

04 THE IRREDUCIBLE SPHERICAL TENSOR TECHNIQUE, APPLIED TO NONLINEAR PROCESSES IN GASES: APPLICATION TO COHERENT ANTI-STOKES RAMAN SCATTERING (CARS)

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The calculation of nonlinear susceptibilities for atoms and molecules is of great interest both for device applications (e.g. harmonic generation and frequency conversion) and for spectroscopy. An example of the latter is the recent interest in CARS, which has experimental advantages over Raman scattering.

These calculations can be carried out using cartesian tensors alone, but for gases, where individual molecules are considered and then orientation averaged, such a procedure would be

Table 1
Angular dependence of intensity on direction of polarisation vectors (*all beams linearly polarised*).

K	0	1	2
Raman	$\frac{1}{3} \cos^2 \beta_S$	$\frac{1}{2} \sin^2 \beta_S$	$\frac{1}{6} (3 + \cos^2 \beta_S)$
CARS	$\frac{1}{9} \cos^2 \beta_S \cos^2 \beta_{AS}$	$\frac{1}{4} \sin^2 \beta_S \sin^2 \beta_{AS}$	$\frac{1}{36} [\cos(\beta_{AS} - \beta_S) (3 + \cos^2 \beta_S) - \sin(\beta_{AS} - \beta_S) \sin \beta_S \cos \beta_{AS}]^2$

β_S is the angle between Stokes and pump polarisation vectors, β_{AS} is the angle between anti-Stokes and pump polarisation vectors.

algebraically clumsy and unclear. Because of their rotational properties, the use of irreducible spherical tensors (IST's) is ideally suited to these calculations.

We therefore present, from the general outlook afforded by the use of spherical tensors, a unified scheme for orientation averaging, for obtaining selection rules and angular distributions of intensity and for absolute numerical calculations. The case of CARS is discussed in detail as an illustrative example, and is compared with Raman Scattering.

By using the ISR technique, it will be seen that the nonlinear polarisation can be written as a product of two parts, one containing electric field vectors, the other cartesian susceptibility components. These parts are linked by common labels, K_2, K_3, \dots which are determined by selection rules internal to the susceptibility. Once the labels are known the angular dependence on field vectors may be written down.

After orientation averaging, only the isotropic IST in the decomposition survives, and as this is a known linear combination of cartesian susceptibility components (referred to the molecule-fixed axes) one can thus immediately write down the averaged form.

As an example consider CARS, for which the susceptibility may be written in a form resembling the product of a Raman and a "CARS" polarisability. The IST scheme preserves this form, and it will be seen that only one label, K , appears: $K = 0, 2$ corresponds to Placzek's isotropic and anisotropic scatterers respectively; $K = 1$ implies $\alpha_{ij} \neq \alpha_{ji}$ for both the polarisabilities. This same labelling applies to pure Raman scattering, and it is thus not surprising to find they have the same selection rules for K , viz. that the direct product of the representations of the initial and resonant excited states (molecular point group G) with the decomposition of the representation $D_+^{(K)}$ of the rotation-reflection group, under G , should contain the identity representation of G .

Once K has been fixed, the angular distribution follows; some examples are given in table 1. As the CARS intensity depends on the modulus squared of the susceptibility, its angular distributions resemble the square of the corresponding Raman ones (this is exact if $\beta_S = \beta_{AS}$ in table 1).

It is clear therefore that no new information is to be obtained from CARS as opposed to Raman Scattering, apart from that allowed by the improved experimental conditions.

The IST formalism is readily extended to detailed numerical work, and its application to parametric generation in diatomic molecules will be discussed.