

# Rotationally adapted studies of *ab initio*-computed collision-induced hyperpolarizabilities: The H<sub>2</sub>-Ar pair

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In this work we investigate the collision-induced (CI) dipole moment  $\Delta\mu_i(R)$ , the CI polarizability tensor  $\Delta\alpha_{ik}(R)$ , and the first dipole-hyperpolarizability tensor  $\Delta\beta_{ijk}(R)$  of the H<sub>2</sub>-Ar pair as a function of the intermolecular distance  $R$ , and the relative orientation of the intermolecular vector  $\hat{\mathbf{R}}$  and the H<sub>2</sub> molecule. For each type of spectroscopy the induction operator should be given in the symmetry adapted form. In our case the components of the CI dipole hyperpolarizability are expressed in such a way that their rotational behavior is unambiguously defined. The above description is based on the spherical rotationally adapted method presented here. Spherical rotationally adapted components  $\Delta\beta_{\lambda L}^{(s,K)}(R)$  of the *vector* ( $K=1$ ) and the *septor* ( $K=3$ ) parts of the first dipole-hyperpolarizability tensor  $\Delta\beta(R)$  are computed and discussed. Results are applied to the case of H<sub>2</sub>-Ar pair. Asymptotic long-range analytical formulas are proposed for the multipole-induced spherical rotationally adapted components  $\Delta\beta_{\lambda L}^{(s,K)}(R)$  of  $\Delta\beta(R)$ , respectively. Reasonable agreement is observed between the long-range analytical and *ab initio* numerical data.

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## I. INTRODUCTION

Interaction-induced dipole moment and polarizability are of central importance to the interpretation of fundamental spectroscopic investigations such as collision-induced absorption (CIA) and collision-induced light scattering (CILS). A wealth of experimental data concerning CIA and CILS observations has been collected in comprehensive texts [1,2]. In recent years we have reported several CILS studies for a number of significant cases such as the isotropic and anisotropic CILSs by gaseous carbon tetrafluoride [3,4], the isotropic CILS by carbon tetrafluoride in a Raman vibrational band [5], the isotropic CILS spectra from gaseous sulfur hexafluoride [6], the polarization components of rototranslational light-scattering spectra from gaseous sulfur hexafluoride [7], and the multipolar polarizations of methane from isotropic and anisotropic CILSs [8]. More recently, we have extended our efforts to investigate collision-induced hyper-Rayleigh scattering (CIHR). In this phenomenon the key element is the CI first dipole hyperpolarizability  $\Delta\beta(R)$ . The studies have brought forth many important aspects of the description of hyper-Rayleigh scattering in various systems, as gaseous sulfur hexafluoride [9], Ne-Ar [10], Kr-Xe [11], He-Ne [12], and He-Ar [13].

In this work we investigate the CI first dipole-hyperpolarizability tensor  $\Delta\beta_{ijk}(R)$  [14–17] of the H<sub>2</sub>-Ar pair as a function of the intermolecular distance  $R$ , and the relative orientation of the H<sub>2</sub> molecule and the intermolecular vector  $\hat{\mathbf{R}}$ . Special care must be taken when a pair includes at least one molecule. When this system starts to move, during

fly-by encounter of its components, besides their transient translational motion the entire molecule rotates. The rotational degrees of freedom (the rotation of the H<sub>2</sub> molecule as well as the relative “translational” angular momentum of the interacting pair) are excited in the presence of the incident radiation. The only efficient way to deal with the rotational motions relies on the angular-momentum methods [18,19]. Then for each kind of the CI spectroscopy the induction operator should be given in the language of irreducible symmetry adapted spherical tensors. In our case the components of the CI hyperpolarizability have to be expressed with their rotational behavior univocally defined [20,21]. This description is based on the spherical rotationally adapted method presented here.

Theory and quantum-chemistry computational methods are presented in Sec. II. The symmetry allowed form of spherical harmonic expansion of  $\Delta\beta(R)$  is given in Sec. III. In this section the method of computing the rotationally adapted components  $\Delta\beta_{\lambda L}^{(s,K)}(R)$  of  $\Delta\beta(R)$  is proposed as well. The long-range model asymptotic pair multipolar hyperpolarizability tensor is given in Sec. IV. Two multipole-like spherical rotationally adapted components,  $\Delta\beta_{23}^{(s,1)}(R)$  and  $\Delta\beta_{23}^{(s,3)}(R)$  of the vector and the septor parts of  $\Delta\beta(R)$ , respectively, are discussed numerically. Good agreement between analytical and *ab initio* numerical data for these components has been found. Section V concludes the paper.

## II. THEORY AND COMPUTATION

For determination of the interaction dipole moment, polarizability, and first hyperpolarizability of H<sub>2</sub>-Ar, we lean heavily on previous experience on the calculations of electric properties of interaction species [22–28]. We will give only a few significant details here, with an emphasis on basis set

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selection. The energy of the uncharged molecule in a weak homogeneous electric field can be expanded as [29]

$$E^P = E^0 - \boldsymbol{\mu}_i F_i - \frac{1}{2} \boldsymbol{\alpha}_{ij} F_i F_j - \frac{1}{6} \boldsymbol{\beta}_{ijk} F_i F_j F_k - \frac{1}{24} \boldsymbol{\gamma}_{ijkl} F_i F_j F_k F_l + \dots, \quad (1)$$

where  $F_i$  is the field and  $E^0$  is the energy of the free molecule. The coefficients of the expansion (in bold) are the dipole moment ( $\boldsymbol{\mu}_i$ ), the dipole polarizability ( $\boldsymbol{\alpha}_{ij}$ ), the first dipole-hyperpolarizability ( $\boldsymbol{\beta}_{ijk}$ ), and the second dipole-hyperpolarizability ( $\boldsymbol{\gamma}_{ijkl}$ ) Cartesian components. A repeated subscript implies summation over  $x$ ,  $y$ , and  $z$ . The number of independent components needed to specify the above tensors is regulated by symmetry. In this work  $z$  is the  $\text{H}_2$  molecular axis with  $\text{H}_2$ -Ar in the  $xz$  plane. For the linear L-shaped (Ar on the positive  $z$  axis,  $C_{\infty v}$ ), T-shaped (Ar on the positive  $x$  axis,  $C_{2v}$ ), and planar (Ar on the  $45^\circ$  direction) configurations,  $\Delta\boldsymbol{\beta}_{ijk}(\mathbf{R})$  has two, three, and six independent components, respectively. The interaction properties were calculated via the Boys-Bernardi counterpoise correction method [30], as

