THEORETICAL SPECTROSCOPIC CHARACTERIZATION AT LOW TEMPERATURES OF S-METHYL THIOFORMATE AND O-METHYL THIOFORMATE

R. Domínguez-Gómez[1], C. Puzzarini[2], M.L.Senent[3], and M. Hochlaf[4], M. Carvajal[5]

[1]Departamento de I. C.T. Hidráulica y Energética, U.D. de Química, E.T.S Ingeniería Civil, Universidad Politécnica de Madrid, SPAIN.
[2]Dipartimento di Chimica, "Giacomo Ciamician", Università di Bologna, Via F. Selmi 2, I-40126, Bologna, Italy
[3]Departamento de Química y Física Teóricas, Instituto de Estructura de la Materia (IEM), C.S.I.C., Serrano 121, Madrid 28006, Spain
[4] Université Paris-Est, Laboratoire de Modélisation et Simulation Multi Echelle, MSME UMR 8208 CNRS, 5 boulevard Descartes, 77454 Marne-la-Vallée, France.
[5]Departamento de Física Aplicada, Unidad Asociada al IEM-CSIC, Universidad de Huelva, 21071 Huelva, SPAIN

Highly correlated ab initio methods are employed to determine spectroscopic properties at low temperatures of two S-analogs of methyl formate: S-methyl thioformate CH_3-S-CHO (MSCHO) and O-methyl thioformate CH_3-O-CHS (MOCHS). Both species can play important roles for astrochemistry. Molecular properties are compared with those of the O-analog, methyl formate.

Equilibrium geometries and equilibrium rotational constants have been evaluated at the CCSD(T)/CBS(Q,5)+CV(CQ) level. Both isomers present two conformers cis and trans. cis-CH_3-S-CHO represents the most stable structure lying at 4372.2 cm^{-1} below cis-CH3-O-CHS. The energy difference between the cis and trans forms is drastically lower for MSCHO (1134 cm^{-1}) than for MOCHS (1963.6 cm^{-1}). Harmonic and anharmonic fundamentals and the corresponding intensities, rotational constants for the ground vibrational states and first excited torsional states, as well as centrifugal-distortion constants, are provided.

Low torsional energy levels are determined by solving variationally a two dimensional Hamiltonian depending on the two torsional modes. The corresponding 2D potential energy surfaces are determined at the CCSD(T)/aug-cc-pVTZ level. The methyl torsional barriers V3(cis) are determined to be 139.7 cm^{-1} and 670.4 cm^{-1} for MSCHO and MOCHS, respectively. The A/E splitting of the torsional ground state is 0.438 cm^{-1} for CH_3-S-CHO, while is negligible for CH_3-O-CHS.

[1] M.L. Senent, C. Puzzarini, M. Hochlaf, R. Domínguez-Gómez and M. Carvajal (in preparation)