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Research paper

Electric multipole moments of XeCuX (X = F, Cl, Br, I)

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ABSTRACT

We have calculated reference CCSD values for the electric moments of the XeCuX, X = F, Cl, Br, I molecules. Our values for the dipole moment are $\mu/ea_0 = -2.8399$, -2.9875, -2.9935 and -2.9486 for XeCuF, XeCuCl, XeCuBr and XeCuI, respectively. A quantitative benchmark analysis over a series of widely used functionals reveals that from all DFT methods included in this work BHandHLYP yields values closest to the reference CCSD ones.

1. Introduction

Experimental research has brought forth new classes of noble-gas compounds. Significant work has also been recently reported on weakly bound systems formed by some of these molecules [1]. Theoretical investigations have examined closely various physicochemical properties. Emphasis has been put on electric (hyper)polarizabilities. The potential of these new molecules to be used as building blocks for the design of novel architectures with enhanced NLO (nonlinear optical) properties has never been lost sight of.

Electric multipole moments are properties of importance for the modelling of intermolecular interactions. There is continuous theoretical interest in their calculation [2]. Little systematic work has been reported on these properties for noble-gas compounds. See for instance recent work on HXeI [3] and HXeH [4]. Electric moments, especially high-order ones, are not easily amenable to experiment. Experimental work on electric multipole moments appears sporadically in the literature. Important results on higher electric moments have been published on small molecules as carbon monoxide [5] and dinitrogen [6]. In both cases, the higher-order moments were extracted from far-infrared absorption measurements in CO-Ar and N_2-Xe, respectively.

In this work we turn our attention to the electric moments of XeCuX, X = F, Cl, Br and I. From the above sequence the first three members XeCuX, X = F, Cl and Br have been recently characterized theoretically by Fang and Zhang [7]. An important experimental and theoretical spectroscopic investigation of XeCuF and XeCuCl was reported earlier by Michaud and Gerry [8]. Our calculations of the electric properties rely on **ab initio** and Density Functional Theory (DFT) methods. The former group consists of both Møller-Plesset perturbation theory (MP) and coupled cluster (CC) calculations. Very large, flexible basis sets of gaussian-type functions (GTF) are employed throughout this investigation.

It should be noted here that on a purely computational basis, DFT techniques offer an economical alternative to costly **ab initio** methods. This constitutes a substantial advantage for rapid, low-cost evaluations of electric multipole moments of large, complex molecular architectures. We are keen on gathering reliable information on the relative performance of DFT techniques and their comparison to **ab initio** methods.

2. Theory

We adopt and follow Buckingham's definitions and conventions throughout this paper [9].

When a polar linear molecule interacts with a distant proton lying on the molecular axis at R from the origin, the 1st order interaction energy can be written as [10]

$$E_{int} = \mu/R^2 + \Theta/R^3 + \Omega/R^4 + \Phi/R^5 + \cdots \quad (1)$$

where μ, Θ, Ω, Φ are the dipole, quadrupole, octopole and hexadecapole moments, respectively. There is only one independent multiple moment of any order for a linear molecule, so we write simply (with z as the molecular axis) $\mu \equiv \mu_z$, $\Theta \equiv \Theta_{zz}$, $\Omega \equiv \Omega_{zzz}$ and $\Phi \equiv \Phi_{zzzz}$.

In previous work we have calculated electric multipole moments via a finite-field method [11]. The properties are

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extracted from the perturbed energy of the molecule in the presence of distant, strategically placed point charges. In the present investigation we lean on previous experience [12] and we calculate the electric moments from the electron density.

We have had recourse well-test **ab initio** methods to calculate reference electric multipole moments. These are: **SCF**, self-consistent-field, **MP2**, second-order Møller-Plesset perturbation theory (MP) and **CCSD**, singles and doubles coupled cluster. Comprehensive and accurate presentations of these methods are available in standard references [13,14]. As regards density-functional theory based approaches we select the widespread and confidently used B3LYP, BHandHLYP, B3PW91, PBEPBE, mPW1PW91 and CAM-B3LYP. We adopt the versions implemented in the GAUSSIAN 03 [15] and GAUSSIAN 09 [16] programmes.

In order to produce solidly quantitative arguments about the performance of the theoretical methods employed in the present investigations we lean heavily on a theoretical tool introduced in early work [17]. Only a few central points of our methodology are given here. A well-defined theoretical method is practically associated to a string of values $Q_{\alpha i}$ (the subscript α denotes the property and i the method). We label this string a theoretical description (TD_i). We define distance/proximity in the space of all theoretical descriptions TD_i by introducing a generalized form of the Minkowski metric

$$D_{ij} = \left(\sum_{\alpha} \frac{|Q_{i\alpha} - Q_{j\alpha}|^p}{\left(\max_{ij}|Q_{i\alpha} - Q_{j\alpha}|\right)^p} \right)^{1/p}, \; p \geqslant 1 \tag{2}$$

Here, we rely exclusively on the Euclidean metric, that is p = 2. Similarity between two theoretical descriptions TD_i and TD_j is then defined on the basis of proximity as

$$S_{ij} = 1 - \frac{D_{ij}}{\max_{ij} D_{ij}}, \; 0 \leqslant S_{ij} \leqslant 1 \tag{3}$$

Sometimes, we write directly S($Method_i$, $Method_j$) or, e.g. S(SCF, MP2) to refer to the particular quantity.