$$P_{\text{int}}(\text{H}_2 \cdots \text{Ar})(\mathbf{R}) = P(\text{H}_2 \cdots \text{Ar})(\mathbf{R}) - P(\text{H}_2 \cdots \text{X})(\mathbf{R}) - P(\text{X} \cdots \text{Ar})(\mathbf{R}), \quad (2)$$

where  $\mathbf{R}$  determines the geometrical configuration of the system.  $P(\text{H}_2 \cdots \text{X})(\mathbf{R})$  and  $P(\text{X} \cdots \text{Ar})(\mathbf{R})$  denote the results of calculations of the property of subsystems  $\text{H}_2$  and Ar in the presence of the ghost orbitals of Ar and  $\text{H}_2$ , respectively. All calculations were performed at the second-order Møller-Plesset perturbation theory [MP2(Full)] level of theory with the GAUSSIAN 98 program [31]. All electrons were correlated. Full descriptions of the MP2 method are available in standard textbooks [32]. For our choice of the MP2 method, we lean heavily on previous experience on interaction (hyper)polarizability calculations. For instance, in the case of NeAr at an internuclear separation of  $5.0 a_0$ , we obtain an interaction mean first hyperpolarizability  $\beta_{\text{int}}/e^3 a_0^3 E_h^{-2}$  of 8.0 for MP2 and 7.9 for the presumably more accurate coupled-cluster approach CCSD(T) [singles and doubles coupled cluster theory with an estimate of connected triple excitations obtained via perturbational treatment] (see Table IV of [23]).

The selection of suitable basis sets is of central importance for the interaction (hyper)polarizability calculations. Special attention is needed for atomic systems for which unusually difficult cases are easily recognized [33–35]. In this work we relied on a [8s6p5d4f] basis set used and tested systematically in previous work (see Refs. [22,24]). This basis gives the Ar dipole polarizability at the self-consistent field (SCF) level of theory  $\alpha/e^2 a_0^2 E_h^{-1} = 10.66$  to be compared with the numerical Hartree-Fock (NHF) [36] value of 10.758. For  $\text{H}_2$  we rely on previous experience [37] to propose a [6s4p2d] basis set. This is an augmented version of the [6s4p1d] purpose-oriented basis set used previously in the calculations on  $\text{H}_2$ - $\text{H}_2$  (see Ref. [22]) which contains an additional diffuse  $d$ -GTF (Gaussian-type functions) with exponent  $\eta_d = 0.0464 a_0^{-2}$ .

TABLE I. Interaction dipole moment, polarizability, and hyperpolarizability for  $\text{H}_2$ -Ar [Ar on the  $z$  axis;  $\Delta\alpha_{xx}(\mathbf{R}) = \Delta\alpha_{yy}(\mathbf{R})$ ,  $\Delta\beta_{xxz}(\mathbf{R}) = \Delta\beta_{yyz}(\mathbf{R})$ ].

$R/a_0$	$\Delta\mu_z(\mathbf{R})$	$\Delta\alpha_{xx}(\mathbf{R})$	$\Delta\alpha_{zz}(\mathbf{R})$	$\Delta\beta_{xxz}(\mathbf{R})$	$\Delta\beta_{zzz}(\mathbf{R})$
2.0	1.8723	19.5322	48.2450	-58.20	-2477.15
2.5	1.3318	3.3338	23.3411	89.55	-423.25
3.0	0.8090	-0.7363	11.5702	34.87	-32.22
4.0	0.2341	-1.4128	3.9675	4.23	31.19
5.0	0.0630	-0.8981	2.0622	0.50	17.53
6.0	0.0192	-0.5256	1.3620	0.12	7.12
7.0	0.0079	-0.3244	0.9437	0.05	2.63
8.0	0.0041	-0.2163	0.6509	0.00	1.13
9.0	0.0023	-0.1530	0.4499	0.02	0.48
10.0	0.0014	-0.1116	0.3188	0.090	0.13
12.0	0.0007	-0.0652	0.1755	0.090	0.13
14.0	0.0006	-0.0402	0.1092	0.10	-0.20
16.0	0.0003	-0.0262	0.0757	0.03	0.07
18.0	0.0002	-0.0184	0.0529	0.09	0.25
20.0	0.0001	-0.0134	0.0384	0.01	0.02
25.0	0.0000	-0.0068	0.0196	0.00	0.01
30.0	0.0000	-0.0040	0.0113	0.00	0.01

The electric properties obtained for the Ar and  $\text{H}_2$  monomers at the MP2 level are: for Ar,  $\alpha/e^2 a_0^2 E_h^{-1} = 11.19$ ,  $\alpha_2/e^2 a_0^4 E_h^{-1} = 53.09$ ,  $B/e^3 a_0^4 E_h^{-2} = -166$ , and  $\gamma/e^4 a_0^4 E_h^{-3} = 1211$  (the five innermost MO were kept frozen in the Ar monomer calculations). Definitions of the higher polarizabilities ( $\alpha_2$ —quadrupole polarizability,  $B$ —dipole-dipole-quadrupole hyperpolarizability, and  $\gamma$ —second dipole hyperpolarizability) have been given in our previous work [38].

