

STATIC DIPOLE POLARIZABILITIES AND HYPERPOLARIZABILITIES OF X_3^- ANIONS ($X \in \{F, Cl, Br, I\}$). A QUANTUM CHEMICAL HF, MP2 AND DENSITY FUNCTIONAL FINITE-FIELD STUDY

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Abstract. Static dipole polarizability and second hyperpolarizability tensor components are reported for the X_3^- anions (where $X \in \{F, Cl, Br, I\}$). The static electrical properties for the mentioned species were calculated using the finite-field methodology, at various theoretical levels. Both uncorrelated HF wavefunctions, as well as the correlated MP2 and density functional ones were employed. The density functional calculations were performed with two combinations of the exchange-correlation functionals: Becke's exchange with the Lee-Yang-Parr correlation one (BLYP), as well as the Becke's three-parameter hybrid functional with the LYP correlation one (B3LYP). The LANL2DZ basis set was used to solve the SCF or Kohn-Sham equations. The obtained dependencies of the calculated energies on the applied finite electrostatic field (in various orientations) were used to extract the corresponding tensor components. The importance of the inclusion of the dynamic electron correlation effects in the finite-field calculations is discussed.

Key words: trihalide anions, static dipole polarizability, static dipole hyperpolarizability, finite-field methodology, dynamical electron correlation.

1. Introduction

Trihalide anions of the type X_3^- (where $X \in \{F, Cl, Br, I\}$) have attracted a lot of attention, from both experimental and theoretical aspects [1-14]. These anions are usually described as additional products of a halide ion (acting as a Lewis base) with one halogen molecule (acting as a Lewis acid). Higher polyhalides of the form X_5^- , X_7^- and X_9^- have also been detected and described as weakly interacting X_{2n+1}^- with X_2 . However, the trihalide systems are of importance because of their hypervalency, violating the "Lewis octet rule". The behavior of these systems in solutions has been thoroughly studied. Both in solutions and in noble gas matrices they have shown to possess linear and symmetrical structures. However, both symmetrical and unsymmetrical species have been shown to be stable in other solid phases.

The up-to-date *ab initio* studies of the X_3^- species have mainly been devoted to equilibrium geometries and harmonic vibrational frequencies. Both free and solvated species were studied. Solvation studies were limited to the application of the generalized Born (GB) formula [12]. However, in all of the studies, practically only the F_3^- and Cl_3^- species were considered, which are the most unstable ones. On the other hand, the heavier species, especially the I_3^- ion, are significantly more important in solution chemistry [14]. No theoretical study on the static electrical properties of these species, such as polarizabilities or hyperpolarizabilities has been published.

Regarding the static electrical properties of molecular species in general, their role in the effect of an electric field on the energies and intermolecular interactions have long been recognized. On the other hand, the hyperpolarizabilities are involved in variety of nonlinear optical phenomena, such as the Kerr effect, DC induced second- and third-harmonic generation, etc. Nowadays, with the advent of CW laser techniques, there is a possibility for direct experimental measurement of molecular hyperpolarizabilities.

2. Theoretical and computational details

2. 1. Molecular system in a finite field

The energy of a molecular system placed in a weak, static and homogeneous finite field may be written as:

$$E = E^0 - \mu_\alpha F_\alpha - (1/2)\alpha_{\alpha\beta} F_\alpha F_\beta - (1/6)\beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma - (1/24)\gamma_{\alpha\beta\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta - \dots$$

where E^0 is the energy of the unperturbed system, F is the field strength, while the Greek subscripts denote the vector or tensor components. In the previous equation, the Einstein summation convention was assumed (a repeated Greek subscript implies summation over the Cartesian coordinates). The coefficients in the series are known as the (static) dipole moment, dipole polarizability, and the first, second, etc. polarizabilities. Based on the previous expansion, approximate formulae for the particular tensor components may be derived, allowing their calculation at a relatively low computational effort.

2. 2. The wavefunctions employed

In the present study, both uncorrelated Hartree-Fock wavefunctions, as well as the correlated ones (based on the many-body perturbation theory - MP2 or the Kohn-Sham density-functional approach) were employed. The density functional calculations were performed with two combinations of the exchange-correlation functionals: Becke's exchange with the Lee-Yang-Parr correlation one (BLYP), as well as the Becke's three-parameter hybrid functional with the LYP correlation one (B3LYP). The LANL2DZ basis set (D95 on the first row elements, Los Alamos ECP plus DZ on Na-Bi) was used to solve the SCF or Kohn-Sham equations. This basis contains an effective core potential (ECP) representation of the core electrons. It was chosen in order to obtain consistent results on all of the studied systems. The geometries of the trihalide species were optimized at the mentioned levels of theory, with Berny's optimization algorithm (calculating the energy derivatives analytically). Numerical harmonic vibrational analyses were performed for the stationary points found at the anionic potential energy hypersurfaces. The absence of the imaginary frequencies and negative eigenvalues of the Hessian matrix indicated that the stationary points found correspond to real minima on the surfaces. All calculations were performed with Gaussian94w series of programs [15].

