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Infrared spectra of jennite and tobermorite from first-principles

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ABSTRACT

The infrared absorption spectra of jennite, tobermorite 14 Å, anomalous tobermorite 11 Å, and normal tobermorite 11 Å are simulated within a density-functional-theory scheme. The atomic coordinates and the cell parameters are optimized resulting in structures which agree with previous studies. The vibrational frequencies and modes are obtained for each mineral. The vibrational density of states is analyzed through extensive projections on silicon tetrahedra, oxygen atoms, OH groups, and water molecules. The coupling with the electric field is achieved through the use of density functional perturbation theory, which yields Born effective charges and dielectric constants. The simulated absorption spectra reproduce well the experimental spectra, thereby allowing for a detailed interpretation of the spectral features in terms of the underlying vibrational modes. In the far-infrared part of the absorption spectra, the interplay between Ca and Si related vibrations leads to differences which are sensitive to the calcium/silicon ratio of the mineral.

1. Introduction

Concrete is a widely used building material, but its microscopic structure is not yet fully understood [1]. The main binding phase in most types of concrete consists of calcium silicate hydrates (C–S–H) and is responsible for its strength properties [2]. Therefore, it is important to characterize the microscopic structure of C–S–H. Since the C–S–H in concrete are poorly crystalline, their atomic structure cannot be solved by X-ray diffraction experiments (XRD) [3]. Moreover, the calcium to silicon (C/S) ratio can vary from 1.2 to 2.1 in a given cement paste [4].

To overcome these difficulties, research has focused on several crystalline model systems of given C/S ratio which show similar structural arrangements as C–S–H. Through XRD experiments, Bernal et al. showed similarities between C–S–H in cement paste and tobermorite, a mineral that can be found in nature [5]. Similarly, the mineral jennite is often considered to describe the properties of C–S–H with higher C/S ratios [6]. Jennite and tobermorite are both mostly composed of Ca–O sheets connected on both sides by infinite silicate chains named 'dreierketten' [1]. These chains give rise to typical signatures identifying twofold coordinated Si tetrahedra in both nuclear magnetic resonance [7,8] and Raman spectroscopy [9] experiments. The Ca – O sheets in jennite are corrugated [10] giving a C/S ratio much larger than that of tobermorite (1.5 for jennite vs. 0.83 or less for tobermorite). Tobermorite and jennite structures generally serve as starting point for the construction of C–S–H models [8,3,11], which are then used to advance our understanding of this phase. These minerals have been the object of extensive experimental investigation in the last decade. Merlino, Bonaccorsi and co-workers have characterized the structures of tobermorite 11 Å [12], tobermorite 14 Å [13], and jennite [10] through XRD experiments. The proposed protonation scheme of O atoms in jennite has been confirmed later by first-principles molecular dynamics [14]. Structural properties and elastic constants have been investigated through first-principles methods for jennite and various forms of tobermorite [15].

Infrared (IR) spectroscopy techniques have also been used to investigate C–S–H of various C/S ratios [16]. IR spectroscopy is an analytical technique which is sensitive to vibrational modes, thereby indirectly providing information on the local atomic structure. To interpret the IR spectra obtained for C–S–H, analogous spectra were obtained for jennite and tobermorite [16]. IR spectra of C–S–H with a C/S ratio greater than 1.7 were found to show similarities with that of jennite, whereas those with C/S ratios lower than 1.7 resembled that of tobermorite. Theoretical modeling of infrared spectra has remained limited. The IR spectrum of tobermorite 14 Å has only been studied through semi-empirical simulations [17]. First-principles calculations of infrared spectra have been performed on small molecular clusters intended to model C–S–H [18]. However, IR spectra of tobermorite and jennite minerals have so far not been achieved through first-principles simulations.

In this work, we model the infrared absorption spectra of jennite, tobermorite 14 Å, and tobermorite 11 Å through first principles in order to provide a detailed description of the underlying active vibrational modes. For tobermorite 11 Å, we consider both the anomalous and the normal structure [12]. In particular, we aim at understanding to what extent this knowledge can be used to infer structural properties of C–S–H from their infrared spectra. Our investigation is composed of several parts. First, a fully geometrically optimized structure is obtained for each mineral and compared with previous experimental and

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theoretical studies. In particular, we analyze the structural properties leading to specific vibrational signatures. Next, the vibrational frequencies and modes are calculated and analyzed in terms of atom-specific contributions. The vibrational modes are also distinguished by considering their projections on the tetrahedra composing the silicate chains, the oxygen atoms in differing environments, the water molecules, and the OH groups. The infrared spectra are obtained by considering the coupling between the vibrational modes and an electric field. The simulated infrared spectra are found to give a good description of their experimental counterparts, allowing us to establish a correspondence between calculated and measured peaks. This correspondence provides the basis for the interpretation of the experimentally observed peaks in terms of the underlying vibrations. Finally, we highlight specific features in the absorption spectra of each mineral and relate them to their underlying structural properties. The relevance of the present results for the interpretation of the infrared spectra of C–S–H is discussed.

The article is organized as follows. In Section 2, we describe the methods used for the calculation of IR spectra and give the computational parameters. In Section 3, we describe the structures obtained upon full geometrical optimization. In Section 4, we present and analyze the vibrational modes. The IR spectra and their interpretation are given in Section 5. In Section 6, the spectra of various minerals are compared and the conclusions are drawn.