For  $\text{H}_2$ , with  $z$  as the molecular axis, we obtain for the quadrupole and the hexadecapole moments  $Q = 0.49 e a_0^2$  and  $\Phi = 0.34 e a_0^4$ , dipole polarizability  $\alpha_{zz} = 6.81 e^2 a_0^2 E_h^{-1}$  and  $\alpha_{xx} = 4.79 e^2 a_0^2 E_h^{-1}$ , second hyperpolarizability  $\gamma_{zzzz} = 753 e^4 a_0^4 E_h^{-3}$ ,  $\gamma_{xxxx} = 638 e^4 a_0^4 E_h^{-3}$ , and  $\gamma_{xxzz} = 233 e^4 a_0^4 E_h^{-3}$ , dipole-octopole polarizability  $E_{z,zzz} = 4.41 e^2 a_0^4 E_h^{-1}$  and  $E_{x,xxx} = -1.71 e^2 a_0^4 E_h^{-1}$ , and dipole-dipole-quadrupole hyperpolarizability  $B_{z,z,zz} = -101 e a_0^4 E_h^{-2}$ ,  $B_{x,x,xx} = -67 e a_0^4 E_h^{-2}$ ,  $B_{x,z,xz} = 42 e a_0^4 E_h^{-2}$ , and  $B_{x,x,xx} = -74 e a_0^4 E_h^{-2}$ . See Ref. [37] for a convenient choice of tensor components for the electric properties of this molecule. All calculations on  $\text{H}_2$  pertain to a bond length of  $1.449 a_0$ . In Tables I and II we show the calculated dipole moments, polarizabilities, and hyperpolarizabilities for Ar on the  $z$  and  $x$  axes, respectively. In Table III we give the computed dipole moments and polarizabilities with Ar on 45 degrees, whereas in and Table IV we present the computed hyperpolarizabilities for 45 degrees geometry. As expected, the magnitude of the interaction properties increases very rapidly as the Ar atom approaches the  $\text{H}_2$  molecule. In the linear case, the axial interaction hyperpolarizability  $\Delta\beta_{zzz}$  is very large and negative for short distances but changes the sign for  $3 < R/a_0 < 4$  and remains significantly high for  $4 < R/a_0 < 10$ .

Our calculated values of the collision-induced dipole moment are very similar to those obtained by Meyer and From-

TABLE II. Interaction dipole moment, polarizability, and hyperpolarizability for H<sub>2</sub>-Ar (Ar on the *x* axis).

$R/a_0$	$\Delta\mu_x(R)$	$\Delta\alpha_{xx}(R)$	$\Delta\alpha_{yy}(R)$	$\Delta\alpha_{zz}(R)$	$\Delta\beta_{xxx}(R)$	$\Delta\beta_{xyy}(R)$	$\Delta\beta_{xzz}(R)$
2.0	0.7843	80.9818	26.4944	32.1131	-1940.74	25.66	95.65
2.5	0.4529	19.8459	1.3421	1.8367	-46.11	64.17	90.34
3.0	0.2096	6.6522	-1.1976	-1.4640	21.15	16.09	24.27
4.0	0.0288	1.5169	-1.2545	-1.6224	7.77	1.84	3.46
5.0	-0.0039	0.8990	-0.7811	-1.0413	0.85	0.19	0.67
6.0	-0.0058	0.7395	-0.4675	-0.6400	-1.01	-0.02	0.16
7.0	-0.0038	0.5691	-0.2947	-0.4107	-1.00	-0.02	0.06
8.0	-0.0022	0.4120	-0.1982	-0.2787	-0.64	-0.01	0.03
9.0	-0.0013	0.2950	-0.1404	-0.1982	-0.39	-0.01	0.01
10.0	-0.0009	0.2152	-0.1032	-0.1461	-0.22	-0.01	0.01
12.0	-0.0004	0.1237	-0.0604	-0.0858	-0.10	-0.01	0.00
14.0	-0.0002	0.0776	-0.0383	-0.0545	-0.06	0.00	0.00
16.0	-0.0001	0.0519	-0.0257	-0.0367	0.20	0.07	0.07
18.0	-0.0001	0.0364	-0.0181	-0.0258	-0.03	0.00	0.00
20.0	-0.0001	0.0265	-0.0132	-0.0189	0.01	0.01	0.01
25.0	0.0000	0.0136	-0.0068	-0.0097	0.00	0.00	0.00
30.0	0.0000	0.0079	-0.0039	-0.0056	0.00	0.00	0.00

mhold [39]. These authors have calculated the interaction dipole moment of H<sub>2</sub>-Ar employing the coupled-electron pair approximation (CEPA). At a distance of  $5.0a_0$  in the collinear approach they calculate  $\mu_{\text{int}}/ea_0=0.060\ 717$ , to be compared to our MP2 value of 0.0630. We note that our CI dipole moment is very close to data computed in [39] for each intermolecular distance considered and for all considered configurations. Moreover, our data were computed for the  $2.5a_0-20a_0$  intermolecular distance range comparing with the  $5a_0-9a_0$  range of [39].

### III. CI PAIR HYPERPOLARIZABILITY FOR $D_{\infty h}$ MOLECULE-ATOM SYSTEM: ROTATIONALLY ADAPTED SPHERICAL FORM

We assume a  $D_{\infty h}$  symmetry molecule-atom system fixed in the  $xz$  plane with the atom on the positive side of the  $z$  axis. The *ab initio* computed hyperpolarizability components have been transformed to this coordinate frame. We consider the induced first dipole-hyperpolarizability tensor  $\Delta\beta_{ijk}^{(s)}$  of H<sub>2</sub>-Ar to be fully symmetric (*s*) with respect to its indices

 TABLE III. Interaction dipole moment and polarizability for H<sub>2</sub>-Ar (Ar on 45 degrees).

