Computational Aromaticity Studies on Metallic Four-Membered Rings

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Aromaticity is a concept introduced to account for the unusual stability of an important class of organic aromatic compounds. In recent times the concept of aromaticity has been extended to all metal molecules in order to explain the stability of some small clusters observed in laser vaporization experiments. A particular class of molecules that have been subject to many studies are the lithium -aluminum clusters consisting of Al_4^{2-} and Al_4^{4-} cores. These systems were first both experimentally and theoretically studied by Boldyrev *et al.*[1] The aromaticity was later studied using nucleus-independent chemical shift (NICS) analysis by Schleyer *et al.* and using ipsocentric CTOCD-DZ by Fowler and Havenith.[2,3] Although much studied, the exact nature of their aromaticity has still not been completely determined.

Wannere *et al.*[4] recently studied computationally four-membered ring species of coinage metals, such as bipyramidal Cu_4Li_2, Ag_4Li_2, and Au_4Li_2 clusters of D_{4h} symmetry and used NICS calculations to access their aromaticity. Moreover, they considered these coinage-metal clusters as the first example of *d*-orbital aromatic molecules. .

In the present work, we first report the generation of Cu_4Na^- and Au_4Na^- clusters in the gas phase and their characterizations experimentally using PES and computationally at correlated *ab initio* levels.[5] The molecular structures of Cu_4Na^- and Au_4Na^- are found to be pyramidal of D_{4h} symmetry and planar cluster of D_{2v} symmetry, respectively. It shows the importance of both PES experiments and computational spectrum in order to identify the molecular structures of observed clusters.

Moreover, we have applied the GIMIC method[6] to three different metallic systems for understanding their nature of aromaticity: Al_4^{2-}, Al_4^{4-}, and Cu_4^{2-}.[5,7]

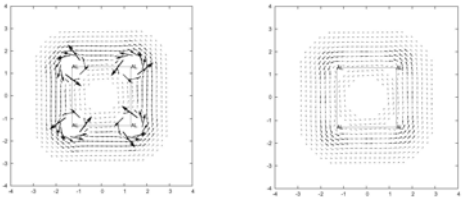

Figure 1. Vector representation of the current density in Al_4Li_2:
(a) in the plane,
(b) 1 a.u. above the plane in the π-bond

The magnetically induced current is invariant to transformations of the magnetic gauge origin. In practice, however, gauge invariance is hard to achieve. GIMIC is a method for calculating the components of the magnetically induced current tensor using gauge-including atomic orbitals (GIAO). The use of GIAOs represents an elegant solution to remedy the gauge-origin problem. The ring-current strengths are obtained directly via explicit numerical integration over the net current flow through one of the bond cross -section within the considered molecular ring.

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