Geophysical Research Abstracts, Vol. 8, 08430, 2006
SRef-ID: 1607-7962/gra/EGU06-A-08430

Theoretical and Experimental Evaluation of Low-frequency Spectra of Nitric Acid Hydrates

R. Escribano (1), H. Grothe (2), D. Fernández-Torre (1), B. Maté (1), I. K. Ortega (1), B. Martín and V. J. Herrero (1)

(1) Instituto de Estructura de la Materia, CSIC, Serrano 123, 28006 Madrid, Spain, (2) Institute of Materials Chemistry, Vienna University of Technology, Veterinärplatz 1/GA, A-1210, Vienna, Austria

The low-frequency region (below 175 cm^{-1}) of the spectra of solid samples can provide valuable information on vibrational modes related to large amplitude motions, intermolecular vibrations or vibrations associated to weak linkages. Whereas far-infrared spectroscopy exhibits rather broad bands for solid hydrates, among other drawbacks of this technique, Raman spectroscopy produces narrow signals in this spectral region. On the other hand, the prediction of spectra from first principles is currently at a higher level of development for infrared absorption than it is for Raman scattering. This contribution presents the application of two techniques to the study of samples of atmospheric relevance, namely the hydrates of nitric acid.

The experimental part consists in the Raman spectra of samples of the nitric acid mono-, di- and trihydrates, and mixtures of them. The samples were prepared by sudden cooling of a solution of nitric acid and water at the desired concentration contained in a capillary. More details are given in a recent publication [1].

Predictions of spectral line positions have been obtained for the same nitric acid hydrates by means of the SIESTA program. These calculations are based on a refinement of the geometrical structure of the unit cell of the crystal, followed by an evaluation of the atomic forces induced by the Cartesian displacements of the atoms, and hence the prediction of the vibrational modes related to all systems within the unit cell.

This contribution to the Conference will present a comparison between the experimental Raman spectra and the predicted vibrations of the nitric acid hydrates under study. An interpretation of the spectra will be proposed based on the atomic displacements observed for the corresponding modes, according to the theoretical model.

Reference:

[1] H. Grothe, C. E. Lund Myhre, C. Nielsen J. Phys. Chem. A 110 (2006) 171-176.