$R/a_0$	$\Delta\mu_x(R)$	$\Delta\mu_z(R)$	$\Delta\alpha_{xx}(R)$	$\Delta\alpha_{yy}(R)$	$\Delta\alpha_{xz}(R)$	$\Delta\alpha_{zz}(R)$
2.0	0.8521	1.1471	34.1214	20.8071	18.7609	47.2433
2.5	0.5592	0.7655	10.9078	2.2229	9.9393	13.584
3.0	0.3227	0.4001	3.6568	-1.0469	5.2914	4.5385
4.0	0.0905	0.0854	0.5814	-1.3373	2.1290	0.6176
5.0	0.0249	0.0131	0.2522	-0.8382	1.2164	0.2326
6.0	0.0082	0.0001	0.2233	-0.4963	0.8126	0.2306
7.0	0.0082	0.0001	0.1801	-0.3087	0.5584	0.1999
8.0	0.0021	-0.0008	0.1294	-0.2055	0.3865	0.1503
9.0	0.0013	-0.0005	0.0898	-0.1444	0.2728	0.1081
10.0	0.0009	-0.0003	0.0632	-0.1056	0.1981	0.0783
12.0	0.0004	-0.0002	0.0344	-0.0614	0.1137	0.0445
14.0	0.0002	-0.0001	0.0209	-0.0387	0.0712	0.0278
16.0	0.0001	0.0000	0.0137	-0.0260	0.0476	0.0185
18.0	0.0001	0.0000	0.0095	-0.0183	0.0334	0.0130
20.0	0.0001	0.0000	0.0069	-0.0133	0.0243	0.0095
25.0	0.0000	0.0000	0.0035	-0.0068	0.0124	0.0049
30.0	0.0000	0.0000	0.0020	-0.0039	0.0072	0.0028

$ijk$ . For  $C_s$  symmetry we have six independent Cartesian components of the hyperpolarizability  $\Delta\boldsymbol{\beta}$  tensor [29,40,41]:

$$\Delta\beta_{xxx}, \Delta\beta_{zzz}, 3\Delta\beta_{xzz}, 3\Delta\beta_{xyy}, 3\Delta\beta_{zxx}, 3\Delta\beta_{zyy}.$$

We study the irreducible spherical components of  $\Delta\boldsymbol{\beta}$  for  $C_s$ ,  $C_{2v}$ , and  $C_{\infty v}$  symmetries [42–44], assuming the standard Condon and Shortley [45] phase convention. For  $C_s$  symmetry we have six independent irreducible totally symmetric ( $s$ ) spherical components [42]:

(a) two for the vector part

$$\begin{aligned} \Delta\beta_0^{(s,1)} &= -\sqrt{\frac{3}{5}}(\Delta\beta_{zzz} + \Delta\beta_{xzz} + \Delta\beta_{yyz}), \\ \Delta\beta_{\pm 1}^{(s,1)} &= \pm \frac{3}{\sqrt{30}}(\Delta\beta_{xxx} + \Delta\beta_{xyy} + \Delta\beta_{xzz}), \end{aligned} \quad (3)$$

(b) and four for the septor part

$$\begin{aligned} \Delta\beta_0^{(s,3)} &= \frac{1}{\sqrt{10}}(2\Delta\beta_{zzz} - 3\Delta\beta_{xzz} - 3\Delta\beta_{yyz}), \\ \Delta\beta_{\pm 1}^{(s,3)} &= \mp \frac{3}{\sqrt{120}}(\Delta\beta_{xxx} + \Delta\beta_{xyy} - 4\Delta\beta_{xzz}), \\ \Delta\beta_{\pm 2}^{(s,3)} &= \frac{3}{\sqrt{12}}(\Delta\beta_{xzz} - \Delta\beta_{yyz}), \\ \Delta\beta_{\pm 3}^{(s,3)} &= \mp \frac{1}{\sqrt{8}}(\Delta\beta_{xxx} - 3\Delta\beta_{xyy}). \end{aligned} \quad (4)$$

We note that this set reduces to the three  $\Delta\beta_0^{(s,1)}$ ,  $\Delta\beta_0^{(s,3)}$ , and  $\Delta\beta_{\pm 2}^{(s,3)}$ , independent components for  $C_{2v}$  symmetry (for T-shaped geometry), and finally to the two  $\Delta\beta_0^{(s,1)}$  and  $\Delta\beta_0^{(s,3)}$  independent components for  $C_{\infty v}$  symmetry (for L-shaped geometry).

We discuss the hyperpolarizability tensor both in Cartesian and irreducible spherical forms, starting from the brief review of main principles these two approaches.

### A. Hyperpolarizability tensors in spherical irreducible form

Vector quantities can be given either in a Cartesian basis  $|i\rangle$  with  $i=x,y,z$  or in a spherical basis  $|1\mu\rangle$  with  $\mu=1,0,-1$ . The transformation  $\langle i|1\mu\rangle$  between these two bases is unitary. For higher ( $i \geq 2$ ) rank quantities (tensors) the transformation from Cartesian tensors  $\Delta\beta_{(i)}$  to irreducible spherical tensors  $\Delta\beta_m^{(\tau,j)}$  is still unitary

$$\Delta\beta_{(i)} = \langle (i)|\tau jm\rangle \Delta\beta_m^{(\tau,j)}; \quad \Delta\beta_m^{(\tau,j)} = \langle \tau jm|(i)\rangle \Delta\beta_{(i)}, \quad (5)$$

where  $(i)$  stands for a whole set of Cartesian indices and the convention of summation over repeated indices is assumed.

The Cartesian rank- $i$  tensor  $\Delta\beta_{(i)}$  has  $3^i$  components. This tensor can be decomposed into irreducible spherical tensors. The most general reduction spectrum of  $\Delta\beta_{(i)}$  to the irreducible form is [18,44,46]

$$\Delta\beta_{(i)} = \sum_{\oplus \tau, j} \Delta\beta^{(\tau,j)}. \quad (6)$$

If several linearly independent irreducible tensors of the same weight  $j$  exists in the reduction in  $\Delta\beta_{(i)}$ , they can be distinguished by an additional superscript  $\tau$ , called the seniority index.

We can project out of any tensor the part which has a particular symmetry under Cartesian tensor index permutation. An important, interesting, and often encountered task is the way of extracting a tensor having fully permutational symmetric behavior of its indices from some given general tensor. In the case of the first dipole-hyperpolarizability tensor, we denote this fully symmetrical part by  $\Delta\beta_{ijk}^{(s)}$ . The projector  $\sigma(3)$  on the symmetric tensor subspace is called the symmetrizer. It gives

$$\Delta\beta_{ijk}^{(s)} = \frac{1}{3!} \sum_P \Delta\beta_{ijk}, \quad (7)$$

where  $\sum_P$  stands for the summation over all the permutations of a set of indices  $(ijk)$ .

