Vibrational signatures of chemical- and density-induced structural changes in simulated amorphous silica

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Abstract: Molecular dynamics simulations show that vibrational modes in glassy SiO$_2$ are affected differently by density-induced changes to the structural order compared with those induced by specific cationic substitutions (Al, P, Na). Using standard measures of local and midrange positional order, we find that P disrupts network order in terms of second nearest neighbours, but preserves local order. In contrast, Al decreases local order while maintaining network order. Increased density preserves structural correlations in the network although the length scale shrinks. The complex short-range and long-range structural trends in these modified glasses coincide with changes in distinct regions in the vibrational density of states (VDOS). This suggests that a greater role for VDOS as a tool to link simulation and experiment in amorphous materials.

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Résumé : Des simulations de dynamique moléculaire montrent que les modes de vibration dans le SiO$_2$ vitreux sont affectés différemment par les changements induits par la densité à l’ordre structural comparés à ceux induits par des substitutions cationiques spécifiques (Al, P, Na). Utilisant des mesures standard d’ordre de positionnement à courte et moyenne portée, nous trouvons que P perturbe le réseau (de verre) au niveau des deuxièmes voisins, mais laisse intact l’ordre local, alors que Al perturbe l’ordre local et laisse l’ordre du réseau intact. Une augmentation de la densité préserve les corrélations structurelles du réseau, même si l’échelle de longueur diminue. Les tendances structurelles complexes à courte et à longue portée dans ces verres modifiés coïncident avec des changements dans des régions distinctes dans les densités d’états de vibration (VDOS). Ceci suggère que VDOS peut jouer un plus grand rôle pour lier simulations et expérimentation dans les matériaux amorphes. [Traduit par la Rédaction]

1. Introduction

Glasses are inherently aperiodic materials, yet this lack of three-dimensional periodicity does not mean that they lack order. For example, there can be very good local order in a well-formed glass. While there are well-established experimental tools that can probe the two extremes of local order (e.g., X-ray absorption fine structure) and long-range periodicity (e.g., diffraction), it is an ongoing challenge to quantify changes to the midrange order in materials, regardless of whether they are glassy or crystalline [1, 2]. Vibrational properties are one assessment method that can span from local to long-range effects, yet vibrational density of states (VDOS) is not the primary tool in theoretical studies of glasses. Midrange order differences are important because they have been implicated in many important material behaviours including crystallization–devitrification products [3, 4], links between defect states (VDOS) is not the primary tool in theoretical studies of glasses. Midrange order differences are important because they have been implicated in many important material behaviours including crystallization–devitrification products [3, 4], links between defect states (VDOS) is not the primary tool in theoretical studies of glasses. Midrange order differences are important because they have been implicated in many important material behaviours including crystallization–devitrification products [3, 4], links between defect states (VDOS) is not the primary tool in theoretical studies of glasses. Midrange order differences are important because they have been implicated in many important material behaviours including crystallization–devitrification products [3, 4], links between defect states (VDOS) is not the primary tool in theoretical studies of glasses. Midrange order differences are important because they have been implicated in many important material behaviours including crystallization–devitrification products [3, 4], links between defect...
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hoover thermostat with a time constant of 1 ps. The radial cutoff
1000–1200 cm\(^{-1}\), which includes the two highest energy
peaks that are derived primarily from modes that are along-axis Si–O bond vibrations with a distinct local character (Figs. 1a and 1b). This region is the only one that is dominated by local modes that affect the dilation of individual tetrahedra. The second region is 800–950 cm\(^{-1}\), which contains a shoulder that is almost exclu-
sibly related to twisting modes (Fig. 1c) that affect the relative
orientation of the tetrahedra, rather than their volume, and are thus more strongly affected by the connectivity of the SiO\(_4\) tetra-
hexa. While there are other VDOS peaks at lower energy that are also related to network connectivity and lattice modes, this shoul-
der is the only region that has a dominant contribution from a single twisting mode. To summarize, we associate disruptions in
network connectivity to changes in the shoulder near 850 cm\(^{-1}\). Our work will show that simple distinctions in the VDOS data show qualitative trends that correlate well with the more standard quantitative measures of local positional order \( g(r) \) and its integral \( n(r) \), and long-range positional order \( S(q) \).

