SUPERALKALI MOLECULES CONTAINING HALOGENOIDS

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Abstract

The structure and properties of hypermetalated Li_2X, Na_2X (X=SCN, OCN, and CN), Na_4OCN molecules and their corresponding daughter cations were investigated using *ab initio* methods at the CCSD(T)/6-311+G(3df)//MP2/6-311+G(d) level of theory. The vertical ionization potentials of the Li_2X, Na_2X and Na_4OCN radicals were calculated at the outer valence Green function level (OVGF) with the 6-311+G(3df) basis set. It was found that all Na_2X molecules studied possess the vertical ionization potentials (VIP) that are smaller than the IP of the Na atom (5.14 eV) and thus may be termed *superalkali molecules*, whereas the Li_2X radicals exhibit slightly larger IPs. The VIP predicted for Na_4OCN superalkali molecules (4.117-4.640 eV) are substantially lower than those estimated for Na_2OCN species (4.747-5.072 eV). The smallest VIP of 4.478 eV was calculated for the global minimum of the Na_4OCN structure. The IP dependence on the structure and singly occupied molecular orbital (SOMO) character is also discussed.