### B. Vector part of hyperpolarizability tensor

It is easy to note that the irreducible vector part of the totally index symmetric first dipole-hyperpolarizability rank-3 tensor results from two routes (a)  $\{1,1\} \Rightarrow 0$  and then  $\{1,0\} \Rightarrow 1$ , and moreover (b)  $\{1,1\} \Rightarrow 2$  and then  $\{1,2\} \Rightarrow 1$ . Let us consider this problem in some detail. The irreducible part with weight  $j$  of the totally symmetric tensor ( $s$ ) is a direct sum of the orthogonal tensors  $\sigma(3)\Delta\beta^{(\tau,j)}$  [44]:

$$\Delta\beta^{(s,j)} = \sum_{\tau} \sigma(3)\Delta\beta^{(\tau,j)}. \quad (8)$$

The rank-3 totally symmetric tensor  $\Delta\beta_{ijk}^{(s)}$  has three parts  $\Delta\beta^{(0,1)}$ ,  $\Delta\beta^{(2,1)}$ , and  $\Delta\beta^{(2,3)}$  which are mutually orthogonal. It is possible only if each tensor is proportional to  $\Delta\beta^{(s,j)}$ :

$$\sigma(3)\Delta\beta^{(\tau,j)} = U_{\tau}^{3,j} \Delta\beta^{(s,j)}. \quad (9)$$

Consequently we write

$$\Delta\beta_m^{(s,j)} = \sum_{\tau} U_{\tau}^{3,j} \Delta\beta_m^{(\tau,j)}. \quad (10)$$

Here we apply the genealogical coefficients  $U_{\tau}^{3,j}$ . For the vector part of the hyperpolarizability tensor, we obtain  $U_0^{3,1} = \frac{\sqrt{5}}{3}$ ,  $U_2^{3,1} = \frac{2}{3}$ . We use these results in Sec. IV.

### C. Symmetry allowed form of the hyperpolarizability spherical harmonic expansion

We expand the irreducible spherical components  $\Delta\beta_{\mu}^{(s,K)}(R)$  of CI hyperpolarizability tensor dependent on the orientation of  $H_2$  molecule,  $\Omega$ , and intermolecular separation,  $\mathbf{R}$ , and given by Eqs. (3) and (4) in a series of spherical harmonics [21,47]. We choose the vector,  $\mathbf{R}$ , to be parallel to the  $z$  axis; hence  $Y_{LM} = \sqrt{\frac{2L+1}{4\pi}} \delta_{M0}$  and then the series reads [48]:

$$\Delta\beta_{\mu}^{(s,K)}(R) = \left(\frac{4\pi}{2K+1}\right)^{1/2} \sum_{\lambda L} (2L+1)^{1/2} \Delta\beta_{\lambda L}^{(s,K)}(R) \times Y_{\lambda\mu}(\Omega) C_{\lambda\mu L0}^{K\mu}, \quad (11)$$

where  $C_{\alpha\beta\gamma}^{c\gamma}$  stands for the Clebsch-Gordan coefficient [19]. We note that, for totally symmetric hyperpolarizability tensor  $\Delta\beta$ ,  $K$  must be equal to one and/or three. For homonuclear molecules (such as for  $H_2$  in the  $H_2$ -Ar pair)  $\lambda$  from Eq. (11) must be even integer whereas  $\lambda+L$  must be odd. Moreover  $|K-\lambda| \leq L \leq K+\lambda$ . Using

$$Y_{km}(\theta\phi) = (-1)^m \left(\frac{2k+1}{4\pi}\right)^{1/2} \left(\frac{(k-m)!}{(k+m)!}\right)^{1/2} P_{km}(\cos\theta) e^{im\phi}, \quad (12)$$

where  $P_{km}(\cos\theta)$  denotes the associated Legendre polynomial, with the notation  $D_{km} = \left(\frac{(k-m)!}{(k+m)!}\right)^{1/2}$  and  $x = \cos(\theta)$ . We obtain for the symmetry allowed forms of  $\Delta\beta_{\lambda L}^{(s,K)}(R)$ :

(a) For vector component

$$\Delta\beta_0^{(s,1)}(R) = \sum_j \left\{ \sqrt{j+1} \Delta\beta_{jj+1}^{(s,1)}(R) - \sqrt{j} \Delta\beta_{jj-1}^{(s,1)}(R) \right\} P_{j0}(x), \quad (13)$$

$$\Delta\beta_1^{(s,1)}(R) = \frac{1}{\sqrt{2}} \sum_j \left\{ \sqrt{j} \Delta\beta_{jj+1}^{(s,1)}(R) + \sqrt{j+1} \Delta\beta_{jj-1}^{(s,1)}(R) \right\} \times (R) \left\{ D_{j1} P_{j1}(x) \right\}. \quad (14)$$

(b) For septor component

$$\Delta\beta_0^{(s,3)}(R) = \sum_j \left\{ \left( -\frac{\sqrt{\frac{3}{2}} \sqrt{j} \sqrt{1+j} \sqrt{2+j}}{\sqrt{-1+2j} \sqrt{5+2j}} \Delta\beta_{jj+1}^{(s,3)}(R) + \frac{\sqrt{\frac{3}{2}} \sqrt{-1+j} \sqrt{j} \sqrt{1+j}}{\sqrt{-3+2j} \sqrt{3+2j}} \Delta\beta_{jj-1}^{(s,3)}(R) \right) \times D_{j1} + \sqrt{\frac{5}{2}} \left( \frac{\sqrt{1+j} \sqrt{2+j} \sqrt{3+j}}{\sqrt{3+2j} \sqrt{5+2j}} \Delta\beta_{jj+3}^{(s,3)}(R) + \frac{\sqrt{-2+j} \sqrt{-1+j} \sqrt{j}}{\sqrt{-3+2j} \sqrt{-1+2j}} \Delta\beta_{jj-3}^{(s,3)}(R) \right) D_{j3} \right\} P_{j0}(x), \quad (15)$$

