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Spectral mode assignment for binary silicate glasses using molecular dynamics simulations

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ABSTRACT

The vibrational behavior of binary silicate glasses is modeled using molecular dynamics (MD) simulations. The prevailing procedure for assigning vibrational modes to structural features is through comparison with spectra of known substances. The explicit knowledge of atomic trajectories from MD simulations allows for a direct observation of vibrational motion in specific frequency bands and decomposition into the predominant vibrational modes. We demonstrate a Fourier transform method for determining the vibrational motion associated with a particular frequency. We compare literature assignments for α-cristobalite, vitreous silica, β $Na_2O-2SiO_2$ and vitreous $Na_2O-2SiO_2$ to this method. Our analysis shows that while it is necessary for the network to be disrupted and non-bridging oxygen atoms to form for vibrational motion to occur at 1205 cm^{-1}, the mode is in fact not specific to that structural moiety.

1. Introduction

Silica glasses are among the most prevalent amorphous engineering materials, vital to technologies that include optical fiber telecommunications, modern electronics, high-performance optical components, fiberglass insulation, windowpanes and containers. While extensive experimental work has been done, the quest for a more complete structural characterization of silicate glasses is ongoing. Vibrational spectroscopy, such as infrared (IR) and Raman spectroscopy, has long been an important experimental tool for identifying structural details in non-crystalline materials. Raman and IR spectroscopy are based on the coupling between electromagnetic radiation and the fluctuations in the polarizability and dipole moment of the material, respectively, are sensitive to structural symmetries in complementary ways, and have been used extensively in the study of amorphous SiO_2 and various silicates [1–4]. Spectra so obtained are typically deconvoluted, assuming Gaussian or Lorentzian theoretical line shapes, to yield the positions and magnitudes of all discernible spectral bands. Assignment of these spectral bands to vibrational modes of specific molecular species thought to be present in the material under investigation can be based on a variety of tools, including group theory, molecular mechanics calculations, and, to a significant extent, comparison with databases of spectra recorded for known substances [1] In this respect, however, amorphous materials pose a particular challenge. The ubiquitous structural disorder eliminates symmetry, which complicates the assignment of vibrational modes considerably. Furthermore, satisfying the bonding requirements of the various species within such a topological disorder imposes mechanical constraints that can distort the force fields that govern the vibrations of atoms and lead to erratic shifts and broadening of spectral bands. Here we describe an approach based on molecular dynamics (MD) simulations aimed at refining the interpretation of vibrational spectra for the purpose of deriving information about the structure of an amorphous material. To demonstrate this approach we provide new insights into the origins of the high-frequency spectral bands for alkali-modified silica network structures.

Generally, experimental infrared spectra of silica and silicate glasses contain three major bands as well as other minor peaks [5]. The 1111 cm^{-1} peak is associated with the asymmetric stretching of Si–O–Si bonds, the 802 cm^{-1} with bending, and the 474 cm^{-1} band with the rocking motion of this structural unit. A weak peak sometimes seen near 600 cm^{-1} is attributed to deformation modes of ring structures [5]. Peaks associated with lattice modes are generally found in the 275–500 cm^{-1} region of the spectra [6].

Few studies of vibrational spectra of $xNa_2O\cdot(1-x)SiO_2$ have been reported to date [3,6–10]. The addition of alkali oxides results in the modification of the silica network, i.e., the replacement of bridging oxygen (BO), found in Si–O–Si units, by forming two terminal non-bridging oxygens (NBO), found in $Si-O^-$ units. Glasses already exhibit broad spectral features compared to crystalline structures of the SiO_2 polymorphs, underlining the lack of structural clarity. The disruption of the silica network introduces new degrees of freedom for atomic motion, resulting in increased complexity of the corresponding IR spectra. Most notably and characteristically, an additional shoulder is seen near 1200 cm^{-1}, which consequently has been assigned to the asymmetric stretching motion of NBO. With the present analysis we

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seek to clarify the role of NBO in the vibrational spectra of binary silicate glasses, using sodium disilicate ($Na_2O\cdot 2SiO_2$) as a model system. Discussion of the compositional dependence of vibrational spectra of multi-component glasses is beyond the scope of this manuscript and will be reported elsewhere.

