

Validity of the minimum polarizability principle in molecular vibrations and internal rotations: An ab initio SCF study

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Molecular vibrations in ammonia (NH_3) and hydrogen sulfide (H_2S), and internal rotations in hydrogen peroxide (HOOH), hydrogen thioperoxide (HSOH), hydrogen persulfide (HSSH), and ethylene (C_2H_4) are studied using ab initio SCF methods at the Hartree-Fock level using a standard Pople 6-311G** basis set. Polarizability values are calculated using both Pople's and Sadlej's basis sets. Any nontotally symmetric distortion in bond length or bond angle along the vibrational symmetry coordinates of a molecule around its equilibrium geometry decreases the equilibrium hardness value and increases the equilibrium polarizability value. During rotational isomerization the minimum energy conformation corresponds to the maximum hardness and minimum polarizability values and the maximum energy conformation corresponds to the minimum hardness and maximum polarizability values. Density functional calculations confirm these observed trends. In general we have found that the conditions of maximum hardness