

## **MOLIM scientific report for ECOST-STSM-CM1405-150417-085764**

### *Spectroscopic characterization of the HOC(O)O radical for its identification in Earth's atmosphere*

15.4-23.4: During this STSM we (R. Linguerri and C. Puzzarini) decided the best approaches and run corresponding computations for determining accurate spectroscopic parameters that can guide future detection and experimental characterization of the atmospherically relevant HOC(O)O radical.

In particular, the discussion was first focused on the selection of the best post-Hartree Fock approaches to determine accurate geometric parameters and rotational constants for the ground and the first excited electronic states. We agreed that a suitable approach should include corrections for basis set incompleteness and account for core correlation effects. We decided to use standard CCSD(T) and the explicitly-correlated CCSD(T)-F12b methods for this task, together with suitable atomic basis sets, for the evaluation of core-valence corrections to the frozen-core approximations.

Calculations are currently performed with the CFOUR and MOLPRO suites of ab initio programs that are both available on the workstations at University of Paris-Est Marne-la-Vallée (R. Linguerri) and Bologna (C. Puzzarini).

Vibrational ground state rotational constants obtained by augmenting the equilibrium rotational constants with vibrational corrections at the CCSD(T)/cc-pVTZ level are being evaluated.

Quartic centrifugal distortion constants will be calculated at the CCSD(T)/cc-pVTZ and CCSD(T)/aug-cc-pVTZ levels, and sextic centrifugal distortion constants at the CCSD(T)/cc-pVTZ level.

We discussed the computational details to simulate the IR spectrum of the ground state with an approach based on second order vibrational perturbation theory that includes anharmonic effects in both energies and intensities. This task will be performed in collaboration with M. Biczysko (SNS, Pisa, Italy).

Anharmonic force-field computations are carried out with CFOUR by numerical differentiation of analytic harmonic force constants obtained at the CCSD/aug-cc-pVDZ level of theory. A suitable representation of the PES is given in terms of harmonic CCSD(T)/aug-cc-pVTZ and anharmonic CCSD/aug-cc-pVDZ force fields. Then, the dipole moment surface will be obtained by combining harmonic IR intensities, at the

CCSD(T)/aug-cc-pVTZ level, with anharmonic corrections computed by numerical differentiation of B3LYP/aug-cc-pVTZ analytic first derivatives with the GAUSSIAN code. Second-order vibrational perturbation theory is used in conjunction with the above PES and dipole surface to perform anharmonic computations, according to the framework developed by Barone and Bloino, as implemented in GAUSSIAN. This allows the evaluation of thermodynamic properties as well as vibrational and IR transition energies.

A publication based on these data is in preparation.

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