and similarly for other septor components. The system of equations defined by relations (11)–(15) have been solved for the  $\Delta\beta_{\lambda L}^{(s,K)}(R)$  coefficients from the known *ab initio* computed  $\Delta\beta_{\mu}^{(s,K)}(R)$  given by Eqs. (3) and (4) for selected intermolecular orientations and selected molecule-atom distances. Using these equations we are able to compute four spherical irreducible rotationally adapted components  $\Delta\beta_{01}^{(s,1)}(R)$ ,  $\Delta\beta_{21}^{(s,1)}(R)$ ,  $\Delta\beta_{23}^{(s,1)}(R)$ , and  $\Delta\beta_{45}^{(s,1)}(R)$  of the vector part of the first hyperpolarizability tensor. For the septor part of the hyperpolarizability tensor, we computed seven spherical irreducible symmetry adapted components, namely:  $\Delta\beta_{03}^{(s,3)}(R)$ ,  $\Delta\beta_{21}^{(s,3)}(R)$ ,  $\Delta\beta_{23}^{(s,3)}(R)$ ,  $\Delta\beta_{25}^{(s,3)}(R)$ ,  $\Delta\beta_{41}^{(s,3)}(R)$ ,  $\Delta\beta_{43}^{(s,3)}(R)$ , and  $\Delta\beta_{45}^{(s,3)}(R)$ . The fitting analytical formulas are also available [48]. The rotationally adapted vectorlike hyperpolarizability components  $\Delta\beta_{\lambda L}^{(s,1)}(R)$  are plotted in Fig. 1. Additionally, the

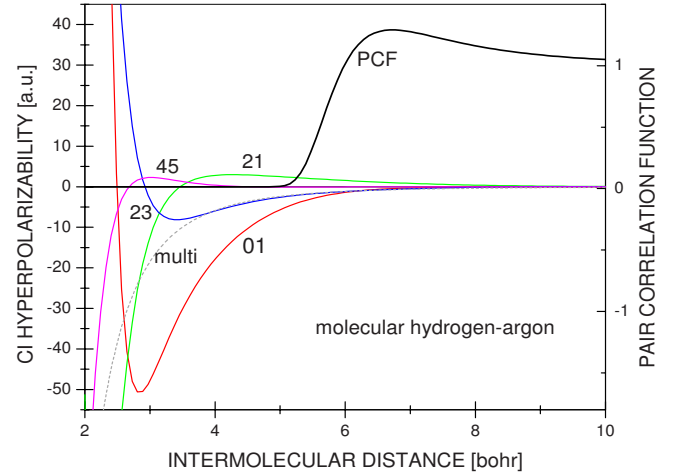


FIG. 1. (Color online) The  $R$  dependence of the  $\Delta\beta_{\lambda L}^{(s,1)}(R)$  irreducible spherical rotationally adapted component of the vector part of the CI first dipole-hyperpolarizability tensor for  $H_2$ -Ar versus intermolecular distance  $R$ , in atomic units. Long-range multipolar  $\Delta\beta_{23}^{(s,1)}(R)$  hyperpolarizability is also shown. Curves are labeled by  $\lambda L$  and *multi*. Moreover the plot of the  $H_2$ -Ar semiclassical pair-correlation function (PCF)  $g(r)$  is also given. For  $g(r)$  values, see the right side scale of the graph.

most important  $\lambda=0$  and  $\lambda=2$  rotationally adapted septorlike hyperpolarizability components  $\Delta\beta_{\lambda L}^{(s,3)}(R)$  are given in Fig. 2. We have estimated [48] that the zeroth moments of the  $\lambda=4$  septor rotationally adapted components amount to less than 1.5% of the total zeroth moment of the septor part of  $\Delta\beta(R)$ . That part of  $\Delta\beta(R)$  is not shown here. We note that the rotationally adapted components of the vector part of  $\Delta\beta(R)$  having, in some sense, the meaning of a *mean* or *average* CI hyperpolarizability [49] displays much shorter range behavior than the rotationally adapted components

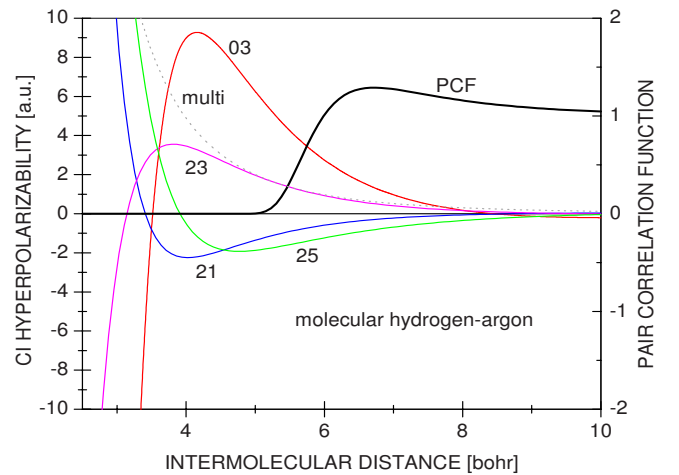


FIG. 2. (Color online) The  $R$  dependence of the  $\Delta\beta_{\lambda L}^{(s,3)}(R)$  irreducible spherical rotationally adapted component of the septor part of the CI first dipole-hyperpolarizability tensor for  $H_2$ -Ar versus intermolecular distance  $R$ , in atomic units. Curves are labeled by  $\lambda L$  and *multi*. Moreover the plot of the  $H_2$ -Ar semiclassical pair-correlation function  $g(r)$  is also given. For  $g(r)$  values, see the right side scale of the graph.

$\Delta\beta_{\lambda L}^{(s,3)}(R)$  of its septor part. The situation is similar to the case of CI polarizability  $\Delta\alpha(R)$  when the mean CI polarizability part is shorter range than its anisotropy [50].

