The HOBr Molecule Revisited: Accurate Near-Equilibrium Potential from Composite Calculations

Antonio G. S. de Oliveira-Filho, Fernando R. Ornellas

Depto. de Química Fundamental, Instituto de Química, Universidade de São Paulo, São Paulo, Brazil

Halogen-containing species, such as halogen oxides and hypohalous acids, are known by their importance to atmospheric chemistry due to the central role they play on the destruction of stratospheric ozone. In this study, the well investigated hypobromous acid is revisited. A total of 84 configurations were sampled to obtain an accurate three-dimensional near-equilibrium potential that was used to calculate equilibrium structural parameters and vibrational frequencies for HOBr. At each configuration a composite *ab initio* approach based on the Feller-Peterson-Dixon procedure was used: the fronzen-core CCSD(T) complete basis set limit was estimated from a extrapolation with a l^{-3} formula using the aug-cc-pVQZ(-PP) and aug-cc-pV5Z(-PP) basis sets, corrections for outer core/valence correlation effects were included at the CCSD(T)/aug-cc-pwCVQZ(-PP) level, scalar relativistic effects were described with second-order Douglas-Kroll-Hess (DKH) CCSD(T) (frozen-core) calculations using the aug-cc-pV5Z-DK basis set, contributions of higher-order correlation were included at the CCSDT/cc-pVTZ + CCSDTQ/cc-pVDZ levels, and the diagonal Born-Oppenheimer correction was considered at the HF/aug-cc-pVTZ level of theory. An excellent agreement between experimental and theoretical results was observed: the calculated equilibrium structural parameters are 1.8311 Å for R_{BrO}, 0.9643 Å for r_{OH}, and 102.94º for the bond angle, while the experimental values are, respectively, 1.8280 Å, 0.9460 Å, and 102.99º; the computed fundamental vibrational frequencies are 3621.0, 1166.7, and 623.1 cm^{-1}, and the experimentally determined values are 3614.9, 1162.6, and 620.2 cm^{-1}.