

RESEARCH ARTICLE

Atomistic insights on the elasticity and Raman spectra of C-S-H from quantum-mechanical simulations

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Abstract

The strength of Portland cement is primarily due to the products of its hydration: Calcium silicate hydrates (C-S-H). The poorly ordered nature of these phases at the atomic scale is a limiting factor for the applicability of quantum-mechanical simulations relying on periodic boundary conditions (PBC). This is because large supercells are usually needed within PBC to capture the structural complexity of amorphous materials, with associated high, when not prohibitive, computational costs. Here, we devise a strategy to design small and symmetric PBC-compliant structural models of C-S-H with different Ca/Si ratios, allowing efficient quantum-mechanical atomistic simulations via the density functional theory (DFT). The mechanical and dynamical stability of the proposed models is assessed from DFT calculations. The effectiveness of the symmetric models in mimicking the actual disordered C-S-H phase is validated against experimental Raman spectra and bulk moduli.

KEYWORDS

C-S-H, cement, density functional theory, elastic constants, Raman spectroscopy

1 | INTRODUCTION

The calcium silicate hydrate (C-S-H) phase is the primary component responsible for the mechanical properties and durability of Portland cement. Consequently, understanding chemical and structural properties of this phase is fundamental to comprehending the behavior of cementitious materials. Several key macroscopic properties of C-S-H, such as porosity, which affects the permeability of concrete, and the distribution and size of pores, are critical parameters that determine the material's resistance to aggressive substances like sulfates and chlorides. Additionally, the interaction with water, including its ability to absorb and retain moisture, significantly impacts the hardening properties and overall durability of concrete. Beyond mechanical characteristics, the dimensional stability of C-S-H is essential for maintaining structural

integrity, as volume changes due to drying, hydration, secondary phases, and temperature variations can lead to cracking and structural failures.^{1,2}

The C-S-H phase forms during the hydration of Portland cement when calcium silicates in the clinker react with water, resulting in a complex, amorphous structure that gives the desirable properties to concrete. A detailed understanding of the formation mechanisms, atomic and molecular structure, and chemical interactions within the C-S-H phase is critical for the development of cements with optimized properties.^{1,3,4}

Atomic-scale computational modeling has emerged as an invaluable tool for the investigation and development of novel materials, allowing for the detailed examination of a wide range of properties and applications.^{5,6} In particular, the application of quantum theory, especially through the density functional theory (DFT), in materials science and

engineering has grown significantly with advances in theoretical models, data processing, and with the availability of increasingly powerful computers.^{7–9}

And yet, the structural complexity of C-S-H and in particular its amorphous nature represent a challenge to atomistic computational modeling. Indeed, quantum-mechanical calculations of materials rely on periodic (i.e., long-range ordered) structural models. Supercells containing a large number of atoms are thus required to mimic the structure of an amorphous material, which critically impacts the associated computational cost. As a consequence, many computational studies for the characterization of C-S-H have employed large structural models with thousands of atoms and classical molecular dynamics (MD) instead of quantum approaches.^{2,10–14} On the other hand, DFT is generally limited to systems with a few hundred atoms, making it less suitable for modeling highly disordered systems.^{15,16} As such, DFT studies of the C-S-H phase often resort to its crystalline analogs, such as tobermorite and jennite, with the former being one of the most studied minerals in this context.^{2,15}

In this study, we present a strategy to design small and symmetric periodic structural models of C-S-H with different Ca/Si ratios, which allows us to perform accurate DFT simulations of advanced properties of the C-S-H phase in terms of its mechanical and lattice dynamical response. We validate the effectiveness of the approach—that is, use of symmetric ordered models to mimic the actual disordered C-S-H phase—through critical comparison with experimental Raman spectra and bulk moduli.

2 | METHODS AND COMPUTATIONAL DETAILS

2.1 | Computational details

The CRYSTAL23 program for electronic structure of materials is used for all calculations reported in this study.¹⁷ The basis set of local atom-centered Gaussian-type functions (GTFs) is the same already adopted by some of the authors in a previous study on major oxides of Portland' clinker, with the addition of that of hydrogen.¹⁸ The Ca, Si, Al, Fe, O, and H atoms are described by contractions of primitive GTFs as follows: 8(s)651l(sp)2l(d), 8(s)631l(sp)l(d), 8(s)621(sp)l(d), 8(s)641l(sp)4l(d), 8(s)41l(sp)l(d), and 2(s)l(p), respectively.¹⁹ The exchange-correlation functional used is Perdew–Burke–Ernzerhof (PBE),²⁰ belonging to the generalized-gradient approximation (GGA) family, complemented by a correction for missing dispersive interactions through Grimme's-D3 approach,

referred to as PBE-D3 in what follows. The truncation thresholds for the infinite Coulomb and exchange lattice series are set to their default values in all calculations. Reciprocal space is sampled using a Monkhorst-Pack grid with a shrinking factor set to 2 for tobermorite and C-S-H, corresponding to sampling over eight independent **k**-points within the first Brillouin zone. The energy convergence criterion for the self-consistent field (SCF) procedure is set to the tight value of 10^{-10} hartree for harmonic lattice dynamics calculations.

