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Infrared and Raman spectroscopic features of clinochlore  $Mg_6Si_4O_{10}(OH)_8$ : A density functional theory contribution

This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

*Published Version:*

Ulian G., Moro D., Valdrè Giovanni (2020). Infrared and Raman spectroscopic features of clinochlore  $Mg_6Si_4O_{10}(OH)_8$ : A density functional theory contribution. APPLIED CLAY SCIENCE, 197, 1-11 [10.1016/j.clay.2020.105779].

*Availability:*

This version is available at: <https://hdl.handle.net/11585/782000> since: 2024-02-13

*Published:*

DOI: <http://doi.org/10.1016/j.clay.2020.105779>

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# 1 **Infrared and Raman spectroscopic features of Clinochlore**

## 2 **Mg<sub>6</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>8</sub>: a Density Functional Theory contribution**

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9

### **Abstract**

10 Mineral identification and analysis are often performed by using vibrational spectroscopies, namely  
11 infrared and Raman techniques. However, very few spectroscopy data are available on clinochlore, an  
12 important phyllosilicate with manifold applications in several fields. In the present work, *ab initio*  
13 Density Functional Theory simulation was employed to calculate the infrared and Raman spectra at  $\Gamma$   
14 points and the phonon dispersion at different  $\mathbf{k}$ -points of the magnesium end-member of clinochlore,  
15 with ideal chemical formula Mg<sub>6</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>8</sub> and space group *C2/m*. Each phonon mode of the mineral  
16 was assigned to specific vibrations of the ionic groups in the structure. The theoretical results were found  
17 in good agreement with the available experimental data in literature, further extending the knowledge on  
18 the vibrational properties of clinochlore, which could be useful for experimental characterization of this  
19 mineral phase in various and different fields of research.

20 **Keywords:** Clinochlore, infrared and Raman spectroscopies, phonon dispersion relations, Density  
21 Functional Theory

22

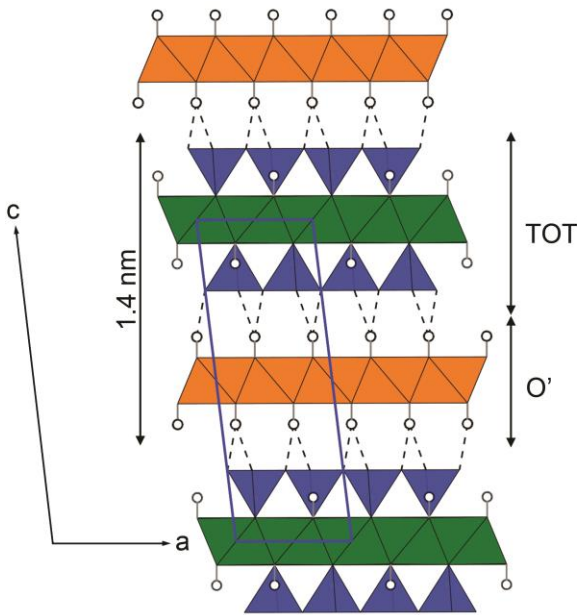
## 23 1. Introduction

24 Clinochlore is a phyllosilicate mineral of the chlorite group whose ideal formula is  
25  $\text{Mg}_3^{\text{IV}'}\text{Mg}_3^{\text{VI}}\text{Si}_4^{\text{IV}}\text{O}_{10}(\text{OH})_8$ , composed by alternately stacked brucite-like (labelled as O') and talc-like  
26 (2:1 or TOT) layers (see Figure 1) held together by hydrogen bonds. According to conventional  
27 mineralogical rules, the superscripts VI', VI, and IV refer to six-fold coordination of the octahedral  
28 interlayer cation, six-fold coordination of the TOT layer octahedral cation and the four-fold coordination  
29 of the tetrahedral cation, respectively (Bayliss, 1975; Wiewiora, 1990).

30 Clinochlore is an interesting clay mineral due to its peculiar surface properties. In fact, when cleaved,  
31 its surface often presents remainders of the O' layer above an intact TOT layer, resulting in a  
32 simultaneous exposition of regions related to the two layers. According to previous atomic force  
33 microscopy, Kelvin-probe force microscopy studies and quantum-mechanical simulations (Valdrè et al.,  
34 2011c; Valdrè et al., 2012; Moro et al., 2016; Moro et al., 2019a), the brucite-like layer is hydrophobic,  
35 whereas the 2:1 layer is hydrophilic, hence they present different features as adsorbents and/or catalysts.  
36 To cite some example, chlorite is able to adsorb, organize and self-assemble nucleotides, RNA and DNA  
37 (Valdrè, 2007; Valdrè et al., 2011a; Valdrè et al., 2011b), and amino acids, *e.g.* glycine and L-alanine  
38 (Moro et al., 2015; Moro et al., 2019b). The cited biomolecules were found selectively adsorbed on the  
39 brucite-like sheet and atomic force microscopy revealed different molecular conformations at the mineral  
40 surface. For example, RNA filaments adsorbed on atomic flat terraces were found as globular structures,  
41 whereas they were linearized on the edges of the brucite-like sheet (Valdrè et al., 2011b). DNA molecules  
42 were mainly found on the edges of the  $\text{Mg}(\text{OH})_6$  zones both in network-like and linear conformations  
43 and, in some cases, also as “bridges” between two parallel brucite-like stripes. In the case of amino acids,  
44 they were experimentally found as dot-like structures (single molecules), agglomerates and filament-like  
45 structures (Moro et al., 2015; Moro et al., 2019b). Very high adsorption energy between single molecules

46 and the brucite-like sheet was calculated from *ab initio* simulations, whose value was in the range 77 –  
47 82 kJ/mol for glycine and 110 – 280 kJ/mol for L-alanine, depending on the local crystal-chemistry. The  
48 positive sign here indicates the energy necessary to desorb the molecule from the surface.

49 In addition zeolitic-type Brønsted-Lowry sites, which are known to control catalytic processes, were  
50 discovered on atomic flat surfaces (bi-dimensional systems) in chlorites and modelled by *ab initio*  
51 techniques (Valdrè et al., 2011c). For these reasons, there are many and various important applications  
52 of clinochlore (and clay minerals, in general) in several fields, from petrochemical refining, fine-  
53 chemical production, to water and air purification (Phuakkong et al., 2011; Stueckenschneider et al.,  
54 2014).



55  
56 **Figure 1.** View along the **b**-axis of an ideal clinochlore mineral structure (s.g. *C2/m*). Talc-like (2:1,  
57 TOT) and brucite-like (O') structural units are indicated. Blue tetrahedrons represent the SiO<sub>4</sub>, whereas  
58 orange and green octahedrons represent MgO<sub>6</sub> groups in the O' and TOT units, respectively. The blue  
59 solid line shows the crystallographic unit cell, whereas the dashed lines indicate the hydrogen bonds  
60 between the structural units.

61 One of the leading and simplest methods to investigate bulk structures and/or processes occurring at  
62 the surface is vibrational (infrared, IR or Raman) spectroscopy. For example, IR/Raman experiments are  
63 employed to recognize the presence of a mineral phase, by comparing the acquired spectrum with those  
64 available in databases (Fries and Steele, 2018), or to study fluid inclusions in minerals (Rosso and  
65 Bodnar, 1995). For surface processes, Attenuated Total Reflectance – Fourier Transform Infrared (ATR-  
66 FTIR) and confocal Raman spectroscopy are useful tools to investigate surfaces and reactions between  
67 minerals and the environment (*e.g.* molecules of gas/liquid) or intra-phase processes (King and Geisler,  
68 2018). Very recently, infrared and Raman spectroscopy at the nanoscale, *i.e.* nano-FTIR, near-field FTIR  
69 and tip-enhanced Raman spectroscopy (TERS), are leading for promising applications and researches at  
70 the sub-micrometre level with very high resolution (Dominguez et al., 2014; Firkala et al., 2018;  
71 Bhattarai and El-Khoury, 2019; Kumar et al., 2019). The common factor between different applications  
72 is that a detailed knowledge of the vibrational modes of the mineral phase is required. For clinocllore,  
73 very few data on the infrared and Raman properties are available in literature (Gopal et al., 2004;  
74 Lafuente et al., 2016). In addition, the interpretation of experimental spectra is often difficult for several  
75 reasons, such as (1) the presence of impurities in both natural and synthetic samples, (2) the morphology  
76 of the samples (3) the presence of overtones and/or combination bands; (4) the impossibility to observe  
77 modes associated with weak intensities (low transition moments), (5) the availability only of poor  
78 crystalline samples, resulting in band broadening with extensive overlap of the signals, (6) polarization  
79 anisotropy in nano-FTIR and Raman and (7) residual strains in the minerals. In this perspective, *ab initio*  
80 quantum-mechanical simulations represent an effective tool to overcome the issues mentioned above,  
81 because they allow for the calculation of the phonon modes of solids. From the analysis of the vibrational  
82 motion of the atoms in the unit cell, it is also possible to successfully identify and assign to specific  
83 normal modes all of the fundamental vibrational transitions of the system in consideration, a task that is  
84 still very difficult by experimental means.

