STRUCTURAL CHARACTERIZATION AND BAND ASSIGNMENT OF THE RAMAN SPECTRA OF OXAMMITE MINERAL BY DENSITY FUNCTIONAL THEORY

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Introduction: Ammonium oxalate monohydrate mineral oxammite, $(NH_4)_2(C_2O_4) \cdot H_2O$ is a fundamental oxalate mineral widespread in nature [1]. Oxammite is a fundamental organic mineral that has attracted attention because it exhibits the phenomenon of negative linear compressibility (NLC) [6]. The characterization of oxalate minerals is extraordinarily important since these organic minerals are indicators of environmental events and of the presence of biological origin. These minerals are nowadays under study to investigate the possible biological activity on Mars [1-2].

The identification of these compounds is usually performed by X-Ray diffraction [3] and Raman spectroscopy [1-2]. Theoretical calculations are of great value for the study and interpretation of the results of these experimental techniques. In this work, oxammite mineral was studied by first principle calculations based on the density functional theory using plane waves and pseudopotentials [4]. The computed structure of oxammite reproduces the one determined experimentally [3]. Raman spectrum was then computed by means of density functional perturbation theory and compared with the experimental spectrum [1]. A normal mode analysis of the theoretical spectra was carried in order to assign the main bands of the Raman spectrum.

Methods: CASTEP code [4], a module of the Materials Studio package, was employed to model oxammite mineral structure. The generalized gradient approximation (GGA) together with PBE functional and Grimme empirical dispersion correction, the DFT-D2 approach were used [5]. Geometry optimization was carried out by using the Broyden–Fletcher–Goldfarb–Shanno optimization scheme. The optimization was performed with a cut-off of 900 eV and a K mesh of 3 x 2 x 7 (8 K points). For the calculations of Raman spectra, the linear response density functional perturbation theory (DFPT) was used.

Results. Structure: The computed structure of oxammite (see Figure 1) reproduces quite well the structure determined experimentally by X-Ray diffraction [3] (orthorhombic symmetry, spatial group $P2_12_12$; lattice parameters a=8.017 Å, b=10.309 Å; c=3.735 Å). The lattice parameters, bond lengths, bond angles and X-Ray powder pattern (see Figure 2 and Table 1) were found

to be in very good agreement with their experimental counterparts [3].
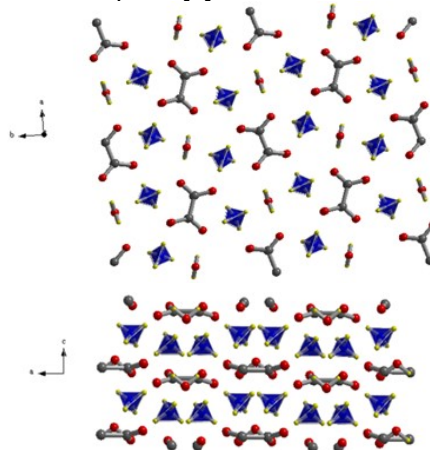
Figure 1: Computed Oxammite structure. Views of a 2x2x2 supercell from [001] and [010]. Color code: N-Blue, C-Gray, O-Red, H-Yellow.
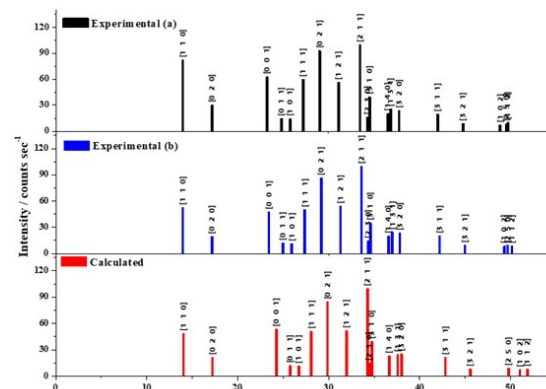
Figure 2. X-ray powder pattern of oxammite: a) Experimental diffractogram (pattern 87-660 from PDF-2 database); b) X-ray powder pattern computed from experimental geometry [3]; c) X-ray powder pattern computed from calculated geometry.

