Tetrafluoroberrylate(2) Ions as Hydrogen-Bond Proton Acceptors: Quantum Chemical Considerations

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TETRAFLUOROBERRYLATE(2-) IONS AS HYDROGEN-BOND PROTON ACCEPTORS: QUANTUM CHEMICAL CONSIDERATIONS

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ABSTRACT

The experimentally observed lower proton acceptor ability of the tetrafluoroberrylate(2-) anion, compared to that of the sulphate(2-) and selenate(2-) anions, was explained on the basis of various quantum chemical approaches. The geometries of the above-mentioned XY_4^{2-} anions were fully optimised at the *ab initio* HF SCF and MP2 levels of theory, as well as within the DFT (BLYP and B3LYP) approach, using the 6-311+G* and LANL2DZ basis sets. The 6-311++G(3df,3pd)

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basis set was also used within the DFT BLYP approach. The molecular charge distribution was partitioned among the atomic centers using the Mulliken as well as the natural population analysis. All levels of theory (both with and without inclusion of the electron correlation effects), regardless of the basis set employed, predict lower (by absolute value) atomic charge on the fluorine atom in the tetra-fluoroberrylate(2-) anion than that on oxygen atoms in sulphate(2-) and selenate(2-) anions. The quantum chemical predictions are fully in line with the spectroscopically observed order of the proton acceptor abilities in these anions.

INTRODUCTION

Our previous IR studies of several pairs (or triads) of isotypic (preferably isomorphous) compounds containing BeF_4^{2-}, SO_4^{2-} and/or SeO_4^{2-} anionic species [1-4], allowed us to derive interesting conclusions regarding the proton acceptor abilities of these anions. The experimental results could not be explained at all on the basis of the simple electronegativity-based concepts [5-9], even with the usage of intuitively appealing quantitative models such as that proposed by Sanderson [5, 6]. It became obvious that a more fundamental theoretical approach is required to explain the experimentally observed order of the proton acceptor abilities in the mentioned series of XY_4^{2-} species. The preliminary *ab initio* results, reported in our previous work [10], were in line with the experimentally observed trends. To get a deeper theoretical insight into this problem, a quantum chemical study of the structures and charge distributions in BeF_4^{2-}, SO_4^{2-} and SeO_4^{2-} anions was performed at various levels of theory and within several basis sets, both with and without an explicit inclusion of the electron correlation effects. Various charge assignment schemes were employed for that purpose, in order to take into account both the advantages and disadvantages of the quantum chemical approaches.

COMPUTATIONAL DETAILS

The geometries of the tetrafluoroberrylate(2-), sulphate(2-) and selenate(2-) anions were fully optimized both at the HF SCF level and at several levels of theory that include explicitly the electron correlation effects. Of the latter, second order Møller-Plesset perturbation theory (MP2) [11] and Density Functional Theory (DFT) [12,13] methodologies were applied. All optimizations were performed using Berny's algorithm [14] (analytically computing the energy derivatives) in redundant internal coordinates. The method of initial guess of the second derivative matrix was applied. The stationary points found on molecular potential energy hypersurfaces were characterized by standard numerical harmonic vibrational analysis.

MP2 calculations were done within the frozen-core (FC) approximation (excluding the inner shell electrons from the correlation energy calculations). The MP2 densities were used for charge partitioning. The applicability of the Møller-Plesset perturbational approach for each particular case was confirmed performing stability testing of the corresponding Hartree-Fock wavefunction.

Within the DFT methodology, two combinations of exchange and correlation functionals were used. In the first one, Becke's 1988 exchange functional[1] [15] was used with the correlation functional of Lee, Yang, and Parr[2] [16] (BLYP - gradient-corrected DFT). The second approach was based on hybrid methodology (Becke's three parameter functional [17] was used along with the correlation functional of Lee, Yang and Parr (B3LYP)).

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[1] It includes the Slater exchange [15] along with corrections involving the density gradient.

[2] Including both local and non-local terms.

In all of the approaches, the 6-311+G* [18] and LANL2DZ basis sets were used. The first basis contains diffuse functions for a better description of the anionic wavefunction, as recommended for such species [19]. The LANL2DZ basis is, in fact, the Dunning/Huzinaga full double zeta for the first-row elements [20], and the Los Alamos ECP plus DZ for Na to Bi [21]. The very large 6-311++G(3df,3pd) basis set was also used for calculations at DFT BLYP level.

The charge partitioning (at the optimized geometry) was performed using the corresponding densities for each method. Both Mulliken scheme [22] and the natural population analysis [23] were applied. All calculations were done with the Gaussian 94w series of programs (Revision B.3) [24].

RESULTS AND DISCUSSION

The optimized X–Y bond lengths for the XY_4^{2-} species (with T_d symmetry) at various levels of theory are summarised in Table 1.

The results from the harmonic vibrational analyses, together with the harmonic vibrational frequencies determined on the basis of experimental data regarding anharmonicity constants for isomorphously isolated XY_4^{2-} species will be published elsewhere [25].