#### IV. LONG-RANGE ASYMPTOTIC PAIR MULTIPOLAR HYPERPOLARIZABILITY TENSOR

The long-range pair multipole CI hyperpolarizability tensor has been recently discussed [51]. Note that equations given in [51] give an opportunity to write analytical long-range formulas for each separate multipole-induced rotationally adapted component of  $\Delta\beta(R)$ . For the  $H_2$ -Ar pair the rotationally adapted multipole-induced component  $^{(\text{multi})}\Delta\beta_{\lambda L}^{(s,K)}(R)$  in self-explanatory notations reads:

$$\begin{aligned} &^{(\text{multi-B}\alpha)}\Delta\beta_{\lambda L}^{(s,K)}[(11)\tau_1](R) \\ &= -\sqrt{3}(2K+1)^{1/2} \sum_{l_A, l_B} R^{-(L+1)} \left( \frac{(2L)!}{(2l_A)!(2l_B)!} \right)^{1/2} \\ &\quad \times \left[ (-1)^{K+L+\tau} \left\{ \begin{matrix} K & L & \lambda \\ l_A & \tau & 1 \end{matrix} \right\} {}_{(H_2)}\tilde{B}_{\lambda 0}[(11)\tau l_A] {}_{(Ar)}\tilde{\alpha}_{00}[1l_B] \right. \\ &\quad \left. - \sqrt{3}(-1)^\lambda (2l_A+1)^{-1/2} \delta_{\tau l_A} \right. \\ &\quad \left. \times \left\{ \begin{matrix} K & L & \lambda \\ l_B & 1 & l_A \end{matrix} \right\} {}_{(Ar)}B_{00}[(11)l_A l_A] {}_{(H_2)}\tilde{\alpha}_{\lambda 0}[1l_B] \right], \quad (16) \end{aligned}$$

$$\begin{aligned} &^{(\text{multi-}\gamma Q)}\Delta\beta_{\lambda L}^{(s,K)}[(11)\tau_1](R) \\ &= -\frac{1}{\sqrt{3}}(-1)^{K+L}(2K+1)^{-1} R^{-(L+1)} \left( \frac{(2L)!}{(2K)!(2\lambda)!} \right)^{1/2} \\ &\quad \times (2\lambda+1)^{-1/2} {}_{(Ar)}\tilde{\gamma}_{00}[[11)\tau_1]KK] {}_{(H_2)}\tilde{Q}_{\lambda 0}, \quad (17) \end{aligned}$$

In the last two equations, we have used a set of square brackets [...] to indicate the coupling scheme of the (hyper)polarizability tensors [52]. In Eqs. (16) and (17)  $L=l_A+l_B$  and moreover

$$\left\{ \begin{matrix} a & b & c \\ d & e & f \end{matrix} \right\}$$

is the  $6-j$  Wigner symbol,  $\mathbf{B}_j[(11)\tau l_A]$  is the irreducible  $j$ th rank spherical tensor of the dipole-dipole- $2^{l_A}$  pole hyperpolarizability in a coupling scheme where at first the dipole moments and then the  $\mathbf{Q}_{l_A}$  multipole moment are coupled [47,51], whereas  $\alpha_k[1l_B]$  stand for the irreducible  $k$ th rank spherical dipole- $2^{l_B}$  pole polarizability tensor. We note that the lowest-rank multipole-induction contribution to  $\Delta\beta(R)$  is of the quadrupole-type ( $l_B=2$ ) and then the CI hyperpolarizability is of order  $R^{-4}$ .

For the *vector* part ( $K=1$ ) of the totally index symmetric  $\Delta\beta$ , using the coefficients calculated in Sec. III B, we have

$$\Delta\beta^{(s,1)} = \frac{\sqrt{5}}{3} \Delta\beta^{(1)}[(11)01] + \frac{2}{3} \Delta\beta^{(1)}[(11)21]. \quad (18)$$

For numerical discussion we select the multipole-like  $\Delta\beta_{23}^{(s,1)}(R)$  spherical irreducible symmetry adapted component. Then using Eqs. (16) and (17) we obtain:

$$\begin{aligned} \Delta\beta_{23}^{(s,1)}(R) &= \left( -\sqrt{5} {}_{(H_2)}\tilde{B}_{20}[(11)02] {}_{(Ar)}\alpha_{00}[11] \right. \\ &\quad \left. + \frac{6}{5} \sqrt{\frac{3}{2}} {}_{(H_2)}\Delta\tilde{\alpha}_{20}[11] {}_{(Ar)}B_{00}[(11)22] \right. \\ &\quad \left. - \frac{2\sqrt{35}}{35} {}_{(H_2)}\tilde{B}_{20}[(11)22] {}_{(Ar)}\alpha_{00}[11] \right. \\ &\quad \left. - \sqrt{5} {}_{(Ar)}\gamma {}_{(H_2)}Q_{20} \right) R^{-4}. \quad (19) \end{aligned}$$

In our numerical calculations we use the following values:  ${}_{(H_2)}\tilde{B}_{20}[(11)02]=9.82$  a.u. for the (02) part of dipole-dipole-quadrupole-hyperpolarizability tensor [47] of  $H_2$ ,  ${}_{(H_2)}\tilde{B}_{20}[(11)22]=92.96$  a.u. for its (22) part,  ${}_{(Ar)}\alpha_{00}[11]=-19.38$  a.u. for the isotropic part of dipole-dipole polarizability of Ar,  ${}_{(Ar)}\tilde{B}_{00}[(11)22]=-455.16$  a.u. for the isotropic part of the dipole-dipole-quadrupole-hyperpolarizability tensor of Ar,  ${}_{(H_2)}\Delta\tilde{\alpha}_{20}[11]=1.65$  a.u. for the anisotropic part of the dipole-dipole polarizability of  $H_2$ ,  ${}_{(Ar)}\gamma=1211$  a.u. for the second dipole hyperpolarizability of Ar, and  ${}_{(H_2)}Q_{20}=0.49$  a.u. for the quadrupole moment of  $H_2$ . Then we obtain

$$^{(\text{multi})}\Delta\beta_{23}^{(s,1)}(R) = (-69.2 - 1326.9)R^{-4} = -1396.1R^{-4}. \quad (20)$$

