

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

The Raman spectrum of diopside: a comparison between ab initio calculated and experimentally measured frequencies

This is a pre print version of the following article:

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/61753> since 2016-06-22T15:10:08Z

Published version:

DOI:10.1127/0935-1221/2012/0024-2178

Terms of use:

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)

This is the author's final version of the contribution published as:

MAURO PRENCIPE; LUCIANA MANTOVANI; MARIO TRIBAUDINO;
DANILO BERSANI; PIER PAOLO LOTTICI. The Raman spectrum of
diopside: a comparison between ab initio calculated and experimentally
measured frequencies. EUROPEAN JOURNAL OF MINERALOGY. 24 pp:
457-464.

DOI: 10.1127/0935-1221/2012/0024-2178

The publisher's version is available at:

<http://www.ingentaconnect.com/content/schweiz/ejm/2012/00000024/00000003/art00005>

When citing, please refer to the published version.

Link to this full text:

<http://hdl.handle.net/2318/61753>

TITLE:

The Raman spectrum of diopside: a comparison between *ab initio* calculated and experimentally measured frequencies

RUNNING TITLE:

Raman spectrum of diopside

Abstract

Introduction

Experimental

Computational details

Raman spectroscopy

Results and discussion

Comparison between different Hamiltonians

Experimentally determined frequencies

Normal modes

Conclusions

Dipartimento di Scienze Mineralogiche e Petrologiche

Via Valperga Caluso 35 – 10125 Torino – Italy

E-mail: mauro.prencipe@unito.it

Tel. +0039 011 6705131

Fax +0039 011 2365131

Windows 7 – Microsoft Office 2007

32.025 characters

The Raman spectrum of diopside: a comparison between *ab initio* calculated and experimentally measured frequencies

Mauro PRENCIPE^{1*}, Luciana MANTOVANI², Mario TRIBAUDINO², Danilo BERSANI³ and Pier Paolo LOTTICI³

¹Dipartimento di Scienze Mineralogiche e Petrologiche, Via Valperga Caluso 35, 10125 Torino, Italy

*Corresponding author, e-mail: mauro.prencipe@unito.it

² Dipartimento di Scienze della Terra, Parco Area delle Scienze 157A, 43124 Parma, Italy

³ Dipartimento di Fisica, Parco Area delle Scienze 7A, 43124 Parma, Italy

Abstract: The Raman spectrum of diopside has been calculated by using three *purely* Density Functional Theory (DFT) Hamiltonians (PBE, WCPBE, LDA), the Hartree-Fock Hamiltonian (HF) and three hybrid HF/DFT ones (B3LYP, WC1LYP, PBE0). A comparison has been done between the calculated frequencies with those measured by Raman spectroscopy on a natural sample, along with several different orientations and beam polarizations, or retrieved from literature; such a comparison demonstrated the excellent performances of the hybrid Hamiltonians in reproducing the vibrational spectrum of the mineral, in line with what it is generally observed in literature concerning other mineral phases. In particular, the mean average absolute discrepancies of the calculated frequencies with respect to the experimental data were: 3.2 (WC1LYP), 4.7 (B3LYP), 6.5 (PBE0), 18.0 (PBE), 9.7 (WCPBE), 7.3 (LDA) and 40.6 cm⁻¹ (HF). The very good quality of the WC1LYP results, allowed for a reliable assignment of all of the experimentally observed Raman signals, and the corresponding assignments to specific patterns of atomic vibrational motion (normal modes).

Key-words: Diopside, Raman Spectrum, Vibrational Modes Assignment, First Principles Calculations

1 **1. Introduction**

2 Raman spectroscopy is a rapid and non destructive method of analysis of growing interest in
3 Materials, Earth and Space sciences. Among minerals, Raman studies of pyroxenes are especially
4 interesting, as pyroxenes are found in several materials where sampling and/or destructive analysis
5 is critical, like extraterrestrial materials or ceramics in cultural heritage studies. Therefore several
6 experimental studies were performed to provide a careful description of the Raman spectrum of
7 pyroxenes. Most investigation focussed on the holotypic pyroxene diopside ($\text{CaMgSi}_2\text{O}_6$) whose
8 Raman spectrum was measured at different crystal orientations and beam polarizations (Etchepare,
9 1972; Swami *et al.*, 1997; Downs, 2006). These studies provided the basis to study the changes in
10 the Raman spectra in pyroxenes due to temperature, pressure and composition (Richet *et al.*, 1998;
11 Chopelas & Serghiou, 2002; Huang *et al.*, 2000).

12 Peak assignment was also a subject of interest. In diopside, group analysis predicts 14 A_g
13 and 16 B_g Raman-active modes (Etchepare, 1972; Tomisaka & Ishi, 1980). Although the signals
14 from most of them are rather weak to be detected, careful Raman spectroscopic experimental
15 analysis from a single crystal, beam polarized measurements could be able to detect most of the
16 predicted 30 Raman-active modes and to perform the symmetry assignment (Etchepare, 1972). In
17 order to assign the observed signals to specific vibrational modes, the frequencies of the vibrational
18 spectrum were calculated by semi-empirical models (lattice dynamics; Tomisaka & Ishi, 1980;
19 Pilati *et al.*, 1996; Swamy *et al.*, 1997). In particular Swamy *et al.* (1997), by using a quasi-
20 harmonic lattice dynamics simulation together with the CMAS94 potential by Matsui (1996), were
21 able to model the experimental results. Semiempirical methods are however dependent on the
22 specific choice of the pair potential, and are based on the classical models of atomic interactions. At
23 present this is not fully satisfactory, as developments in quantum-mechanical calculations for
24 crystals, coupled with the ever increasing availability of computational resources at a relatively low
25 cost, enable the *ab-initio* calculation of fundamental frequencies and their assignement also in
26 minerals having a relatively complex structure like diopside. Such *ab-initio* approach has been