3. Computational strategy

The choice of suitable basis sets is of central importance to computational quantum chemistry. As regards electric polarizability calculations, we can reasonably design flexible basis sets for small systems as atoms [18], diatomics [19], small symmetric polyatomics [20]. More complex situations arise in calculations on clusters [21] where more often than not the choice of basis sets is understandably limited. It is less clear how one can define or select suitable basis sets for the calculation of electric multipole moments.

In this work we rely on previous experience in order to pick suitable basis sets for the calculation of the electric moments of XeCuX, X = F, Cl, Br and I. For Xe we used the [9s8p7d1f] basis set from previous work on Xe-Xe [22]. The [8s7p7d1f] from previous work on Cu_2 was used for Cu [23]. For F we relied on the [9s6p4d1f] basis from our study on F_2 [24]. A [9s6p5d2f] basis optimized on Cl_2 was used for Cl [25]. A [11s8p6d2f] basis from Br was taken from previous work on HBr [25]. Last, the [11s10p8d2f] used on I is a smaller version of the [11s10p10d3f] one used on HI [26].

All molecules are on the z axis with the centre of mass on the origin and the halogen along the positive part of the axis. The higher multipole moments are relative to the centre of mass.

Unless otherwise indicated, atomic units are used in this work. Conversion factors to SI units are [27]: length, 1 a_0 = 0.529 177 210 92(17) × 10^{-10} m, μ, 1 ea_0 = 8.47835326(19) × 10^{-30} cm, Θ, 1 ea_0^2 = 4.486551331(99) × 10^{-40} cm^2, Ω, 1 ea_0^3 = 2.374180719987994 × 10^{-50} cm^3 and Φ, 1 ea_0^4 = 1.256362331623284 × 10^{-60}. Molecular property values are given as pure numbers, i.e. R/a_0, μ/ea_0, Θ/ea_0^2, Ω/ea_0^3 and Φ/ea_0^4.

4. Results and discussion

4.1. Molecular geometry

Molecular geometries for all XeCuX structures were determined at the MP2(FULL) level of theory. All calculations rely on Sapporo basis sets [28]. The DZP basis set used in this work are, in contracted form: Xe = [7s6p4d1f], Cu = [6s4p3d1f], F = [4s3p1d], Cl = [5s4p2d], Br = [6s5p3d1f] and I = [7s6p4d1f]. For instance, the uncontracted form for the basis for the iodine atom is {7,432,211/742,121/7222/2}. The calculated bond lengths at the MP2(FULL) level are R(Xe-Cu)/Å and R(Cu-X)/Å = 2.4550 and 1.7275 (XeCuF), 2.4893 and 2.0566 (XeCuCl), 2.5011 and 2.1845 (XeCuBr), 2.5198 and 2.3616 (XeCuI).

For comparison, Fang and Chang [7] reported theoretical CCSD (T) values of R(Xe-Cu)/Å and R(Cu-X)/Å = 2.429 and 1.743 (XeCuF), 2.469 and 2.048 (XeCuCl), 2.485 and 2.1882 (XeCuBr). The experimental r_0 values of Michaud and Gerry [8] are R(Xe-Cu)/Å and R (Cu-X)/Å = 2.4327(5) and 1.754(1) (XeCuF), 2.471(7) and 2.058(1) (XeCuCl).

4.2. Atomic charges

Relying on the Sapporo Gaussian basis sets used in the molecular geometry calculations, see above, we have obtained atomic charges via a natural bond orbital (NBO) analysis. The relevant calculations were performed at the MP2(FULL) level of theory. The NBO charges are

XeCuF:	0.1177(Xe),	0.6180(Cu),	−0.7357(F)
XeCuCl:	0.1219(Xe),	0.6049(Cu),	−0.7268(Cl)
XeCuBr:	0.1211(Xe),	0.5833(Cu),	−0.7044(Br)
XeCuI:	0.1209(Xe),	0.5335(Cu),	−0.6544(I)

The charge on Xe is more or less stable at ≈0.12. For Cu the charge reduces monotonically for the sequence XeCuF → XeCuCl → XeCuBr → XeCuI. Accordingly, the charge on the halogen is negative and reduces in magnitude in the above sequence.

4.3. Electric multipole moments

The calculated electric multipole moments are given in Table 1.

Our most accurate dipole moment values are calculated at the CCSD level of theory and are (SCF values in parentheses): −2.8399 (−3.0031) for XeCuF, −2.9875 (−3.1756) for XeCuCl, −2.9935 (−3.2046) for XeCuBr and −2.9486 (−3.2311) for XeCuI. The electron correlation correction, defined as CCSD-SCF, is systematically positive for all molecules. It is worth noticing that the BHandHLYP method is closest to the reference CCSD for all four molecules. Overall, we observe that the dipole moments of the four molecules are quasi-identical, due to the fact that even though the charges decrease with the halogen from F to I, the bond lengths increase.

The CCSD quadrupole moment values reduce considerably in magnitude in the sequence XeCuF → XeCuCl → XeCuBr → XeCuI. The respective CCSD (SCF) values are −15.1682 (−17.8483), −13.0776 (−15.8228), −6.8428 (−9.3777) and −0.9847 (−3.4344). The electron correlation correction (see definition above) is consistently positive. Again, the BHandHLYP method provides values in reasonable agreement with the CCSD one. The