



Laboratory IR Spectroscopy of Nitric Acid Hydrates Relevant to PSC Research

V. J. Herrero

Instituto de Estructura de la Materia, CSIC, Serrano 123, 28006 Madrid, Spain
(vherrero@iem.cfmac.csic.es / Phone: 34-915901605)

Nowadays it is generally accepted that nitric acid hydrates are basic constituents of polar stratospheric clouds (PSCs) and contribute to ozone depletion. From a thermodynamic point of view, the most favourable form of nitric acid hydrate, under typical conditions of the polar stratosphere in winter, is the β -phase of the tri-hydrate (β -NAT), but the possible presence of the di-hydrate (NAD) has also been suggested. The actual identification of these hydrates in field measurements has been difficult and not always free from controversy [1].

In a recent work [2] a spectroscopic feature peculiar to β -NAT, a peak at 820 cm^{-1} , was found in IR limb-emission measurements of PSCs. The same investigation revealed no evidence for the presence of NAD in these clouds. The identification of crystalline solids with IR spectra requires in general a simulation of the measured data with the corresponding refractive indices. Different sets of optical constants have been reported for β -NAT [1,3] and although all of them have been derived from solid samples of the hydrate [3,4] they are not entirely coincident. An assessment of the available data seems thus timely.

In this work we present transmission and RAIR spectra of β -NAT films, together with simulations performed with the available sets of optical constants. In many cases noteworthy differences are obtained between the measured and simulated spectra. Different causes like, film preparation procedure, sample history, and orientation effects could be at the root of the observed discrepancies and will be discussed at the conference. The discussion will include results from theoretical calculations of the crystalline spectra [5]. Analogous investigations have been carried out for films of α -NAT[6] and α -NAD[7] and will be also presented at the conference

Acknowledgement We are indebted to M. Höpfner for providing us with the refractive indices of β -NAT reported in ref. [2].

References

- [1] C. Voigt et al. *Science* 290 (2000) 1756.
- [2] M. Höpfner, B. P. Luo, P. Massoli, F. Cairo, R. Spang, M. Snels, G. Di Donfrancesco, G. Stiller, T. vob Clarman, H. Fischer,, U. Biermann,. *Atmos. Chem. Phys. Discuss.* 5 (2005) 1685.
- [3] O. B. Toon, M. A. Tolbert, B. G. Koehler, A. M. Middlebrook A. M. Jordan, *J. Geophys. Res.* 99 (1994) 25631.
- [4] U. Biermann, Ph D Thesis, Universität Bielefeld, 1998. Cuvillier Verlag, Göttingen.
- [5] D. Fernández, V. Botella, V. J. Herrero, R. Escribano, *J. Phys. Chem. B* 107 (2003) 10608.
- [6] B. Maté, I. K. Ortega, M. A. Moreno, R. Escribano, V. J. Herrero, *Phys. Chem. Chem. Phys.* 6 (2004) 4047.
- [7] B. Maté, I. K. Ortega, M. A. Moreno, V. J. Herrero, R. Escribano, submitted for publication