COMMENTS

Comment on "A Theoretical Study of Bonding in Lanthanide Trihalides by Density Functional Methods"

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Recently, Adamo and Maldivi[1] have tested the performance of various density functional methods together with different treatments of relativistic effects in the calculation of bonding and geometry of a series of lanthanide trihalides. This comment concerns *only* their approach to, discussion of, and conclusions about molecular geometry.

With its increasing capabilities, computational chemistry has become a partner on a par with the best experimental techniques. For simple organic molecules a computation may be as good or better as the best experiments in determining molecular geometry. Although detailed comparisons between computed and measured geometries often suffer from the nonavailability of the "experimental error" of the computed structures, this difficulty is alleviated by the availability of a large and consistent body of accumulated data for and experience with simple organic molecules.

The situation is different for inorganic systems where each element, or group of elements, has its own unique bonding peculiarities while accumulated experience on computed structures is relatively scarce, and where the available experimental information lacks yet the consistency of that for simple organic systems. Recently, considerable efforts have been made to scrutinize the molecular structures of metal halides. These molecules represent complex systems for structure determination because of their often fluxional character, low volatility, and the possible complexity of their vapor composition. A combined approach involving careful experiment and extensive computations has proved to be fruitful in the reliable determination of these structures, see, e.g., ref 2. At the same time, this approach has necessitated a rigorous probe into the differences of the physical meaning of the internuclear distance provided by various techniques (see, e.g., refs 3, 4) before a meaningful comparison can be made between them.

The largely uncharted areas of inorganic structures are inviting for computational studies while the caveat mentioned above may be easily overlooked. Hence we would like to call for vigilance in assessing the relevant literature.

In their abstract, Adamo and Maldivi[1] state that "All data were found to be in very good agreement with experimental data." This aspect of their paper needs scrutiny in the light of the above caveat. Their Table 3 lists the bond lengths and bond angles of 12 lanthanide trihalides calculated by different approaches. These values are compared with relevant experimental data and the "mean absolute error on the bond length" is calculated for each method, i.e., the differences between the experimental and calculated bond lengths for the 12 molecules are averaged. This approach is not only oversimplifying, it is also grossly misleading.

First of all, Adamo and Maldivi[1] quote the experimental geometrical data without their uncertainties. The experimental error is as important part of a parameter as the parameter itself. The experimental error usually, though not always, includes both the standard deviation of the analysis procedure, which is basically a random error, and the systematic errors of the experiment. Together they provide the *precision* of the parameter. Any detailed comparison should take the precision of the parameters into account, but this is only a necessary but not yet sufficient condition of a meaningful comparison.

Another factor overlooked in ref 1 is the *accuracy* of the parameters. Different physical techniques determine geometrical parameters of different physical meaning. Hence, these parameters will differ from their "true" values to different extents. The relatively rigid organic molecules pose a much smaller problem in this respect than many of the inorganic systems, including the metal halides, known for their low-frequency, large-amplitude vibrations, especially for deformation modes. As is known, the computed geometry is the equilibrium geometry, a hypothetical motionless structure, corresponding to the minimum of the potential energy surface. On the other hand, an experimental geometry is always an average structure; the nature of averaging depends on the particular technique used. The greater the fluxionality of a molecule, and the greater the degree of anharmonicity of its vibrations, the more important will be the difference between, for example, a thermal average internuclear distance (r_g) and the corresponding distance between average nuclear positions (r_α). The parameters used for comparison in ref 1 were all determined by gas-phase electron diffraction, yet their physical meanings are not all the same. Some represent the ill-defined r_a operational distance, while others represent the well-defined thermal average distance, r_g. There is an approximate relationship between the two, $r_g \sim r_a + l^2/r_a$, which again points to the importance of the magnitude of intramolecular motion since l is the mean vibrational amplitude. In addition to the lanthanide trihalide molecules being rather fluxional, the experimental conditions of their studies are invariably characterized by high temperatures, between 1000 and 1800 Kelvin for the molecules in question, undoubtedly enhancing the magnitude of intramolecular motion. Thus the r_g, let alone the r_a, representation is far from the equilibrium distance (r_e) coming out of the computations.

Fortunately, there are ways to convert the r_g thermal average distance into others that are considerably closer to the true equilibrium distance. This is done with appropriate vibrational corrections. One such parameter is r_α, vide supra, that differs from the equilibrium distance only by an anharmonic term. In an ideal case, the computed equilibrium distance should be compared with an experimental equilibrium distance, which can be estimated by applying both harmonic and anharmonic corrections to the r_g parameter.