2.1.1 | Simulated Raman spectra

Within the harmonic approximation, peak locations are derived from harmonic phonon frequencies ω_p computed at the Γ point (i.e., the center of the first Brillouin zone in reciprocal space). These frequencies are obtained by diagonalization of the mass-weighted Hessian matrix $\mathbf{W}^\Gamma$ of the second derivatives of the energy, E , with respect to atomic displacements $\mathbf{u}$. The elements of the mass-weighted Hessian matrix are defined as:

$$W_{ai,bj}^\Gamma = \frac{H_{ai,bj}^0}{\sqrt{M_a M_b}} \quad \text{where} \quad H_{ai,bj}^0 = \left. \frac{\partial^2 E}{\partial u_{ai}^0 \partial u_{bj}^0} \right|_{\text{eq}}, \quad (1)$$

where $H_{ai,bj}^0$ is the interatomic force constant between atoms a and b in the reference cell (denoted by the superscript 0), with atomic masses M_a and M_b . The subscripts i and j represent Cartesian displacement directions (x, y, z). Raman Stokes intensities I_{ij}^p for a phonon mode p associated with the component α_{ij} of the polarizability tensor α , are computed as:

$$I_{ij}^p \propto \frac{(\omega_L - \omega_p)^4}{30\omega_p \left[1 - \exp\left(-\frac{\hbar\omega_p}{K_B T}\right) \right]} \left(\frac{\partial \alpha_{ij}}{\partial Q_p} \right)_{\text{eq}}^2, \quad (2)$$

where T is the temperature (here set to 300 K), ω_L is the laser frequency (values corresponding to wavelengths of 532 and 632.8 nm are used for the simulation of tobermorite and C-S-H, respectively),²¹ $\hbar$ is the reduced Planck constant, K_B is Boltzmann's constant, and Q_p is the normal coordinate for the phonon mode p . The derivatives of the polarizability tensor with respect to normal coordinates in Equation (2) are computed analytically using the coupled-perturbed Kohn–Sham (CPKS) method.^{22,23} A Raman spectral profile is subsequently simulated from the computed phonon frequencies ω_p and intensities I_{ij}^p by superposition of Lorentzian profiles. A full width at half maximum (FWHM) value of 20 cm^{-1} is used for all simulated spectra.

2.1.2 | The elastic tensor

The fourth-order elastic tensor describes the mechanical behavior of a material in the elastic regime. Its elements, the elastic constants, are defined as second energy derivatives with respect to pairs of infinitesimal strain components:

$$C_{ijkl} = \frac{1}{V_0} \left(\frac{\partial^2 E}{\partial \epsilon_{ij} \partial \epsilon_{kl}} \right)_{\epsilon=0} \quad (3)$$

A fully automated algorithm for calculating the elastic tensor, has been implemented in the CRYSTAL program.²⁴ The elastic tensor can conveniently be represented using a two-index Voigt notation ($C_{ijkl} \rightarrow C_{vu}$), where $v, u = 1, \dots, 6$ ($1 = xx, 2 = yy, 3 = zz, 4 = yz, 5 = xz, 6 = xy$).²⁵ This symmetric 6×6 matrix has 21 independent elements for $P1$ triclinic systems, which are reduced to 13 for monoclinic systems of $P2_1/c$ space group, such as those used in this study to model tobermorite and C-S-H. Various elastic properties, such as the bulk modulus, K , shear modulus, G , Young's modulus, E , Poisson's ratio, ν , can be derived from the elastic constants.²⁵

2.2 | The search for a symmetric model for C-S-H

As already recalled, the C-S-H phase exhibits a complex, disordered structure, which requires some care in the definition of appropriate periodic boundary conditions compliant structural models. The strengths and limitations of several models that have been used to run simulations on C-S-H have recently been highlighted.² Apart from the direct use of mineral structures, no symmetric models of C-S-H have been reported. Let us note that symmetry preservation proves particularly challenging while varying the Ca/Si ratio to explore typical experimental ranges.