27 followed with success in several other cases, as in calcite (Prencipe *et al.*, 2004), beryl (Prencipe *et*
28 *al.*, 2006) and lizardite (Prencipe *et al.*, 2009). However, in general the reliability of the results
29 depends on several factors and computational details, including the choice of the Hamiltonian. The
30 purpose of this work was to calculate the frequencies of the Raman spectrum in diopside, using the
31 quantum-mechanical approach, and to compare the relative performances of several Hamiltonians.
32 The calculated frequencies were compared with those from Raman measurements on a single
33 crystal, for different crystallographic orientation and beam polarization.

34

35 **2. Computational details**

36 Geometry optimization and spectral calculations on diopside were performed by means of
37 the *ab-initio* CRYSTAL09 code (Dovesi *et al.*, 2009), which implements the Hartree-Fock and
38 Kohn-Sham, Self Consistent Field (SCF) method for the study of periodic systems (Pisani *et al.*,
39 1988), by using a Gaussian type basis set. The latter consists of a 86-511d3G contraction for Ca
40 (Prencipe *et al.*, 2004), a 85-11d1G contraction for Mg (Valenzano *et al.*, 2007) and 88-31d1G and
41 8-411d2G contractions for Si and O, respectively (Prencipe *et al.*, 2006).

42

43 **2.1. Hamiltonian**

44 Seven different Hamiltonians, proposed in previous similar quantum mechanical
45 investigations, were employed for the calculations of the mode frequencies: B3LYP, WC1LYP,
46 PBE0, PBE, WCPBE, LDA and HF. The first three Hamiltonians are hybrid HF/DFT ones, in that
47 they contain a percentage of the *exact non-local* Hartree-Fock (HF) exchange correcting for the
48 approximate DFT exchange functional. B3LYP (Becke, 1993) is one of the most suitable and
49 largely employed Hamiltonian for *the ab initio* calculation of the vibrational properties of
50 molecules, as documented by Koch & Holthausen (2000), as well as for solid state calculations,
51 where it has been shown to provide excellent results for geometries and vibrational frequencies,
52 superior to those obtained by LDA- (Local Density Approximation) or GGA- (Generalized

53 Gradient Approximation) type functionals (Pascale *et al.*, 2004a; Prencipe *et al.*, 2004; Pascale *et*
54 *al.*, 2005a; Pascale *et al.*, 2005b; Prencipe *et al.*, 2009). WC1LYP is based on the relatively new
55 DFT exchange functional proposed by Wu & Cohen (2006), mixed to the HF exchange (16%) and
56 coupled with the LYP correlation functional of Lee *et al.* (1988); though not being extensively
57 tested, such Hamiltonian proved to be very successful in the reproduction of elastic and vibrational
58 properties of minerals (Ungureanu *et al.*, 2010; Prencipe *et al.*, 2011). PBE0 (Adamo & Barone,
59 1999) employs PBE exchange and correlation functionals (Perdew *et al.*, 1996), and a fraction of
60 HF exchange (25%). PBE (Perdew *et al.*, 1996) and WCPBE (Wu & Cohen, 2006) are purely DFT-
61 GGA Hamiltonians. LDA is the *standard* DFT Hamiltonian in the Local Density Approximation
62 (Dirac, 1930; Vosko *et al.*, 1980) and HF is the Hartree-Fock Hamiltonian.

63

64 **2.2. Computational parameters**

65 The DFT exchange and correlation contributions to the total energy were evaluated by
66 numerical integration, over the cell volume, of the appropriate functionals; a (75, 974)*p* grid has
67 been used, where the notation (n_r, n_ω)*p* indicates a pruned grid with n_r radial points and n_ω angular
68 points on the Lebedev surface in the most accurate integration region (see the ANGULAR keyword
69 in the CRYSTAL09 user's manual, Dovesi *et al.*, 2009). Such a grid corresponds to 115447
70 integration points in the primitive unit cell. The accuracy of the integration can be measured from
71 the error in the integrated total electron density, which amounts to $-4 \cdot 10^{-5} |e|$ for a total of 216
72 electrons (in the primitive cell). The thresholds controlling the accuracy of the calculation of
73 Coulomb and exchange integrals have been set to 7 (*ITOL1* to *ITOL4*) and 16 (*ITOL5*; Dovesi *et al.*,
74 2009). The diagonalization of the Hamiltonian matrix was performed at 6 independent **k** vectors in
75 the reciprocal space (Monkhorst net; Monkhorst & Pack, 1976) by setting to 2 the shrinking factor
76 IS (Dovesi *et al.*, 2009).