In the following we attempt to illustrate how seriously different a high-temperature experimental bond length may be from the estimated experimental equilibrium bond length which, in

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TABLE 1: Comparison of Computed and Experimental Bond Lengths (in Å) of some Lanthanide Trihalides

	comp[a] "BP/QR"	expt[b]	diff[c] (expt − comp)	expt[d]	expt, r_e/r_α	diff[g] (expt, r_e − comp)
LaF_3	2.124	2.22	0.096	r_a 2.22(3)	2.13(6)[e]	0.006
LaI_3	2.983	2.99	0.007	r_a 2.98(3)	2.86(3)[e]	−0.123
GdF_3	2.031	2.053	0.022	r_g 2.053(3)	2.016(6)[f]	−0.015
$GdCl_3$	2.481	2.489	0.008	r_g 2.488(5)	2.445(7)[f]	−0.036
$GdBr_3$	2.630	2.640	0.01	r_g 2.641(4)	2.590(9)[f]	−0.040
GdI_3	2.868	2.84	−0.028	r_g 2.840(4)	2.704(7)[f]	−0.164

[a] Column 1 of Table 3 from reference 1. [b] Column 9 of Table 3 from reference 1. [c] Difference of values in previous two columns. [d] Experimental data with indicated uncertainties and physical meaning from original publications. LaF_3 and LaI_3 from reference 5; gadolinium halides from ref 6. [e] r_α, calculated by us using vibrational correction terms from normal coordinate analysis based on vibrational wavenumbers from reference 1. [f] Experimental equilibrium distance from reference 6. [g] Difference of values in columns 5 and 1 of this table.

turn, is the parameter to be ideally compared with the computed equilibrium bond length. Six of the 12 lanthanide trihalides that are dealt with in ref 1 were chosen for this comparison.

The first two columns of Table 1 list the computed and experimental bond lengths for the six LnX_3 molecules exactly the way as given in Table 3 of ref 1. The third column lists the difference of these two values. These are the ones used by Adamo and Maldivi[1] to calculate the "mean absolute errors" of the computed bond lengths (0.021 Å for the BP/QR approach, considering all 12 molecules).

In the fourth column of Table 1 the experimental distances are given together with their experimental errors quoted from the original reports,[5,6] and their physical meaning is also indicated. Notice that the precisions of these distances vary in a broad range. For two of them it is 0.03 Å, while for the four more recent determinations it is only 0.003 to 0.005 Å. Discussing differences to thousandths of an angstrom for parameters with a precision of three hundredth of an angstrom, as is done in ref 1, is of questionable value, to say the least.

The original publication of the experimental data for the gadolinium trihalides actually gives not only the thermal average r_g distances but also the "harmonic" experimental r_e distances that were determined by a joint electron diffraction and vibrational spectroscopic analysis.[6] As is expected for such floppy high-temperature species, the corrections are large. The next column of Table 1 gives the converted r_α parameters for the two lanthanum trihalides and the "harmonic" experimental equilibrium distance, r_e, for the gadolinium trihalides.[7]

The differences between the experimental r_α/r_e and the computed r_e distances are given in the last column of Table 1. This difference column is very different from that in ref 1. While for LaF_3 their comparison showed a difference of 0.096 Å between computation and experiment, the vibrational corrections diminish this difference to 0.006 Å. This is as good an agreement as it may be worth noting, considering the large experimental error of this bond length. The next difference, for LaI_3, on the other hand, changed from 0.007 to −0.123 Å, an increase by 0.13 Å. Considering the differences of experimental vs computed bond lengths for the gadolinium trihalides, while the four values in column 3 (from ref 1) show a random pattern, the differences in the last column (that is the differences between the experimental and computed equilibrium bond lengths) show a trend. This difference increases with the size of the halogen atom, from the moderate −0.015 Å for GdF_3 to the extreme −0.164 Å for GdI_3.

This observation also shows that calculating a "mean absolute error" to indicate the applicability of a certain computational technique for a series of inorganic molecules is lacking merit; the applicability of a method seriously depends on the size of the atoms in the molecules in question.

Conclusions

(1) Further work is needed to establish the most appropriate computational approaches to study various inorganic systems, especially if they have unknown bonding peculiarities and are known to be floppy.

(2) Experimentalists should be taking a second look at many of the inorganic molecular structures that have been around unchallenged for a long time. We anticipate that the precision of many of the early structure determinations will not measure up to the enhanced and increasing computational capabilities.

(3) Computational works should be more rigorous in using experimental information for confronting computational data.[8]

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References and Notes

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(7) The vibrational corrections for LaF_3 and LaI_3 were calculated with a normal coordinate analysis that uses harmonic approximation. Similarly, the gadolinium trihalide equilibrium bond lengths were obtained by a harmonic approximation. This introduces an uncertainty into the correction terms and may somewhat overemphasize the difference, but this uncertainty should be considerably smaller than the actual values of these corrections.

(8) There is another misunderstanding or misinterpretation of less general importance by Adamo and Maldivi when they state that the low-frequency bending mode may not be detected in electron diffraction and they refer to their ref 42 (Hargittai, M. *Coord. Chem. Rev.* **1988**, *91*, 35). In fact, for these very low-frequency bending modes, electron diffraction has been used to estimate wavenumbers at least as good as could be measured by vibrational spectroscopy.