Here, we start from a small and symmetric model of the tobermorite mineral (characterized by a Ca/Si ratio of 0.83) proposed by Richardson as an idealized model of 11 Å clinotobermorite.²⁶ This model, graphically represented in panel (a) of Figure 1, is based on space group $C2/c$ and consists of 18 symmetry-independent atoms. Note that this model lacks information on the actual positions of the hydrogen atoms within the structure: only the positions of the oxygen atoms associated with water molecules are given. Symmetry can be reduced when hydrogen atoms are taken into account. Another common issue in complex mineral models is represented by fractional site occupancy. While the canonical approach to resolve this problem involves creating supercells to explore distinct configurations in which replicated sites can host atoms or not,

such a method conflicts with the goal of finding efficient models. We follow a different strategy to preserve stoichiometry, explicitly insert the hydrogen atoms, and resolve the issue of fractional site occupancy. The result is shown in Figure 1B: a model of space group $P2_1/c$, with 45 symmetry-independent atoms (total of 160 atoms per cell), which preserves the four symmetry operators of the starting $C2/c$ structure.

As mentioned above, one of the key challenges is the preservation of symmetry while increasing the Ca/Si ratio from 0.83 in tobermorite to higher values, as C-S-H in early-age Portland cement typically exhibits a Ca/Si ratio ranging from 1.2 to 2.1.²⁷ Figure 1C–E shows different symmetry-preserving models (all of $P2_1/c$ space group) that we have designed with Ca/Si ratios of 1.00, 1.10, and 1.38, respectively. The models were obtained by removing Si and O atoms and by adding Ca or H atoms, paying attention to the stoichiometry of the system to avoid the creation of charged structures.

Further clarifications on the models design process are provided in Figure S1 and in the corresponding discussion. Let us note that, in principle, the Ca/Si ratio could also be increased by substituting Si with Al. However, although the substitution of $[\text{SiO}_4]^{4-}$ with $[\text{AlO}_4]^{5-}$ would affect the ratio, it would not fundamentally alter the type of site. In summary, the designed models are as follows: tobermorite with Ca/Si = 0.83 and 160 atoms with chemical formula $\text{Ca}_{20}\text{Si}_{24}\text{O}_{68} \cdot 16\text{H}_2\text{O}$; C-S-H model with Ca/Si = 1.00 with 154 atoms and chemical formula $\text{Ca}_{20}\text{Si}_{20}\text{O}_{62}\text{H}_2 \cdot 16\text{H}_2\text{O}$; C-S-H model with Ca/Si = 1.10 with 152 atoms and chemical formula $\text{Ca}_{22}\text{Si}_{20}\text{O}_{62} \cdot 16\text{H}_2\text{O}$; and C-S-H model with Ca/Si = 1.38 with 140 atoms and chemical formula $\text{Ca}_{22}\text{Si}_{16}\text{O}_{54} \cdot 16\text{H}_2\text{O}$.

3 | RESULTS AND DISCUSSION

3.1 | Structure

The structure of all models has been fully optimized (atomic positions and lattice parameters) within the symmetry constraints presented in Section 2.2 (Crystallographic Information Files, CIFs, are reported in the Supporting Information). The geometry optimization process of the C-S-H models poses significant challenges due to the complex nature of their potential energy surface (PES) and the high energy starting point. The convergence to a stable, low-energy minimum is a necessary condition to ensure mechanical and dynamical stability. The accurate determination of equilibrium positions of the many hydrogen atoms within each model required a complex strategy with multiple optimizations for each model starting from different initial configurations. Moreover, the use

