Nonlinear properties and collisional spectra in hydrogen-(heavy) noble-gas-atom mixtures

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Abstract. In a series of previously published works the phenomenon of collision induced nonlinear hyper-Rayleigh scattering of light (CIHRS) was studied on the basis of the numerical quantum chemistry (QC) methods confronted with a theoretical approach. A class of supermolecular systems composed of hydrogen (H$_2$) and lighter inert gas atoms (Rg) was considered. In this report a development of this research work is presented with more massive and highly polarizable, Kr and Xe, perturbers involved. The collision-induced hyperpolarizability tensorial values, $\Delta \beta$ obtained by means of the QC ab initio methods are applied in order to produce the CIHRS spectral distributions; the influence of $\Delta \beta$ features on the line shapes is compared with the earlier theoretical predictions. Namely, the validity of the multipole-induced-multipole (MIM) mechanism is assessed. In particular, its relevance to reproduce long-range functional behavior of the so-called symmetry adapted (SA) components of the hyperpolarizability tensor $\Delta \beta (R)$ is discussed. A thorough analysis of the translational CIHRS spectra is then performed to identify the role of the hyperpolarizability spatial distribution in forming particular sections of the line shapes. An extension of the dipole-induced-quadrupole analytical model is suggested and tested with regard to its ability to reproduce more accurate profiles.

1. Introduction

In view of the continuous development of experimental and numerical methods of investigation of still more subtle effects related to light scattered by molecular media, a growing demand for data sets of relevant molecular properties and for analysis of validity of their values is observed. Nonlinear hyper-Rayleigh scattering occurrences, particularly those in which a significant role is played by intermolecular interactions and correlations, no doubt belong to this category of phenomena.

The hyper-Rayleigh (HR) process can be observed, when there is a non-negligible probability of two absorbed photons of laser frequency $\omega$ to initiate a nonlinear response of the medium resulting in emission of a photon at a frequency of about $2\omega$. The most pronounced spectral properties of the HR scattered signal are mainly determined by the first hyperpolarizability tensor, $\beta$, of a given microsystem. It may be expected, however, that there are also certain non-negligible contributions to the HR effect induced by interactions between the atoms and/or molecules during their fly-by encounters. This is the so-called collision-induced hyper-Rayleigh
scattering (CIHRS) that can be especially conspicuous in molecular media that consist of microscopic entities whose intrinsic symmetry forbids the occurrence of the single-molecule HR effect. The hyperpolarizability property of the short-lived compounds can be evaluated both by means of numerical and theoretical procedures [1, 2], each having its specific domain of validity attributed, for instance, to characteristic frequency regions of the scattered light. Analysis of applicability of these methods is the main aim of the research presented.

2. Objectives
The above stated general idea of the study determines more detailed objectives to be achieved:

- to extend the set of the CIHRS-active compounds previously considered [3, 4, 5, 6, 7] to systems including the heavier noble gas atoms of Kr and Xe; as found earlier, the more polarizable the perturbers the greater is the intensity of the scattered signal, which offers a better chance for foreseeable experimental methods to detect it;
- to determine ab initio values of the supermolecules’ collisional hyperpolarizabilities and their counterparts obtained analytically;
- to assess and compare the ability of the data sets obtained by means of the procedures mentioned to render particular frequency area of the CIHRS spectral lines.

3. Outline of the method
3.1. Spectral distributions
The intensity of the hyper-Rayleigh scattered light related to a collisional hyperpolarizability SA component $\Delta \beta_{KL}^\alpha(R)$, defined later on in Eq. 4, can be expressed on the basis of the quantum mechanical approach (QM) by the formula:

$$\left( \frac{\partial^2 I_2}{\partial \Omega_1 \partial \omega} \right) / I_0^2 \sim \sum_{\Lambda,\lambda,j,j'} \Pi_{j,j'}^2 P_j \left( \begin{array}{ccc} j & j' & \lambda \\ 0 & 0 & 0 \end{array} \right) \int_0^\infty \left| \Psi^*(R; E + \hbar \omega, j') \Delta \beta_{KL}^\alpha(R) \Psi(R; E, j) dR \right|^2,$$

where the wave functions $\Psi$ are obtained by means of solving numerically the radial Schrödinger equation [8, 9].

3.2. Hyperpolarizability
According to the symmetry properties of the H$_2$Rg systems, there are only two spherical tensor components of $\Delta \beta$: the vector- and septon-like of rank 1 and 3, respectively. The ab initio (QC) evaluation of the SA components is performed on the following assumptions: all the calculations are accomplished at the coupled-cluster theory with singles and doubles level; the Gaussian 03 computing procedure is used with the basis sets: [6s4p3d] for H$_2$, [8s7p6d1f] for Kr and [9s8p7d1f] for Xe. For the details of the method see [1, 10].

Within the MIM model some of the SA hyperpolarizability components can be expressed in terms of analytical formulae of the shape akin to the one given below [2]:

$$\Delta \beta_{03}^{(3)}(R) = -3 \left( \langle H_2 \rangle \tilde{B}_{00} \rangle (11)22 \langle H_e \rangle \tilde{a}_{00}[11] - \langle H_e \rangle \tilde{B}_{00}^\dagger (11)22 \langle H_2 \rangle \tilde{a}_{00}[11] \right) R^{-4};$$

$B_j[(11) 22]$ is the dipole-dipole-quadrupole hyperpolarizability, $\tilde{a}_{00}[11]$ denotes the dipole-dipole polarizability tensor. After having substituted proper values of the molecular and atom quantities one can derive, for example, for H$_2$Xe:

$$\Delta \beta_{23}^{(3)}(R) = -2959.4 R^{-4}. \quad (3)$$

This individual contribution of the lowest order effect, induced by the dipole-induced-quadrupole (DIQ) interaction, can be subsequently refined by extending the collisional series expansion into
terms representing other kinds of intermolecular interactions, firstly—the higher order multipolar mechanisms (EMIM) and secondly—the overlap, dispersion and exchange forces. The details of the method are given in [2].