3. Computational details
We carry out molecular dynamics simulations using GROMACS v4.5.5 [16–19]. Pure liquid silica (SiO\(_2\)) simulations employ the van Beest – Kramers – van Santen potential [20] for a system of 444 SiO\(_2\) units in a cubic simulation cell with periodic boundary conditions at eight densities: 2.31, 2.45, 2.61, 2.80, 3.01, 3.26, 3.55, and 3.90 g/cm\(^3\). All simulations are carried out at \( T = 3000 \) K using the Nosé–Hoover thermostat with a time constant of 1 ps. The radial cutoff is 1 nm for all real space pair interactions. Coulomb interactions are handled with the particle mesh Ewald algorithm with a Fou-
rier spacing of 0.1 nm and interpolation of order four (cubic). We add to the van Beest – Kramers – van Santen potential a short
range interaction, described in ref. 21, to prevent the system from exploring the unphysical attraction occurring at small distances. At this \( T \), the model exhibits glassy dynamics and at the lowest densities, the tetrahedral network is well formed, resulting in an approach to Arrhenius dynamics [21–23]. The simulations are car-
ried out for 6 ns, sufficient to equilibrate the least diffusive state point (2.31 g/cm\(^3\)), for which Si ions diffuse an average distance of 0.31 nm (one Si–Si distance) in roughly 2.5 ns.

Substitutional impurities are gradually added to the 2.31 g/cm\(^3\) system by replacing Si ions in such number ratios as to preserve charge balance. For example, five Si ions are replaced by 12 Na ions before simulating for another 6 ns. The simulations with impurities are carried out at a constant pressure of \(-1.6 \) GPa to match the conditions at 2.31 g/cm\(^3\) for this silica model. The constants used for the pair potentials for the impurity ions are taken from ref. 24. We note the partial charges for the cations: 2.40 for Si, 1.40 for Al, 3.40 for P, and 1.00 for Na. We report results for which there are 60 impurity ions.

To obtain VDOS, configurations drawn from the liquid are each quenched, using the conjugate gradient algorithm, to a local po-
tential energy minimum. At this minimum, the mass-weighted
Hessian is evaluated and diagonalized, with the spectrum of eigenfrequencies yielding the VDOS. GROMACS conveniently pro-
vides utilities to carry out these calculations. To characterize the structure of the liquids, we calculate the partial Si–Si structure factor, \( S(q) \), the radial distributions function, \( g(r) \), and its integral, \( n(r) \), to get the number of atoms in the coordination sphere of radius \( r \). The radial distribution function, \( g(r) \), gives the dimen-
sionless orientational average of local positional order, while \( S(q) \), related to the Fourier transform of \( g(r) \), indicates periodicitities in density fluctuations [25].

4. Results and discussion
Figure 2 shows noticeable changes in the VDOS when we either increase the density (in compositionally pure silica) or change the type of substitutional impurity (in silica equilibrated at a constant pressure). In all cases, the peaks between 1000 and 1200 cm\(^{-1}\) show slight energy shifts and decreases in intensity. These peaks show a more considerable change in intensity as density increases, but with no significant change in position until the highest densities. We note that this is a very large range of densities. For the shoulder near 850 cm\(^{-1}\), P preserves the intensity, Na attenuates it, while Al impurities cause it to increase in a way that is similar to the effect of increasing density.

