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Molecular Constants of Aluminum Monohalides: Caveats for Computations of Simple Inorganic Molecules

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Quantum chemical calculations have become an everyday tool in chemistry. There are commercial program packages and downloadable basis sets for most needs. However, many chemists rarely go beyond the routine use of these programs, rarely, if ever, checking the original references for basis sets. In this letter, we point out some of the pitfalls of such an approach. Structural parameters of the aluminum-monohalides, AlF, AlCl, AlBr, and AlI, have been calculated using the Gaussian 03 program package and different basis set combinations.

Introduction

We have been involved with computations of metal halide molecular structures in order to augment our experimental studies.[1] Since our objects often involve heavy atoms, either as the halogen or, especially, as the metal, the beginning these computations often resulted in geometries far away from the experimental findings.[2,3] Recently, however, there has been a remarkable development in new basis sets and, especially, pseudopotentials for heavy atoms, allowing a more meaningful comparison between experimental and computed bond lengths.

At the same time, we find it useful to point out some details that are well-known for computational chemists but might be missed by those who merely use these methods. Our experimental and computational studies of aluminum trihalides have prompted us to calculate the bond lengths of the aluminum monohalides as well. This was especially worthwhile since, for all four aluminum monohalides, good-quality molecular constants are available from microwave spectroscopy.[4] We wanted to find the best level of computation in order to get bond lengths comparable with the experiment, and see whether these bond lengths would correspond to the "complete basis set limit". Our experience with these calculations is the topic of this letter.

All calculations were performed with the Gaussian 03 (G03) program package; this is the program mostly used by non-specialists.[5] The MP2 and CCSD(T) methods were applied. Our objectives could be grouped into two parts: for AlF and AlCl, all-electron calculations were performed, while, for AlBr and AlI, the basis sets were mixed, as pseudopotentials were used for the halogen atom. The all-electron bases for F, Cl, and Al were the correlation consistent cc-pV*n*Z bases from double-ζ (DZ) to sextuple-ζ quality (the latter only when available).[6] For bromine and iodine, different pseudopotentials (ECPs) were tested; the simplest being the "large-core" ECPs of the Stuttgart group (all electrons below the valence shell are treated by the ECP), together with the associated basis sets, SDB-cc-pV*n*Z ($n = 2-4$).[7] Further, we checked the "small-core" ECPs (the electrons of the ($n - 1$) shell are described by the basis set together with the valence shell);[8] the accompanying basis sets were of the cc-pV*n*Z-PP type ($n = 2-5$). Next we tested the cc-pwCV*n*Z weighted core-valence basis sets of Peterson et al., from DZ to 5Z quality for Al, F, and Cl,[9] and the corresponding ones for Br and I, developed to be used with the appropriate pseudopotentials.[10] Diffuse functions on the halogens were also tested.

We checked different possibilities concerning electron correlations that are offered by G03, correlating only the valence electrons (this is the default, called "frozen core" or FC), including the ($n - 1$)spd shell in the correlation calculation (FC1), including all electrons in it (full) and, finally, the so-called "read window" option, in which case the electrons to be included in the correlation calculations are to be specified. Note that, for AlF and AlCl, the difference between the FC1 and full calculations is merely the inclusion of the 1s electrons of Al and Cl in calculating the electron correlation; the difference between the two sets of results is marginal. However, it should be kept in mind that the results of FC1 and "full" computations could be quite different depending on the types and number of atoms in the molecule.

One important caveat is mentioned here: all the applied cc-pV*n*Z basis sets and cc-pV*n*Z-PP ECP-based sets were developed for *valence-only correlation*. The cc-pwCV*n*Z basis sets (and the corresponding cc-pwCV*n*Z-PP ECP-based ones), on the other hand, were developed for *valence plus (n − 1)spd correlation* calculations, which correspond to the FC1 option in Gaussian. Strictly speaking, the basis sets should *only* be used in the calculations for which they were developed; all other correlation calculations, even if they happen to give relatively good results, are in principle not correct.

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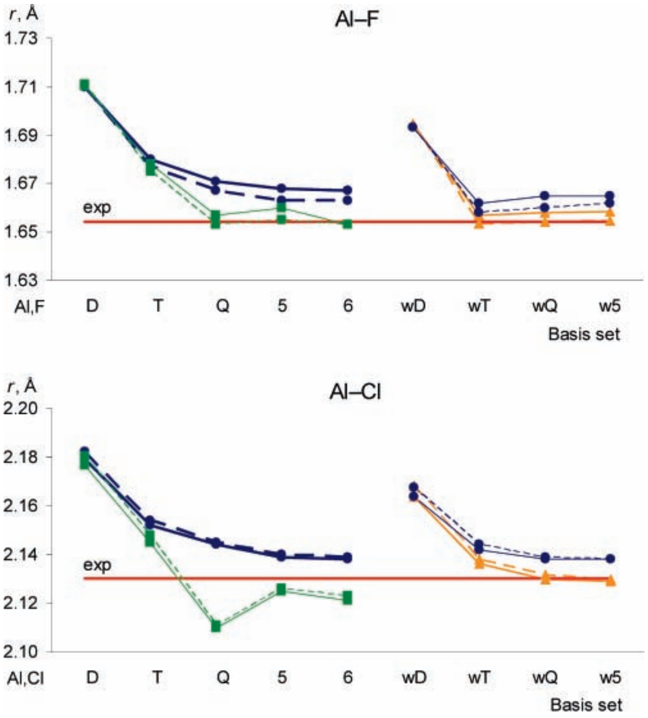

