Second Harmonic Elastic Light Scattering by Gases Composed of Centrosymmetric Molecules. The Case of H_2-Ar.

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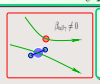
Abstract

A numerical and theoretical study of nonlinear collisional electrical and/or optical properties of van der Waals weakly bound complexes composed of a linear nonpolar molecule and an atom is presented. The basic stage of the procedure developed consists of computational quantum chemistry (QC) efforts of determining values of the first hyperpolarizability for several intermolecular configurations in order to produce its symmetry adapted (SA) components, which are finally used so that the spectral distributions of the collision-induced hyper-Rayleigh (CIHR) light scattering could be determined. Translational parts of these functions have served as an assessment tool to judge about the role played by a particular SA contribution in the overall tensorial property. Three computational methods based on quantum and semiclassical approach have been compared.

The phenomenon

In centrosymmetric molecules/atoms and molecular systems the first hyperpolarizability third rank tensor, β_{xyz}, has all its components identically equal zero as a result of geometrical properties of a system and indices permutational symmetry.

Two colliding identical entitites form a centrosymmetric unit with no nonzero hyperpolarizability.



In systems composed of two unlike molecules/atoms the nonzeroth hyperpolarizability appears

A compound of two dissimilar molecules/atoms during their encounters may posses a collective (the so-called—collisional hyperpolarizability, which results from intermolecular interactions and noncentrosymmetric geometry of the supermolecule.

Geometrical considerations

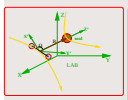
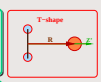


Fig.1 Coordinate system.

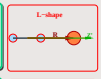
The geometrical properties of the system, a choice of the reference frame and permutational properties of the hyperpolarizability tensor indices determine number of the tensor components and the shape of the formulas needed.

Three geometrical arrangements are taken into account in the QC computations determining a number of independent tensorial components (spherical).

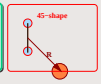
$\Delta\beta_0^1(R), \Delta\beta_2^3(R) = \Delta\beta_{-2}^3(R), \Delta\beta_0^3(R)$



$\Delta\beta_0^1(R), \Delta\beta_0^3(R)$



$\Delta\beta_0^1(R), \Delta\beta_0^3(R), \Delta\beta_1^3(R), \Delta\beta_2^3(R), \Delta\beta_3^3(R)$



Ab initio QC computations

The QC calculations of the hyperpolarizabiity components were performed under the following assumptions:

- Boys-Bernardi conterpoise-correction method was used,
- calculations are performed at the second-order MP2(Full) level of theory,
- Gaussian 98 algorithm applied,
- basis set: [6s4p2d] for H_2 and [8s6p5d4f]

A more daetailed description of the method is given in [1].

Symmetry adapted components

The radial/orientational dependence of the hyperpolarizability can be evaluated in the form of a series expansion with the so-called symmetry adapted (SA) components of $\Delta\beta$ [2](in the equation below in red); their dependence on R is illustrated in Fig.2:

$$\Delta\beta_\mu^{(s,K)}(R) \sim \sum_{\lambda L} (2L+1)^{1/2} \Delta\beta_{\lambda L}^{(s,K)}(R) \times Y_{\lambda\mu}(\Omega)\, C_{\lambda\mu\, L0}^{K\mu},$$

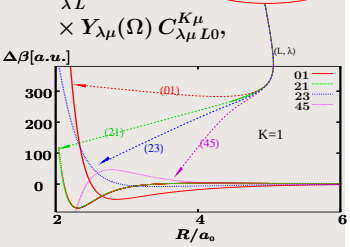


Fig.2 The radial dependence of the SA components, $\Delta\beta_{\lambda L}^{s,1}$, of the vector part of $\Delta\beta$, for different allowed λ and L values calculated by the QC method.

Translational spectra

A theory of the nonlinear collision-induced hyper-Rayleigh (CIHR) light scattering, for which the hyperpolarizability property is exclusively responsible, has been developed in order to analyze the role played by the particular SA components. The intensity of the CIHR scattered light is given by:

$$\left(\frac{\partial^2 I^{2\omega}}{\partial\Omega\partial\omega}\right)/I_0^2 \sim \sum_{\lambda,L}\sum_{j,j'} \Pi_{jj'}^2 P_j \begin{pmatrix} j & \lambda & j' \\ 0 & 0 & 0 \end{pmatrix}^2 g_{\lambda L}^{(K)}(\Delta\omega)$$

