Theoretical Raman spectra of carbonate minerals

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The Raman spectra of the majority of $MeCO_3$ minerals, with Me=alkali elements, calc-alkali elements or combinations thereof, are determined using density functional perturbation theory in the ABINIT implementation. We consider more than a dozen different minerals, most of them with rhombohedral, i.e. calcite-like, or orthorhombic, i.e. aragonite-like, structures [1].

We start with the experimental structure and perform two distinct structural relaxations: one at experimental density, i.e. experimental volume, and one at theoretical 0GPa pressure. During these structural relaxations we minimize the energy, the residual forces on the atoms and the non-hydrostatic stresses on the unit cell. Consequently in the end we obtain to distinct sets of data. We find that the relative intensities of the major Raman peaks are in good agreement with respect to experiment. The positions of the peaks are consistently shifted relative to the experiment. As a general rule, the best agreement between theory and experiment is obtained for the calcualtions performed at experimental density.

We find that all spectra are dominated, as expected, by the stretching modes of the planar CO_3 groups. Their theoretical frequency varies from as low as 1066 in paralstonite [$BaCa(CO_3)_2$] up to high as 1113 cm-1 in eitelite [$Na_2Mg(CO_3)_2$]. The low-frequency modes are dominated by the heavy cations. Their degeneracy is directly determined by the symmetry of the structure. We performed a detailed comparative study to be able to identify identification trends.

Finally we discuss C and O isotope fractionation patterns. We compute $\log(\beta)$ functions based on the vibrational information contained in the Brillouin zone center. Though not complete, this information is already enough to give us a reasonable estimation of the partitioning.

References:
Caracas, R., Bobocioiu, E. (2011), American Mineralogist, vol. 96, pp. 437-443.