging to next-generation photonic devices: prominent examples extend from the nonlinear optical characterization of pharmaceutical formulations [115] to the creation of multi-channel holograms – for example ref. [116]. Now, generalizing an explicit development of theory to underpin experimental studies [19], the present symmetry analysis paves the way for developing and fully systematizing the interpretation of experiments in this rapidly growing field.

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