3.3. Spatial dependence of SA components
The SA adapted components of hyperpolarizability, defined in the formula below (in bold):

$$\Delta \beta^{(K)}_{\mu}(R) \sim \sum_{\lambda L} (2L + 1)^{1/2} \Delta \beta^{(K)}_{\lambda L}(R) Y_{\lambda \mu}(\Omega) C_{\lambda L}^{K \mu},$$

are obtained by solving appropriate sets of equations resulting from this equation [2]. To this end, initial tensorial data sets of $\Delta \beta^{(K)}_{\mu}$ are calculated for three intra supermolecular orientations (0°, 45° and 90°) by the ab initio (QC) tools as well as by the multipole-induced-multipole analytical means. A simple model in which a kind of ‘exchange interactions’ influence is expressed in terms of a fitted exponential function combined with the EMIM model:

$$\Delta \beta(R) = (a_1 R^2 + a_2 R + a_3) \exp(a_4 R + a_5) + EMIM,$$

is additionally taken into account in the considerations hereafter.

The approaches mentioned above are assumed to render a satisfactory description in different regions of colliding distances. Thus, their applicability of shaping particular parts of the CIHRS lines is worth determination, which is done by benchmarking the translational CIHRS spectra against model profile lines [6] calculated by using a kind of ‘best fit’ (BF) $\Delta \beta(R)$ dependence. The form of the BF functions is established assuming that the relative root mean square deviation (RRMSD) of their shape from the points representing the ab initio data sets should not exceed a level of 0.5%. This requirement is fulfilled in general for the $R$ distances below 10 $a_0$, whereas above this limit a relatively poorer precision of the QC methods used results in a more scattered ab initio point pattern. The RRMSD values in this case reach a level of up to several percent (the 123 and 323 components). On the other hand, the distance $R$ equal 10 $a_0$ makes the lower bounds of the MIM model applicability region.

In Fig. 1 the ab initio values are compared with the functional dependence $\Delta \beta(R)$ resulting from the analytical models. In fact, the EMIM lines are in an acceptable agreement with the
*ab initio* set for remote distances, beginning at $R \sim 9 \ a_0$; while the EMIM+’exchange’ case, in almost every point considered, provides an accurately fitted plot. It must be noted, however, that for significantly larger $R$s the *ab initio* results happen not to follow a smooth functional pattern. Rather obviously, these constatations provide a rationale for the idea of blending the QC profiles with the MIM-obtained lines into overall spectral CIHR shapes.

4. Spectra

The complete roto-translational (R-T) spectra expressed via Eq. 1 are obtained as the convolution of the rotational (so called— ’stick’) structure and superimposed translational envelope combined of contributions related to the SA translational components of $\Delta \beta (R)$.

![Figure 2. R-T total spectral lines.](image)

Analysis of the diagrams in Fig. 2 shows that the section of the translational profiles significantly influencing the resulting R-T line shape spans within approximately 350 cm$^{-1}$ of the frequency range to the sides of each rotational stick line. Therefore, only such a frequency

![Figure 3. Translational spectral contributions obtained on the grounds of: *ab initio*/'best fit’ approach (*fit3*$\Lambda L$), dipole-induced-quadrupole model (Eq. 3; *diq*), ‘extended’ EMIM method (*mim*), and EMIM/exchange approach (*mimex*).](image)
displacement should be taken into consideration, when analyzing the role of the particular hyperpolarizability models on the individual translational spectral contributions.

The spectral patterns in Fig. 3 illustrate the rather widely accepted fact that the pure DIQ approximation cannot be used in order to reflect adequately enough the spectral CIHRS properties within the 350 cm$^{-1}$ frequency limit. Indeed, the RRMS deviation from the ‘best fit’ shape in this case amounts to about 32%, 67% and 58% for $K\Lambda L = 123$, 303 and 323, respectively (all examples for H$_2$Kr). Moreover, it is also rather evident, that the extended multipolar series expansion, EMIM, does not seem to improve the picture (RRMSD $\sim$ 21%, 27% and 43%). Unfortunately, even though slightly better, these lines are not satisfactory enough in the line center as well (see the bottom enlargement panels, where RRMSD $\sim$ 10%, 11% and 12% for the EMIM shapes).

Instead, a tangible improvement can be noted, once the exponential ‘exchange’ term (Eq. 5) has been added to the model collisional mechanism (RRMSD $\sim$ 1.5%, 4% and 5%). Usually, this contribution is associated with the short-range intermolecular correlations (and thus—related to the frequency tails of the spectra), yet the examples in Fig. 3 suggest that its influence seems crucial even for the line cores so that to have them yielded properly.

5. Final remarks
To sum up, the analysis presented leaves one with the conclusion that none of the numerical and theoretical tools considered, if applied single-handedly, is capable of producing CIHRS R-T lines satisfactory enough from the experimental point of view, even within a specific area of applicability. On the one hand, the ab initio values of $\Delta \beta(R)$, though extremely precise for the short- and mid-range $R$ values [6], should be supplemented by the data sets provided by the MIM long-distance relevant models. The latter procedure, on the other hand, need to be supported with correcting terms stemming from the other types of interactions. Therefore it turns out to be apparently inevitable to combine all the approaches mentioned so that a reliable overall functional dependence of $\Delta \beta$ on $R$ could be determined. The procedures suggested in our previous work seem to pave the way towards this goal [6, 7].

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