

## Computational study of vibrational spectra and thermodynamic properties of the sulphuric acid monohydrate complex

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Water and some of its complexes are greenhouse gases in the Earth's atmosphere. Stretching vibrational overtone spectroscopy in the near-infrared region is interesting for the experimental observation of these species under atmospheric conditions. Cloud formation is another area where some of these complexes such as the water sulphuric acid complex play an important role. Consequently, to obtain thermodynamic properties and the equilibrium constant of the water sulphuric acid complex, we have computed vibrational states of those low-frequency vibrational modes which connect different in energy close-lying conformers. For spectroscopic purposes, we have computed high-frequency OH stretching and HOH bending vibrational overtones of this complex.

In particular, we employ *ab initio* methods to find stable geometries and to calculate potential energy surfaces and vibrational wavenumbers for the sulphuric acid monohydrate [1]. Geometry optimizations are carried out with the explicitly correlated coupled-cluster approach that includes single, double, and perturbative triple excitations (CCSD(T)-F12a) with a valence double- $\zeta$  basis set (VDZ-F12). Four different stable geometries are found, and the two lowest are within  $0.41 \text{ kJ mol}^{-1}$  (or  $34 \text{ cm}^{-1}$ ) of each other. Vibrational harmonic wavenumbers are calculated at both the density-fitted local spin component scaled second-order Møller–Plesset perturbation theory (DF-SCSLMP2) with the aug-cc-pV(T+d)Z basis set and the CCSD-F12/VDZ-F12 level. Water O–H stretching vibrations and particularly the two highly anharmonic large amplitude motions connecting the three lowest potential energy minima are considered by limiting the dimensionality of the corresponding potential energy surfaces to two- or three-dimensional subspaces that contain only strongly coupled vibrational degrees of freedom. In these anharmonic domains, the vibrational problem is solved variationally using potential energy surfaces calculated at the CCSD(T)-F12a/VDZ-F12 level of theory.

[1] L. Partanen, V. Hänninen, L. Halonen, *J. Phys. Chem. A* **2012**, *116*, 2867.