2. Methods

The simulations in this work are performed within density functional theory (DFT) [19,20] using the plane-wave implementation in the QUANTUM ESPRESSO (QE) suite of electronic structure codes [21]. We use the generalized-gradient approximation (GGA) to the exchange-correlation functional as proposed by Perdew, Burke, and Ernzerhof [22]. The interaction of the valence electrons with the nuclei and the core electrons is described through ultrasoft pseudopotentials (US-PP) [23]. All the US-PP are taken from the official website of QE. The Ca 3*s* and 3*p* semi-core states are included among the valence states. After detailed convergence tests, the kinetic energy cutoffs are set at 50 and 550 Ry for the wave functions and the electron charge density, respectively [24,25].

For the optimization of the structures, we simultaneously minimize the forces acting on the atoms and the stress acting on the cell. For the tobermorite structures, the initial atomic positions and cell parameters are taken from experimental data [12,13], while we find it more convenient to start the jennite optimization from previous coordinates found from first-principles [14]. The structural optimizations are continued until each component of the atomic forces is below 0.006 eV/Å and each component of the stress tensor is below 0.1 kbar. Jennite is simulated using a triclinic cell with two *k*-points along the shortest direction of the cell (**b** axis, see also Table 1). Tobermorite cells are simulated through monoclinic cells with 2 *k*-points along the two shortest directions (axes **a** and **b**). Convergence with respect to *k*-point sampling and size of the basis set is carefully checked.

A finite-difference method is used to build the force-constant matrix. To obtain the numerical derivatives of the forces, each atom is displaced by $+\Delta x$ and $-\Delta x$ along the three Cartesian directions. The size of the displacements results from a trade-off: it needs to be large enough to avoid numerical errors, but small enough to remain in the harmonic region of the potential. The value of the displacement is set at $\Delta x = 0.05$ Å. For jennite, we check that the vibrational density of states obtained in this way closely agrees with that obtained through density functional perturbation theory [21,26].

To simulate the infrared spectra, the coupling with an electric field is achieved within density functional perturbation theory [21,26]. We calculate the Born effective charge tensors of each atom in our model systems. The Born effective charge tensor is defined as the variation of the polarization induced by a given atomic displacement [26]:

$$Z_{I,ij} = \Omega \frac{\partial P_i}{\partial r_{Ij}}, \tag{1}$$

where P_i is the polarization along direction i, r_{Ij} is the displacement of ion I along j, and Ω is the volume of the unit cell. The high frequency dielectric constant is given by:

$$\epsilon_\infty^{ij} = \delta_{ij} + 4\pi \frac{\partial P_i}{\partial E_j}, \tag{2}$$

where E_j is the electric field along direction j.

It is convenient to introduce the oscillator strengths:

$$\mathcal{F}_i^n = \sum_{Ij} Z^*_{I,ij} \frac{\xi^n_{Ij}}{\sqrt{M_I}}, \tag{3}$$

where ξ^n_{Ij} corresponds to the displacement of atom I along j in the vibrational mode n and M_I is the mass of ion I. The real part of the dielectric function in the long wavelength limit can be written as [27–29]:

$$\epsilon_1(\omega) = \epsilon_\infty - \frac{4\pi}{3\Omega} \sum_n \frac{|\mathcal{F}^n|^2}{\omega^2 - \omega_n^2}, \tag{4}$$

and the imaginary part as:

$$\epsilon_2(\omega) = \frac{4\pi^2}{3\Omega} \sum_n \frac{|\mathcal{F}^n|^2}{2\omega_n} \delta(\omega - \omega_n). \tag{5}$$

The frequency-dependent refractive index can then be expressed in terms of the dielectric functions:

$$n(\omega) = \sqrt{\frac{\epsilon_1(\omega) + \sqrt{\epsilon_1(\omega)^2 + \epsilon_2(\omega)^2}}{2}}. \tag{6}$$

Table 1
Calculated cell parameters of jennite and tobermorite structures compared to experimental data [10,13,12]. The present results are also compared with previous DFT calculations (DFT-GGA) obtained with a single *k*-point [15]. α, β, and γ are the angles between axes **b** and **c**, **a** and **c**, and **a** and **b**, respectively.

		a (Å)	b (Å)	c (Å)	α	β	γ
Jennite	Present	10.66	7.31	10.97	100.87°	97.86°	109.31°
	DFT-GGA [15]	10.70	7.34	10.89	102.11°	95°	109.82°
	Expt. [10]	10.58	7.27	10.93	101.30°	96.98°	109.65°
Tobermorite 14 Å	Present	6.64	7.41	28.18	90.00°	89.99°	121.66°
	DFT-GGA [15]	6.87	7.43	28.49	89.96°	90.05°	123.47°
	Expt. [13]	6.74	7.43	27.99	90°	90°	123.25°
Tobermorite 11 Å (anomalous)	Present	6.82	7.47	22.70	90°	90°	123.22°
	DFT-GGA [15]	6.80	7.51	22.57	89.83°	89.05°	123.43°
	Expt. [12]	6.74	7.39	22.49	90°	90°	123.25°
Tobermorite 11 Å (normal)	Present	6.82	7.46	22.67	90.27°	89.12°	123.24°
	Expt. [12]	6.73	7.37	22.68	90°	90°	123.18°