Rydberg bonding - the non-valence long-range covalent bond

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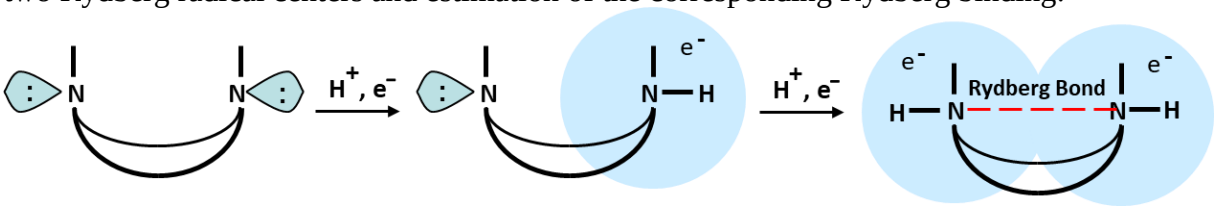
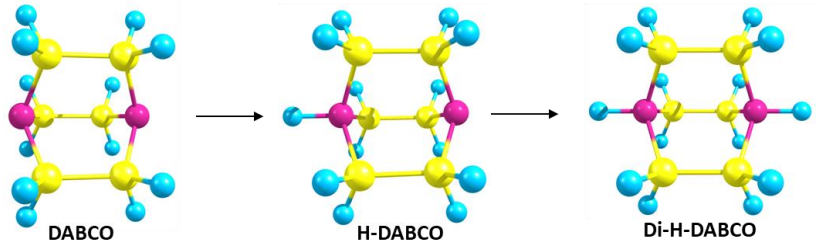
The first experimental study of Rydberg species - •NH4 was reported by Herzberg in 1981 [1]. This radical is not stable, but it could be stabilized by the complexation in ammonia cluster.
3s-AO Rydberg origin was reported for the different alkyl-substituted amines [2,3]. Calculations of pyrrole-ammonia [4], pyrazole-pyrazole and imidazole-imidazole [5] complexes show that the proton shift is escorted by shift of a Rydberg orbital from the excited to the ground state.
Chemical binding of two monovalent Rydberg radicals •NH_4 to form a dimer with non-valence Rydberg bond was estimated to be about 8 kcal/mol [6]. However, the dimer $(NH_4)_2$ is unstable towards dissociation into ammonia and molecular hydrogen [7].
The goal of this study is a design of thermodynamically and kinetically stable compounds with two Rydberg radical centers and estimation of the corresponding Rydberg binding:



Different diaza-derivatives of cyclohexane and some polycycles were studied computationally on CASCF, CAS-MP2 and DFT levels of theory. Probably, the optimal position of N-centers for the Rydberg binding is 1,4-diaza location. Addition of hydrogens to the two N-atoms of 1,4-diazapiperazine or DABCO leads to strong and long-range bonding between two Rydberg N-centers. The strength of N-N Rydberg bond could reach 0.9eV as was calculated for the 1,4-dihydro-DABCO adduct (di-H-DABCO). Calculations show both thermodynamic and a kinetic stabilization for the molecules with a Rydberg N-N bond for the different 1,4-diaza-derivatives.



VB analysis of the 3s-3s AOs binding between two N-atoms shows the dominant covalent character of the Rydberg N-N bond.

References

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