85 In the present work, a fundamental and detailed theoretical analysis of the infrared and Raman  
86 responses of monoclinic clinochlore ( $C2/m$  space group) is provided to fill the knowledge gap on this  
87 important clay mineral phase. The chemical composition here considered is that of an ideal, clinochlore  
88 end-member, where every T and M sites are occupied by silicon and magnesium, respectively. This  
89 monoclinic clinochlore model was geometrically optimized and its vibrational features at  $\Gamma$  point were  
90 investigated in detail using Density Functional Theory. Finally, the theoretical phonon dispersion  
91 relations of this mineral phase is reported and compared with the few data reported by Collins et al.  
92 (1993) on the acoustic phonons.

93

## 94 **2. Theoretical methods**

95 All the simulations related to the geometry optimization and the calculation of the phonon properties  
96 of clinochlore were performed within the Density Functional Theory (DFT) framework using the  
97 CRYSTAL17 periodic code (Dovesi et al., 2018), whereas graphical representations were carried out  
98 with the molecular graphics program VESTA (Momma and Izumi, 2011) and Moldraw (Ugliengo et al.,  
99 1993).

100 The chosen Hamiltonian was the hybrid B3LYP (Lee et al., 1988; Becke, 1993), where 20% of Hartree-  
101 Fock energy contributes to the DFT exchange term, because of its suitability for the *ab initio*  
102 investigations of vibrational properties of both molecular and solid (periodic) systems (Pascale et al.,  
103 2004; Pascale et al., 2005). The total energy (exchange/correlation) was evaluated on a pruned grid with  
104 75 radial points and 974 angular points, subdivided in 5 intervals of 86, 194, 350, 974 and 350 points  
105 according to the Gauss-Legendre quadrature and Lebedev schemes (Prencipe et al., 2004). The thresholds  
106 controlling the accuracy of the calculation of the Coulomb and exchange integrals have been set to  $10^{-8}$   
107 (ITOL1 to ITOL4) and  $10^{-16}$  (ITOL5); this means that when the overlap between two atomic orbitals is

108 lower than  $10^{-\text{ITOL}}$ , the corresponding integral is either discarded or treated with less precision, as  
109 explained by Dovesi et al. (2018). The Hamiltonian matrix has been diagonalized through the Monkhorst  
110 and Pack scheme (Monkhorst and Pack, 1976), using a  $6 \times 6 \times 2$  k-mesh, which leads to 26 reciprocal lattice  
111 points (**k**-points). Weak intermolecular interactions, such as van der Waals forces, play a relevant role in  
112 determining the internal geometries of the crystal and its related properties. For this reason, a modified  
113 DFT-D2 scheme proposed by Grimme (2006) was employed to include those energy contributions to the  
114 final energy (Civalleri et al., 2008).

115 Within the Linear Combination of Atomic Orbitals (LCAO) approach, atomic and crystalline orbitals  
116 have been described by Gaussian-type orbitals basis sets. In particular, for magnesium and oxygen a 8-  
117 511d1G and a 8-411d11G (Valenzano et al., 2006; Ulian et al., 2016, 2018) basis sets were employed,  
118 respectively. Silicon and hydrogen were described by a 88-31G\* (Nada et al., 1996; Ulian and Valdrè,  
119 2015; Ulian et al., 2018) and a 3-1p1G basis sets (Gatti et al., 1994; Moro et al., 2015; Ulian et al., 2018),  
120 respectively. The chosen basis sets are well balanced, allowing accurate calculations in both molecular  
121 and crystal structures with sustainable computational costs.

122 The geometry of monoclinic clinoclone  $\text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_{10}$  (space group  $C2/m$ ) was taken from the  
123 experimental refining of Welch and Marshall (2001) on a synthetic sample, which represents the closest  
124 structure to start with. All the simulations on this model were performed on the primitive cell, but  
125 structural results are referred to the crystallographic cell to ease the comparison (*vide infra*).

126 The cell parameters and internal coordinates of each model were optimized using the analytical  
127 gradient method for the atomic positions and a numerical gradient for the unit-cell parameters, to find  
128 the equilibrium geometry. The self-consistent field (SCF) procedure for the total energy calculations was  
129 considered converged when the energy difference between the last step and the previous one was less  
130 than  $10^{-8}$  Ha during geometry optimization. The convergence on the structural optimization was reached  
131 when each component of the gradient was smaller than  $3 \cdot 10^{-5}$  hartree bohr<sup>-1</sup> and displacements with

132 respect to the previous step were smaller than  $12 \cdot 10^{-5}$  bohr. The Hessian matrix was upgraded with the  
 133 Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm. The structure parameters and atomic coordinates  
 134 of the optimized clinocllore model (crystallographic cell) are reported in Table 1.

135

**Table 1.** Crystallographic cell structure (lattice parameters and atomic positions) of monoclinic stoichiometric clinocllore (s.g.  $C2/m$ ), optimized at the Density Functional Theory/B3LYP-D\* level, compared to experimental results.

<b>B3LYP-D*</b>					<b>Experimental (Welch and Marshall, 2001)</b>				
<i>a</i>	<i>b</i>	<i>c</i>	$\beta$	<i>V</i>	<i>a</i>	<i>b</i>	<i>c</i>	$\beta$	<i>V</i>
5.3297	9.2309	14.8947	96.829	727.590	5.332	9.224	14.414	97.07	703.52
<b>Internal geometry</b>					<b>Internal geometry</b>				
<i>Atom</i>	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>Wyckoff</i>	<i>Atom</i>	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>Wyckoff</i>
H1	0.2130	0.5000	0.1364	4i	H1	0.200	0.500	0.142	4i
H2	0.6204	0.5000	0.3639	4i	H2	0.117	0.320	0.358	4i
H3	0.1220	0.3338	0.3641	8j	H3	0.120	0.000	0.371	8j
Mg1	0.0000	0.0000	0.0000	2a	Mg1	0.000	0.000	0.000	2a
Mg2	0.5000	0.1663	0.0000	4g	Mg2	0.000	0.160	0.500	4g
Mg3	0.0000	0.3337	0.0000	4h	Mg3	0.000	0.353	0.000	4h
Mg4	0.0000	0.5000	0.5000	2d	Al4*	0.000	0.500	0.500	2d
O(a)	0.1910	0.1668	0.0739	8j	O1	0.185	0.172	0.080	8j
O(b)1	0.2136	0.0000	0.2209	4i	O2	0.228	0.000	0.234	4i
O(b)2	0.5029	0.2369	0.2210	8j	O3	0.509	0.220	0.231	8j
O(h)1	0.1907	0.5000	0.0715	4i	O4	0.181	0.500	0.068	4i
O(h)2	0.1424	0.0000	0.4283	4i	O5	0.168	0.000	0.435	4i
O(h)3	0.1432	0.3336	0.4285	8j	O6	0.135	0.337	0.430	8j
Si1	0.2277	0.1667	0.1844	8j	Si1 <sup>†</sup>	0.224	0.166	0.193	8j

Notes: The experimental sample contained an Al-substitution in the O' layer (Al4 atom, marked with an asterisk) corresponding to the Mg4 atom in the simulated stoichiometric model and a partial substitution (25%) of silicon (Si1, marked with †) with aluminium.

136

137 There is an overall good agreement between the theoretical and experimental results of Welch and  
 138 Marshall (2001), with the main difference residing in the *c*-axis length. Indeed, the synthetic Mg-rich  
 139 clinocllore refined in the  $C2/m$  space group presented a chemical formula  
 140  $(Mg_2Al)^{IV}Mg_3^{VI}(AlSi_3)^{IV}O_{10}(OH)_8$ , characterized by the following cation occupation:  $T = 0.25Al +$   
 141  $0.75Si$ ,  $M1 = M2 = M3 = Mg$ ,  $M4 = Al$ , whereas the simulated model has chemical composition  
 142  $(Mg_3)^{IV}Mg_3^{VI}(Si_4)^{IV}O_{10}(OH)_8$ . The presence of some fraction of aluminium substitutions in both the  
 143 tetrahedral sheet of the TOT layer and the O' layer increases the Coulomb (ionic) interactions between  
 144 them, resulting in a lowered TOT – O' distance.



145 Harmonic phonon modes and vibrational frequencies were calculated at the  $\Gamma$  point on the optimized model of  
146 monoclinic clinochlore by diagonalizing the mass-weighted Hessian matrix (dynamical matrix), whose elements  
147 are the second derivatives of the lattice potential with respect to mass-weighted atomic displacements (Pascale et  
148 al., 2004). For these calculations, strict threshold criteria ( $10^{-10}$  Ha) were applied for the energy convergence to  
149 improve the accuracy of the vibrational results. Also, an anharmonic correction for OH stretching modes was  
150 applied, following the procedure described by Tosoni and co-workers (2005).

151

### 152 **3. Results and discussion**

153 Monoclinic, stoichiometric clinochlore  $\text{Mg}_3(\text{OH})_6\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$  (space group  $C2/m$ , point group  
154  $C_{2h}$ ) has a single unit formula per primitive unit cell (36 atoms). The phonon modes of this mineral phase  
155 are then  $36 \times 3 = 108$ , subdivided in three modes related to acoustic phonons (translations of the whole  
156 lattice) and 105 to optical ones. The presence of an inversion centre in the mineral leads to (1) vibrational  
157 modes active only in infrared or in Raman, but not in both (mutual exclusion rule), (2) the subdivision  
158 of the modes in *gerade* (labelled as *g*) and *ungerade* (*u*), namely vibrations that are symmetric or  
159 antisymmetric with respect to the inversion centre, respectively and (3) the absence of the longitudinal  
160 optical (LO) - transverse optical (TO) splitting. The LO-TO splitting is common in many layered  
161 silicates, in which atoms that vibrates perpendicularly to the layers (the so-called polar modes, or Fröhlich  
162 modes) should vibrate at their longitudinal optical frequency (Balan et al., 2001; Prencipe et al., 2009);  
163 however, the presence of the inversion centre nullify this effect (Prencipe et al., 2009).