Figure 1. Bond lengths of AlF and AlCl. Left sets: calculations with the cc-pV*n*Z basis sets (*n*). Right sets: calculations with the cc-pwCV*n*Z basis sets (w*n*). Full lines: MP2; broken lines: CCSD(T). Electrons taken into account in correlation calculation: circles: sp only (FC); triangles: FC1; squares: full. Thick lines indicate the G03 default calculation. The experimental bond length is indicated by a straight line.

TABLE 1: Molecular Constants of Aluminum Monohalides[a]

	AlF	AlCl	AlBr	AlI
r_e(Al−X), Å	1.655[b]	2.130[b]	2.295[c]	2.534[c]
r_e(Al−X), Å[d]	1.657	2.136	2.297	2.531
r_e(Al−X)$_{exp}$ Å	1.65436(2)[e]	2.13011(3)[f]	2.29480(3)[f]	2.53709(3)[f]
ω_e, cm^{-1}	802.6	483.2	381.7	321.2
$\omega_{e,exp}$, cm^{-1}	802.85(25)[e]	481.67(14)[f]	378.19(6)[f]	316.25(2)[f]
IP, eV[g]	9.4/9.5	9.1/9.2	8.9/9.0	8.7/8.8
IP$_{exp}$, eV	9.73(1)[h]	9.4(3)[i]	9.3(3)[i]	9.3(3)[i]
D_e, kcal/mol	163	121	107	96
$D_{e,exp}$, kcal/mol[j]	160(2)	119(2)	102(5)	88(5)

[a] Electron correlation calculations include the (*n*-1)spd shell (FC1 option in G03), bond lengths at different levels (see below), harmonic vibrational frequencies, ionization potentials, and dissociation energies at the MP2 level with cc-pwCVTZ and cc-pwCVTZ-PP basis sets and related pseudopotentials. [b] CCSD(T)/cc-pwCV5Z. [c] CCSD(T)//cc-pwCVQZ/cc-pwCVQZ-PP. [d] MP2/cc-pwCVTZ(−PP). [e] From ref 4a. [f] From ref 4b. [g] Adiabatic/vertical ionization potentials. [h] Adiabatic ionization potential, ref 11. [i] Threshold appearance potential, ref 12. [j] From ref 13.

All-Electron Calculations

Figure 1 shows the Al−F and Al−Cl bond lengths from different levels of computations with different basis sets. A straight line indicates the experimental bond lengths. All calculated bond lengths are given in the Supporting Information, while the best ones for all molecules are given in Table 1. This table also gives the harmonic vibrational frequencies, ionization potentials, and dissociation energies from one set of calculations together with the experimental values.

Calculations with the cc-pV*n*Z bases are given on the left side of Figure 1. For both molecules, the FC CCSD(T) calculations give longer bonds than the experimental ones, and they seem to converge at values that are about 0.009 Å longer than the experimental ones. Calculations with full electron correlation, from the quadruple-ζ bases on, seem to agree well with the experiment for AlF, but this may be fortuitous. For AlCl, the values above TZ quality are smaller than the experimental ones and do not show a converging pattern; this is the result of trying to correlate more electrons than the basis set is designed for. The cc-pV*n*Z bases were optimized for valence-only correlation, and they are only single-ζ in the core; therefore, the full correlation calculation might result in "borrowing" basis functions from the other center (i.e., basis set superposition error). Since this approach is not right, we cannot expect any systematic behavior with increasing basis size, except that, with larger ones, there are more basis functions that can be used to replace the missing core functions, so the bond lengths might improve. These computations clearly show that using larger correlations than what the given basis sets were optimized for might lead to very strange results.

The sets on the right in Figure 1 were calculated with the cc-pwCV*n*Z basis sets, with FC and FC1 options ("full" gives the same bond lengths as FC1). The results of the FC1 calculations (especially the CCSD(T) ones) are very good, and they converge at the experimental value. Since the basis sets were optimized for the FC1 level, these are the proper calculations. It is noteworthy that the difference between the default FC and the FC1 calculation is only the inclusion of the 2s2p electrons of Al for AlF and the 2s2p electrons of Al and Cl for AlCl; still the differences in bond lengths are noticeable, indicating the effect of core−valence correlation.