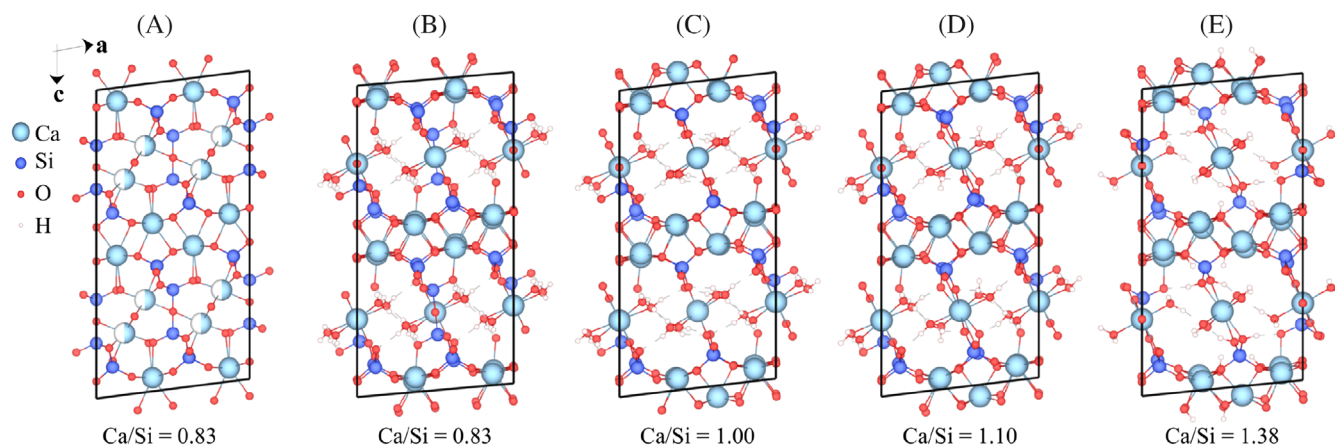


FIGURE 1 Atomic-scale structure of (A) the $C2/c$ tobermorite model²⁶; (B) the $P2_1/c$ model for tobermorite used in this study ($\text{Ca/Si} = 0.83$); (C) our $P2_1/c$ model for C-S-H with $\text{Ca/Si} = 1.00$; (D) our $P2_1/c$ model for C-S-H with $\text{Ca/Si} = 1.10$; and (E) our $P2_1/c$ model for C-S-H with $\text{Ca/Si} = 1.38$.

of tight convergence criteria on both forces and atomic displacements (10 times tighter than default settings in the CRYSTAL package) was required to ensure finding a robust, reproducible optimized structure.

To better characterize the different structural models, it is convenient to introduce some nomenclature commonly used in the study of glasses with techniques such as Raman spectroscopy, ^{29}Si and ^{17}O nuclear magnetic resonance (NMR), and oxygen 1s x-ray photoelectron spectroscopy (XPS). The most relevant features of such spectra can indeed be traced back to structural moieties constituted by differently coordinated SiO_4 tetrahedra. Each tetrahedron is denoted as Q^n , where $n = 0, 1, 2, 3, 4$ represents the number of its oxygen atoms that form Si–O–Si bridges (i.e., that are shared with neighboring tetrahedra). See Figure S2 for a graphical representation of these different structural moieties. The relative abundance of different Q^n species determines the degree of “silicon polymerization” and strongly influences chemical and physical properties of these materials, producing specific fingerprint features in the Raman spectra, see below.^{28,29}

Let us analyze the optimized structural parameters of the models with different Ca/Si ratio. For the structure with $\text{Ca/Si} = 0.83$ ($V = 1801.4 \text{ \AA}^3$), the lattice parameters are $a = 11.1368 \text{ \AA}$, $b = 7.3403 \text{ \AA}$, $c = 22.1204 \text{ \AA}$, and $\beta = 94.9940^\circ$. These values indicate a relatively elongated structure along the c axis and a β angle slightly greater than 90° , suggesting a slight distortion of the unit cell relative to Richardson’s model.²⁶ The structure presents Q^2 (20 Si atoms/cell) and Q^3 (4 Si atoms/cell) species, with an average Si–O distance of $1.64 \pm 0.03 \text{ \AA}$, Ca–O distance of $2.4 \pm 0.1 \text{ \AA}$, and with a basal spacing of $11.11 \text{ \AA}$. Increasing the Ca/Si ratio to 1.00 ($V = 1727.8 \text{ \AA}^3$), the lattice parameters undergo minor changes: $a = 11.0637 \text{ \AA}$, $b = 7.2847 \text{ \AA}$, $c = 21.5903 \text{ \AA}$, and $\beta = 96.8008^\circ$. The slight decrease

($<0.8\%$) in the a and b parameters and the decrease (2.4%) in c , along with the increase (1.9%) in the β angle, indicate a compression of the structure along the c axis (basal spacing of $10.84 \text{ \AA}$) and a greater angular distortion. The structure presents Q^1 (8 Si atoms/cell) and Q^2 (12 Si atoms/cell) species, with an average Si–O distance of 1.65 ± 0.03 and Ca–O of $2.5 \pm 0.2 \text{ \AA}$. Moreover, this model exhibits a Si–OH/Si ratio of 0.2, which agrees well with values presented by Casar et al.³⁰ In the structure with $\text{Ca/Si} = 1.10$ ($V = 1715.2 \text{ \AA}^3$), the parameter a decreased almost to the same extent as $\text{Ca/Si} = 1.00$ – $11.0600 \text{ \AA}$, with almost no modification of parameter b with $7.3281 \text{ \AA}$, and with $c = 21.3198$ and $\beta = 96.9509^\circ$, which presents a variation of -3.4% and 2.1% , respectively (basal spacing of $10.70 \text{ \AA}$). This model also only contains Q^1 (8 Si atoms/cell) and Q^2 (12 Si atoms/cell) species, with an average Si–O distance of 1.65 ± 0.04 and Ca–O of $2.5 \pm 0.1 \text{ \AA}$. At variance with the model with $\text{Ca/Si} = 1.00$, this structure does not contain any hydroxyl bond. Finally, for the structure with $\text{Ca/Si} = 1.38$ ($V = 1686.9 \text{ \AA}^3$), a slight increase in the a parameter to $11.1853 \text{ \AA}$ and a decrease in the b and c parameters to $7.1187 \text{ \AA}$ and $21.2900 \text{ \AA}$, respectively, are observed. The β angle is 95.6921° , showing a distortion similar to that observed at $\text{Ca/Si} = 1.10$ for the c parameter but with a more compact arrangement (basal spacing of $10.67 \text{ \AA}$). These values are indicative of a more compact structure in all directions, and especially along the c axis. This model exhibits Q^0 (8 Si atoms/cell) and Q^1 (8 Si atoms/cell) species, with an average Si–O distance of 1.66 ± 0.04 and Ca–O of $2.4 \pm 0.1 \text{ \AA}$. During the optimization process of the C-S-H model with Ca/Si ratio of 1.38, spontaneous dissociation of most water molecules was observed, leading to the formation of many hydroxyl bonds within the structure: only four of the initial sixteen water molecules were preserved as molecular units at the end of the optimization process. This