164 The  $\Gamma$ -point vibrational modes can be classified according to the irreducible representation of the  $C_{2h}$   
165 point group of the mineral as  $\Gamma_{\text{total}} = \Gamma_{\text{acoustic}} + \Gamma_{\text{optic}} = 27A_g + 24A_u + 24 B_g + 33A_u$  (Kroumova et al.,  
166 2003). The  $A_u$  and  $B_u$  modes are active in infrared spectroscopy, whereas  $A_g$  and  $B_g$  ones are Raman  
167 active. The three acoustic phonons are given by  $A_u + 2B_u$  modes. A site symmetry analysis according to

168 Kroumova et al. (2003) is reported in Table 2. Each atom contributes to all active vibrational modes,  
 169 Mg1 and Mg4 atoms in the trioctahedral sheet of the talc-like layer and of the brucite-like layer,  
 170 respectively, are not associated with any *gerade* mode, which are those active in Raman spectroscopy.

**Table 2.** Site symmetry analysis for monoclinic clinocllore (s.g. *C2/m*).

<i>Atom</i>	<i>Layer</i>	<i>Wyckoff</i>	<i>Symmetry</i>
H1	TOT	4i	$2A_g + A_u + B_g + 2B_u$
H2	O'	4i	$2A_g + A_u + B_g + 2B_u$
H3	O'	8j	$3A_g + 3A_u + 3B_g + 3B_u$
Mg1	TOT	2a	$A_u + 2B_u$
Mg2	TOT	4g	$A_g + A_u + 2B_g + 2B_u$
Mg3	O'	4h	$A_g + A_u + 2B_g + 2B_u$
Mg4	O'	2d	$A_u + 2B_u$
O(a)	TOT	8j	$3A_g + 3A_u + 3B_g + 3B_u$
O(b)1	TOT	4i	$2A_g + A_u + B_g + 2B_u$
O(b)2	TOT	8j	$3A_g + 3A_u + 3B_g + 3B_u$
O(h)1	TOT	4i	$2A_g + A_u + B_g + 2B_u$
O(h)2	O'	4i	$2A_g + A_u + B_g + 2B_u$
O(h)3	O'	8j	$3A_g + 3A_u + 3B_g + 3B_u$
Si1	TOT	8j	$3A_g + 3A_u + 3B_g + 3B_u$
Total			$27A_g + 24A_u + 24B_g + 33B_u$

171

172 In Table 3, the calculated  $\Gamma$ -point frequencies of the transverse optical vibrational modes of monoclinic  
 173 clinocllore, together with their transition moment corresponding to infrared and Raman activity are  
 174 reported. The infrared spectrum of clinocllore was analytically calculated using the classical absorption  
 175 formula as explained by Maschio et al. (2012):

$$176 \quad A(\nu) = \frac{1}{3} \sum_{ii=1}^3 \frac{4\pi}{\lambda\rho} \text{Im}[n_{ii}(\nu)]$$

177 where  $A(\nu)$  is the infrared absorption,  $\lambda$  if the wavelength of the incident light,  $\rho$  is the density of the  
 178 mineral,  $n$  is the complex refractive index and  $ii$  represents the polarization direction. The real and  
 179 imaginary parts of the refractive index  $n_{ii}$  were calculated as:

$$180 \quad \{\text{Re}[n_{ii}(\nu)]\}^2 - \{\text{Im}[n_{ii}(\nu)]\}^2 = \text{Re}[\varepsilon_{ii}(\nu)]$$

181  $2 \operatorname{Re}[n_{ii}(\nu)] \cdot \operatorname{Im}[n_{ii}(\nu)] = \operatorname{Im}[\varepsilon_{ii}(\nu)]$

182 where  $\varepsilon_{ii}(\nu)$  is the complex dielectric tensor, computed for each inequivalent polarization direction

183 according to a classical Drude-Lorentz model:

184 
$$\varepsilon_{ii}(\nu) = \varepsilon_{\infty,ii} + \sum_p \frac{f_{p,ii} \nu_p^2}{\nu_p^2 - \nu^2 - i\nu\gamma_p}.$$

185 In the previous equation,  $\varepsilon_{\infty}$  indicates the optical dielectric tensor, which was calculated using a couple-  
 186 perturbed Kohn-Sham approach (Ferrero et al., 2008a; Ferrero et al., 2008b), whereas  $\nu_p, f_p$  and  $\gamma_p$  are the  
 187 transverse optical frequency, oscillator strength and damping factor of the  $p^{\text{th}}$  vibrational mode,  
 188 respectively. The damping factor represents the full width at half maximum of each vibrational mode  
 189 and was set to 8, which is a value that provides band broadening similar to that of experimental samples  
 190 and also the default employed by CRYSTAL, as described by Maschio and co-workers (2012).

191 For what regards the Raman spectrum of clinocllore, it was calculated for a polycrystalline powder  
 192 by using the transverse optical vibrational modes by means of a pseudo-Voigt functional form (Maschio  
 193 et al., 2013a, b):

194 
$$A(\nu) = \eta L(\nu) + (1 - \eta) G(\nu)$$

195 where, in this case,  $A(\nu)$  represents the Raman intensity and  $L(\nu)$  and  $G(\nu)$  are given by:

196 
$$L(\nu) = \sum_p \frac{I_p}{\pi} \frac{\gamma_p/2}{(\nu - \nu_p)^2 + (\gamma_p/2)^2}$$

197 
$$G(\nu) = \sum_p 2\sqrt{\frac{\ln 2}{\pi}} \frac{I_p}{\gamma_p} \exp\left[-\frac{4 \ln 2 (\nu - \nu_p)^2}{\gamma_p^2}\right]$$

198 with  $I_p$  the computed Raman intensities for the  $p^{\text{th}}$  vibrational mode and  $\eta$  is the Lorentz factor. A pure  
199 Lorentzian form, which is the default of CRYSTAL (Maschio et al., 2013a), corresponding to  $\eta = 1$ , was  
200 employed to obtain the typical sharp peaks of Raman spectra (Dovesi et al., 2018). The infrared and  
201 Raman spectra for monoclinic clinocllore calculated as described above are reported in Figure 2a and  
202 Figure 2b, respectively.

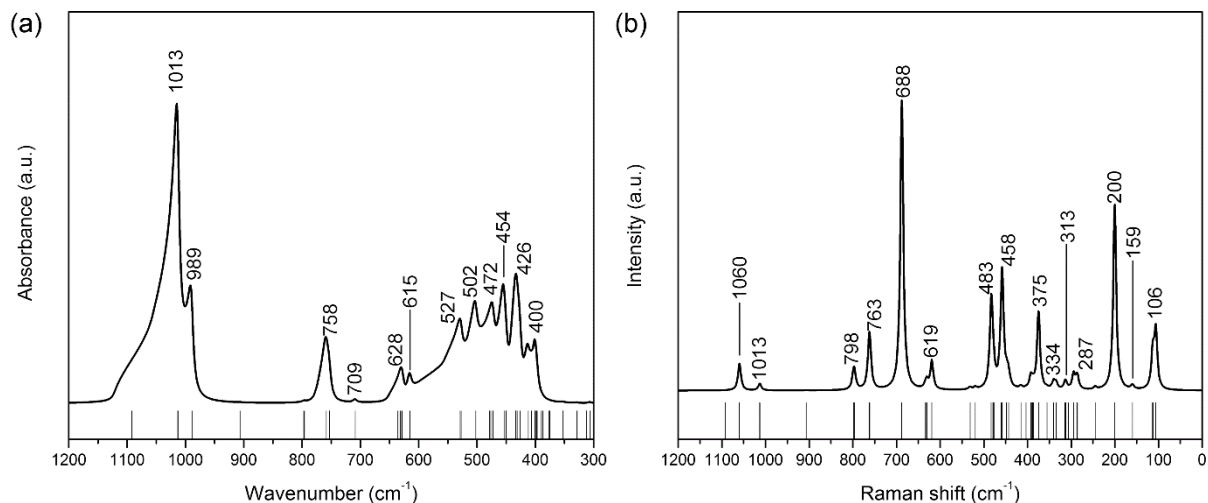
203

204

**Table 3.** Phonon frequencies ( $\nu$ ) and their irreducible representation (IRREP) of monoclinic clinoclone  $\text{Mg}_3(\text{OH})_6\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$  (s.g. C2/m) as obtained from Density Functional Theory simulations at the B3LYP-D\* level. Amplitude is referred to transition moments in infrared (Ampl. IR) and Raman (Ampl. R).

