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Abstract Introduction Experimental Computational details Raman spectroscopy Results and discussion Comparison between different Hamiltonians Experimentally determined frequencies Normal modes Conclusions

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

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**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<sup>-1</sup> (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 (CaMgSi<sub>2</sub>O<sub>6</sub>) 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 Ag 13 and 16 Bg Raman-active modes (Etchepare, 1972; Tomisaka & Ishi, 1980). Although the signals from most of them are rather weak to be detected, careful Raman spectroscopic experimental 14 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 order to assign the observed signals to specific vibrational modes, the frequencies of the vibrational 17 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 assignment also in 26 minerals having a relatively complex structure like diopside. Such *ab-initio* approach has been

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

34

#### 35 **2.** Computational details

Geometry optimization and spectral calculations on diopside were performed by means of
the *ab-initio* CRYSTAL09 code (Dovesi *et al.*, 2009), which implements the Hartree-Fock and
Kohn-Sham, Self Consistent Field (SCF) method for the study of periodic systems (Pisani *et al.*,
1988), by using a Gaussian type basis set. The latter consists of a 86-511d3G contraction for Ca
(Prencipe *et al.*, 2004), a 85-11d1G contraction for Mg (Valenzano *et al.*, 2007) and 88-31d1G and
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 al., 2005a; Pascale et al., 2005b; Prencipe et al., 2009). WC1LYP is based on the relatively new 54 55 DFT exchange functional proposed by Wu & Cohen (2006), mixed to the HF exchange (16%) and coupled with the LYP correlation functional of Lee et al. (1988); though not being extensively 56 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  $(n_r, n_{\omega})p$  indicates a pruned grid with  $n_r$  radial points and  $n_{\omega}$  angular 68 points on the Lebedev surface in the most accurate integration region (see the ANGULAR keyword in the CRYSTAL09 user's manual, Dovesi et al., 2009). Such a grid corresponds to 115447 69 70 integration points in the primitive unit cell. The accuracy of the integration can be measured from the error in the integrated total electron density, which amounts to  $-4 \cdot 10^{-5}$  |e| for a total of 216 71 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 the total energy, in the SCF cycles, was set to 10<sup>-10</sup> hartree (TOLDEE parameter in CRYSTAL09). 90 91 Raman spectroscopy.

92

#### 93 **3. Experimental details**

94 A single crystal of pale green diopside from rhodingitic 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 (Ca<sub>0.99</sub>Na<sub>0.01</sub>)(Mg<sub>0.94</sub>Fe<sub>0.07</sub>)Si<sub>1.99</sub>O<sub>6</sub>, The crystal has a tabular shape, sized  $6x5x1 \text{ mm}^3$  and elongated along the cleavage, i.e. along the c axis. The crystal orientation was 98 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 apparatus, with spatial resolution of  $\sim 1 \, \text{um}$  and a spectral resolution of  $\sim 1 \, \text{cm}^{-1}$ . The 632.8 nm line 101 102 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 **a**\*, **b** and **c** crystallographic axes, hereafter referred as **x**, **y** and **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 **a**<sup>\*</sup>, **b** and **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 the strongest peak in each spectrum are reported in Tables S2 and S3 (deposited). The collected 114 115 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 error between the 18 measured positions in the strong and well resolved peaks at 667 and 1013 cm<sup>-1</sup> 119 was calculated: the value are respectively 666.7(5) and 1013.6(3)  $\text{cm}^{-1}$ , with a standard deviation 120 below the experimental uncertainty of  $\approx 1 \text{ cm}^{-1}$  usually taken for Raman spectroscopy. 121

- 122 Experimentally measured Raman frequencies are reported in Table 2, together with the123 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  $\Gamma_{tot} = 14A_g + 14A_u + 16B_g + 16B_u$ 

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

- 157 value; the corresponding experimental datum is about 920 cm<sup>-1</sup>). 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
- and -25 cm<sup>-1</sup>, respectively; Table 1]. The Hartree-Fock Hamiltonian (HF) largely overestimates
- 164 frequency up to 90 cm<sup>-1</sup>, with an average discrepancy of 38 cm<sup>-1</sup>.
- 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 Többens 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 parallel polarized spectra, only the symmetry allowed B<sub>g</sub> modes are expected for cross polarization 173 (with non-vanishing polarization tensors elements  $a_{yz}$  and  $a_{xz}$ ). The present assignments (Table 2) 174 175 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<sub>g</sub> 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

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

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

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

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

207 At 1047 and 1050 cm<sup>-1</sup> two peaks,  $A_g$  and  $B_g$  are predicted. We observed a single peak at 208 1048 cm<sup>-1</sup>, 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  $1048 \text{ cm}^{-1}$ , and both are reported in Table 2.