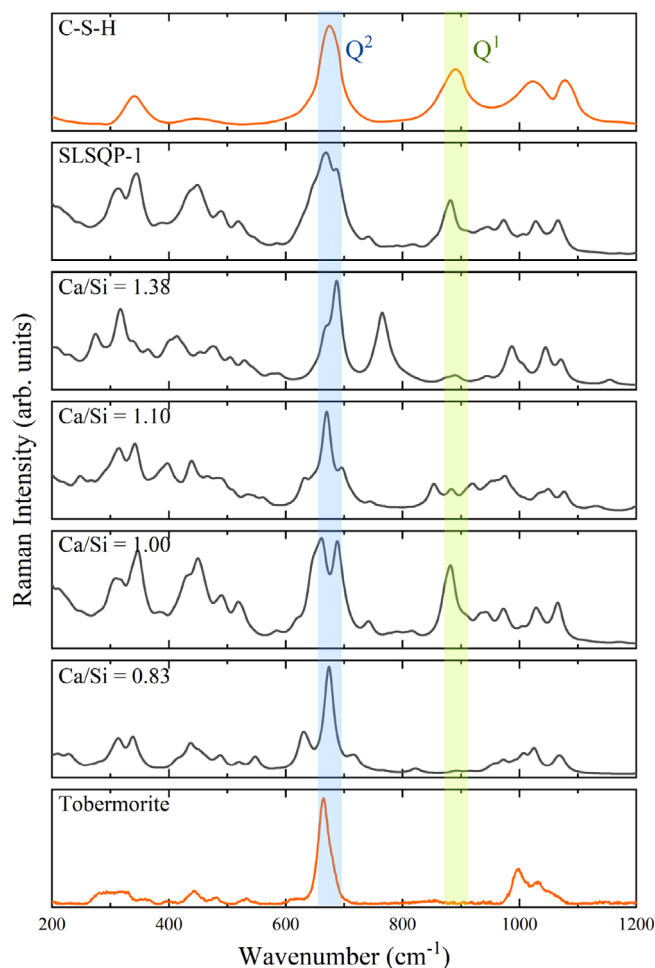


FIGURE 2 Comparison of simulated (black) and experimental^{31,32} (orange) Raman spectra, arranged from bottom to top corresponding to increasing Ca/Si ratios. The simulated spectrum obtained from SLSQP is also reported (see text for more details). Two guide lines are reported to highlight spectral regions associated with Q^2 (blue) and Q^1 (green) species.

corresponds to a Si–OH/Si ratio of 0.5 and a Ca–OH/Ca ratio of 0.6, which is outside of the proportions assumed stable by Casar et al.³⁰ We are going to further assess the (in)stability of this model below.

3.2 | Raman spectra and dynamical stability

We have performed harmonic vibration frequency calculations for all structural models, and simulated the corresponding Raman spectra. We report all simulated Raman spectra in Figure 2, where experimental data of tobermorite³¹ and C-S-H³² are also reported for comparison in the bottom and top panels, respectively. Let us start by underlining the remarkable agreement between the experimental spectrum of tobermorite and our

simulated spectrum from the tobermorite structural model with Ca/Si ratio of 0.83 (see also Figure S3 for a more detailed comparison). Apart from an overall slight blue shift of the simulated spectrum relative to the experimental one—likely due to the slight underestimation of the calculated volume by 3.4%—all main features are correctly reproduced by our model. The peaks around 628 and 674 cm^{-1} are attributed to symmetric bending vibrations of the Si–O–Si bonds of Q^3 and Q^2 species, respectively. We stress that the band width of the latter is often associated with the degree of silicon polymerization in the structure.³² Although the tobermorite model is widely recognized as one of the most reliable starting points for simulating C-S-H,² it remains a highly polymerized system, lacking Q^0 and Q^1 species that are present in C-S-H, as discussed by Ortaboy et al.³² This distinction becomes particularly evident when comparing the bottom (tobermorite) and top (C-S-H) panels in Figure 2. Indeed, the latter exhibits an intense spectral feature around 900 cm^{-1} associated to Q^1 species, which the former lacks.