As can be seen from Table 1, the results are fully in line with the intuitive chemical expectations based on the atomic radii concepts. Inclusion of the electron correlation, of course, leads to an increase of the bond lengths compared to those obtained within the Hartree-Fock theory in all of these anionic species.

The calculated atomic charges for the Y atoms, using the Mulliken charge-

TABLE 1

Optimised X–Y Bond lengths of the XY_4^{2-} species (within the T_d symmetry) at various levels of theory

Method	Basis set	Optimized bond length / pm		
		Be–F	S–O	Se–O
HF SCF	6-311+G*	159.8	148.3	163.5
	LANL2DZ	161.8	164.3	172.8
MP2	6-311+G*	161.6	151.7	167.4
	LANL2DZ	164.8	166.9	175.3
BLYP	6-311++G(3df,3pd)	161.7	152.4	170.1
	6-311+G*	163.3	155.4	172.5
	LANL2DZ	162.8	171.0	179.3
B3LYP	6-311+G*	161.5	152.6	169.1
	LANL2DZ	161.9	167.7	176.2

partitioning scheme are presented in Table 2. The values refer to the optimized geometries of the tetrahedral anions at the corresponding levels.

Irrespective of whether the particular approach does or does not include explicitly the electron correlation effects, or on the basis set employed, the predicted order of the proton acceptor ability is, thus: $SeO_4^{2-} > SO_4^{2-} > BeF_4^{2-}$. This order is, it should be recalled, fully in line with the spectroscopic data regarding the hydrogen bond strengths in series of the studied isostructural or isomorphous compounds which contain the examined anions participating in this specific interaction [1-4].

Of course, one may argue that no charge assignment scheme can partition the molecular charge distribution uniquely, since the atomic charge is not quantum

TABLE 2

The calculated Mulliken charges of the Y atoms for the fully optimized XY_4^{2-} anionic species at various levels of theory

Method	Basis set	Mulliken charge of atom Y / e		
		BeF_4^{2-}	SO_4^{2-}	SeO_4^{2-}
HF SCF	6-311+G*	-0.626	-0.772	-0.930
	LANL2DZ	-0.740	-0.932	-0.975
MP2	6-311+G*	-0.584	-0.634	-0.795
	LANL2DZ	-0.684	-0.863	-0.897
BLYP	6-311++G(3df,3pd)	-0.697	-0.755	-0.953
	6-311+G*	-0.550	-0.568	-0.726
	LANL2DZ	-0.579	-0.768	-0.798
B3LYP	6-311+G*	-0.567	-0.619	-0.782
	LANL2DZ	-0.621	-0.811	-0.844

mechanical observable. The method for population analysis suggested by Mulliken also suffers from several well documented weaknesses [23]. However, as has been shown [26].in a series of molecular/ionic species this scheme is able to consistently predict *the trends* and only the *absolute value* of the atomic charge at particular center can not be predicted uniquely. Since this quantity can not be determined uniquely from the experimental data either, this weakness of the Mulliken partitioning scheme is not of fundamental importance for the current analysis. The consistency of the predictions at all levels of theory gives further support for the correctness of this approach for such problems.

Although the previously outlined arguments seem to be convincing enough, it appeared interesting to see whether the predictions of some other charge assignment

TABLE 3

The calculated natural charges of the Y atoms for the fully optimized XY_4^{2-} anionic species at various levels of theory

Method	Basis set	Natural charge of atom Y / e		
		BeF_4^{2-}	SO_4^{2-}	SeO_4^{2-}
HF SCF	6-311+G*	-0.939	-1.187	-1.240
	LANL2DZ	-0.931	-1.107	-1.195
MP2	6-311+G*	-0.920	-1.110	-1.158
	LANL2DZ	-0.902	-1.071	-1.146
BLYP	6-311++G(3df,3pd)	-0.926	-1.113	-1.139
	6-311+G*	-0.923	-1.082	-1.108
	LANL2DZ	-0.886	-0.992	-1.062
B3LYP	6-311+G*	-0.928	-1.111	-1.146
	LANL2DZ	-0.901	-1.037	-1.111

schemes would further support the obtained results. This especially refers to those schemes which are based on more exact physical concepts, unlike the equal partitioning method of Mulliken. Therefore, the charge assignment to atomic centers was performed using also the natural bond orbital (NBO) population analysis algorithm (NPA) [27], which was proposed as an alternative, or better as an improvement to the Mulliken one. As it was outlined in the original work [23], it does not suffer from many of the main weaknesses of the Mulliken algorithm.

The results obtained with NPA are presented in Table 3. As is obvious from this table, the charges derived from the natural population analysis further support the previously obtained conclusions regarding the proton acceptor abilities of the

SeO_4^{2-}, SO_4^{2-} and BeF_4^{2-} anionic species. Both schemes fully explain the spectroscopically observed trends.

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