

COMMENTS

Comment on “Instability of the Al_4^{2-} ‘All-Metal Aromatic’ Ion and Its Implications”

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Lambrecht, Fleig, and Sommerfeld¹ recently presented study on implications of instability of Al_4^{2-} . In their thorough ab initio investigation they showed that the Al_4^{2-} dianion is metastable with a very short lifetime of 9 fs. They also demonstrated that the adequate description of the dianion requires the admixture of scattering solutions to the bound-state wave functions. Thus, they made a conclusion that calculations of molecular properties can give essentially arbitrary results for such ill-defined systems. The instability of isolated Al_4^{2-} toward electron autodetachment was recognized in our first publication on this system.² Nevertheless, we performed geometry optimization, calculated harmonic frequencies and analyzed chemical bonding in this system using B3LYP and CCSD(T) methods with compact 6-311+G* basis set. Though we agree that accurate description of this dianion requires taking the continuum (unbound) states $\text{Al}_4^- + \text{free e}$ into account, we still believe that our calculations of molecular properties of Al_4^{2-} performed with compact basis set do make sense. It is common in chemistry to partition complex systems into simpler “building blocks”. For example, all inorganic salts are usually represented by the simplest stoichiometric ratio of cations and anions, even though some of these anions may not be stable in the isolated form. When theoreticians run calculations of such unstable anions, they try to model properties of these objects in the condensed phase, where these objects are stabilized by the external field. Within the same conceptual framework, we considered Al_4^{2-} as a building block of electronically stable systems such NaAl_4^- or Na_2Al_4 . In this case calculations of Al_4^{2-} with compact basis sets serve for modeling purposes because the bound state of individual Al_4^{2-} is an adequate model of the Al_4^{2-} in stabilizing environment such as in NaAl_4^- or Na_2Al_4 species. This is because the compact basis sets used in our calculations adequately describe the part of the potential energy surface inside the repulsive Coulomb barrier. This part of the potential energy surface should not be significantly affected by the external field of Na^+ cation as we show below. When Al_4^{2-} is stabilized by the external field, the “tails” of continuum solutions can be disregarded.

To prove our statement and validate this modeling approach, we compare properties (obtained at B3LYP with compact 6-311+G* basis set) of bound state description of isolated Al_4^{2-} with corresponding properties of Al_4^{2-} in the electronically stable NaAl_4^- and Na_2Al_4 species where perfect square shape of Al_4^{2-} unit is preserved (Figure 1 and Table 1). In Figure 1b we presented localized description of chemical bonding in Al_4^{2-} ,

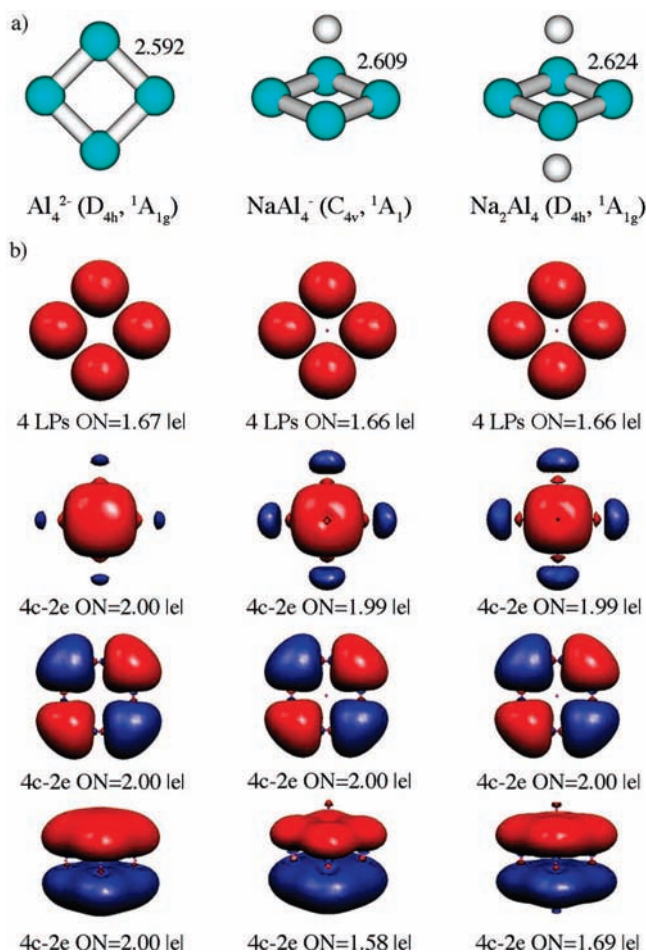


Figure 1. (a) Optimized geometries (Al–Al distances are in Å) and (b) localized nc-2e bonds (obtained by the AdNDP) for Al_4^{2-} (D_{4h} , $^1A_{1g}$), NaAl_4^- (C_{4v} , 1A_1), and Na_2Al_4 (D_{4h} , $^1A_{1g}$). All calculations are performed at B3LYP/6-311+G*.