Mode	$\nu$ ( $\text{cm}^{-1}$ )	IRREP	Ampl. IR	Ampl. R	Mode	$\nu$ ( $\text{cm}^{-1}$ )	IRREP	Ampl. IR	Ampl. R
1	0	B <sub>u</sub>	0.0	0.0	55	450	A <sub>u</sub>	596.0	0.0
2	0	B <sub>u</sub>	0.0	0.0	56	454	B <sub>u</sub>	1404.5	0.0
3	0	A <sub>u</sub>	0.0	0.0	57	458	B <sub>g</sub>	0.0	56.4
4	22	B <sub>u</sub>	1.8	0.0	58	458	A <sub>g</sub>	0.0	55.4
5	25	A <sub>u</sub>	2.3	0.0	59	460	B <sub>g</sub>	0.0	13.3
6	82	B <sub>u</sub>	0.2	0.0	60	472	A <sub>u</sub>	712.3	0.0
7	106	B <sub>u</sub>	3.5	0.0	61	476	A <sub>g</sub>	0.0	4.0
8	106	A <sub>g</sub>	0.0	58.2	62	476	B <sub>u</sub>	16.7	0.0
9	112	B <sub>g</sub>	0.0	17.4	63	479	B <sub>g</sub>	0.0	2.7
10	114	A <sub>g</sub>	0.0	20.1	64	479	A <sub>u</sub>	24.1	0.0
11	158	B <sub>u</sub>	2.8	0.0	65	481	A <sub>g</sub>	0.0	23.5
12	159	B <sub>g</sub>	0.0	4.2	66	483	A <sub>g</sub>	0.0	75.2
13	179	B <sub>u</sub>	4.6	0.0	67	502	B <sub>u</sub>	662.7	0.0
14	185	A <sub>u</sub>	2.9	0.0	68	519	B <sub>g</sub>	0.0	2.3
15	200	A <sub>g</sub>	0.0	191.0	69	527	B <sub>u</sub>	371.9	0.0
16	245	B <sub>g</sub>	0.0	2.6	70	529	A <sub>u</sub>	4.2	0.0
17	245	B <sub>u</sub>	1.0	0.0	71	531	A <sub>g</sub>	0.0	2.5
18	273	B <sub>u</sub>	22.4	0.0	72	615	B <sub>u</sub>	199.5	0.0
19	285	B <sub>g</sub>	0.0	7.8	73	619	A <sub>g</sub>	0.0	29.3
20	287	A <sub>g</sub>	0.0	7.5	74	628	B <sub>u</sub>	264.0	0.0
21	294	A <sub>g</sub>	0.0	15.6	75	629	A <sub>u</sub>	0.7	0.0
22	298	A <sub>u</sub>	0.0	0.0	76	630	A <sub>g</sub>	0.0	5.5
23	306	B <sub>u</sub>	11.1	0.0	77	631	B <sub>u</sub>	4.0	0.0
24	307	B <sub>g</sub>	0.0	0.4	78	631	B <sub>g</sub>	0.0	3.2
25	312	A <sub>u</sub>	0.7	0.0	79	635	B <sub>g</sub>	0.0	2.2
26	313	A <sub>g</sub>	0.0	6.8	80	636	A <sub>u</sub>	0.6	0.0
27	314	B <sub>g</sub>	0.0	2.5	81	688	A <sub>g</sub>	0.0	298.7
28	329	B <sub>u</sub>	7.9	0.0	82	709	B <sub>u</sub>	17.7	0.0
29	334	A <sub>g</sub>	0.0	6.2	83	753	B <sub>u</sub>	351.3	0.0
30	340	B <sub>g</sub>	0.0	7.8	84	758	A <sub>u</sub>	373.7	0.0
31	353	A <sub>u</sub>	12.7	0.0	85	761	B <sub>g</sub>	0.0	30.7
32	355	B <sub>g</sub>	0.0	0.9	86	763	A <sub>g</sub>	0.0	31.4
33	375	A <sub>g</sub>	0.0	80.3	87	796	A <sub>g</sub>	0.0	12.7
34	375	A <sub>u</sub>	1.1	0.0	88	796	B <sub>u</sub>	3.8	0.0
35	377	B <sub>u</sub>	2.2	0.0	89	797	A <sub>u</sub>	2.2	0.0
36	387	A <sub>g</sub>	0.0	3.1	90	798	B <sub>g</sub>	0.0	13.1
37	387	B <sub>u</sub>	7.1	0.0	91	906	B <sub>g</sub>	0.0	0.2
38	388	B <sub>g</sub>	0.0	1.9	92	907	A <sub>u</sub>	2.4	0.0
39	390	A <sub>u</sub>	1.8	0.0	93	989	B <sub>u</sub>	1945.4	0.0
40	390	B <sub>g</sub>	0.0	0.1	94	1013	A <sub>u</sub>	2672.1	0.0
41	392	A <sub>g</sub>	0.0	11.3	95	1013	B <sub>g</sub>	0.0	3.5
42	397	A <sub>u</sub>	242.6	0.0	96	1013	B <sub>u</sub>	2678.2	0.0
43	398	B <sub>u</sub>	140.6	0.0	97	1013	A <sub>g</sub>	0.0	3.5
44	400	B <sub>u</sub>	515.4	0.0	98	1060	A <sub>g</sub>	0.0	27.9
45	400	A <sub>u</sub>	656.5	0.0	99	1092	B <sub>g</sub>	0.0	0.0
46	403	B <sub>g</sub>	0.0	0.4	100	1092	A <sub>u</sub>	0.2	0.0
47	407	B <sub>u</sub>	380.1	0.0	101†	3697	B <sub>u</sub>	130.2	0.0
48	412	A <sub>u</sub>	846.9	0.0	102†	3698	A <sub>g</sub>	0.0	111.6
49	415	A <sub>g</sub>	0.0	2.5	103†	3831	B <sub>g</sub>	0.0	2.7
50	426	B <sub>u</sub>	1730.2	0.0	104†	3831	A <sub>u</sub>	4.9	0.0
51	431	A <sub>u</sub>	1215.7	0.0	105†	3832	B <sub>u</sub>	10.9	0.0
52	434	B <sub>u</sub>	398.3	0.0	106†	3832	A <sub>g</sub>	0.0	12.1
53	443	B <sub>g</sub>	0.0	11.8	107†	3843	B <sub>u</sub>	513.0	0.0
54	448	A <sub>g</sub>	0.0	10.2	108†	3844	A <sub>g</sub>	0.0	1000.0

Notes: modes 1 – 3 are acoustic phonons. IRREP is the irreproducible representation of the mode. Ampl. IR and Ampl. R are the calculated infrared and Raman transition amplitudes, respectively. Modes labelled with † are corrected for anharmonicity as of the model of Tosoni and co-workers (2005).



206

207 **Figure 2.** Simulated infrared (a) and Raman (b) spectra of monoclinic clinocllore

208  $\text{Mg}_3(\text{OH})_6\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$  (space group  $C2/m$ ).

209 Three regions were calculated in both the infrared and Raman spectra: a low-frequency region 0 – 500  
 210  $\text{cm}^{-1}$ ; an intermediate-frequency region between 500 and 1100  $\text{cm}^{-1}$ ; and a high-frequency region up  
 211 in the 3700 – 4000  $\text{cm}^{-1}$ . The assignment of each normal mode was carried out by means of (1) graphical  
 212 animation of the atom motions using Moldraw (Ugliengo et al., 1993), (2) analysis of the vibrational  
 213 eigenvectors and of the potential energy distribution (PED), provided by CRYSTAL and (3) isotopic  
 214 substitutions, in particular  $^{25}\text{Mg} \rightarrow ^{24}\text{Mg}$ ,  $^{29}\text{Si} \rightarrow ^{28}\text{Si}$  and  $^2\text{D} \rightarrow ^1\text{H}$ . CRYSTAL can easily calculate  
 215 isotopic shifts because the vibrational frequencies and normal modes are obtained from the  
 216 diagonalization of the mass-weighted dynamical matrix  $W$ , which is defined as:

217 
$$W_{\alpha,\beta}(\mathbf{k} = 0) = \frac{H}{\sqrt{M_\alpha M_\beta}}$$

218 where  $H$  is the dynamical matrix (matrix of the second-derivatives of the energy with respect to atom  
 219 displacements) and  $M_\alpha$  and  $M_\beta$  are the masses of the atoms associated to the vibrational motion.  
 220 Vibrational isotopic shifts related to the  $^{25}\text{Mg} \rightarrow ^{24}\text{Mg}$ ,  $^{29}\text{Si} \rightarrow ^{28}\text{Si}$  substitutions are reported in Tables

221 4, whereas Table 5 shows those of the deuterium  $\rightarrow$  hydrogen substitution. In the following, the results  
222 are discussed in details for the three spectral regions and compared to the available experimental results.

223

### 224 **3.1. The 0–500 $\text{cm}^{-1}$ region**

225 In this region, 64 optic modes were computed, of which 33 are IR active (14  $A_u$  + 19  $B_u$ ) and 31 are  
226 active in Raman (16  $A_g$  + 15  $B_g$ ). Up to about 400  $\text{cm}^{-1}$ , IR modes have very low intensity, which make  
227 them very difficult to observe experimentally. Even at theoretical level, the calculated amplitudes are  
228 very low. For the sake of an example, the analysis of the potential energy distribution revealed that the  
229  $B_u$  mode at 106  $\text{cm}^{-1}$  is related to a rotation of the Si – O(b) basal triangle, which is a mode with very  
230 low transition dipole moment in IR.

