Reply to the Comment "A theoretical study of bonding in lanthanide trihalides by density functional methods" by M. Hargittai

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The above-mentioned comment criticizes one particuliar part of our recently published paper[1], i.e., the comparison of our theoretical results with experimental data on molecular structures of lanthanide trihalides species. This Comment may be analyzed in terms of one general criticism on the way we have presented the comparisons and several faultfindings on more specific points in our text, and we wish to reply to both.

The main reproach expressed by M. Hargittai is therefore that we have compared our calculated interatomic equilibrium distances with the available experimental values given in various publications.[2−6] The problem in these compounds is that their are very fluxional and may adopt quite easily either a pyramidal or planar structure. Their potential curve is very flat, resulting in non negligible anharmonicity effects. Moreover, experimental conditions require high temperatures thus emphasizing significantly the contribution of intramolecular motions in the estimation of the interatomic Ln−X bond length.

Of course, this picture, as presented in the above Comment is the most rigorous one, but theoreticians wishing to compare their computed estimations with experimental data primarily refer to the existing tabulated values given in the literature. This is what we have done, as it had been done in several other theoretical papers already published in the same field,[2−6] and we urge M. Hargittai to have a look at these publications. Of course, in those papers, as in ours, the purpose was to compare results given by various methodologies (influence of the effective core potential, of the basis set, of the functional, ...) first and then to compare them to experimental data. We have followed exactly the same approach, and it was therefore evident to reuse the same tabulated experimental data as those already used in precedent theoretical papers, in order to make a coherent comparison! As a matter of fact, our main source of information was the complete review of M. Hargittai[7] (Table 12 on p 41) where several distances of lanthanide trihalides are reported as estimated, which means that the error on such distances might be greater, and at least is not known.

Now we also wish to reply to more specific points, because even if they seem of less importance, the way they have been written up contributes to a general unpleasant feeling for the reader.

First, the averaging of the difference between calculated and experimental data for all compounds was included as an *additional* parameter. All of our computed and "experimental" data were given, so that each individual difference for a given compound could be readily calculated from our tables. We do not understand why it should be considered as an "oversimplification", whereas it was just complementary information.

A completely rigourous quotation of experimental data should have included of course the experimental errors, but, in that case, why not include in the criticism a great number of other theoretical papers? This is not an excuse, but this remark illustrates the deliberately overemphasizing character of the Comment.

Second, in footnote 8 of the Comment, it is suggested that we have not a clear understanding of techniques which give access to the vibrational motions of a molecule. But maybe this was merely a misunderstanding of our sentence (first column, p 6815 in our paper) concerning the experimental uncertainties of the techniques. We have stated in the first part of the sentence that "electron diffraction experiments only give average values of the bend angle": effectively this has been quoted from the review of M. Hargittai (see p 39).[7] In the second part, we have stated that the low-bending mode could not be detected: it is said, always in ref 7 by Hargittai,[7] that "these bending frequencies are often unavailable as they occur in a far infrared region". One example may also be quoted in ref 5, for LaI_3 and $LaBr_3$, where the corresponding band was outside the detection limit. One should note also that, in ref 6a cited in Hargittai's Comment, electron diffraction data are interpreted by some kinds of models, whose precision is evaluated using other better known molecules. There is thus no warranty to obtain the same error.

We hope to have clearly expressed our response, but we wish to add a final comment. The fact that our paper has been alone the subject of such criticisms whereas most of them could be adressed to some other papers already published in the same field (whether these reproaches were justified or not) clearly points to the subjective character of these criticisms, thus weakening them.

The only positive point in that controversy is, once again, an illustration that theoreticians must constantly be watchful, when analyzing computed values against experimental data published in the literature, about their uncertainness and their meaning.

References and Notes

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