Critical analysis of the calculated frequency shifts of hydrogen-bonded complexes.

Autorzy

Bernard Silvi

Robert Wieczorek

Zdzisław Latajka

M. E. Alikhani

A. Dkhissi

Y. Bouteiller

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Streszczenie

The frequency shift of the proton donor in hydrogen bonded complexes is an important quantitywhich enables to discuss the nature of the hydrogen bond. Calculations of frequency shifts byquantum chemical methods are usually performed within the harmonic approximation and thereforethe comparison with experimental data is biased. We have investigated the importance ofanharmonic corrections in the case of twelve complexes in which either FH or ClH is the protondonor. Hartree–Fock, Moîller–Plesset second and third order~MP2, MP3!, density functional theory~DFT!, and hybrid Hartree–Fock/DFT methods have been used for the calculations. It is shown thatthe anharmonic contribution to the frequency shift is rather method dependent. Its magnitude isusually 10%–20% of the total shift though it can be as large of;50% for~ClH!2. Onceanharmonicity is taken into account, most methods tend to noticeably overestimate the frequencyshifts. In the case of DFT related approaches this trend is interpreted in terms of a poor descriptionof the exchange in the intermolecular region.

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