231 Below 400  $\text{cm}^{-1}$ , Raman spectroscopy is more informative and sensitive. The weak band at 106  $\text{cm}^{-1}$   
232 is again related to the Si – O(b) triangle rotation as noted from IR. Two extremely weak signals were  
233 calculated at 112 and 114  $\text{cm}^{-1}$ , which were assigned to bending modes of  $\text{Si}_2\text{O}_5$  layers. The mode at 159  
234  $\text{cm}^{-1}$  was related, instead, to a combination of the out-of-plane vibration of the magnesium ions and to  
235 librations of the OH groups in the brucite-like interlayer. There is a quite intense peak at 200  $\text{cm}^{-1}$  related  
236 to a symmetric  $\text{MgO}_6$  vibration that moves also the T sheets along the *c*-axis direction. These results are  
237 in good agreement with the experimental observations of Rinaudo et al. (2004) on phlogopite, where  
238 these signals were measured at 102, 120, 153 and 195  $\text{cm}^{-1}$ . The only exception is the assignment of the  
239 mode at 102  $\text{cm}^{-1}$ , which the authors correlated to  $\text{MO}_6$  vibrations. Three very weak bands were observed  
240 at 334, 313 and 287  $\text{cm}^{-1}$ , which were assigned to Si – O(b) – Si bending, Mg – O(h) – Mg bending in  
241 the brucite-like layer and Si – O(b) – Si bending, respectively. A weak band at 375  $\text{cm}^{-1}$  is related to a  
242 Mg – O(h) – Mg bending mode of the TOT layer. Finally, the peaks in the Raman spectrum at 458  $\text{cm}^{-1}$

243 and  $483\text{ cm}^{-1}$  are related to two modes of the O' layer, namely OH librations and Mg – O(h) – Mg  
244 bending, respectively.

245 Above  $400\text{ cm}^{-1}$ , quantum mechanical simulations of the infrared spectrum of clinocllore provided  
246 vibrational signals with higher intensities (about 100 times those below  $400\text{ cm}^{-1}$ ). Between 500 and 600  
247  $\text{cm}^{-1}$ , the spectrum is mainly due to octahedral  $\text{MgO}_6$  modes. The first peak ( $400\text{ cm}^{-1}$ ) is given by two  
248 optic modes related to Mg – O(h) – Mg bending mode of the TOT layer, one showing Mg displacement  
249 normal to the layer and the second with Mg motion parallel to the (001) plane. There are two strong  
250 signals at  $426\text{ cm}^{-1}$  and  $431\text{ cm}^{-1}$  related to OH librations (Mg – O(h) – H bending) in the O' layer,  
251 normal to [001]. An  $\text{MgO}_6$  deformation parallel to the (001) plane and associated with O(b) – Si – O(b)  
252 bending was calculated at  $434\text{ cm}^{-1}$ , whereas two overlapping modes at  $450\text{ cm}^{-1}$  (1/4 of the intensity of  
253 highest signal) and  $454\text{ cm}^{-1}$  (1/2 of the intensity of highest signal) showed similar Mg-centred motions  
254 together with O(b) – Si – O(a) bending. At  $472\text{ cm}^{-1}$ , collective O – Mg – O bending modes in both the  
255 TOT and O' layers were calculated, whereas two very weak signals at  $476$  and  $479\text{ cm}^{-1}$ , hidden below  
256 the previous one, were mainly due to Mg motions in the brucite-like layer.  $\text{MgO}_6$  stretching modes in  
257 association with O(b) – Si – O(a) bending in the TOT layer were calculated at  $502\text{ cm}^{-1}$  (medium  
258 intensity, 1/4 of the highest signal) and  $527\text{ cm}^{-1}$  (medium to low intensity, 1/7 of the highest signal).

259 Making a comparison with the experimental results by Gopal et al. (2004), it is interesting to note that  
260 this region presents a single, strong signal centred between  $435 - 450\text{ cm}^{-1}$ , with many shoulders and  
261 small sub-peaks, which are overall in good agreement with the present theoretical simulation. The small  
262 discrepancies are mainly due to the aluminium substitutions in both the TOT layer ( $\text{Al}^{3+}/\text{Si}^{4+}$   
263 substitutions) and the O' layer ( $\text{Al}^{3+}/\text{Mg}^{2+}$  substitutions) that are a common feature of real samples and  
264 also affects the mineral structure (Gopal et al., 2004; Valdrè et al., 2009; Moro et al., 2016; Moro et al.,  
265 2019a; Moro et al., 2019b). The different crystal-chemistry not only affects, for example, the unit cell



266 structure (*e.g.* the larger **c**-axis parameter in Table 1) or the elastic properties of the mineral (Ulian et al.,  
267 2018), but also the chemical environment of the anionic/cationic groups, and IR/Raman spectroscopies  
268 are very sensitive to these variations. Also, it is important to stress that in the low-frequency region the  
269 modes are expected to be affected by an extremely limited anharmonicity, probably smaller than 3–4 cm<sup>-1</sup>,  
270 as also discussed by Prencipe et al. (2009) for lizardite.

271

### 272 **3.2. The 500–1100 cm<sup>-1</sup> region**

273 The theoretical analysis revealed 33 optical modes in this region, whereas few and very broad peaks  
274 were experimentally observed in both IR and Raman spectroscopies. Gopal et al. (2004) reported an  
275 infrared signal at 653 cm<sup>-1</sup> that was assigned to M – OH libration. The same signal calculated at the  
276 B3LYP-D\* level is at 758 cm<sup>-1</sup>, given by two modes at 753 and 758 cm<sup>-1</sup>. This high discrepancy is due  
277 to the anharmonic behaviour of this kind of modes for which the CRYSTAL code does not provide a  
278 correction. Indeed, while the O – H stretching modes are usually uncoupled with other vibrational modes  
279 and a reliable correction for anharmonicity was implemented in CRYSTAL by Tosoni et al. (2005), in  
280 the case of H-bending modes such a correction is not applicable due to the coupling with other modes  
281 having similar frequencies (Prencipe et al., 2009). Very recently, a computational approach based on the  
282 vibrational configuration interaction method was proposed by Erba and co-workers (Erba et al., 2019a;  
283 Erba et al., 2019b) to explicitly calculate the phonon-phonon coupling and evaluate the anharmonic  
284 vibrational states of solids. However, this method is not available in version of the CRYSTAL code here  
285 employed and, in addition, would demand high computational requirements for complex phases such as  
286 layered silicates (Erba et al., 2019a; Erba et al., 2019b).

287 The present Density Functional Theory simulations provided also two very small IR peaks at 615 and  
288 628 cm<sup>-1</sup> that were attributed to OH librations in the brucite-like layer. Given the previous consideration,

289 these signals are affected by anharmonicity and their position in real spectra should be considered with  
290 care.

291 An asymmetric  $\text{SiO}_4$  umbrella bending was calculated at  $709\text{ cm}^{-1}$  in the infrared spectrum, but this  
292 mode has an extremely low intensity and it could not be observable by experimental equipment or could  
293 appear as a shoulder on the OH libration band. The symmetric counterpart, which is Raman active, was  
294 calculated at  $688\text{ cm}^{-1}$ , and it is the signal with highest intensity in the  $0 - 1100\text{ cm}^{-1}$  spectral region.

295 The asymmetric Si – O(a) and Si – O(b) stretching modes were calculated at 989 (one mode) and 1013  
296  $\text{cm}^{-1}$  (two modes) in the infrared spectrum, which are in good agreement with the experimentally  
297 measured values of 958 and  $998\text{ cm}^{-1}$  reported by Gopal et al. (2004). Another Si – O(b) stretching mode  
298 was calculated at  $1092\text{ cm}^{-1}$ , appearing as a shoulder of the more intense Si – O(b) vibration. The Raman  
299 spectrum contained the symmetric Si – O modes, with two Si – O(b) vibrations overlapping at about  
300  $1015\text{ cm}^{-1}$  and one Si – O(a) stretching mode at  $1060\text{ cm}^{-1}$ . At  $906\text{ cm}^{-1}$  an asymmetric Si – O(a) was  
301 calculated in the Raman spectrum, but it presented almost zero intensity (1/5000 of the most intense  
302 peak).

303

304

**Table 4.** Calculated isotopic shifts ( $\text{cm}^{-1}$ ) according to the  $^{25}\text{Mg} \rightarrow ^{24}\text{Mg}$  and  $^{29}\text{Si} \rightarrow ^{28}\text{Si}$  substitutions (see paragraph 3 for details).