Calculations Involving Pseudopotentials

For the AlBr and AlI molecules, aluminum is described by all-electron bases, and the halogen is described by a pseudopotential with associated basis sets. We noticed that the commands in G03 do not work the same way for atoms described by ECPs as they do for atoms that are described by all-electron bases. In this case, the default (FC) calculation correlates not only the valence electrons, but also all the active electrons described by the basis set. For "large core" ECPs, which retain all core electrons below the valence shell, this is correct. However, for small-core ECPs, the (*n* − 1)spd shell is also part of the basis set, and G03 includes it in the FC correlation calculation. As expected, this gives shorter bonds that are closer to the experimental ones. There is one potential problem here though: the atoms of the molecule that are described by all-electron bases (here Al) are treated according to the original meaning of FC, and only their valence electrons are considered in the correlation calculation. For example, in AlBr, for bromine the 4s4p and 3s3p3d electrons will be taken into account (altogether 25), while for aluminum only its 3s3p electrons are considered (i.e., 3). This can give a rather unbalanced treatment.

We carried out different computations for AlBr and AlI, and some of the results are given in Figure 2. The leftmost sets of data for both molecules show the results of the large-core calculations, while the central sets show those of the small-core calculations with the cc-pV*n*Z/cc-pV*n*Z-PP basis sets. In both cases, the full option, especially the quadruple-ζ set, yields unreasonable results for reasons discussed before; these are not recommended. We calculated the proper FC combination (having only the valence electrons correlated) for the central set with the read window option ("sp-only", blue upper curve in the central set); these give bond lengths similar to the large-core FC calculations. The default option of G03 with the small-core bases, having more electrons correlated, gives shorter bonds than the strictly *n*sp correlation.

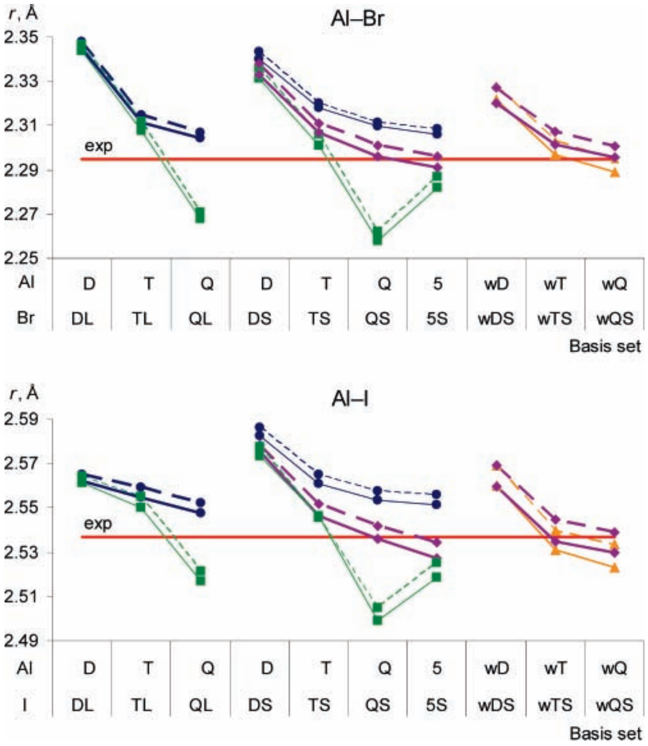

Figure 2. Bond lengths of AlBr and AlI. Left sets: large core calculations (Al: *n*, Br,I: *n*L); central sets: small-core calculations with the cc-pV*n*Z basis sets (Al: *n*, Br,I: *n*S); right sets: small-core calculations with the cc-pwCV*n*Z basis sets (Al: w*n*, Br,I: w*n*S). For further explanation, see caption of Figure 1; moreover, diamonds indicate Gaussian default calculations.

The bond lengths are much improved if we use the cc-pwCV*n*Z and cc-pwCV*n*Z-PP-based bases, in which the ($n-1$) shells are also correlated, for both atoms in the molecules (rightmost sets); the best results are obtained with the CCSD(T) method. Again, it is interesting to mention the observable difference between the default and FC1 calculations; here it is due merely to the inclusion of the 2s and 2p electrons of aluminum in the correlation calculation, and clearly indicates the importance of core−valence correlation in determining accurate molecular constants. Last, we need to mention that adding diffuse functions to the halogens (or also to Al) does not result in any appreciable difference in the bond lengths (see Supporting Information), except at the double-ζ level, which does not give reliable bond lengths for these molecules with either method/basis set combination.

Conclusion

Calculations for the diatomic molecules of aluminum monohalides indicate that, even for the simplest systems containing atoms beyond the first two periods, commercial quantum chemistry programs should be used with care and not mechanically.

- It is advisable to look up in the original publication the level of electron correlation considered during the development of the basis sets and apply the bases accordingly. Calculating full-electron correlation with bases that were developed for valence-only correlation may lead to unreliable results.
- We suggest carefully confirming how many electrons a particular option of a particular program takes into account in calculating electron correlation. This is especially important if we use all-electron bases for some atoms and pseudopotentials with their associated basis sets for others in the molecule.
- It is preferable to use basis sets that take core−valence correlation into account for calculating structural parameters.

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Supporting Information Available: Computed bond lengths of aluminum monohalides at all computational levels discussed above. This material is available free of charge via the Internet at http://pubs.acs.org.

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