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

215

#### 216 4.3. Normal modes

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

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

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

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

242

#### 243 **5.** Conclusions

244 Due to the very high cost of the computational evaluation of the exact non local Hartree-Fock (HF) exchange, when plane wave basis sets are employed, hybrid HF/DFT Hamiltonians are 245 246 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 ones ( $<|\Delta|>$ ) are below 4-5 cm<sup>-1</sup> (WC1LYP and B3LYP), whereas such figures can be much higher 253 for purely DFT Hamiltonians ( $<|\Delta|>=18 \text{ cm}^{-1}$  for PBE). 254

# 1 **References** 2

- Adamo, C. & Barone, V. (1999): Toward reliable density functional methods without adjustable
   parameters: the PBE0 model. *Journal of Chemical Physics*, **110**, 6158-6170.
- Becke, A.D. (1993): Density-functional thermochemistry 3. The role of exact exchange. *Journal of Chemical Physics*, 98, 5648-5652.
- Chopelas, A. & Serghiou, G. (2002): Spectroscopic evidence for pressure-induced phase transitions
  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.
- De La Pierre, M., Orlando, R., Maschio, L., Doll, K., Ugliengo, P., Dovesi, R. (2011): Performance
   of six functionals (LDA, PBE, PBESOL, B3LYP, PBE0, and WC1LYP) in the simulation
   of vibrational and dielectric properties of crystalline compounds. The case of forsterite
   Mg<sub>2</sub>SiO<sub>4</sub>. *Journal of Computational Chemistry*, **32**, 1775-1784.
- Demichelis, R., Civalleri, B., Ferrabone, M., Dovesi, R. (2010): On the performance of eleven DFT
   functionals in the description of the vibrational properties of aluminosilicates. *International Journal of Quantum Chemistry*, **110**, 406-415.
- Dirac, P.A.M. (1930): Note on Exchange Phenomena in the Thomas Atom. *Mathematical Proceedings of the Cambridge Philosophical Society*, 26, 376-385.
- Dovesi, R., Saunders, V. R., Roetti, C., Orlando, R., Zicovich-Wilson, C. M., Pascale, F., Civalleri,
  B., Doll, K., Harrison, N. M., Bush, I. J., D'Arco, P., Llunell, M. (2009): CRYSTAL09
  User's Manual. University of Torino, Torino.
- Downs, R. T. (2006): The RRUFF Project: an integrated study of the chemistry, crystallography,
   Raman and infrared spectroscopy of minerals. Program and Abstracts of the 19th General
   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
- R.W., Ellis B. ed., Amorphous materials International Conference on Noncrystalline Solids,
  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.
- Koch, W., and Holthausen, M.C. (2000): A chemist's guide to density functional theory. Wiley VCH Verlag GmbH, Weinheim.