$\nu$ ( $\text{cm}^{-1}$ )	IRRE P	Isotopic shift					$\nu$ ( $\text{cm}^{-1}$ )	IRRE P	Isotopic shift				
		Mg1	Mg2	Mg3	Mg4	Si			Mg1	Mg2	Mg3	Mg4	Si
22	B <sub>u</sub>	0.0	0.0	-0.1	0.0	0.0	431	B <sub>u</sub>	0.0	-1.5	0.0	0.0	-0.2
25	A <sub>u</sub>	0.0	0.0	-0.1	0.0	0.0	443	B <sub>g</sub>	0.0	-3.1	0.0	0.0	-1.5
82	B <sub>u</sub>	0.0	-0.1	-0.3	-0.1	-0.1	448	A <sub>g</sub>	0.0	-3.6	0.0	0.0	-0.8
106	B <sub>u</sub>	0.0	0.0	0.0	0.0	0.0	450	A <sub>u</sub>	-1.7	-2.7	0.0	0.0	-1.4
106	A <sub>g</sub>	0.0	0.0	0.0	0.0	0.0	454	B <sub>u</sub>	-0.1	-0.6	0.0	0.0	-1.1
112	B <sub>g</sub>	0.0	0.0	0.0	0.0	-0.9	458	B <sub>g</sub>	0.0	0.0	-0.1	0.0	0.0
114	A <sub>g</sub>	0.0	0.0	0.0	0.0	-0.9	458	A <sub>g</sub>	0.0	-0.1	-0.1	0.0	-0.1
158	B <sub>u</sub>	0.0	0.0	-0.7	-1.4	0.0	460	B <sub>g</sub>	0.0	-2.6	0.0	0.0	-1.1
159	B <sub>g</sub>	0.0	0.0	-2.1	0.0	0.0	472	A <sub>u</sub>	-0.9	-0.1	-0.1	-0.3	-1.1
179	B <sub>u</sub>	-0.5	-0.8	0.0	0.0	-0.5	476	A <sub>g</sub>	0.0	0.0	-5.1	0.0	0.0
185	A <sub>u</sub>	-0.4	-0.9	0.0	0.0	-0.5	476	B <sub>u</sub>	0.0	0.0	-1.8	-3.4	0.0
200	A <sub>g</sub>	0.0	0.0	0.0	0.0	-1.4	479	B <sub>g</sub>	0.0	0.0	-5.2	0.0	0.0
245	B <sub>g</sub>	-1.5	-2.4	0.0	0.0	-0.3	479	A <sub>u</sub>	0.0	0.0	-1.6	-3.3	0.0
245	B <sub>u</sub>	0.0	-0.5	0.0	0.0	-0.3	481	A <sub>g</sub>	0.0	-1.4	0.0	0.0	-0.4
273	B <sub>u</sub>	-0.3	-1.2	0.0	0.0	-0.4	483	A <sub>g</sub>	0.0	0.0	-0.1	0.0	0.0
285	B <sub>g</sub>	0.0	0.0	0.0	0.0	0.0	502	B <sub>u</sub>	-1.5	-1.6	-0.3	-0.2	-0.1
287	A <sub>g</sub>	0.0	0.0	0.0	0.0	0.0	519	B <sub>g</sub>	0.0	-0.1	0.0	0.0	-0.3
294	A <sub>g</sub>	0.0	0.0	0.0	0.0	-0.5	527	B <sub>u</sub>	-0.5	-0.5	-0.2	-0.1	-0.2
298	A <sub>u</sub>	-0.1	0.0	0.0	0.0	-0.4	529	A <sub>u</sub>	0.0	0.0	0.0	0.0	-0.1
306	B <sub>u</sub>	-0.2	0.0	-0.1	-0.1	0.0	531	A <sub>g</sub>	0.0	-0.1	0.0	0.0	-0.1
307	B <sub>g</sub>	0.0	-1.1	-0.1	0.0	-0.1	615	B <sub>u</sub>	-0.2	-0.5	-1.3	-0.5	-0.1
312	A <sub>u</sub>	0.0	-0.1	0.0	-0.1	-0.4	619	A <sub>g</sub>	0.0	0.0	0.0	0.0	0.0
313	A <sub>g</sub>	0.0	0.0	-0.2	0.0	-0.1	628	B <sub>u</sub>	-0.1	-0.3	-3.2	-1.8	-0.1
314	B <sub>g</sub>	0.0	-0.4	-0.1	0.0	-0.3	629	A <sub>u</sub>	0.0	0.0	0.0	0.0	-0.3
329	B <sub>u</sub>	-2.1	-0.7	0.0	0.0	-0.3	630	A <sub>g</sub>	0.0	0.0	0.0	0.0	-0.3
334	A <sub>g</sub>	0.0	0.0	0.0	0.0	-0.1	631	B <sub>u</sub>	0.0	0.0	-0.1	-0.5	-0.3
340	B <sub>g</sub>	0.0	-1.4	0.0	0.0	-0.5	631	B <sub>g</sub>	0.0	0.0	-0.7	0.0	-0.2
353	A <sub>u</sub>	-2.0	-0.5	0.0	-0.1	-2.6	635	B <sub>g</sub>	0.0	0.0	-0.4	0.0	-0.2
355	B <sub>g</sub>	0.0	-2.4	-0.1	0.0	-2.3	636	A <sub>u</sub>	0.0	0.0	0.0	0.0	-0.2
375	A <sub>g</sub>	0.0	-1.1	0.0	0.0	-0.2	688	A <sub>g</sub>	0.0	0.0	0.0	0.0	-2.2
375	A <sub>u</sub>	-0.2	-1.3	0.0	0.0	-0.8	709	B <sub>u</sub>	-0.8	-1.5	-0.1	0.0	-2.7
377	B <sub>u</sub>	-0.9	-0.8	0.0	-0.1	-0.7	753	B <sub>u</sub>	-0.1	0.0	0.0	0.0	-1.1
387	A <sub>g</sub>	0.0	-0.1	-3.3	0.0	0.0	758	A <sub>u</sub>	0.0	0.0	0.0	0.0	-0.9
387	B <sub>u</sub>	0.0	0.0	-1.1	-2.7	0.0	761	B <sub>g</sub>	0.0	-0.2	0.0	0.0	-1.5
388	B <sub>g</sub>	0.0	-0.9	-1.8	0.0	-0.8	763	A <sub>g</sub>	0.0	0.0	0.0	0.0	-1.4
390	A <sub>u</sub>	-0.1	0.0	-2.1	-2.0	0.0	796	A <sub>g</sub>	0.0	0.0	0.0	0.0	-10.6
390	B <sub>g</sub>	0.0	-0.1	-1.5	0.0	0.0	796	B <sub>u</sub>	0.0	0.0	0.0	0.0	-11.0
392	A <sub>g</sub>	0.0	-2.2	-0.1	0.0	-0.7	797	A <sub>u</sub>	0.0	0.0	0.0	0.0	-11.2
397	A <sub>u</sub>	0.0	0.0	-1.6	-1.5	0.0	798	B <sub>g</sub>	0.0	-0.1	0.0	0.0	-10.6
398	B <sub>u</sub>	0.0	-1.3	-2.1	-1.2	0.0	906	B <sub>g</sub>	0.0	0.0	0.0	0.0	-4.1
400	B <sub>u</sub>	-1.8	-1.8	0.0	0.0	-0.1	907	A <sub>u</sub>	0.0	0.0	0.0	0.0	-4.1
400	A <sub>u</sub>	-0.7	-0.5	0.0	0.0	-0.4	989	B <sub>u</sub>	0.0	-0.1	-0.1	-0.1	-6.5
403	B <sub>g</sub>	0.0	0.0	-2.3	0.0	0.0	1013	A <sub>u</sub>	0.0	0.0	0.0	0.0	-4.6
407	B <sub>u</sub>	0.0	0.0	-1.6	-1.5	0.0	1013	B <sub>g</sub>	0.0	0.0	0.0	0.0	-4.6
412	A <sub>u</sub>	0.0	0.0	-0.6	-0.2	0.0	1013	B <sub>u</sub>	0.0	0.0	0.0	0.0	-4.6
415	A <sub>g</sub>	0.0	0.0	0.0	0.0	0.0	1013	A <sub>g</sub>	0.0	0.0	0.0	0.0	-4.6
426	B <sub>u</sub>	-0.2	0.0	-0.2	-0.1	0.0	1060	A <sub>g</sub>	0.0	0.0	0.0	0.0	-7.6
434	A <sub>u</sub>	-4.7	0.0	-0.1	-0.1	0.0	1092	B <sub>g</sub>	0.0	0.0	0.0	0.0	-1.6

**Table 5.** Calculated isotopic shifts ( $\text{cm}^{-1}$ ) according to the  $^2\text{D} \rightarrow ^1\text{H}$  substitutions (see paragraph 3 for details).