77

78

79 **2.3. Geometry optimization and calculation of frequencies**

80 Cell parameters and fractional coordinates were optimized by analytical gradient methods,
81 as implemented in CRYSTAL09 (Civalleri *et al.*, 2001; Dovesi *et al.*, 2009). Geometry
82 optimization was considered converged when each component of the gradient (TOLDEG parameter
83 in CRYSTAL09) was smaller than 0.00001 hartree/bohr and the displacements (TOLDEX) with
84 respect to the previous step were smaller than 0.00004 bohr. Results (cell parameters, optimized
85 fractional coordinates) are reported in Table S1 of supplementary material; compared calculation
86 results are shown in Table 1. Vibrational frequencies and normal modes were calculated within the
87 limit of the harmonic approximation, by diagonalizing a mass weighted Hessian matrix, whose
88 elements are the second derivatives of the full potential of the crystal with respect to mass weighted
89 atomic displacements (see Pascale *et al.*, 2004b for details). The threshold for the convergence of
90 the total energy, in the SCF cycles, was set to 10^{-10} hartree (TOLDEE parameter in CRYSTAL09).
91 Raman spectroscopy.

93 **3. Experimental details**

94 A single crystal of pale green diopside from rhodinitic environment sampled at
95 Bellacomba, Aosta valley, Italy, was used. The sample was previously studied by single crystal
96 neutron diffraction (Prencipe *et al.*, 2000). Its chemical composition, as determined by SEM-EDS
97 (Prencipe *et al.*, 2000), is $(\text{Ca}_{0.99}\text{Na}_{0.01})(\text{Mg}_{0.94}\text{Fe}_{0.07})\text{Si}_{1.99}\text{O}_6$. The crystal has a tabular shape, sized
98 $6 \times 5 \times 1 \text{ mm}^3$ and elongated along the cleavage, i.e. along the **c** axis. The crystal orientation was
99 identified on the basis of morphological and optical characteristics, and confirmed by single crystal
100 diffraction. Raman spectroscopy was performed using a Jobin-Yvon Horiba LabRam microRaman
101 apparatus, with spatial resolution of $\sim 1 \mu\text{m}$ and a spectral resolution of $\sim 1 \text{ cm}^{-1}$. The 632.8 nm line
102 of an He-Ne laser was used as the excitation. The laser source has a power of 20 mW, but the use of
103 the filter wheel reduced the power to 1 mW or less on the sample. The calibration was performed
104 with the main Raman peak of Silicon.

105 Raman spectra were collected at different orientations (Table S2, supplementary material),
106 with beam propagation along \mathbf{a}^* , \mathbf{b} and \mathbf{c} crystallographic axes, hereafter referred as \mathbf{x} , \mathbf{y} and \mathbf{z} in a
107 conventional setting. For each orientation both polarized and unpolarized spectra were collected;
108 polarized spectra were collected both in cross and parallel polarization settings. The crystal was
109 oriented so that two of the \mathbf{a}^* , \mathbf{b} and \mathbf{c} crystallographic axes are parallel to the plane polar. Along
110 each orientation the measure was repeated after a 90° rotation of the crystal, so that a total of 18
111 spectra were collected. The peak positions were obtained from baseline-corrected spectra by least-
112 squares analysis using the Labspec Raman spectroscopy software. A Lorentzian profile was used in
113 the peak analysis. The peak positions, with experimental errors and intensities normalized to that of
114 the strongest peak in each spectrum are reported in Tables S2 and S3 (deposited). The collected
115 spectra are shown can be obtained from the authors. With the purpose of comparing our
116 experimental data with those from previous papers, the peak position measured in different spectra
117 for each mode were averaged, excluding those having an unfavourable peak to error intensity ratio
118 (Table 2). To estimate the uncertainty in peak position due to spectrometer offsets, average and
119 error between the 18 measured positions in the strong and well resolved peaks at 667 and 1013 cm^{-1}
120 was calculated: the value are respectively $666.7(5)$ and $1013.6(3)\text{ cm}^{-1}$, with a standard deviation
121 below the experimental uncertainty of $\approx 1\text{ cm}^{-1}$ usually taken for Raman spectroscopy.

122 Experimentally measured Raman frequencies are reported in Table 2, together with the
123 calculated values at the WC1LYP level.

124

125 **4. Results and discussion**

126 **4.1. Comparison between different Hamiltonians**

127 There are 20 atoms in the primitive unit cell of diopside, giving rise to 60 different
128 vibrational normal modes, three of which correspond to pure translations. The symmetry
129 decomposition of the normal modes in the $2/m$ point group of diopside is:

$$130 \quad \Gamma_{\text{tot}} = 14A_g + 14A_u + 16B_g + 16B_u$$

131 The symmetry of the three translations is $A_u + 2B_u$; the A_g and B_g normal modes are Raman active,
132 whereas the A_u and B_u modes are IR active; no silent modes are present.

133 The frequencies of the Raman active normal modes, calculated by the different Hamiltonian,
134 are reported in Table 1, together with the average absolute discrepancy ($\langle|\Delta| \rangle$) and the standard
135 deviation relative to the values of discrepancy (σ_Δ in Table 1), a measure of the scattering of the
136 discrepancies around the average value. The whole set of frequencies, comprising those of the IR
137 active modes, is deposited as supplementary material (Table S4).