Several classical and ab initio molecular dynamics simulations for studying the vibrational modes of *a*-SiO_2 [11–17] have been reported. In the present study, atomic interactions are modeled using a new charge-transfer potential specifically designed to accommodate the chemical differences between BO and NBO, which exhibit different degrees of charge localization. Parameters for this potential have been optimized to reproduce the IR spectra of α-and β-cristobalite, the polymorphs of silica [18] generally accepted as being most structurally similar to glass. Our potential also reproduces the structure of crystalline $Na_2O\cdot 2SiO_2$ accurately, albeit no experimental IR spectra of this compound could be found for comparison. Few interaction models have been able to accurately reproduce the expected spectra [15], though better accuracy has been achieved in replicating Raman than IR spectra [11,13].

In isolated molecules and ordered crystalline systems, the number of independent modes of motion is reasonably small due to the space group and translational symmetries of these structures. Normal modes of motion and the corresponding frequencies can be calculated by determining the eigenvectors and eigenvalues of the Hessian matrix, which describes the dynamical response of the system in its ground state configuration [19]. However, these methods cannot be applied to vitreous systems in a computationally practical manner, because the lack of periodicity requires one to consider configurations of several thousand atoms in order to avoid system size effects. On the other hand, MD simulations yield the actual atomic trajectories, which can be used to compute the vibrational behavior of structures of arbitrary geometric complexity and even account for elastic anharmonicity.

In this paper we describe a unique method of trajectory filtering based on the Fourier transform of the atomic trajectories obtained from MD simulations, which yields the vibrational modes of motion associated with a particular spectral band and allows us to quantify the energy associated with this mode. Since IR spectra reflect the coupling between electromagnetic radiation and fluctuations in the spatial distribution of atomic charge, we also discuss the charge transfer potential we used for this study. Finally, applying this approach to the investigation of sodium disilicate glass, we elucidate the role of NBO in the IR spectra.

2. Computational procedure

2.1. Potential model

Early models used to simulate the structure and properties of silica or binary or ternary silicate glasses are based on formal ionic charges, but in recent studies the need for fractional charges to account for the covalency of Si–O bonds was recognized. While central force potentials effectively reproduce equilibrium structures and structural instabilities [20,21], it appears that only by taking the directional character of covalent bonds through three body interactions into account can dynamical properties such as phonon dispersion and IR spectra be accurately simulated.

Multi-component silicate glasses containing network modifying compounds possess up to three different types of oxygen: BO O^0, NBO, O^-, and free oxygen, O^{2-}. As the nomenclature indicates, these species are characterized by different charges, and in the simulations for this study, it is not a priori known what type is to be attributed to a given oxygen atom. In fact, the type may change in the course of a simulation. The fraction of each type of oxygen present is a result of dynamic equilibrium as the system evolves naturally, allowing for spatial fluctuations of the chemical composition. Assigning oxygen speciation a priori cannot be done without predetermining the resulting structure. Overcoming this limitation was a specific purpose of the potential we developed in the context of earlier work [22]. The potential includes a Coulombic term, a Born–Huggins–Mayer repulsive term [23] and a directional covalent term capable of accommodating multiple coordination states dynamically [18,22]. The balance between the ionic and covalent characters of atomic interactions is achieved through a charge transfer term. Accordingly, the magnitude of charge transfer between atoms upon rupture or formation of bonds depends on the electronegativity difference between species and the ionization potential; it is controlled by a continuously differentiable charge transfer term. The potential energy for a given particle is defined as:

$$\Phi_i = q_i \sum_{j=1}^{N} \frac{q_j}{4\pi\varepsilon_0 r_{ij}} + \sum_{i=1}^{NC} C_{ij} e^{(\sigma_i+\sigma_j-r_{ij})\cdot\rho_{ij}} + \sum_{j=1}^{NC-1} \sum_{k=j+1}^{NC} \left(\varphi_{ij}+\varphi_{ik}\right) e^{-\gamma_{ijk}\left(\bar{\theta}-\theta_{ijk}\right)^2}$$

where ε_0 is the dielectric constant of vacuum, r_{ij} is the interatomic distance, and q_i is the charge. The charge of an atom is evaluated according to $q_i = q_i^{\varnothing} - \sum_{j=1}^{NC}(\delta_{ij}\zeta_{ij})$, where $q_i^{\varnothing}$ is the charge of the isolated atom and $\zeta_{ij} = (1+\exp(b(r_{ij}-a)))^{-1}$ is the charge transfer function, *a* and *b* are empirical parameters. Electroneutrality is assured by requiring that $\delta_{ij} = -\delta_j$. The term $(\varphi_{ij}+\varphi_{ik})\exp(-\gamma_{ijk}(\bar{\theta}\text{-}\theta_{ijk})^2)$, where $\varphi_{ij} = -C_{ij}(\kappa_{ij}/\eta_{ij})\zeta_{ij}\exp((\lambda_{ij}-r_{ij})\eta_{ij})$, $C_{ij} = A_{ij}[1+(z_i/n_i)+(z_j+n_j)]$, and z_i is the valence, and n_i is the number of electrons in the outer shell of atom *i*, models covalent bonding by acting in the radial and angular direction, as defined by triplets of particles.

The long-range Coulomb interactions are evaluated using the Ewald summation method. The magnitude of the attractive covalent terms is modulated by the angular term, $\exp(-\gamma_{ijk}(\bar{\theta}\text{-}\theta_{ijk})^2)$, which is symmetric with respect to an equilibrium bond angle $\bar{\theta}$ between the bond vectors r_{ij} and r_{ik}. In this potential model, both Columbic and three-body terms are complementary, as controlled by the charge transfer function.

The potential parameters were first optimized to reproduce the experimentally observed structure and IR spectra of α-cristobalite. These potential parameters were then adopted for interactions involving silicon and oxygen to simulate crystalline sodium disilicate. The optimization of the three additional pair interactions, Na–Na, Na–Si and Na–O, was based on reproducing the structure and density of known crystalline modifications, as shown in Table 1. A comparison between β-$Na_2O\cdot 2SiO_2$ structures, determined by X-ray diffraction measurements [24], and obtained from simulation using optimized parameters is shown in Fig. 1. The α and γ angles, as well as the *a* and *b* lattice vector lengths resulting from simulations coincide with the experimentally measured ones, while the magnitudes for β and c differ by 4.8% and 3.1%, respectively.

Table 1
Optimized potential parameters for sodium disilicate.

Element	σ_i (nm)	n_i	z_i	$q_i^{\varnothing}$
Na	0.1110	8	+1	+1
Si	0.1010	8	+4	+4
O	0.1430	8	−2	−2

Pair	A_{ij} (10^{-19} J)	ρ_{ij} (nm^{-1})	λ_{ij} (nm)	η_{ij} (nm)	κ_{ij} (nm^{-1})
Na–Na	0.5327	35.0	0.0	0.0	35.0
Na–Si	0.1450	35.0	0.0	0.0	35.0
Na–O	0.1977	35.0	0.0	0.0	35.0
Si–Si	0.1600	34.5	0.0	0.0	34.5
Si–O	0.1400	38.7	2.6	3.2	38.7
O–O	0.2500	19.5	0.0	0.0	19.5

Charge transfer	δ_{ij} (*e*)	*a* (nm)	*b* (nm^{-1})
Si–O	0.2170	0.24	80

Triplet	γ_{ijk} (rad^{-2})	θ_{ijk} (rad)
O–Si–O	0.1	1.91
Si–O–Si	0.2	2.48