$\nu$ ( $\text{cm}^{-1}$ )	IRREP	Isotopic shift			$\nu$ ( $\text{cm}^{-1}$ )	IRREP	Isotopic shift		
		H1	H2	H3			H1	H2	H3
0	B <sub>u</sub>	0.0	0.0	0.0	450	A <sub>u</sub>	-4.3	-0.3	-1.7
0	B <sub>u</sub>	0.0	0.0	0.0	454	B <sub>u</sub>	-13.9	0.0	-0.6
0	A <sub>u</sub>	0.0	0.0	0.0	458	B <sub>g</sub>	-3.2	-14.1	-14.7
22	B <sub>u</sub>	0.0	-0.1	-0.1	458	A <sub>g</sub>	-0.2	-10.0	-10.0
25	A <sub>u</sub>	0.0	0.0	-0.1	460	B <sub>g</sub>	-2.6	0.0	-3.2
82	B <sub>u</sub>	-0.1	-0.3	-0.6	472	A <sub>u</sub>	-14.1	-0.4	-4.4
106	B <sub>u</sub>	0.0	0.0	0.0	476	A <sub>g</sub>	-9.5	-3.2	-10.6
106	A <sub>g</sub>	0.0	0.0	0.0	476	B <sub>u</sub>	0.0	-2.4	-9.2
112	B <sub>g</sub>	0.0	-0.1	0.0	479	B <sub>g</sub>	0.0	-1.6	-7.4
114	A <sub>g</sub>	0.0	0.0	0.0	479	A <sub>u</sub>	-0.1	-0.1	-5.0
158	B <sub>u</sub>	0.0	-6.4	-8.9	481	A <sub>g</sub>	-5.0	-2.0	-5.7
159	B <sub>g</sub>	0.0	-3.9	-11.3	483	A <sub>g</sub>	0.0	-2.2	-2.2
179	B <sub>u</sub>	-1.0	0.0	0.0	502	B <sub>u</sub>	-2.6	-0.1	-5.8
185	A <sub>u</sub>	-0.3	0.0	-0.1	519	B <sub>g</sub>	-1.0	-0.4	-15.7
200	A <sub>g</sub>	-0.2	0.0	0.0	527	B <sub>u</sub>	-2.7	-0.8	-22.9
245	B <sub>g</sub>	-2.6	-0.1	-0.1	529	A <sub>u</sub>	-0.2	0.0	-29.5
245	B <sub>u</sub>	-1.4	0.0	-0.3	531	A <sub>g</sub>	-0.7	-0.1	-35.8
273	B <sub>u</sub>	-5.0	0.0	0.0	615	B <sub>u</sub>	-38.4	-52.9	-86.8
285	B <sub>g</sub>	0.0	-0.3	-0.3	619	A <sub>g</sub>	-41.5	-53.1	-87.8
287	A <sub>g</sub>	0.0	-1.0	-0.1	628	B <sub>u</sub>	-13.7	-7.9	-41.5
294	A <sub>g</sub>	-0.9	-5.2	-3.0	629	A <sub>u</sub>	-54.2	-86.7	-100.5
298	A <sub>u</sub>	-0.2	-1.7	-12.8	630	A <sub>g</sub>	-11.1	-4.4	-45.6
306	B <sub>u</sub>	-0.2	-8.6	-15.8	631	B <sub>u</sub>	-3.3	-2.5	-10.0
307	B <sub>g</sub>	-3.3	-3.7	-11.4	631	B <sub>g</sub>	-49.7	-76.3	-111.8
312	A <sub>u</sub>	-0.1	-5.2	-7.2	635	B <sub>g</sub>	-3.1	0.0	-24.5
313	A <sub>g</sub>	-0.6	-6.1	-10.5	636	A <sub>u</sub>	-5.7	-0.1	-31.9
314	B <sub>g</sub>	-1.6	-2.1	-3.8	688	A <sub>g</sub>	-56.5	-0.2	-0.2
329	B <sub>u</sub>	-2.7	-1.6	-0.3	709	B <sub>u</sub>	-76.8	-0.2	-0.4
334	A <sub>g</sub>	-2.4	-0.2	-0.5	753	B <sub>u</sub>	-44.6	-0.2	-0.5
340	B <sub>g</sub>	-0.1	0.0	-1.6	758	A <sub>u</sub>	-122.4	-0.1	-0.4
353	A <sub>u</sub>	0.0	-3.2	-36.1	761	B <sub>g</sub>	-125.8	-0.2	-0.4
355	B <sub>g</sub>	0.0	-1.2	-8.1	763	A <sub>g</sub>	-75.1	-0.3	-0.5
375	A <sub>g</sub>	-7.1	-20.6	-23.5	796	A <sub>g</sub>	-2.3	-1.1	-1.5
375	A <sub>u</sub>	-2.3	-15.4	-24.1	796	B <sub>u</sub>	-2.3	-0.9	-1.4
377	B <sub>u</sub>	-1.9	-25.9	-45.9	797	A <sub>u</sub>	-1.7	-0.9	-1.9
387	A <sub>g</sub>	-0.1	-11.9	-14.7	798	B <sub>g</sub>	-2.7	-0.6	-1.8
387	B <sub>u</sub>	0.0	-10.2	-10.3	906	B <sub>g</sub>	-0.5	-0.1	-0.3
388	B <sub>g</sub>	-0.3	-11.5	-32.9	907	A <sub>u</sub>	-0.5	-0.1	-0.3
390	A <sub>u</sub>	0.0	-14.3	-16.8	989	B <sub>u</sub>	-0.1	-0.2	-0.4
390	B <sub>g</sub>	0.0	-1.4	-7.5	1013	A <sub>u</sub>	-0.1	0.0	0.0
392	A <sub>g</sub>	-0.7	-2.8	-15.5	1013	B <sub>g</sub>	-0.1	0.0	0.0
397	A <sub>u</sub>	-1.5	-6.7	-14.3	1013	B <sub>u</sub>	-0.1	0.0	0.0
398	B <sub>u</sub>	-1.2	-10.9	-17.5	1013	A <sub>g</sub>	-0.1	0.0	0.0
400	B <sub>u</sub>	-1.8	0.0	-0.3	1060	A <sub>g</sub>	-0.2	0.0	0.0
400	A <sub>u</sub>	-3.5	0.0	0.0	1092	B <sub>g</sub>	0.0	-0.1	-0.1
403	B <sub>g</sub>	0.0	-2.6	-14.6	1092	A <sub>u</sub>	0.0	-0.1	-0.1
407	B <sub>u</sub>	0.0	-0.1	-6.3	3849	B <sub>u</sub>	-1037.0	0.0	0.0
412	A <sub>u</sub>	0.0	-7.2	-9.5	3850	A <sub>g</sub>	-1036.4	0.0	0.0
415	A <sub>g</sub>	0.0	-21.3	-22.3	3975	B <sub>g</sub>	0.0	0.0	-1074.9
426	B <sub>u</sub>	0.0	-17.7	-18.8	3975	A <sub>u</sub>	0.0	0.0	-1074.9
434	A <sub>u</sub>	-0.1	-17.7	-20.5	3976	B <sub>u</sub>	0.0	-1072.5	4.7
431	B <sub>u</sub>	-0.7	-0.2	-0.1	3976	A <sub>g</sub>	0.0	-1071.7	5.0
443	B <sub>g</sub>	-12.3	-37.4	-38.7	3987	B <sub>u</sub>	0.0	-4.7	-1082.8
448	A <sub>g</sub>	-11.0	-19.3	-44.6	3988	A <sub>g</sub>	0.0	-4.9	-1081.9

### 306 3.3. The 3700–4000 cm<sup>-1</sup> region.

307 This is the region dominated by the hydroxyl stretching modes of both the talc-like and the brucite-  
308 like layer. Here, 8 optical modes were computed, four IR-active ( $A_u + 3B_u$ ) and four active in Raman  
309 spectroscopy ( $3A_g + B_g$ ). Within the harmonic approximation, the calculated vibrational frequency of the  
310 infrared OH-modes were 3849 cm<sup>-1</sup>, 3975 cm<sup>-1</sup>, 3976 cm<sup>-1</sup> and 3987 cm<sup>-1</sup>, whereas the frequencies of  
311 Raman-active modes were 3850 cm<sup>-1</sup>, 3975 cm<sup>-1</sup>, 3976 cm<sup>-1</sup> and 3988 cm<sup>-1</sup>. As reported in Table 2, the  
312 anharmonic constant for these modes is quite remarkable, of about 150 cm<sup>-1</sup>, in agreement with previous  
313 theoretical observations (Tosoni et al., 2005; Prencipe et al., 2009). This is a well-known issue related to  
314 the very low mass of hydrogen, whose vibrational displacement is often large, whereas the assumption  
315 of harmonic oscillators requires small nuclear movements. For this means, the correction proposed by  
316 Tosoni and co-workers (2005), which is based on a numerical solution of the Schrödinger equation along  
317 the O – H coordinate for fully decoupled hydroxyl stretching modes, was employed. The interested  
318 readers can find further details in the work of Tosoni et al. (2005).

319 By considering the anharmonic vibrational frequencies, the first two lines (101,  $B_u$  and 102,  $A_g$ )  
320 reported in Table 2, centred at about 3700 cm<sup>-1</sup>, were related to OH stretching modes of the TOT layer,  
321 whereas the other six vibrations at higher frequencies (3830 – 3850 cm<sup>-1</sup>) are due to O – H vibrations in  
322 the O' layer. These figures are quite different from those experimentally measured by Gopal et al. (2004),  
323 who reported these signals between 3438 cm<sup>-1</sup> and 3678 cm<sup>-1</sup>, and can be explained by the different  
324 crystal-chemistry of the O' and TOT layers, which commonly present  $Al^{3+}/Mg^{2+}$  and  $Al^{3+}/Si^{4+}$   
325 substitutions, respectively.