138 The Raman frequencies experimentally measured in this work, and those from the literature
139 are reported in Table 2, together with the calculated WC1LYP values. In Table 1, the WC1LYP
140 frequencies are taken as reference, as they showed the smallest average absolute discrepancy ($\langle|\Delta| \rangle$
141 = 3.2 cm⁻¹) with respect to the experimental Raman (see the discussion below and the experimental
142 data in Table 2), among the set of frequencies obtained by means of the different Hamiltonians.
143 Indeed, such average discrepancies are 4.7, 6.5, 18.0, 9.7, 7.3 and 40.6 cm⁻¹, for the B3LYP, PBE0,
144 PBE, WCPBE, LDA and HF Hamiltonians, respectively. With respect to the WC1LYP data,
145 B3LYP frequencies are slightly underestimated (4 cm⁻¹, on average; Table 1), with a maximum
146 underestimation of 13 cm⁻¹; σ_Δ (B3LYP) is 4 cm⁻¹, a relatively small value. PBE0 slightly
147 overestimates the frequencies, and the magnitude of such overestimation apparently more at higher
148 frequencies (Δ is greater than 10 cm⁻¹, at frequencies higher than 800 cm⁻¹). PBE largely
149 underestimates the frequencies by up to -42 cm⁻¹ with respect to the WC1LYP values, with an
150 average discrepancy of 21 cm⁻¹ and a relatively high dispersion [σ_Δ (PBE) is 10 cm⁻¹]; as in the case
151 of PBE0 the absolute value of the discrepancies increases at high frequency. As the WC1LYP
152 frequencies are very close to the experimental data, the discrepancies of the PBE values with
153 respect to the WC1LYP ones also reflect a relatively large underestimation of the PBE frequencies
154 with respect to the experiments: as reported above, such underestimation amounts to 18 cm⁻¹, on
155 average, on the whole set of Raman active modes; it increases to 27 cm⁻¹ if only modes above 500
156 cm⁻¹ are considered, with a maximum underestimation of 45 cm⁻¹ at a frequency of 875 cm⁻¹ (PBE

157 value; the corresponding experimental datum is about 920 cm^{-1}). The behaviour of the PBE
158 Hamiltonian, here reported, parallels that observed in other cases, as lizardite (Prencipe *et al.*,
159 2009). The WCPBE Hamiltonian performs slightly better than PBE: like PBE it works frequencies,
160 but with a smaller average discrepancy ($\langle|\Delta|\rangle = 11\text{ cm}^{-1}$). The LDA frequencies are
161 underestimated, but not very far from the WC1LYP ones ($\langle|\Delta|\rangle = 7\text{ cm}^{-1}$), but discrepancies are
162 somewhat scattered [$\sigma_{\Delta}(\text{LDA}) = 10\text{ cm}^{-1}$; the maximum overestimation and underestimation are 15
163 and -25 cm^{-1} , respectively; Table 1]. The Hartree-Fock Hamiltonian (HF) largely overestimates
164 frequency up to 90 cm^{-1} , with an average discrepancy of 38 cm^{-1} .

165 Concerning the relative performances of the different Hamiltonians, our results are in line
166 with those obtained by Zicovich-Wilson *et al.* (2004); Demichelis *et al.* (2010) and De La Pierre *et*
167 *al.* (2011). Moreover, the importance of correcting the DFT exchange functional by using fraction
168 of Hartree-Fock exchange (as in WC1LYP, B3LYP and PBE0) has been recently stated by
169 Többsens and Kahlenberg (2011).

170

171 **4.2 Experimentally determined frequencies**

172 The mode assignment as obtained by Raman spectra was done by comparing cross and
173 parallel polarized spectra, only the symmetry allowed B_g modes are expected for cross polarization
174 (with non-vanishing polarization tensors elements a_{yz} and a_{xz}). The present assignments (Table 2)
175 are in good agreement with those from quantum mechanical calculations (WC1LYP Hamiltonian)
176 and with those done by previous authors (Etchepare, 1972; Swamy *et al.*, 1997). In cross polarized
177 setting, however, some of the strong A_g bands were invariably found. This is related to spectral
178 leakage (McMillan & Hofmeister, 1988). Leakage in polarized Raman spectra in pyroxenes was
179 observed by Swamy *et al.* (1997) in diopside and Ghose *et al.*, (1994) in protoenstatite. Our efforts
180 to avoid this leakage by measuring several spectra by accurately controlling the crystal orientations
181 were not successful.

182 Few criticalities in peak assignments, as shown in Table 2, are still found mostly where

183 peaks are grouped together. The B_g- A_g peaks at 230-233 cm⁻¹ are both rather strong; their
184 assignment was resolved as a significant, although small, difference between the peak position in
185 cross and parallel polarized spectra was found: in parallel polarized spectra only the A_g feature is
186 observed.

187 In the range 307 and 323 cm⁻¹ four peaks (2 A_g +2 B_g) are predicted. The Raman feature
188 observed at 302 cm⁻¹ could be ascribed to the B_g calculated at 307 cm⁻¹, whereas of the two
189 predicted peaks at 314 and 323 cm⁻¹ (A_g and B_g respectively) only one was observed at about 311
190 cm⁻¹, here and in Swamy *et al.* (1997); as it was not observed in cross polarization it was assigned
191 to A_g, contrary to the previous B_g mode assignment by Swami *et al.* (1997). No experimental
192 evidence for the B_g mode predicted at 323 cm⁻¹ was obtained in cross polarization here and in
193 literature, likely because it is too faint to be observed and masked by the leakage of the strong A_g
194 peak predicted at 327 cm⁻¹.

