Vibrational properties of a sodium tetrasilicate glass: \textit{Ab initio} versus Classical Force Fields

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Abstract

We have determined the vibrational properties of a sodium tetrasilicate (Na\(_2\)Si\(_4\)O\(_9\)) glass model generated by molecular dynamics simulations. The study has been carried out using a classical valence force fields approach as well as an \textit{ab initio} approach in the framework of the density functional theory. The total and partial vibrational densities of states (VDOS) are presented, as well as some characteristics of the vibrational modes (participation ratios, correlation lengths). For the low-frequency bands below 500 cm\(^{-1}\), we find that the shapes of the two calculated VDOS as well as those of their corresponding partial VDOS are quite similar. For the intermediate- and high-frequency ranges, we observe larger discrepancies between the two calculations. Using the eigenmodes of the dynamical matrix we also calculate the polarized Raman spectra within the bond-polarizability approximation. We find an overall agreement between the calculated parallel polarized (VV) Raman spectra and the corresponding experimental spectrum. Regarding the perpendicular depolarized (VH) Raman spectrum, the comparison of the calculated spectra to the experimental data indicates a need for an adjustment of the VH bond-polarizability parameters.

PACS numbers: 61.43.Bn, 61.43.Fs, 71.15.Pd, 71.23.Cq

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1. Introduction

The nature of the vibrational excitations of silicate glasses and melts represents a challenging problem of condensed matter physics, glass and earth sciences. Significant experimental and theoretical efforts have been made in order to understand the vibrational properties of these materials, because they provide valuable information about the underlying microscopic structure and other anomalous physical properties of silicate glasses [1]. However, the lack of long-range translational order considerably complicates this task and requires new approaches for measurement, analysis and simulations of the vibrational spectra of glasses and melts as well as a careful investigation on how the vibrational spectra depend on the details of the considered glass (chemical composition, thermal history, etc.).

Therefore we compare in the present paper the vibrational density of states (VDOS) and several vibrational characteristics of an \textit{ab initio} model of sodium tetrasilicate glass \(\text{Na}_2\text{Si}_4\text{O}_9\) (denoted hereafter NS4) calculated by two different methods. The first calculation is based on an \textit{ab initio} treatment of the interatomic forces and is performed in the framework of the density functional theory, while the second one is performed in the approximation of a classical valence force fields (VFF) potential which is especially suited for describing the dynamics of partially covalent materials like silicate glasses.

The structure of the NS4 glass has been intensively investigated by different experimental methods [2], reverse Monte Carlo (RMC) [3] as well as classical molecular dynamics (MD) simulations [4,5]. Recently, the structural and electronic properties of the NS4 glass have been modeled by a combined Car-Parrinello and classical MD simulation [6,7]. The attention given to this system is justified by the fact that it can be used as a prototype for more complicated aluminosilicate and hydrous silicate glasses.

The aims of the present study are: (i) to test the quality of the \textit{ab initio} NS4 vibrational dynamics by comparing the calculated and experimental polarized Raman spectra; (ii) to test the quality and the transferability of a previously proposed [5] valence force fields potential for sodium silicate glasses by comparison with \textit{ab initio} calculations; and (iii) to analyse the effects of adding \(\text{Na}_2\text{O}\) to \(\text{a-SiO}_2\) on the character of the vibrational characteristics of the glass. We would like to note that the present \textit{ab initio} calculations using the Car-Parrinello (CP) method involve various approximations (pseudopotentials, truncated plane-wave basis, etc.) Nevertheless we may expect that the CP approach leads to a better estimation of the real interatomic forces by comparison to the VFF approach. On the other hand, the computation time needed to perform a VFF type calculation is generally very small compared to the one used in first principles calculations.
2. Calculation procedures

2.1. The glass models

The amorphous NS4 model used in this study contains 90 atoms (24 silicon atoms, 54 oxygen atoms and 12 sodium atoms) confined in a cubic box of edge length 10.81 Å corresponding to the experimental NS4 mass density of 2.38 g/cm³. The glass model has been generated using combined classical and ab initio molecular dynamics (MD) simulations. For this we have firstly performed the liquid equilibration, the quench, and the initial part of the low temperature relaxation of the system by using a classical force field. Subsequently we have refined the obtained structure within the framework of the ab initio MD. We note that this approach was successfully employed for the study of the structural, electronic and vibrational properties of vitreous SiO$_2$ [9, 10], as well as for a structural and electronic study of vitreous NS4 [6, 7].