326

327

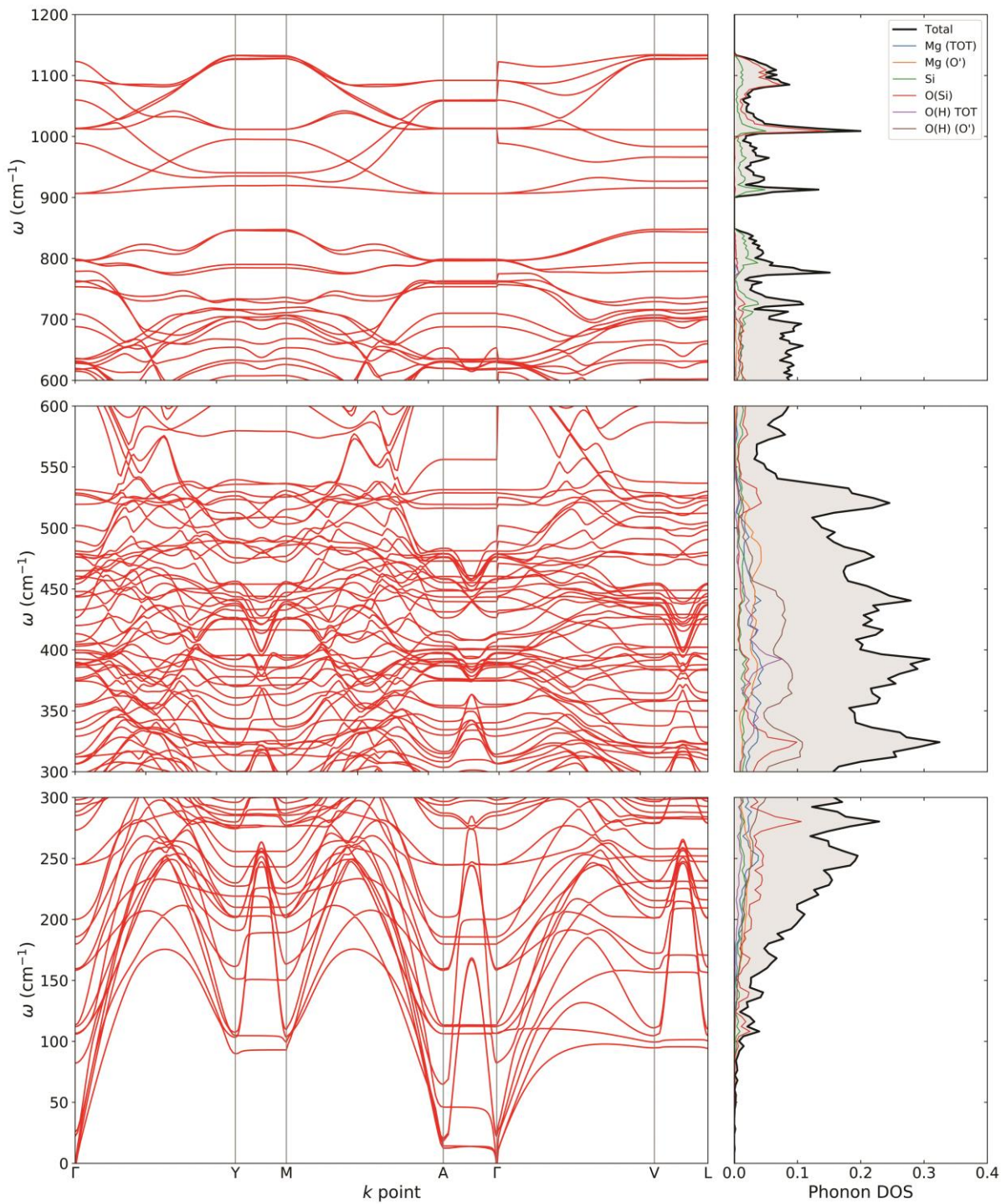
328 **3.4. Phonon dispersion relations.**

329 Phonon dispersion calculations were performed by sampling other  $\mathbf{k}$ -points in the first Brillouin Zone  
330 other than  $\Gamma$  ( $\mathbf{k} = 0$ ) using a direct-space approach (Dove, 1993; Parlinski et al., 1997; Wallace, 1998).  
331 The phonon sampling was conducted on a clinoclone  $2 \times 2 \times 2$  supercell constructed from the primitive  
332 cell of the mineral.

333 Phonon dispersion curves of monoclinic clinoclone in the path  $\Gamma \rightarrow Y \rightarrow M \rightarrow A \rightarrow \Gamma \rightarrow Y \rightarrow V \rightarrow L \rightarrow \Gamma$  is  
334 reported in Figure 3 for the  $0 - 1200 \text{ cm}^{-1}$  range, alongside the calculated total and atom-projected phonon  
335 density of states (DOS). The low-frequency region ( $\nu < 550 \text{ cm}^{-1}$ ) is characterized by magnesium and  
336 oxygen vibrations, whereas at higher wavenumbers ( $750 \text{ cm}^{-1} < \nu < 1200 \text{ cm}^{-1}$ ) the phonon dispersion is  
337 completely dominated by Si – O phonon modes. The spectral region between  $550 \text{ cm}^{-1}$  and  $750 \text{ cm}^{-1}$   
338 shows a small contribution from Mg, Si and O atoms to the total DOS, which is mainly due to vibrational  
339 motion of hydrogen atoms (projection not showed in the figure for the sake of clarity). As previously  
340 discussed, there is a strong anharmonic component in these phonon modes that are not calculated by the  
341 CRYSTAL code at the moment. For this reason, this portion of the phonon spectrum has to be considered  
342 subject to possible shifts at different wavenumbers.

343 Acoustic phonon dispersion curves are in adequate agreement with those experimentally measured by  
344 inelastic neutron scattering technique by Collins et al. (1993), albeit the poor resolution of the phonon  
345 spectra made the comparison difficult.

346



347

348 **Figure 3.** DFT/B3LYP-D\* phonon dispersion relations and phonon density of states (DOS) of  
 349 monoclinic clinocllore (space group  $C2/m$ ) in the frequency range 0 – 1200  $\text{cm}^{-1}$ .

350 As a final note on the phonon properties ( $\Gamma$ -point frequencies and phonon dispersion relations), the  
351 authors are aware that clinocllore is typically found with  $Al^{3+}/Si^{4+}$  substitutions in both the TOT layer  
352 and O' sheet, and other isomorphic substitution may occur in the mineral structure. In general, as reported  
353 by several authors (Pawley and Jones, 2011; Ulian et al., 2014; Jollands et al., 2020), crystal-chemical  
354 variations from stoichiometric structures can deeply affect the vibrational spectrum. Among the possible  
355 effect, it is possible to cite:

356 (i) increasing number of IR/Raman signals due to lower symmetry of the system (*i.e.*, degeneracy loss  
357 of some vibrational modes or activation of silent modes);

358 (ii) blue or red shifts of the peaks because of the different chemical environment around the vibrating  
359 group and/or

360 (iii) more or less intense signals due to variations of the dipole moment (IR) or polarizability (Raman).

361 It is possible to extend these considerations to  $\mathbf{k} \neq 0$ , thus the phonon band structure is more complex  
362 and elaborate in a cationic/anionic-substituted mineral phase than that of the end-member term.

363 However, it was decided to start with the vibrational analysis by considering the simplest clinocllore  
364 system, which is the stoichiometric one, a necessary starting point to assign IR/Raman signals to specific  
365 vibrations in the structure. Although the system is simple, it represents a novelty because to the authors'  
366 knowledge no theoretical information on this subject is present in literature. In addition, Density  
367 Functional Theory simulations involving isomorphic substitutions are very demanding from the  
368 computational side, in particular for the phonon dispersion relations where supercells are required, and  
369 the interpretation of the resulting phonon bands could be a daunting task without those from a reference  
370 phase. A comparison between the present theoretical result for the stoichiometric clinocllore and those  
371 presenting different kinds and degrees of isomorphic substitutions will be the subject of future works,



372 which will also aid the assignment of experimental IR/Raman signals to specific vibrational modes in  
373 the structure.

374

#### 375 **4. Conclusions**

376 In this theoretical work, a detailed and accurate analysis of the vibrational properties of monoclinic  
377 clinochlore was carried out by means of Density Functional Theory simulations. The results were  
378 extensively presented and discussed against the few available experimental findings, with a general good  
379 agreement on both the pattern (peak positions and intensities in the IR/Raman spectra) and assignment  
380 of the normal modes. The theoretical approach provided further details and extended the knowledge on  
381 the vibrational features of this mineral phase, which can be exploited in future studies involving the bulk  
382 and the surface of clinochlore.

383 The small differences between the calculated results and the experimental data in literature are mainly  
384 due to the crystal-chemistry of the simulated model. In fact, it was considered an ideal, completely  
385 magnesian monoclinic clinochlore without any of the typical substitutions occurring in this mineral, *e.g.*  
386  $\text{Al}^{3+}/\text{Si}^{4+}$  or  $\text{Al}^{3+}/\text{Mg}^{2+}$  in the tetrahedral and O' sites, respectively.

387 As a final note, the present results showed the relevance of anharmonic OH-modes in both infrared  
388 and Raman spectra. While an anharmonic correction was employed in this work for the characterization  
389 of the hydroxyl stretching region, at the moment the CRYSTAL code does not calculate the anharmonic  
390 contribution for the Mg – O – H (libration) modes.

391

392

393

394 **Acknowledgments**

395 This work is dedicated to the memory of Professor Emilio Galan, who was a world-known scientist, a  
396 stimulating collaborator of many works, and a sincere good friend.

397

398

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