NaAl_4^- , and Na_2Al_4 using newly developed Adaptive Natural Density Partitioning method.³ One can see that Al_4^{2-} unit has four lone pairs (one on each Al atom) and three delocalized four center – two electron (4c-2e) bonds in each species. Three 4c-2e bonds are responsible for double (σ - and π -) aromaticity in this model system. Sodium cations only introduce relatively small perturbations in this description due to the charge transfer but do not change it qualitatively. On the basis of this chemical bonding analysis, we can expect that other molecular properties of the model dianion Al_4^{2-} will remain close to those of Al_4^{2-} unit within electronically stable NaAl_4^- and Na_2Al_4 species. Indeed, comparison of interatomic distances (Figure 1a), harmonic vibrational frequencies and corresponding force constants (Table 1) confirms this expectation. This good agreement is the criterion for choosing specific compact basis set for modeling purposes. When Na cations are coordinated so that Al_4^{2-} unit loses its perfect square shape (cations coordinated to an edge of the square), perturbations are higher as one should expect, though the qualitative picture of bonding and square-like geometric structure is approximately preserved.

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TABLE 1: Molecular Properties of Model Isolated Al_4^{2-} and Al_4^{2-} in NaAl_4^- and Na_2Al_4^a

Al_4^{2-}	NaAl_4^-	Na_2Al_4
$\omega(\text{a}_{1g}) = 294$ ($k_f = 1.376$)	$\omega(\text{a}_1) = 292$ ($k_f = 1.350$)	$\omega(\text{a}_{1g}) = 283$ ($k_f = 1.269$)
$\omega(\text{b}_{1g}) = 132$ ($k_f = 0.275$)	$\omega(\text{b}_2) = 167$ ($k_f = 0.443$)	$\omega(\text{b}_{1g}) = 147$ ($k_f = 0.345$)
$\omega(\text{b}_{2g}) = 307$ ($k_f = 1.503$)	$\omega(\text{b}_1) = 304$ ($k_f = 1.465$)	$\omega(\text{b}_{2g}) = 289$ ($k_f = 1.327$)
$\omega(\text{b}_{2u}) = 115$ ($k_f = 0.209$)	$\omega(\text{b}_2) = 127$ ($k_f = 0.257$)	$\omega(\text{b}_{2u}) = 186$ ($k_f = 0.550$)
$\omega(\text{e}_u) = 272$ ($k_f = 1.176$)	$\omega(\text{e}) = 266$ ($k_f = 1.124$)	$\omega(\text{e}_u) = 257$ ($k_f = 1.050$)

^a Harmonic frequencies ω are in cm^{-1} , force constants k_f (in parentheses) are in $\text{mDyn}/\text{\AA}$.

On the basis of the analysis of electronic structure of this “ill-defined” system we developed chemical bonding model applicable to a wide range of systems including “well-defined” ones, such as XAl_3^- ($\text{X} = \text{Si}, \text{Ge}, \text{Sn}, \text{and Pb}$) singly charged anions valence isoelectronic with Al_4^{2-} . We predicted that substitution of one Al in Al_4^{2-} by a XIV group atom X with electronegativity close to Al would preserve double aromaticity in electronically stable XAl_3^- clusters and thus their square-like global minimum structures. Indeed, in our joint experimental and theoretical study⁴ we proved that this prediction was correct. In fact, a whole new approach to the description of electronic structure of clusters based on the combined localized and delocalized (aromatic) chemical bonding emerged.⁵⁻⁷

This case is a good example that the calculations of electronically unstable species done with the compact basis sets and disregarding continuum solutions are valuable for the purpose of modeling these systems as parts of the stable chemical objects. Apparently, this modeling approach has certain limitations. There might be cases when calculations of isolated multiply charged anion with compact basis sets would not yield

meaningful results due to either SCF divergence or significant geometry distortions up to complete dissociation of the anion. The main criterion of the validity of model calculations of electronic structure and geometric parameters of isolated electronically unstable anions utilizing compact basis sets is the a reasonable agreement with electronic structure and geometric parameters of the anion in the stabilizing environment.

References and Notes

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