195 Calculations predict three Raman peaks at 359, 362 and 370 cm⁻¹ of A_g, B_g, and B_g
196 symmetries, respectively. However, only two peaks were observed in the Raman spectrum, and
197 their assignment is uncertain: the peak at 356-360 cm⁻¹ was assigned as B_g by Etchepare (1972) and
198 A_g by Swamy *et al.* (1997); the B_g peak at 367 cm⁻¹ was observed here, by Swamy *et al.* (1997)
199 and Richet *et al.* (1998). The peak at 356 cm⁻¹ has been resolved in crossed polarization, its
200 intensity being very small in parallel polarization, and therefore it was ascribed to B_g symmetry. In
201 parallel polarization, when observed, a peak is found at 360 cm⁻¹, suggesting that it is the position
202 of an A_g peak.

203 Predicted B_g features at 908 and 972 cm⁻¹ cannot be clearly detected in Raman spectra; their
204 peak profile could not be refined and only their maximum positions are measured. Also the peak at
205 708 cm⁻¹ is faint, and it was above significance only in two spectra. It was detected these peaks
206 give the higher deviation from the calculated spectrum, here and in literature.

207 At 1047 and 1050 cm⁻¹ two peaks, A_g and B_g are predicted. We observed a single peak at
208 1048 cm⁻¹, irrespectively from the polarization geometry setting. Swamy *et al.* (1997) and Chopelas

209 *et al.* (2002) report the two peaks, in a dubitative manner, without evidence for the split. We suggest
210 here that both peaks are close at 1048 cm^{-1} , and both are reported in Table 2.

211 As a final consideration we notice that the peaks whose assignment was critical are faint or
212 very faint, and can be accurately controlled using polarization geometry. Routine analytical Raman
213 practice takes advantage of few strong peaks, whose assignment is certain, with very small
214 differences between experimental and calculated position.

215

216 **4.3. Normal modes**

217 The general very good agreement between the calculated and the experimental spectra,
218 allows us to discuss about the motion of the atoms within each normal mode; indeed, the relevant
219 information is contained in the eigenvectors of the Hessian matrix, whose diagonalization provides
220 the vibrational frequencies discussed above. CRYSTAL09 (Dovesi *et al.*, 2009) provides several
221 ways to analyse such normal modes, such as the *building units decomposition*, the isotopic shifts or
222 the direct graphical representation. Animations of the normal modes of diopside, as obtained in this
223 work, are provided at the web address

224 <http://www.personalweb.unito.it/mauro.prencipe/vibs/diopside>.

225 As concerns the A_g symmetry, by looking at the animations, it is found that the modes at
226 142 and 235 cm^{-1} can be mainly assigned to tilting of the Si-centred tetrahedra; the modes at 182
227 and 314 cm^{-1} are respectively due to the Ca and Mg vibrations (associated to a tilting of the
228 tetrahedra), whereas the mode at 255 cm^{-1} involves the motion of both Ca and Mg. The modes at
229 frequencies in the $[327, 390\text{ cm}^{-1}]$ range can be associated to tetrahedral tilting, whereas the modes
230 at 515 and 535 cm^{-1} are largely due to O-Si-O bending motion. The A_g mode at 671 cm^{-1}
231 correspond to the Si-O_{br}-Si bending, being O_{br} the bridging oxygen between tetrahedra in the
232 pyroxene tetrahedral chain. The Si-O_{br} stretching mode is at 855 cm^{-1} , whereas the symmetric and
233 anti-symmetric Si-O1, Si-O2 stretchings are at 1013 and 1047 cm^{-1} , respectively.

234 Concerning the modes having B_g symmetry, the three at lowest frequencies are due to Ca
235 vibrations, mixed with chain rotations (168 cm^{-1}) and tetrahedral tilting (199 cm^{-1}); Mg is mainly
236 responsible for the modes at 370 , 397 and 466 cm^{-1} (together with tilting and bending of the
237 tetrahedra), whereas the mode at 323 cm^{-1} involves the motion of both Ca and Mg. The mode at 362
238 cm^{-1} is related to the tilting of the tetrahedra. $\text{Si-O}_{\text{br}}\text{-Si}$ and $\text{O}_{\text{br}}\text{-Si-O}_{\text{br}}$ vibrations occur at 517 and
239 565 cm^{-1} . The Si-O_{br} symmetric and anti-symmetric stretching modes occur at 718 and 972 cm^{-1} ,
240 respectively, whereas the symmetric and anti-symmetric Si-O1 , Si-O2 stretching modes are found
241 to be at 908 and 1050 cm^{-1} , respectively.

242

243 **5. Conclusions**

244 Due to the very high cost of the computational evaluation of the exact non local Hartree-
245 Fock (HF) exchange, when plane wave basis sets are employed, hybrid HF/DFT Hamiltonians are
246 rarely used in solid state calculations, purely DFT Hamiltonians are preferred, at both the LDA and
247 GGA levels of the theory. However, the use of localized atomic basis sets, as in the present case,
248 allows for the calculation of the HF exchange at a relatively low cost, so that hybrid Hamiltonians
249 can effectively be used. The advantages of the HF/DFT approach are evident in their ability to
250 reproduce the experimental spectra, so that correct assignments of the Raman sfeatures can reliably
251 be done, even in spectral regions having an high density of vibrational modes. This is possible as
252 the average absolute discrepancies of the calculated frequencies with respect to the experimental
253 ones ($\langle|\Delta| \rangle$) are below $4\text{-}5\text{ cm}^{-1}$ (WC1LYP and B3LYP), whereas such figures can be much higher
254 for purely DFT Hamiltonians ($\langle|\Delta| \rangle=18\text{ cm}^{-1}$ for PBE).