- Lee. C., Yang, W., Parr, R.G. (1988): Development of the Colle-Salvetti correlation-energy formula
  into a functional of the electron density. *Phys. Rev. B*, 37, 785–789.
- Matsui, M. (1996 b): Molecular dynamics simulation of structures, bulk moduli, and volume
   thermal expansivities of silicate liquids in the system CaO–MgO–Al<sub>2</sub>O<sub>3</sub>– SiO<sub>2</sub>. *Geophys. Res. Lett.*, 23, 395-398.
- 40 Monkhrost, H.J., and Pack, J.D. (1976): Special points for Brillouin-zone integration. *Physical*41 *Review B*, **8**, 5188-5192.
- Pascale, F., Tosoni, S., Zicovich-Wilson, C.M., Ugliengo, P., Orlando, R., and Dovesi, R. (2004a):
  Vibrational spectrum of brucite Mg(OH)<sub>2</sub>: a periodic *ab initio* quantum-mechanical
  calculation including oh anharmonicity. *Chemical Physics Letters*, **396**, 4-6.
- Pascale, F., Zicovich-Wilson, C.M., Lopez Gejo, F., Civalleri, B., Orlando, R., and Dovesi, R.
  (2004b): The calculation of the vibrational frequencies of crystalline compounds and its
  implementation in the CRYSTAL code. *Journal of Computational Chemistry*, 25, 888-897.
- Pascale, F., Zicovich-Wilson, C.M., Orlando, R., Roetti, C., Ugliengo, P., and Dovesi, R. (2005a):
  Vibration frequencies of Mg<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> pyrope. An *ab initio* study with the CRYSTAL code. *Journal of Physical Chemistry B*, **109**, 6146-6152.
- Pascale, F., Catti, M., Damin, A., Orlando, R., Saunders, V.R., and Dovesi R. (2005b): Vibration
   frequencies of Ca<sub>3</sub>Fe<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> andradite: An *ab initio* study with the CRYSTAL code. *Journal 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.
- Pilati, T., Demartin, F., and Gramaccioli, C.M. (1996): Lattice-dynamical evaluation of atomic
   displacement parameters of minerals and its implications; the example of diopside.
   *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.
- Prencipe, M., Tribaudino, M., Pavese, A., Hoser, A., Reehuis, M. (2000): A single-crystal neutron
  diffraction investigation on diopside at 10 K. *Canadian Mineralogist*, 38, 183-189.
- Prencipe, M., Pascale, F., Zicovich-Wilson, C.M., Saunders, V.R., Orlando, R., and Dovesi, R.
  (2004): The vibrational spectrum of calcite (CaCO<sub>3</sub>): an *ab initio* quantum-mechanical
  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 (Al<sub>4</sub>Be<sub>6</sub>Si<sub>12</sub>O<sub>36</sub>) 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	$[Mg_3Si_2O_5(OH)_4]$ at the $\Gamma$ point: a contribution from an <i>ab initio</i> 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 (Al <sub>4</sub> Be <sub>6</sub> Si <sub>12</sub> O <sub>36</sub> ) from <i>ab initio</i> calculations,
74	and observations about the source of thermal expansion. Physics and Chemistry of Minerals,
75	<b>38</b> , 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	<b>24</b> , 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 <sub>3</sub> 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	<b>58</b> , 1200-1211.
95	Wu, Z. and Cohen, R.E. (2006): More accurate generalized gradient approximation for solids. Phys.
96	<i>Rev. B</i> , <b>73</b> , 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 $\alpha$ -Quartz: The Effect of Hamiltonian and Basis
99	Set. Journal of Computational Chemistry, 25, 1873-1881.

	WC1LYP	B3LY	P PBEO		0	PBE		WCPBE		LDA		HF	
Sym	v	v	Δ	v	Δ	V	Δ	v	Δ	v	Δ	V	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
	< \Delta >		4		5		21		11		7		38
	$\sigma_\Delta$				5		10		7		10		28
Ma	Max. overestimation				16		-		1		15		90
Max. underestimation		-13		-3		-42		-24		-25		-	

101 

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

103

Calc (WC1LYP)	Exp1	Exp1		Exp2		Exp3		Exp4		Exp5		Exp6	
v	v	Δ	V	Δ	V	Δ	v	Δ	V	Δ	v	Δ	
A <sub>g</sub> 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	
$B_{a}$ 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	010		971	1				-			
1050	1047	3	1050	0	1051	-1	1045	5	1050	0	1048	2	
< \Delta >		3.6		2.6		3.5		2.2		3.6		3.7	
Max. Overe	estim.	9		8		13		5		14		7	
Max. Underestim.		-7		-12		-9		-5		-9		-1	

104 Table 2: Experimental (Exp) and calculated (calc) frequencies (v, cm<sup>-1</sup>) of Raman active modes. 105 Mode assignment from quanto-mechanical analysis in first column, and compared with

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 ( $\Delta$ , cm<sup>-1</sup>). Exp1 are frequencies measured in this work, whereas

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