

## Supplementary Information

### Resolving interfacial THz dynamics and manifold structuring in setting cements

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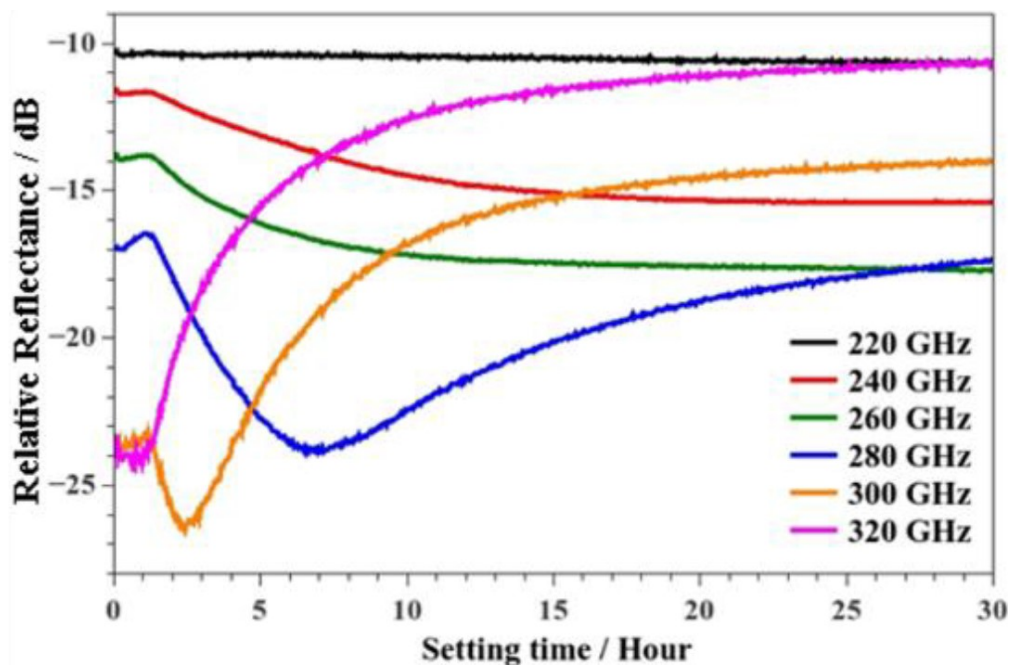
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## Terahertz experiments and spectra

Exemplary outputs at selected frequencies from the coherent terahertz experiments are shown in Figure-S1. These provide a glimpse into the time-dependent influences of the setting cement on the THz signatures; relative reflectance in decibels (dB) in this case. The progression of cementation is shown to be non-monotonic with rises and falls and then subsequent rises at 240, 260, and 280 GHz, whilst the 320GHz frequency shows an initial oscillation through to ~1.5h then only rises with time. The 220GHz frequency showed negligible change over setting. Together these exemplary frequencies evidence the influence of setting, phase and chemical change ongoing on THz frequencies; themselves informative of the evolving interfacial and overall properties in cements.



**Figure S1** Relative reflectance (dB) at selected frequencies as determined in the coherent-THz measurements on the setting cements over time.

## Computational modelling

*Ab initio* (Born-Oppenheimer) molecular dynamics (AIMD) simulations of the commercial glass ionomer G338 were conducted with the electronic structure code CP2K/Quickstep code, version 2.5.1 (Cp2K developers group) [1]. CP2K implements density functional theory (DFT) based on a hybrid Gaussian plane wave (GPW) approach [2]. The PBE was used for the exchange correlation [3] as previous studies have shown that PBE makes accurate predictions of the structural and vibrational properties of and alumino-silicate glasses [4]. Goedecker-Teter-Hutter pseudopotentials [5] were used to describe the core–valence interactions. All atomic species were represented using a double-zeta valence polarized basis set. The plane wave kinetic energy cut off was set to 1000 Ry. k-sampling was restricted to the  $\Gamma$  point of the Brillouin zone. Simulations were carried out with a wave function optimization tolerance of  $10^{-6}$  au that allows for 1.0 fs time steps with reasonable energy conservation. Periodic boundary conditions were applied throughout. The methodological rigorousness of AIMD makes it an ideal tool to investigate the structural and dynamical properties of complex, multicomponent glasses [6]. Moreover, it has been pointed out that the structural and vibrational properties of alumina-silicate glasses prepared by a “full” AIMD calculation are significantly better, compared to the experimental one, than that of the samples prepared by molecular dynamics simulations using empirical forcefields [7].