1 **References**

- 2
- 3 Adamo, C. & Barone, V. (1999): Toward reliable density functional methods without adjustable
4 parameters: the PBE0 model. *Journal of Chemical Physics*, **110**, 6158-6170.
- 5 Becke, A.D. (1993): Density-functional thermochemistry 3. The role of exact exchange. *Journal of*
6 *Chemical Physics*, **98**, 5648-5652.
- 7 Chopelas, A. & Serghiou, G. (2002): Spectroscopic evidence for pressure-induced phase transitions
8 in diopside. *Phys. Chem. Minerals*, **29**, 403-408.
- 9 Civalleri, B., D'Arco, Ph., Orlando, R., Saunders, V.R., Dovesi, R. (2001): Hartree-Fock geometry
10 optimisation of periodic systems with the CRYSTAL code. *Chemical Physics Letters*, **348**,
11 131-138.
- 12 Damen, T.C., Porto, S.P.S., Tell, B. (1966): Raman effect in zinc oxide. *Phys. Rev.*, **142**, 570-574.
- 13 De La Pierre, M., Orlando, R., Maschio, L., Doll, K., Ugliengo, P., Dovesi, R. (2011): Performance
14 of six functionals (LDA, PBE, PBESOL, B3LYP, PBE0, and WC1LYP) in the simulation
15 of vibrational and dielectric properties of crystalline compounds. The case of forsterite
16 Mg_2SiO_4 . *Journal of Computational Chemistry*, **32**, 1775-1784.
- 17 Demichelis, R., Civalleri, B., Ferrabone, M., Dovesi, R. (2010): On the performance of eleven DFT
18 functionals in the description of the vibrational properties of aluminosilicates. *International*
19 *Journal of Quantum Chemistry*, **110**, 406-415.
- 20 Dirac, P.A.M. (1930): Note on Exchange Phenomena in the Thomas Atom. *Mathematical*
21 *Proceedings of the Cambridge Philosophical Society*, **26**, 376-385.
- 22 Dovesi, R., Saunders, V. R., Roetti, C., Orlando, R., Zicovich-Wilson, C. M., Pascale, F., Civalleri,
23 B., Doll, K., Harrison, N. M., Bush, I. J., D'Arco, P., Llunell, M. (2009): CRYSTAL09
24 User's Manual. University of Torino, Torino.
- 25 Downs, R. T. (2006): The RRUFF Project: an integrated study of the chemistry, crystallography,
26 Raman and infrared spectroscopy of minerals. Program and Abstracts of the 19th General
27 Meeting of the International Mineralogical Association in Kobe, Japan, O03-13.
- 28 Etchepare, J. (1972): Study by Raman spectroscopy of crystalline and glassy diopside. Douglas
29 R.W., Ellis B. ed., Amorphous materials International Conference on Noncrystalline Solids,
30 Wiley Interscience, London, 337-346.
- 31 Huang, E., Chen, C.H., Huang, T., Lin, E.H., Xu Ji-An (2000): Raman spectroscopic characteristics
32 of Mg-Fe-Ca pyroxenes. *American Mineralogist*, **85**, pages 473-479.
- 33 Koch, W., and Holthausen, M.C. (2000): A chemist's guide to density functional theory. Wiley-
34 VCH Verlag GmbH, Weinheim.

- 35 Lee, C., Yang, W., Parr, R.G. (1988): Development of the Colle-Salvetti correlation-energy formula
36 into a functional of the electron density. *Phys. Rev. B*, **37**, 785–789.
- 37 Matsui, M. (1996 b): Molecular dynamics simulation of structures, bulk moduli, and volume
38 thermal expansivities of silicate liquids in the system CaO–MgO–Al₂O₃– SiO₂. *Geophys.*
39 *Res. Lett.*, **23**, 395-398.
- 40 Monkhorst, H.J., and Pack, J.D. (1976): Special points for Brillouin-zone integration. *Physical*
41 *Review B*, **8**, 5188-5192.
- 42 Pascale, F., Tosoni, S., Zicovich-Wilson, C.M., Ugliengo, P., Orlando, R., and Dovesi, R. (2004a):
43 Vibrational spectrum of brucite Mg(OH)₂: a periodic *ab initio* quantum-mechanical
44 calculation including oh anharmonicity. *Chemical Physics Letters*, **396**, 4-6.
- 45 Pascale, F., Zicovich-Wilson, C.M., Lopez Gejo, F., Civalleri, B., Orlando, R., and Dovesi, R.
46 (2004b): The calculation of the vibrational frequencies of crystalline compounds and its
47 implementation in the CRYSTAL code. *Journal of Computational Chemistry*, **25**, 888-897.
- 48 Pascale, F., Zicovich-Wilson, C.M., Orlando, R., Roetti, C., Ugliengo, P., and Dovesi, R. (2005a):
49 Vibration frequencies of Mg₃Al₂Si₃O₁₂ pyrope. An *ab initio* study with the CRYSTAL code.
50 *Journal of Physical Chemistry B*, **109**, 6146-6152.
- 51 Pascale, F., Catti, M., Damin, A., Orlando, R., Saunders, V.R., and Dovesi R. (2005b): Vibration
52 frequencies of Ca₃Fe₂Si₃O₁₂ andradite: An *ab initio* study with the CRYSTAL code. *Journal*
53 *of Physical Chemistry B*, **109**, 18522-18527.
- 54 Perdew, J.P., Burke, K., and Ernzerhof, M. (1996): Generalized gradient approximation made
55 simple. *Physical Review Letters*, **77**, 3865–3868.
- 56 Pilati, T., Demartin, F., and Gramaccioli, C.M. (1996): Lattice-dynamical evaluation of atomic
57 displacement parameters of minerals and its implications; the example of diopside.
58 *American Mineralogist*, **81**, 811-821.
- 59 Pisani, C., Dovesi, R., and Roetti, C. (1988): Hartree-Fock *ab-initio* treatment of crystalline
60 systems. *Lecture notes in chemistry*, **48**, Springer, Berlin Heidelberg New York.
- 61 Prencipe, M., Tribaudino, M., Pavese, A., Hoser, A., Reehuis, M. (2000): A single-crystal neutron
62 diffraction investigation on diopside at 10 K. *Canadian Mineralogist*, **38**, 183-189.
- 63 Prencipe, M., Pascale, F., Zicovich-Wilson, C.M., Saunders, V.R., Orlando, R., and Dovesi, R.
64 (2004): The vibrational spectrum of calcite (CaCO₃): an *ab initio* quantum-mechanical
65 calculation. *Physics and Chemistry of Minerals*, **31**, 559-564.
- 66 Prencipe, M., Noel, Y., Civalleri, B., Roetti, C., and Dovesi, R. (2006): Quantum-mechanical
67 calculation of the vibrational spectrum of beryl (Al₄Be₆Si₁₂O₃₆) at the Γ point. *Physics and*
68 *Chemistry of Minerals*, **33**, 519-532.