Table 1. Oxammite lattice parameters.

| Parameter	a (Å)	b (Å)	c (Å)	α	β	γ
Calc.	7.992	10.294	3.670	90	90	90
Exp. [3a]–30K	8.017	10.309	3.735	90	90	90
Exp. [3a]–298 K	8.035	10.309	3.795	90	90	90
Exp. [3b]	8.035	10.309	3.795	90	90	90

Results. Raman spectrum: The computed Raman spectrum was compared with the experimental spectrum [1] (see Figure 3). Since the Raman spectroscopic results were also found to be in agreement with the experimental data, a normal mode analysis of the theoretical spectra

was carried in order to assign the main bands of the Raman spectrum.

The most important bands used to fingerprint this mineral are those placed at 1430, 892, 489 and 224 cm^{-1} and are reproduced theoretically as 1391, 848, 462 and 262 cm^{-1}. These bands are assigned to a combination of CO and CC bond stretching vibrations, HNH twisting vibrations, a combination of OCO bending, CC stretching and HNH twisting vibrations, and ammonium and water translations, respectively.

The theoretical calculations allowed to assign the bands placed at 2344, 2161, 1933, 1902, 1745 and 1725 cm^{-1} which were left unassigned in the experimental works. The 2344, 2161, 1933 and 1902 cm^{-1} bands, missing in the computed spectrum, were identified as combination bands. The band placed at the wavenumber 2879 cm^{-1} is confirmed to be an overtone. Many of the observed bands, previously assigned empirically, were re-assigned. Further, the observed bands, placed at 3030, 2995, 2900, 1475, 489 and 224 cm^{-1} were shown to have two contributing bands.

Conclusions:

- ✓ The computed structure of oxammite reproduces accurately the one determined experimentally by X-Ray diffraction. Lattice parameters, bond lengths, bond angles and X-Ray powder pattern were found in good agreement with the experimental results.
- ✓ Computed Raman spectrum was also found in agreement with the experimental one and, therefore, a normal mode analysis of the theoretical spectra was carried out and used in order to assign the main bands.
- ✓ The previous experimental assignment of the Raman spectra was very incomplete and based on empirical arguments. The assignment allowed assigning rigorously all observed bands including those at very low wavenumbers and those which were left unassigned in the experimental works. Many of the observed bands, assigned empirically, were re-assigned.
- ✓ The computations show clearly that several experimental bands described as single peaks have two contributing bands. Furthermore, several bands are shown to correspond to combination bands. These results are very significant because they emphasize the need of performing a rigorous theoretical assignment for obtaining a correct interpretation of the vibrational spectra. In fact, the same spectral features were found for the Raman spectra of all other oxalate minerals studied so far (for example, natroxalate [7]) and therefore are likely to occur in the spectra of most other oxalate minerals.
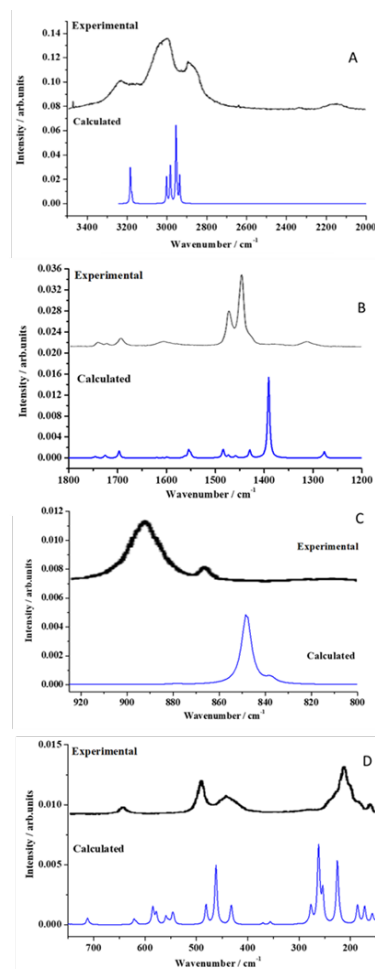
Figure 3: Experimental [1] and theoretical Raman spectra of oxammite mineral.

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