The *full* AIMD melt-and-quench simulation protocol [8,9] was used to generate a 258-atoms model of the commercial G338 glass ( $\text{Si}_{21}\text{Al}_{34}\text{Ca}_9\text{Na}_{17}\text{F}_{56}\text{P}_{11}\text{O}_{110}$ ):

For the calculation of vibrational properties of the Aluminium atoms for our AIMD simulations of the from our AIMD simulations we relied on the velocity-autocorrelation function, defined as

$$VACF_i(t) = \frac{1}{N_O N_{Al}} \sum_{j=1}^{N_O} \sum_{i=1}^{N_{Al}} v_i(t_j) \cdot v_i(t_j + t)$$

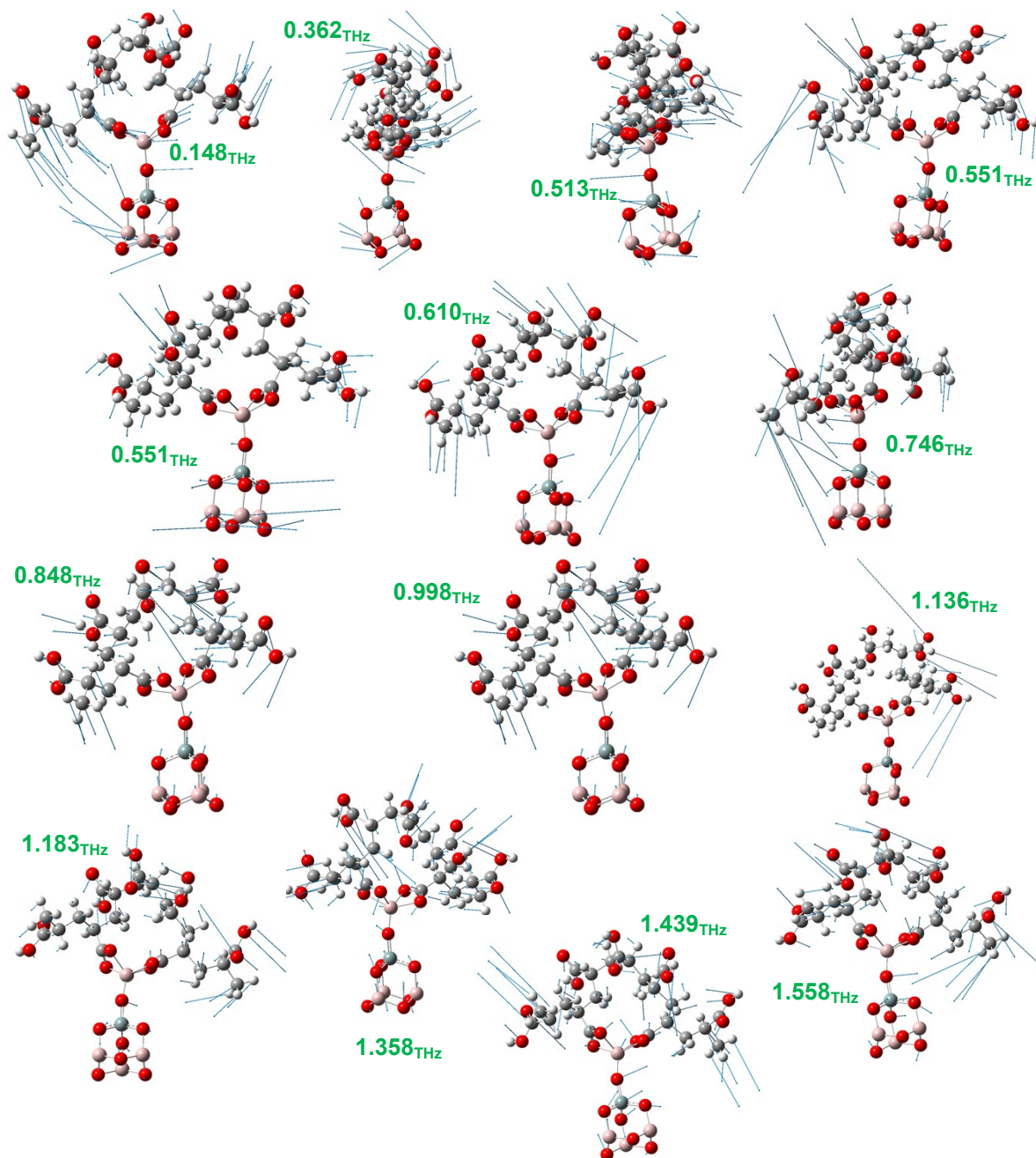
where  $v_i$  is the velocity vector of atom  $i$ ,  $N_O$  and  $N_{Al}$  are the number of time origins spaced by  $t$  and number of Al atoms, respectively. The vibrational density of states (VDOS) projected onto the Aluminium species was calculated as Fourier transform of the VACF [10].

For the DFT models, a model of the polymer-glass linkages was computed for the commercial GIC used in these experiments, was constructed and geometry-optimised, with analytical frequencies determined using the DFT Becke-3-Lee-Yang-Parr correlation (B3LYP) method [11], and an all-electron DGDZVP basis set [12]. Analytical frequency determinations on the geometry-optimised (stable) structures were carried out to determine the frequencies of the normal modes of vibrations as well as their cartesian manifestations.