- 69 Prencipe, M., Noel, Y., Bruno, M., Dovesi, R. (2009): The vibrational spectrum of lizardite-1T
70 $[\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4]$ at the Γ point: a contribution from an *ab initio* periodic B3LYP
71 calculation. *American Mineralogist*, **94**, 986-994.
- 72 Prencipe, M., Scanavino, I., Nestola, F., Merlini, M., Civalleri, B., Bruno, M., Dovesi, R. (2011):
73 High-pressure thermo-elastic properties of beryl ($\text{Al}_4\text{Be}_6\text{Si}_{12}\text{O}_{36}$) from *ab initio* calculations,
74 and observations about the source of thermal expansion. *Physics and Chemistry of Minerals*,
75 **38**, 223-239.
- 76 Richet, P., Mysen, B.O., Ingrin, J. (1998): High-temperature X-ray diffraction and Raman
77 spectroscopy of diopside and pseudowollastonite. *Physics and Chemistry of Minerals*, **25**,
78 401-414.
- 79 Swamy, V., Dubrovinsky, L.S., Matsui, M. (1996b): High-temperature Raman spectroscopy and
80 quasi-harmonic lattice dynamic simulation of diopside. *Physics and Chemistry of Minerals*,
81 **24**, 440-446.
- 82 Többens, D.M., Kahlenberg, V. (2011): Improved DFT calculation of Raman spectra of silicates.
83 *Vibrational Spectroscopy*, **56**, 265-272.
- 84 Tomisaka, T., Iishi, K. (1980): Some aspects of the lattice dynamics of diopside. *Mineral J*, **10**, 84-
85 96.
- 86 Ungureanu, C.G., Prencipe, M., Cossio, R. (2010): *Ab initio* quantum-mechanical calculation of
87 CaCO_3 aragonite at high pressure: thermodynamic properties and comparison with
88 experimental data. *European Journal of Mineralogy*, **22**, 693-701.
- 89 Valenzano, L., Noel, Y., Orlando, R., Zicovich-Wilson, C.M., Ferrero, M., and Dovesi, R. (2007):
90 *Ab Initio* vibrational spectra and dielectric properties of carbonates: magnesite, calcite and
91 dolomite. *Theoretical Chemistry Accounts*, **117**, 991-1000.
- 92 Vosko, S.H., Wilk, L. and Nusair, M. (1980): Accurate spin-dependent electron liquid correlation
93 energies for local spin density calculations: a critical analysis. *Canadian Journal of Physics*,
94 **58**, 1200-1211.
- 95 Wu, Z. and Cohen, R.E. (2006): More accurate generalized gradient approximation for solids. *Phys.*
96 *Rev. B*, **73**, 235116.
- 97 Zicovich-Wilson, C.M., Pascale, F., Roetti, C., Saunders, V.R., Orlando, R., Dovesi, R. (2004):
98 Calculation of the Vibration Frequencies of α -Quartz: The Effect of Hamiltonian and Basis
99 Set. *Journal of Computational Chemistry*, **25**, 1873-1881.