The most crucial part of this expression, from our point of view, i.e. $g_{\lambda L}^{(K)}$, is the spectral density function of the translational part of the CIHR spectrum. In the theory presented it is calculated by means of three methods: the Birnbaum-Cohen model, a quantum-mechanical approach, and a semiclassical treatment, respectively:

$$^{(BC)}g_{\lambda L}^{(K)}(\omega) = \frac{M_0^{(*)}\tau_1}{\pi}\exp[\tau_2/\tau_1]\exp(\omega\,\tau_0)\frac{z\,K_1(z)}{1+(\omega\,\tau_1)^2}$$

$$^{(QM)}g_{\lambda L}^{(K)}(\omega) \sim \sum_{i,i'} P_i \int_0^\infty \left|\Psi_{i'}(R)^* \Delta\beta_{\lambda L}^{(s,K)}(R)\Psi_i(R)dR\right|^2 \delta(\Delta\omega)$$

$$^{(SC)}g_{\lambda L}^{(K)}(\omega) \sim G(\omega)\int_0^\infty s\, f_{MB}(s,T)\, 4\pi s^2 ds \int_0^\infty B_{\lambda L}^K(\omega,q,s)\, 2\pi q\, dq$$

As a result spectral translational profiles have been obtained for both the vector and the septor parts of the hyperpolarizability tensor for different λ, L pairs.

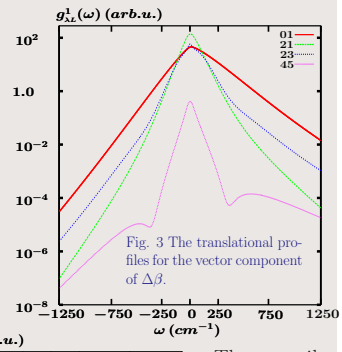


Fig. 3 The translational profiles for the vector component of $\Delta\beta$.

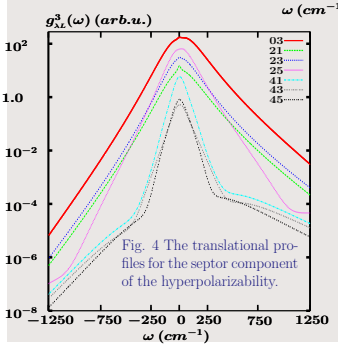


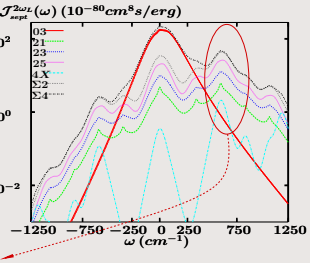
Fig. 4 The translational profiles for the septor component of the hyperpolarizability.

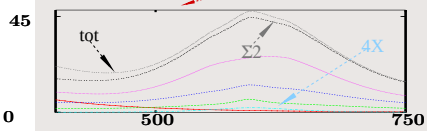
The prevailing role of the profiles for $\lambda = 2$ over those of $\lambda = 4$ indicates a quick convergence of the $\Delta\beta$ series expansion, even for relatively small λ values.

Total spectra

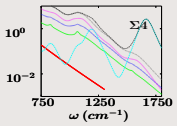
The total resulting CIHR spectra are a convolution product of the transaltional and rotational (stick) profiles. Calculated for a variety of λL pairs combinations they are presented in Fig. 5. One can easily noticed that the order of the intensities shown agrees with the purely translational profiles mainly for the central part of the line sets—for larger intensities the $\lambda = 4$ contributions may gain some importance.

Fig.5 Overall translational/rotational spectrum for the septor part of $\Delta\beta$ Below, an enlargement of the encircled sectoris given and a far wing region of the profile shown to illustrate the λ=4 component importance.





For very remote frequencies the nonnegligible participation of the $\lambda = 4$ contributions becomes more pronounced to end up as a domineering part. However, this region might be rather difficult to reach by means of experimental methods.



To sum up

Numerical efforts to calculate quantum chemistry values of a collisional nonlinear molecular property (the first hyperpolarizability) are presented for systems consisted of a linear nonpolar molecule (H_2) and an atom (Ar) together with a theoretical calculations of the symmetry adapted SA of this quantity.

As a result:

- $\Delta\beta$ collisional values have been obtained numerically (QC method),
- series expansion of the above quantity has been found theoretically,
- $\Delta\beta_{\lambda L}^{(K)}(R)$ components have been derived,
- theory of the CIHR scattering has been developed,
- rapid convergence of the series expansion has been established,
- translational spectra of CIHR have been numerically found for different λL pairs and analyzed with respect to their importance.

A more extended discussion of the above mentioned issues can be found in [3, 4].

References

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