## Normal Modes of Vibrations (0-3.0 THz)

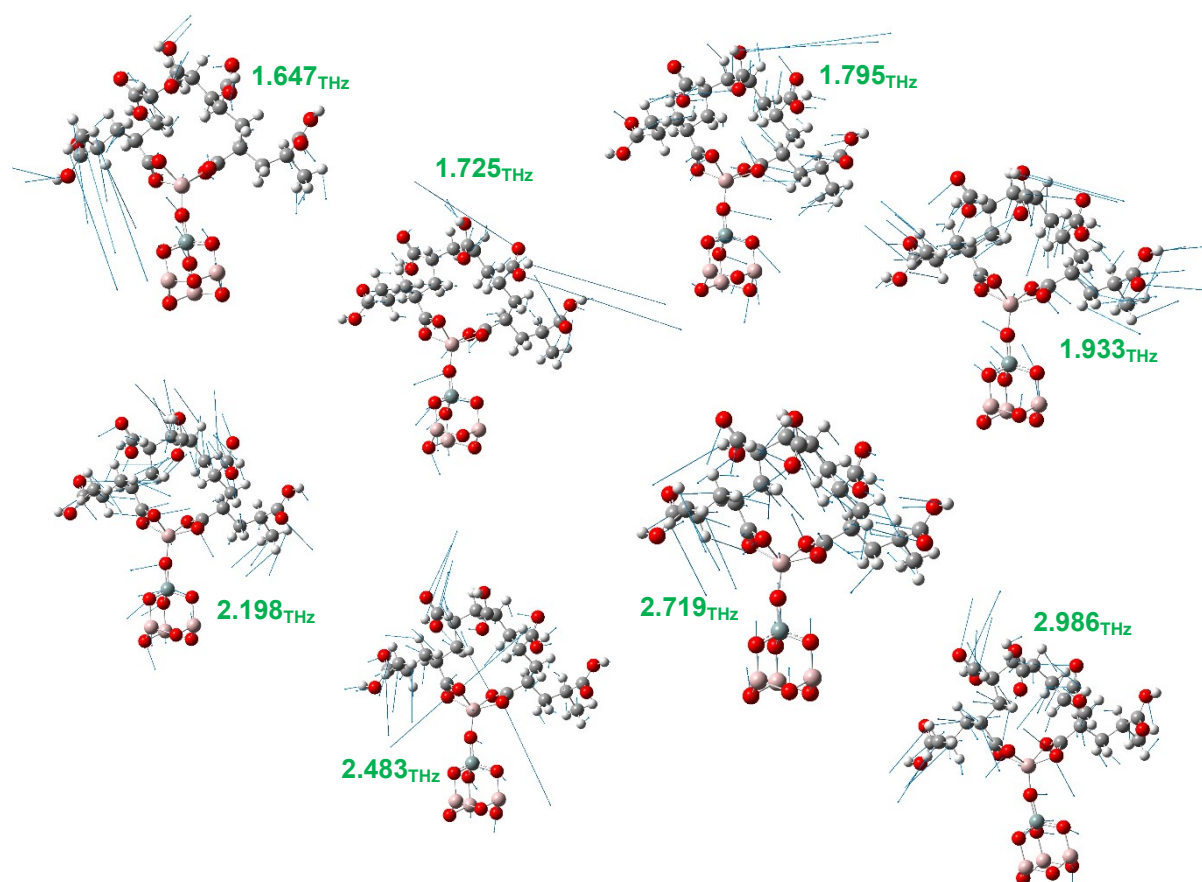
Normal modes of vibration in the 0-3.0 THz range ( $0-100\text{ cm}^{-1}$ ) emerging from the DFT models are shown in Figures S2 and S3. Animated videos from 0-1.5THz and as stills 1.5-3.0THz. Collective all-atom modes are observed up through  $\sim 6\text{THz}$ .

### Animated Images of Vibrational Modes 0-1.5 THz



**Figure S2** The animated video-images of the normal modes with 0-1.5 THz; vibrational frequency in **green text**. Hydrogen, Carbon, Oxygen, Calcium and Aluminium atoms are coloured white, grey, red, teal and rose, respectively. Force vectors on all atoms involved in each normal mode are shown as thin cyan arrows, with arrow-lengths corresponding to magnitudes.

*Still Images of Vibrational Modes 1.5-3.0 THz*



**Figure S3** The still images of the normal modes with 1.5-3.0 THz; vibrational frequency in **green text**. Hydrogen, Carbon, Oxygen, Calcium and Aluminium atoms are coloured white, grey, red, teal and rose, respectively. Force vectors on all atoms involved in each normal mode are shown as thin cyan arrows, with arrow-lengths corresponding to magnitudes.

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