Reply to "Comment on 'Instability of the Al_4^{2-} 'All-Metal Aromatic' Ion and Its Implications'"

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In a recent article on Al_4^{2-},[1] we showed that this species, as an isolated system in the gas phase, has a very short lifetime with respect to electron autodetachment. As for all electronically short-lived systems, standard calculations employing standard basis sets are then highly problematic: Owing to essentially arbitrary mixing with continuum solutions, computations yield arbitrary results for almost all properties. This should not be confused with the normal basis set dependence of all computed properties of electronically stable systems that is orders of magnitude milder.

In their comment[2] Zubarev and Boldyrev point out that standard calculations can nevertheless be used for "modeling purposes" and that, using a 6-311+G* basis set, isolated Al_4^{2-} provides an "adequate model" for Al_4^{2-} embedded in a stabilizing environment.

We agree with this statement. Our and many other calculations suggest that for each metastable species there are basis sets that have approximately the right spatial extent for this purpose, and as Zubarev and Boldyrev show, for Al_4^{2-} the 6-311+G* basis set does a fair job. However, without experimental data, or adequate theoretical treatment, it is by no means clear just how diffuse a basis set for "modeling" purposes should be chosen or whether this conclusion may be transferred to other molecular properties. In fact, our results show clearly that for Al_4^{2-} the computed chemical shifts vary greatly even if only slightly more diffuse functions than the standard "+"-functions are added to the basis and the restriction of doubly occupied determinants is removed (such as in going from closed-shell SCF to correlation approaches or property calculations). Thus, standard calculations are certainly suitable for a posteriori modeling, but lack predictive power, and quantitative results from such calculations are likely to be unreliable.

References and Notes

(1) Lambrecht, D. S.; Fleig, T.; Sommerfeld, T. *J. Phys. Chem. A* **2008**, *112*, 2855.
(2) Zubarev, D. Yu. ; Boldyrev, A. *J. Phys. Chem. A* **2008**, *112*, 7984.

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