ELECTRONIC STRUCTURE OF N_2 DIMER CATION

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Energies of the ground and the lowest excited states of the N_2 dimer cation were calculated. EOM-IP-CCSD method was used for calculations. The goal of this study was to explain experimental data of N_2 dimer dissociation following charge-exchange between nitrogen dimer cation and Cs from R. Continetti group. This system is also very interesting from the theoretical point of view because of the unusual electronic structure and as a model charge-transfer system. We characterized the bonding of the ionized system due to orbital overlaps between the fragments.

To extend EOM-IP-CCSD to large systems, frozen natural orbitals approach can be employed. Benchmark results demonstrating the performance of EOM-IP-CCSD/FNO scheme will be presented. We found that for closed shell molecules the orbital space can be reduced by 40% with minor effect on the ionization energy at EOM-IP-CCSD level (the minimal absolute errors are about 1 kcal/mol).