3. Results and Discussion

The optimized geometry parameters of the X_3^- anionic species ($X \in \{F, Cl, Br, I\}$) are presented in Table 1. According to all of the employed computational strategies, the minima on the anionic potential energy hypersurfaces correspond to $D_{\infty h}$ symmetry. The present finding is in line with the previously presented results. However, as has been mentioned, in

particular condensed phases, other less symmetric structures of these species have been found to exist.

Table 1. Optimized geometry parameters for the trihalide species at various levels of theory (using the LANL2DZ basis set)

Method	R(F-F)/pm	R(Cl-Cl)/pm	R(Br-Br)/pm	R(I-I)/pm
HF	167.86	242.77	271.94	309.25
MP2	179.29	248.51	276.50	313.89
BLYP	179.89	252.93	281.35	318.36
B3LYP	175.44	248.53	277.02	313.73

As obvious from the Table 1, the inclusion of the dynamical electron correlation effects essentially leads to an increase of the X-X bond length.

Within the finite-field approach, the energy series parameters may be obtained through application of different weak fields, and either fitting to the energy data with polynomial model functions, or using the approximate formulae of the form:

$$\alpha_{zz} = 2[SZ(\sigma F) - \sigma^4 SZ(F)] / [(\sigma^4 - \sigma^2)F^2]$$

$$\gamma_{zzzz} = 24[\sigma^2 SZ(F) - SZ(\sigma F)] / [(\sigma^4 - \sigma^2)F^4]$$

and analogously for the other components.

In the previous expressions, F is the strength of the corresponding field component, while:

$$SZ(F) = E(0,0,F) - E^0$$

E^0 being defined previously.

The obtained values of the static dipole polarizabilities and second hyperpolarizabilities for the studied species are summarized in Tables 2 and 3.

Table 2. The computed polarizability tensor zz components for the trihalide species at various levels of theory (using the LANL2DZ basis set)

Method	α_{zz} / atomic units			
	F ₃ ⁻	Cl ₃ ⁻	Br ₃ ⁻	I ₃ ⁻
HF	77.02	11.41	10.04	8.68
MP2	77.13	11.43	10.06	8.69
BLYP	77.36	11.58	10.21	8.83
B3LYP	77.36	11.61	10.24	8.86

As can be seen, the inclusion of the dynamical electron correlation effects has only a subtle effect on the computed values of the polarizability tensor component zz. Generally, the MP2 values are lower than the Density functional ones. The B3LYP values are, on the other hand, higher than the BLYP ones. However, there is a good overall convergence of the computed parameters with the improvement of the theoretical level. It should be noted once again that the presented values in this work are in fact, the static ones (they do not include any *vibrational corrections* which may be of significant importance for particular cases).

Further improvement of the computed values may be achieved by an enlargement of the basis set used for orbital expansions, as well as with an inclusion of the other reference states for a more exact description of the dynamical electron correlation effects.

Table 3. The computed second dipole hyperpolarizability tensor γ_{zzz} component for the trihalide species at various levels of theory (using the LANL2DZ basis set)

Method	γ_{zzz} / atomic units			
	F ₃ ⁻	Cl ₃ ⁻	Br ₃ ⁻	I ₃ ⁻
HF	10.00	104.40	256.60	665.20
MP2	64.20	219.91	465.23	1117.98
BLYP	6.00	34.00	81.80	223.60
B3LYP	2.00	43.00	109.60	285.00

The same conclusions are valid for the second hyperpolarizability tensor components, with one exception. Namely, the convergence of the results with the improvement of the theoretical level is poor.

Апстракт. Компонентите на тензорите на статичките диполни поларизабилности и хиперполаризабилности се пресметани за X₃⁻ анјоните (каде X ∈ {F, Cl, Br, I}). Споменатите електростатички својства се добиени со примена на методологијата на конечно поле, на различни нивоа на теоријата. Ползувани се некорелирани HF бранови функции, како и корелирани MP2 и DFT. DFT испитувањата се изведени вклучувајќи две комбинации на корелациони функционали и функционали на измена: Веcke-ов функционал на измена со Lee-Yang-Parr корелационен функционал (BLYP), како и Веcke-ов тропараметарски хибриден функционал со LYP корелационен функционал (B3LYP). LANL2DZ базисниот сет е ползуван за решавање на стандардните SCF или Kohn-Sham-овите равенки. Од пресметаните зависности на енергиите од применетото поле добиени се соодветните компоненти на тензорите.

4. References

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