CO/H_2O mixtures: computer simulations and prediction of IR spectra

(Inst. Estructura de la Materia, IEM-CSIC, Serrano 123, 28006 Madrid, Spain[a] ,
Institute of Low Temperature Science, Hokkaido Univ., Sapporo[b])
Rafael Escribano[a], Naoki Watanabe[b], Tetsuya Hama[b], Akira Kouchi[b]
e-mail: rafael.escribano@csic.es

Spectra of mixtures of CO and H_2O have been recorded at ILTS, Sapporo, at two different H_2O:CO ratios, namely 1:50 and 1:10. Samples are created by matrix-sublimation of the mixtures deposited at 10 K on a 5 nm thick a-Si substrate. IR spectra of the samples are recorded at increasing temperatures during the CO sublimation experiment, which allows controlling their evolution. At the lowest temperatures, below 50 K, the spectra reveal varying features for the two different mixing ratios, and in particular, the presence of a O-H stretching mode in the low H_2O concentration samples, at 3707 cm^{-1}, which is missing in the high H_2O concentration mixtures. This mode is assigned to a H_2O monomer.

In an attempt to shed light on the analysis of these spectra, we have carried out a series of calculations on theoretical models that simulate the experimental samples. The models consist in amorphous mixtures of CO and H_2O, where the structure is relaxed until a minimum in the potential energy surface is reached. Density Functional Theory is applied, with the Generalized Gradient Approximation and RPBE functionals. The CASTEP and SIESTA sets of programs have been used for the relaxations and predictions of the vibrational spectra.

Our models contain 1 to 4 H_2O molecules, and from 13 to 31 CO molecules. In most cases, the O-H vibration of a non-bound H_2O molecule appears at the highest wavenumber, basically in agreement with the observations. The O-H vibrational mode is stronger when the H_2O molecule is linked by H-bonding to other H_2O molecules.

Predicted spectra will be shown at the meeting.