The classical MD simulations were performed with an interatomic potential which is a modification of the potential proposed by van Beest et al. [11], derived in order to study sodium silicates [12]. The NS4 model was generated by quenching a well equilibrated liquid at 3500 K to 300 K, with a quench rate equal to $5 \cdot 10^{13}$ K/s. The glass model obtained in this way was annealed at 300 K for 70 ps. The final atomic coordinates and velocities after the classical relaxation, were used as initial coordinates and velocities for a short ($\approx 0.5$ ps) ab initio MD simulation. The ab initio simulations were performed in the framework of the Car-Parrinello (CP) method [13, 14] using the CPMD software [15].

In the first principles calculations, the electronic structure calculations were treated via the Kohn-Sham formulation [16] of density functional theory, within the generalized gradient approximation employing the B-LYP functional [17]. The valence Kohn-Sham orbitals were expanded in a plane-wave basis set defined by an energy cutoff of 70 Ry, at the Γ-point of the supercell. The core-valence interactions were described by norm-conserving pseudopotentials of the Bachelet-Hamann-Schlüter type for Si atoms [18] and of the Trouiller-Martins type for O atoms [19]. Further details are given in Ref. [6]. The CP dynamics was performed using a fictitious electronic mass of 800 a.u. and a time step of 0.097 fs. In the present CP calculations, we used for the sodium atoms a semi-core Trouiller-Martins norm-conserving pseudopotential [19] instead of the Goedecker semi-core type used in Ref. [6]. This change allowed a better estimation of the internal pressure of the model. Nevertheless, the same structural modifications as reported in [6] occurred immediately after the CP dynamics was switched on, i.e. the shortening of the Si-NBO bond and the lengthening of the Si-BO and Na-NBO bonds (in the remainder of the text, 'BO' denotes the bridging oxygens, while 'NBO' denotes the non-bridging oxygens). The CP run leads to structural relaxation without changes in the network.
topology, the ring and Q-species distributions being determined in the classical stage.

In order to produce the first NS4 glass model (called the \textit{ab initio} NS4 model) used further for the vibrational calculations, we relaxed to 0 K the glass model obtained at the end of the CP simulation described above. The second glass model was produced by performing a relaxation of the \textit{ab initio} NS4 model with a harmonic valence force field (VFF) potential of the Kirkwood-type (see Ref. \cite{5} for further details as well as the next subsection where we give the values of the VFF potential parameters used in this work). At the end of the VFF relaxation, the NS4 model had practically the same average Si-O and Na-NBO bond lengths as the starting \textit{ab initio} model. However we found a small decrease ($\approx 3\%$) of the Na-BO bond length as well as a decrease of the standard deviation of the average Si-O bond length distribution, from 0.033 Å to 0.019 Å. In addition we observed a decrease of the standard deviation of the intratetrahedral O-Si-O angle distribution (from 3.7 degrees to 2.2 degrees).

\subsection{VDOS and Raman spectra calculations}

Within the first principles approach, the dynamical matrix was computed numerically by evaluating the second derivatives of the total energy with respect to atomic displacements ($\approx 5.3 \cdot 10^{-3}$ Å for each atom), which were calculated using the finite differences of the atomic forces. (We note that, for these latter calculations as well as for the \textit{ab initio} relaxation to 0 K mentioned in the previous subsection, we used an energy cutoff of 90 Ry for the plane-wave basis expansions of the Kohn-Sham orbitals.) The direct diagonalization of the dynamical matrix provides the eigenvalues $\{\omega^{\text{CP}}_p\}$ and the corresponding normalized eigenvectors $\{e^{\text{CP}}(\omega^{\text{CP}}_p)\}$, $p = 1, \ldots, 3N$, where $N = 90$ is the number of atoms in the model. Each eigenvector is a $3N$-dimensional vector which components are proportional to the displacements of the atoms in mode $p$.

