AB INITIO ELECTRONIC AND ROVIBRATIONAL STRUCTURE OF FULMINIC ACID

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Molecules with a non-linear electronic minimum but a low barrier to linearity allowing a large amplitude bending motion may exhibit rovibrational spectra with level patterns reminiscent of molecules with a rigid linear skeleton and are usually referred to as quasilinear molecules. The large amplitude bend contributes a vibrational angular momentum which couples with the overall rotational angular momentum. Furthermore the bending motion is frequently coupled with the high-frequency stretch modes. The combination of these features leads to particularly complicated rovibrational spectra.

Fulminic acid, HCNO, is one of the most important representatives of this class of molecules and has been subjected to extensive previous theoretical and experimental analyses. The electronic structure problem has turned out to be particularly hard leading to strongly method and basis set dependent results such that the equilibrium geometry and the size of the barrier, if there is any, are still unclear. Extensive ab initio calculations of the electronic ground state with coupled cluster and CI techniques with large basis sets have been performed to shed light on the origin of this structural problem and are used for an analysis of the quasilinear ν_5 mode under realistic conditions of the vibrating-rotating molecule. The electronic and rovibrational structures are compared with the isomers cyanic acid, HOCN, and isocyanic acid, HNCO.