The simulated spectra in Figure 2, from bottom to top, show a gradual shift in peak positions and intensities as the Ca/Si ratio increases. The vibrational modes of C-S-H are indeed sensitive to the Ca/Si composition and the changes in spectral features likely reflect variations in the local chemical environment within the C-S-H structures. Let us stress that the assignment of different spectral features to specific local bonding environments is a complex task because of water vibrations, which are present in the entire spectrum, making it challenging to decouple them from the primary peaks associated with the calcium silicate structure. We have used graphical tools for animating the atomic motions involved in the different peaks (more details in the Supporting Information). Notably, our model with a Ca/Si ratio of 1.00 produces a peak due to the symmetric stretching of Q^1 species at 880 cm^{-1} , which agrees well with the experimental counterpart (top panel). The main feature in the region of Q^2 is split into two. This occurs because the intensity and position of the bending of Q^1 are very similar to those of Q^2 for this model. This bending feature also appears at almost the same position in the models with higher Ca/Si ratios (1.10 and 1.38), although with a lower intensity. For Ca/Si = 1.10, also the symmetric stretching of Q^1 is less intense than in Ca/Si = 1.00. The Ca/Si = 1.38 spectrum shows a peak at about 764 cm^{-1} , which we assign to a Q^0 species, that is not visible in the experimental C-S-H spectrum. It is worth mentioning that the model with Ca/Si = 1.38 is the only one to show some degree of lattice dynamical instability (i.e., one imaginary harmonic frequency of $i20 \text{ cm}^{-1}$).

As expected, different structural models capture distinct local bonding environments. This is because of the

small, symmetric and periodic nature of the models we have devised. In order for a single structural model to capture all local chemical environments, its size should be much larger, thus making quantum-mechanical calculations prohibitive. Next, we discuss how it is possible to define a linear combination of the small structural models that mimics the actual complexity of the C-S-H amorphous phase. Chemometrics techniques are routinely applied to spectral analysis when dealing with multi-component mixtures,³³ aiming at the deconvolution of a complex spectrum into a set of simpler well-defined component spectra.^{34–37} We apply a Sequential Least-Square Programming (SLSQP) algorithm to optimize the weights of the linear combination with respect to the experimental Raman spectrum of C-S-H.³⁸ The optimization procedure is limited to the 500–1000 cm^{-1} spectral range as the most relevant peaks are found in this region, as discussed above. We start by considering all four structural models. The Raman spectrum obtained from the SLSQP simulation is reported in the second top panel of Figure 2. The agreement with the experimental spectrum is remarkable, with a Pearson correlation coefficient $r = 0.87$ and a coefficient of determination $R^2 = 0.74$. The optimal calculated weights of the linear combinations are as follows (hereafter referred to as SLSQP-1 model): Ca/Si = 0.83 (21%), Ca/Si = 1.00 (42%), Ca/Si = 1.10 (37%), and Ca/Si = 1.38 (0%). Thus, the structures with intermediate Ca/Si ratios of 1.00 and 1.10 combined contribute nearly 80% of the SLSQP-1 spectrum, and the structure with Ca/Si = 0.83 contributes nearly 20%. Interestingly, the slightly dynamically unstable structure with Ca/Si = 1.38 is fully neglected by the SLSQP algorithm in the average spectrum, likely due to the presence of the strong Q^0 spectral feature around 760 cm^{-1} that does not appear in the experimental spectrum. The improvement of such a SLSQP linear combination approach in the description of the C-S-H spectrum clearly emerges from the analysis of the coefficient of determination R^2 of the four individual spectra: 0.35 for Ca/Si = 0.83, 0.50 for Ca/Si = 1.00, 0.65 for Ca/Si = 1.10, and just 0.08 for Ca/Si = 1.38.

