AB INITIO STRUCTURAL AND RAMAN SPECTROSCOPIC CHARACTERIZATION OF NATROXALATE MINERAL

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Sodium oxalate mineral natroxalate, $Na_2C_2O_4$, is a fundamental oxalate mineral widespread in nature, present in humans, animals and plants, as well as in naturally occurring minerals. The characterization of oxalate minerals is extraordinarily important since these organic minerals are indicators of environmental events and of the presence of biological activity, because usually they have biological origin. These minerals are nowadays under study to investigate the possible biological activity on Mars [1-2].

The identification of these compounds is mainly based in X-Ray diffraction and Raman spectroscopy. Theoretical calculations are of great value for the study and interpretation of the results of these experimental techniques.

In this work, natroxalate mineral was studied by first principle calculations based on the density functional theory (DFT). The computed structure of natroxalate (see Figure 1) reproduces quite well the structure determined experimentally by X-Ray diffraction [3] (monoclinic symmetry, spatial group $P2_1/c$; lattice parameters a=3.449 Å, b=5.243 Å; c=10.375 Å). The lattice parameters, bond lengths, bond angles and X-Ray powder pattern were found to be in very good agreement with their experimental counterparts [3].

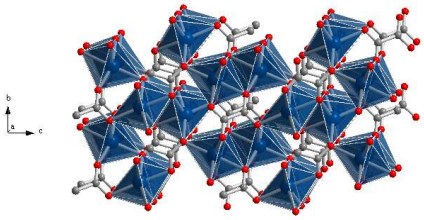

Figure 1: Computed Structure of natroxalate mineral. Color code: Na-Blue, C-Gray, O-Red.

The computed Raman spectrum was compared with the experimental spectrum [1] (see Figure 2). Since the results were also in good agreement, a normal mode analysis of the theoretical spectra was carried out and used in order to assign the main bands of the spectrum. This assignment allowed to complete and improve the experimental assignment of the Raman spectrum. The band observed at 567 cm^{-1} and described as a single peak in the experimental works is shown clearly to have two contributing peaks (Fig. 1.D). It must also be noted that two bands of the observed spectrum were not found in the theoretical spectrum. It may be shown that these bands are an overtone, $2\nu_1$ (ν_1=875 cm^{-1}) and a combination band $\nu_1+\nu_2$ (ν_1,ν_2 =875, 481 cm^{-1}).

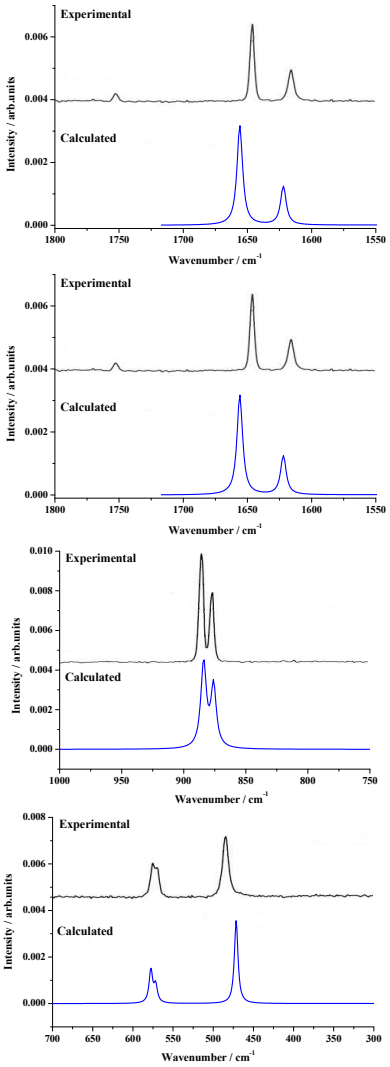

Figure 2: Experimental and theoretical Raman spectra of natroxalate mineral. (A) Region: 1800-1550 cm^{-1}; (B) Region: 1550-1300 cm^{-1}; (C) Region: 1100-750 cm^{-1}; (D) Region: 700-300 cm^{-1}.

[1] R. L. Frost, Y. Jing, Z. Ding, Chin. Sci. Bull. 48 (2003) 1844-1852; R. L. Frost, A. Locke, W. N. Martens, J. Raman Spectrosc. 34 (2003) 776-785.

[2] H. G. M. Edwards, I. B. Hutchinson, R. Ingley, N. R. Waltham, S. Beardsley, S. Dowson, S. Woodward, Spectrosc. Eur. 23 (2011) 6-15.

[3] D. A. Reed, D. A., M. M. Olmstead, Acta Crystallogr. B 37 (1981) 938–939.