We note that the peak near 100 cm\(^{-1}\) is consistent with a Boson peak that is typically observed in silica and other glass forming
materials. Its origins are still debated, but it is generally attributed to modes associated with the SiO₄ tetrahedral units [26, 27]. Recent work by others has shown that Na contributes greatly to this low-energy peak in MD simulations of Na-containing silica glasses [28]. However, we will not discuss the changes in this particular region of the VDOS spectra in detail here.

Based on these comparisons, it appears that the VDOS can tell us very quickly about some important effects induced by different perturbations to the pure SiO₂ glass. First, all perturbations decrease the short-range order in the system, which we infer from the decreased peak intensities at 1200 and 1100 cm⁻¹. Second, and perhaps more interestingly, Al is the most detrimental to local order while boosting the shoulder associated with the connectivity-related twisting modes. In contrast, P causes the least disruption to local order, and has little effect on the connectivity-related shoulder. Na seems to cause disorder on short and intermediate length scales.

To provide more insight on the differences between the density-driven and substitutional impurities, we also track disorder through the radial distribution function, g(r), and its integral, n(r), which provide information about the coordination sphere. As shown in Fig. 3a, there is virtually no difference in n(r) for Si–O when either Na or P is the substitutional impurity. Al substitutions produce slightly higher Si coordination numbers, as the more rapid rise in its n(r) curve indicates. Figures 3b, 3c show how the different substitutional impurities are coordinated to the O and Si atoms, respectively. The P shows a very strong tendency to form PO₄ tetrahedra, whereas the oxygen environment around the Al is generally more variable in terms of both coordination number and in nearest neighbour distances. The Na–O coordination sphere is the most mixed, showing no evidence of plateaus in the n(r) plot and the longest neighbour distances in g(r). For the Si interactions with the substituted species, P–Si is remarkably similar to Si–Si order, which can be inferred from the similarity in g(r) for Si–Si in pure SiO₂ compared with the g(r) for Si–P. Al impurities tend to sit closer to Si atoms than Na impurities, and the Si–impurity correlations become more quickly suppressed with increasing r for the Na compared with the Al or P systems.

Comparing Figs. 3a and 3b with Fig. 3d shows that the changes that occur in the Si–O environments with increasing Al content are the most like those we observe with increasing density. Figure 3d covers a wide range of densities, spanning a correspondingly larger change in the g(r) peak distances and the coordination sphere, n(r). However, for relatively moderate changes in density, the n(r) trends look qualitatively similar to those for the Al–O n(r) shown in Fig. 3b. These findings are consistent with the similarities in the VDOS data for Al substitutions (Fig. 2a) and density changes (Fig. 2b), including the changes in peak intensities between 1000 and 1200 cm⁻¹ and the increase in the intensity of the shoulder region near 850 cm⁻¹.

The effects of substitutional impurities on long-range positional order are also evident in the Si–Si partial structure factor, S(q) (Fig. 4a). The first sharp diffraction peak, occurring near...
17 nm\(^{-1}\) in pure SiO\(_2\) at 2.31 g/cm\(^3\) and which we refer to as the network peak, arises in network-forming liquids as a result of structural correlations beyond nearest neighbours [2]. This peak merges with the nearest-neighbour peak at 27 nm\(^{-1}\) as density increases. It is surprising that the network peak is nearly identical for Al-substituted glass compared with pure SiO\(_2\). These two different glasses also have similar low plateau values for low q, which indicates similar compressibility values and uniformity of Si ions [29]. These similarities suggest that Al does not introduce voids or other medium-length-scale disruptions to the silica structure, even though the g(r) data indicate that it does disrupt local positional order. On the other hand, P and Na both show considerable shifts to larger distances with increasing density, because the network peak is preserved but shifts to larger q values.

### 5. Conclusion

1. Local positional order is best preserved by P substitutions, but this occurs at the expense of long-range positional order.
2. Al substitutions disrupt local order, but enhance midrange order.
3. Density increases preserve structural correlations between second-nearest neighbours but at increasingly smaller distances with increasing density, because the network peak is preserved but shifts to larger q values.

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### References