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A critical investigation of XPS predicted proton affinities

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Abstract

A thermochemical model for predicting gas-phase proton affinities from core ionization energies is investigated for a number of test cases. Deviations from experimental values are attributed to alternate sites of protonation, geometrical relaxation effects and chemical effects on the core replacement energies in the equivalent core approximation. The error types are further explored by ab initio MCSCF calculations, including geometry optimizations, using analytical molecular gradients and hessians. For the protonation of ammonia the thermochemical model is simulated by MCSCF calculations, confirming both the predicted proton affinity and the observed discrepancy vs. the experimental value. The importance of including zero-point vibrational energies in both core ionization and proton affinity calculations is stressed. The calculations suggest that the geometry-related error is small for protonation of nitrogen but considerable for protonation of fluorine, ≈ 1 eV.

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