Let us further inspect the SLSQP-1 model, which exhibits an average Ca/Si ratio of ≈ 1.00 and a Q^1/Q^2 ratio of ≈ 0.60 . This agrees very well with findings by Tajuelo Rodriguez et al.³⁹ who determined that for Ca/Si = 1 the amount of Q^1 and Q^2 species present was 35.7% and 62.0%, respectively, corresponding to a Q^1/Q^2 ratio of ≈ 0.58 . The same authors also reported that the Q^1/Q^2 ratio is expected to increase upon increasing the Ca/Si ratio, which is ≈ 1.6 for the C-S-H experiment in Figure 2. This SLSQP-1 fitted model will be used below in the analysis of the elastic mechanical properties of the C-S-H phase.

3.3 | Elastic tensor and mechanical stability

The forth-rank elastic tensor has been computed for all structural models (the full list of computed elastic constants is provided in Table S2). According to Born's mechanical stability criteria, the elastic tensor of a mechanically stable structure must be positive definite (i.e., must exhibit all positive eigenvalues).^{18,40–44} The only structural model that is found to violate Born's criteria is that corresponding to a Ca/Si ratio of 1.38, having two negative eigenvalues (shear components ϵ_4 and ϵ_5). The analysis of its lattice dynamics reported in Section 3.2 also revealed a dynamical instability of this model. For these reasons, this model will not be further discussed.

We report the computed values of bulk modulus from the stable structural models in Figure 3 (left panel) as full green squares, and compare them with experimental values (full yellow squares),^{45–49} previously simulated values from the DFT (empty black squares),^{50,51} previous MD calculations (empty black circles),^{47,52–54} and previous lattice dynamics simulations (empty triangles).^{55,56} The structure with Ca/Si = 0.83 exhibits the largest bulk modulus among the stable models, with a value of 71 GPa, which aligns well with other theoretical predictions for 11 Å tobermorite,² and is consistent with experimental values ranging between 62 and 94 GPa.^{45,46,48,49} The structure with Ca/Si = 1.00 exhibits a lower modulus of 55 GPa, which agrees nicely with experimental measurements for this ratio spanning from 50 ± 2 to 70 ± 7 GPa.^{46,47} The decrease in bulk modulus with increasing Ca/Si ratio is expected and primarily attributed to the removal of Q^3 species, which serve as critical linkages between neighboring calcium silicate layers, as previously suggested by Jiang et al.⁵⁷ The structure with Ca/Si = 1.10 is instead characterized by a bulk modulus of 70 GPa. This difference with respect to Ca/Si = 1.00 can be explained by the introduction of a calcium atom at a special symmetry position within the interlayer. The dashed horizontal line in the left panel of Figure 3 reports the value of bulk modulus obtained by weighting the bulk moduli of the different structural models according to the weights determined by the previous SLSQP optimization. Overall, our small, symmetric and periodic structural models provide a satisfactory description of the mechanical stiffness of the C-S-H phase, at an affordable computational cost.

The evaluation of the fourth-rank elastic tensor of Equation (3) gives access to the whole anisotropic elastic response of a material. The analysis of the individual components of the tensor (i.e., the elastic constants), as well as their combination, allows to compute a variety of mechanical descriptors: bulk K and shear G moduli,

