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Orientation Effects on Nitric Acid Dihydrate Films

B. Maté, I. K. Ortega, M. A. Moreno, V. J. Herrero and **R. Escribano**
Instituto de Estructura de la Materia, CSIC, Serrano 123, 28006 Madrid, Spain

Nitric acid trihydrate has received considerable attention as the most likely candidate for type I Polar Stratospheric Clouds, due to its thermodynamic stability under polar stratospheric conditions. But some works suggest that nitric acid dihydrate (NAD), a metastable phase, can also form and persist in the winter stratosphere, since the formation of a given species in that region is often not controlled by thermodynamics but by kinetics.

An investigation of orientation effects in films of nitric acid dihydrate (NAD) will be presented based on a systematic study of transmission and Reflection-Absorption infrared (RAIR) spectra of samples of varying thickness. The samples were prepared by vapour deposition on Ge (for transmission spectroscopy) and on Al substrates (for RAIR spectroscopy) at 175 K to produce crystalline α-NAD films. Transmission spectra were recorded at normal incidence and RAIR spectra were recorded at a grazing angle of 75^{o}, with polarized radiation. The observed spectra will be compared with predictions of a classical Fresnel model, in order to test the available optical indices of NAD, which are of great importance for the accurate interpretation of data from remote sensing measurements. Whereas the procedure yields satisfactory results for transmission and s-polarized RAIR spectra, it is found that the agreement is not acceptable for p-polarized RAIR spectra. An explanation will be suggested in terms of a preferential alignment of the films, with the (10-1) crystallographic plane of the crystal situated parallel to the substrate. The (10-1) plane is the one defined by the molecular layers found by X-Ray studies in the structure of the α-NAD crystal. The successive layers are bound by weak van der Waal forces, and thus the adsorption of a layer parallel to the substrate can be energetically favourable since it does not disrupt a strong crystal structure. The infrared activity of a band at $\approx$ 1170 cm^{-1}will be explained in terms of a preferential orientation of the crystal domains in the film.