We note strong cancellation between first, second, and third contributions to Eq. (20) resulting from  $\mathbf{BT}_3\alpha$ , [Eq. (16)], the CI mechanism. The  $\gamma\mathbf{T}_3\mathbf{Q}$ , the CI mechanism dominant in Eq. (20), has been considered by Kielich *et al.* [53,54] and named the cooperative hyper-Rayleigh scattering [55]. The long-range multipolar contribution to  $^{(\text{multi})}\Delta\beta_{23}^{(s,1)}(R)$  is also plotted in Fig. 1 (dashed line). We also note that the long-range behavior of  $\Delta\beta_{23}^{(s,3)}(R)$  fits quite well with the  $R^{-4}$  intermolecular distance dependence (see Fig. 2).

Hyper-Rayleigh scattering is a method widely utilized to measure molecular monomer [42,56–59] and interaction-induced [55] first hyperpolarizabilities [60]. Measurements of hyper-Rayleigh scattering in liquid and vapor  $CCl_4$  have indicated that interaction-induced contributions account for more than half of the scattered intensity from the liquid phase [55]. The spectrum of CIHR light scattering due to  $H_2$ -Ar gas mixture has been computed and described in our recent work [48]. The knowledge of rotationally adapted components of  $\Delta\beta(R)$  enabled the spectral calculations. CIHR scattering has two components: the vector and the septor ones, separable by polarization effects. Both can be measured by the hyper-Rayleigh technique. Moreover, spectral investigations enable us to distinguishing the role played by the separate rotationally adapted components of  $\Delta\beta(R)$  in shaping the resulting CIHR spectrum.

#### V. CONCLUSION

In this work we computed the CI dipole moment  $\Delta\mu_i(R)$ , the CI polarizability tensor  $\Delta\alpha_{ik}(R)$ , and the CI first dipole-

TABLE IV. Interaction hyperpolarizability of H<sub>2</sub>-Ar with Ar on 45 degrees.

$R/a_0$	$\Delta\beta_{xxr}(R)$	$\Delta\beta_{xyy}(R)$	$\Delta\beta_{xxz}(R)$	$\Delta\beta_{yyz}(R)$	$\Delta\beta_{xzz}(R)$	$\Delta\beta_{zzz}(R)$
2.0	-344.88	63.71	-791.52	-81.39	-810.42	-1330.78
2.5	11.69	51.93	-102.88	59.64	-117.5	9.66
3.0	21.82	16.22	-8.25	18.96	-5.78	45.01
4.0	9.32	1.95	5.63	2.06	6.94	13.83
5.0	4.02	0.33	2.89	0.19	3.06	3.76
6.0	1.62	0.12	0.96	-0.02	0.93	0.77
7.0	0.67	0.09	0.21	-0.02	0.19	0.00
8.0	0.32	0.07	0.00	-0.01	0.01	-0.12
9.0	0.19	0.05	-0.03	0.00	-0.02	-0.09
10.0	0.11	0.04	-0.03	0.00	-0.01	-0.06
12.0	0.05	0.02	-0.02	0.00	-0.01	-0.03
14.0	0.03	0.01	-0.01	0.00	0.00	-0.01
16.0	-0.25	-0.08	0.04	-0.04	-0.05	-0.13
18.0	-0.01	0.00	0.03	0.03	-0.03	0.08
20.0	0.00	0.00	0.00	0.00	0.00	-0.01
25.0	0.00	0.00	0.00	0.00	0.00	0.00
30.0	0.00	0.00	0.00	0.00	0.00	0.00

hyperpolarizability tensor  $\Delta\beta_{ijk}(R)$  of the H<sub>2</sub>-Ar pair, each as a function of the intermolecular distance  $R$  and the relative orientation of the H<sub>2</sub> molecule. All calculations were performed at the second-order Møller-Plesset MP2(Full) level of theory with the GAUSSIAN 98 program (also note [61–63]). All electrons were correlated. Using the values of computed *ab initio* Cartesian components of the dipole-hyperpolarizability tensor  $\Delta\beta_{ijk}(R)$ , we propose a procedure to calculate the irreducible spherical rotationally adapted components  $\Delta\beta_{\lambda L}^{(s,K)}(R)$  of  $\Delta\beta(R)$  indispensable for spectroscopic studies. For its *dipolar* (vector) ( $K=1$ ) part we obtain four spherical irreducible rotationally adapted components  $\Delta\beta_{01}^{(s,1)}(R)$ ,  $\Delta\beta_{21}^{(s,1)}(R)$ ,  $\Delta\beta_{23}^{(s,1)}(R)$ , and  $\Delta\beta_{45}^{(s,1)}(R)$ . For the *octopolar* (septor) ( $K=3$ ) part of  $\Delta\beta(R)$ , we get seven octopolar irreducible rotationally adapted components  $\Delta\beta_{\lambda L}^{(s,3)}(R)$ ,

namely,  $\Delta\beta_{03}^{(s,3)}(R)$ ,  $\Delta\beta_{21}^{(s,3)}(R)$ ,  $\Delta\beta_{23}^{(s,3)}(R)$ ,  $\Delta\beta_{25}^{(s,3)}(R)$ ,  $\Delta\beta_{41}^{(s,3)}(R)$ ,  $\Delta\beta_{43}^{(s,3)}(R)$ , and  $\Delta\beta_{45}^{(s,3)}(R)$  from the *ab initio* computed Cartesian components  $\Delta\beta_{ijk}^{(s)}(R)$  of the H<sub>2</sub>-Ar CI hyperpolarizability tensor given in Tables I–IV. Reasonable agreement between analytical long-range and *ab initio* numerical data for two selected multipole-like components  $\Delta\beta_{23}^{(s,1)}(R)$  and  $\Delta\beta_{23}^{(s,3)}(R)$  has been obtained.

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