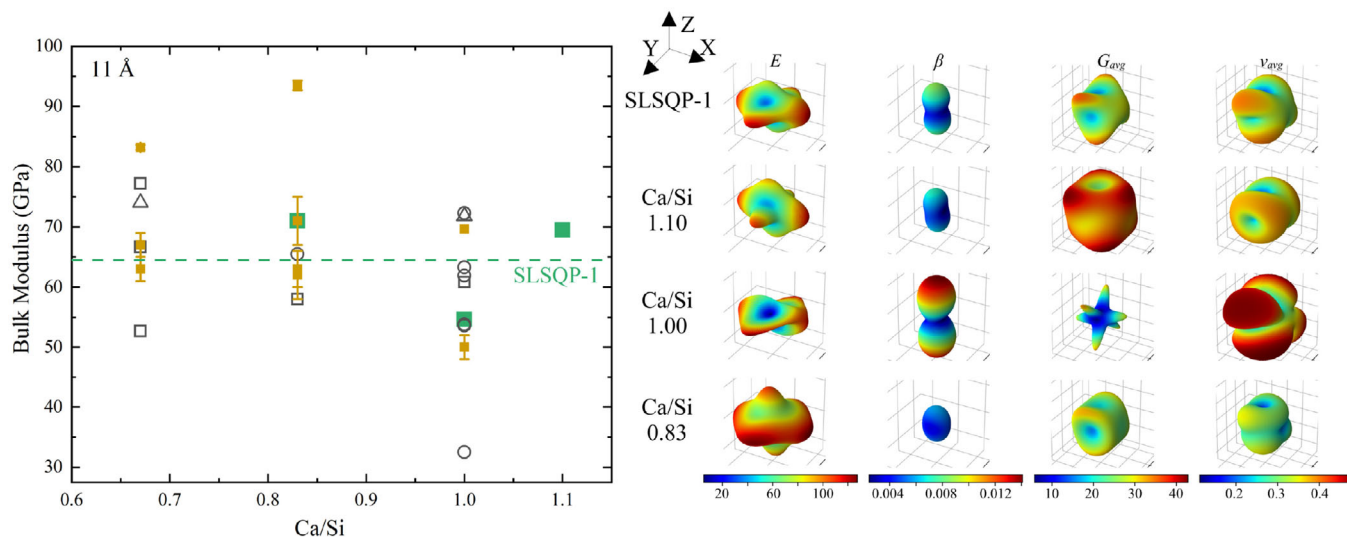


FIGURE 3 Mechanical properties of C-S-H as derived from different structural models with 11 Å tobermorite as a starting point. Left: average bulk modulus K ; present density functional theory (DFT) results are green full squares, experimental values are full yellow squares,^{45–49} previous DFT values are empty black squares,^{50,51} empty black circles are from MD calculations,^{47,52–54} and empty triangles from lattice dynamics simulations.^{55,56} Right: present DFT description of the spatial dependence of various mechanical properties (see text). The 3D plots are produced with the CRYSTALClear⁵⁸ Python interface to CRYSTAL: Young's modulus E and the average shear modulus G_{avg} are in GPa, the linear compressibility β in GPa^{-1} , and Poisson's ratio ν is dimensionless.

Young's modulus E , Poisson's ratio ν , etc. Some of these mechanical descriptors depend on one or more directions in space and their anisotropic behavior can be effectively analyzed in terms of 3D plots, which we report on the right panel of Figure 3. In particular, we report the Young modulus E (i.e., the strain response of a solid to an uniaxial stress, in the direction of the stress), the linear compressibility β (i.e., the linear strain under the application of an external hydrostatic stress), the shear modulus G (i.e., the strain response to a shear stress), and Poisson's ratio ν (i.e., the strain response in the directions orthogonal to a uniaxial stress).⁵⁹ The first two quantities depend on a single direction (and thus on two angles in spherical coordinates), whereas the latter two depend on two directions (if orthogonal, the two directions can be defined in terms of three angles in spherical coordinates). The dependence of G and ν on three angles makes their graphical representation difficult. Here, we follow the same strategy already adopted by other authors,^{60,61} where, for each first direction, the quantities are computed for all values of the third angle and the average is computed. In Figure 3, for each mechanical property, a common scale for the color-bar is used across the different structural models so as to highlight their relative mechanical behavior. Figure 3 clearly shows that there is more to the mechanical behavior of a structure than it is captured by the bulk modulus alone. For instance, the two structural models with Ca/Si ratios of 0.83 and 1.10—both characterized by almost the same value of bulk modulus around 70 GPa—show significantly

different directional mechanical properties, with distinct elastic profiles hinting at a reorientation of the stiffness components along different crystallographic axes.

4 | CONCLUSIONS

Starting from a simplified model of the tobermorite mineral of $C2/c$ space group with no hydrogen atoms and fractional occupations of different lattice sites, we have devised a set of small and symmetric models of $P2_1/c$ space group for atomic-scale quantum-mechanical simulations. All models, characterized by a different degree of “silicon polymerization,” preserve four symmetry operators and do mimic the poorly ordered, structurally complex nature of the C-S-H phase. The optimization of the different structural models posed significant challenges, particularly in the accurate determination of the equilibrium positions of hydrogen atoms, and in the spontaneous dissociation of water molecules with the formation of hydroxyl bonds in an attempt to reduce “silicon polymerization,” through the increase of the Ca/Si ratio. In particular, four distinct models have been created with Ca/Si ratio of 0.83, 1.00, 1.10, and 1.38.

The effectiveness of the models in capturing the most relevant features of the C-S-H phase, at a modest computational cost, is assessed through DFT simulations of their lattice dynamics and mechanical response. Simulated Raman spectra are compared with experimental ones,

which allows to establish that while all models do capture the spectral features related to Q^2 silicon species, some models do also capture the more elusive spectral features of Q^1 silicon species. A SLSQP algorithm has been used to optimize the weights of a linear combination of the various models to maximize the similarity between simulated and experimental spectra. The simulated elastic moduli are also found in remarkable agreement with experimental values for C-S-H. The highest value for the bulk modulus, 71 GPa, is found for the model with Ca/Si ratio of 0.83. The decrease in bulk modulus with increasing Ca/Si ratio is attributed to the reduction of Q^3 silicon species linking different calcium silicate sheets.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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