Sym	WC1LYP		B3LYP		PBE0		PBE		WCPBE		LDA		HF	
	ν	ν	Δ	ν	Δ	ν	Δ	ν	Δ	ν	Δ	ν	Δ	
B_g	120	116	-4	117	-3	111	-9	116	-4	119	-1	122	1	
A_g	142	137	-6	143	1	134	-8	141	-1	148	6	150	8	
B_g	168	167	-1	166	-2	160	-8	162	-6	164	-4	180	13	
A_g	182	180	-2	183	1	175	-7	180	-3	184	2	193	10	
B_g	199	196	-3	200	1	190	-9	194	-5	198	-1	211	12	
B_g	233	229	-4	233	0	221	-12	227	-6	232	-1	248	15	
A_g	235	235	-1	234	-2	222	-13	226	-10	232	-4	251	16	
A_g	256	253	-3	257	1	244	-11	249	-7	254	-2	274	19	
B_g	307	305	-3	308	1	292	-15	299	-9	305	-2	321	14	
A_g	314	307	-7	314	0	299	-15	309	-5	317	2	317	3	
B_g	323	311	-13	326	2	308	-16	324	1	339	15	336	12	
A_g	327	321	-6	328	1	312	-15	321	-7	327	0	346	19	
A_g	359	351	-8	362	3	344	-15	357	-3	371	12	383	24	
B_g	362	356	-5	361	0	344	-17	355	-7	370	8	383	21	
B_g	370	370	0	372	2	355	-15	361	-9	362	-8	400	30	
A_g	391	387	-4	393	2	372	-18	385	-6	396	5	421	30	
B_g	397	396	-1	398	1	377	-20	385	-12	392	-5	429	32	
B_g	466	463	-3	469	3	448	-18	459	-7	472	5	499	33	
B_g	517	517	1	523	6	494	-23	500	-17	503	-14	575	58	
A_g	515	518	4	519	5	490	-25	494	-20	492	-23	577	62	
A_g	535	535	1	537	2	511	-23	518	-17	519	-16	585	50	
B_g	565	569	4	572	8	540	-24	546	-19	540	-25	632	67	
A_g	671	671	0	680	8	641	-30	651	-21	657	-15	744	73	
B_g	718	715	-3	725	7	686	-32	697	-21	712	-6	782	64	
A_g	855	850	-4	870	15	816	-39	834	-20	858	3	929	74	
B_g	908	901	-7	919	11	875	-33	893	-15	911	3	977	68	
B_g	972	971	-2	988	16	930	-42	948	-24	970	-3	1062	90	
A_g	1013	1007	-6	1025	12	979	-34	994	-19	1016	3	1086	73	
A_g	1047	1038	-8	1059	12	1011	-36	1030	-17	1057	10	1124	77	
B_g	1050	1042	-8	1063	13	1016	-34	1034	-16	1062	12	1121	71	
	$\langle \Delta \rangle$		4		5		21		11		7		38	
	σ_Δ		4		5		10		7		10		28	
	Max. overestimation		4		16		-		1		15		90	
	Max. underestimation		-13		-3		-42		-24		-25		-	

Table 1: Results of normal modes frequency calculation using different Hamiltonians.

100
101
102

Calc (WC1LYP)	Exp1		Exp2		Exp3		Exp4		Exp5		Exp6	
	ν	Δ	ν	Δ	ν	Δ	ν	Δ	ν	Δ	ν	Δ
<i>A_g</i> modes												
142	141	1	140	2	140	2	139	3	140	2		
182	181	0	182	0	182	0	184	-2	183	-1		
235	233	2	235	0	235	0			234	1		
256	255	1	256	0	256	0	258	-2	257	-1	255	1
314	311	3										
327	323	4	326	1	326	1	329	-2	325	2	325	2
359	360	1	360	-1	360	-1	363	-4	362	-3	360	-1
391	389	2	390	1	390	1			391	0		
515	509	6	508	7	508	7			509	6	508	7
535	529	6	530	5	530	5	537	-2	531	4	528	7
671	667	4	668	3	668	3	675	-4	668	3	665	6
855	856	-1	858	-3	856	-1			857	-2	852	3
1013	1013	0	1016	-3	1014	-1	1011	2	1015	-2	1012	1
1047	1047	0			1049	-2			1033	14		
<i>B_g</i> modes												
120			118	2	113	7			115	5		
168	164	4	169	-1	163	5	168	0	166	2		
199	195	5	198	1	194	5	197	2	196	3		
233	230	3	232	1	229	4	233	0	231	2	230	3
307	302	5	305	2	301	6	306	1	303	4		
323					310	13						
362	356	6	358	4					357	5		
370	367	3			367	3	372	-2				
397	391	6	395	2	392	5	397	0	393	4	392	5
466	463	3	468	-2	465	1	471	-5	466	0		
517	515	2	517	0	515	2	514	3	517	0		
565	559	6	560	5	560	5	566	-1	561	4	559	6
718	709	9	710	8	710	8			708	10		
908	915	-7	920	-12	917	-9			917	-9		
972	964	8			971	1						
1050	1047	3	1050	0	1051	-1	1045	5	1050	0	1048	2
< Δ >		3.6		2.6		3.5		2.2		3.6		3.7
Max. Overestim.		9		8		13		5		14		7
Max. Underestim.		-7		-12		-9		-5		-9		-1

104 Table 2: Experimental (Exp) and calculated (calc) frequencies (ν , cm^{-1}) of Raman active modes.
105 Mode assignment from quanto-mechanical analysis in first column, and compared with
106 experimental datasets on diopside. Exp 1, 2 and 3 were done in defined polarization geometry and
107 give a mode assignment, as reported in the first column. The difference between experimental and
108 calculated frequencies is reported (Δ , cm^{-1}). Exp1 are frequencies measured in this work, whereas

109 Exp2 to Exp6 are taken from literature [(Exp2: Etchepare, 1972; Exp3: Swamy *et al.*, 1997; Exp4:
110 Richet *et al.*, 1998; Exp5: Chopelas & Sergiou, 2002; Exp6: Huang *et al.*, 2000)].