Within the VFF approach, the dynamical matrix was calculated analytically and was diagonalized using the Householder method. The detailed expressions of the dynamical matrix elements are given elsewhere \cite{21}. The obtained vibrational frequencies will be denoted $\{\omega^{\text{VFF}}_p\}$ and the corresponding eigenvectors $\{e^{\text{VFF}}(\omega^{\text{VFF}}_p)\}$, $p = 1, \ldots, 3N$. In the present work we used the following values for the stretching force constants $\alpha_{ij}$: $\alpha_{\text{Si-BO}} = 465$ N/m, $\alpha_{\text{Si-NBO}} = 655$ N/m, $\alpha_{\text{Na-BO}} = 25$ N/m, and $\alpha_{\text{Na-NBO}} = 30$ N/m, while the bending force constants $\beta_{ijk}$ were $\beta_{\text{BO-BO-Si}} = \beta_{\text{BO-NBO}} = \beta_{\text{NBO-Si-NBO}} = 35$ N/m and $\beta_{\text{Si-BO-Si}} = 14$ N/m. We note that we have used larger Na-O stretching and slightly larger Si-BO-Si bending force constants than the values reported in Ref. \cite{5} since these values led to a better agreement between the calculated and experimental heat capacities for sodium silicate glasses \cite{20}.

The knowledge of all the eigenmodes allows us to calculate the reduced polarized Raman spectra of the NS4 glass model using the bond polarizability approximation
(BPA) \cite{22} presented in details in Refs. \cite{24,23}. The BPA parameters used in the present work are: $A'_{\text{Si-BO}} = 0.5 \text{Å}^3$, $\gamma_{\text{Si-BO}} = 0.05 \text{Å}^3$, $A'_{\text{Si-NBO}} = 1 \text{Å}^3$, $\gamma_{\text{Si-NBO}} = 0.05 \text{Å}^3$, $A'_{\text{Na-O}} = 0.05 \text{Å}^3$, $\gamma_{\text{Na-O}} = 0 \text{Å}^3$, where $A'_{\alpha-\beta}$ is the derivative of the parallel bond polarizability parameter with respect to the length of the bond between atoms $\alpha$ and $\beta$, while $\gamma_{\alpha-\beta}$ is the perpendicular bond polarizability parameter for the $\alpha-\beta$ bond ($\alpha, \beta=\text{Si,Na,BO,NBO,O}$). Recently, a comparison of the Raman scattering mechanism in $\alpha$-quartz using both ab initio and BPA methods has shown that the BPA reproduces the ab initio Raman intensities within 15\% \cite{24}. For amorphous silica models generated by ab initio molecular dynamics simulations, the use of the BPA gives rise to Raman spectra in good agreement with experimental data \cite{25}. This gives strong support for the application of the BPA for the calculation of the Raman spectra of large models of silicate glasses. The comparison of the Raman spectra calculated independently from the CP and the VFF eigenmodes will allow us to investigate separately the effects of the BPA parameters and the eigenmodes on the accuracy of the Raman spectra calculations.

3. Results

In Fig. 1 we compare the CP and VFF vibrational densities of states. Both VDOS are normalized to one, and we have used the same uniform Gaussian broadening of full width at half maximum $2\sigma = 40 \text{cm}^{-1}$. In both spectra we can distinguish three ranges: a low-frequency range ($0 - 500 \text{cm}^{-1}$), an intermediate frequency range ($500 - 900 \text{cm}^{-1}$), and a high-frequency range ($900 - 1200 \text{cm}^{-1}$). The low-frequency bands arise generally from Na-O stretching and bending as well as from Si-O bending and rocking motions. The strong mid-frequency band near $800 \text{cm}^{-1}$ arises from complex motion with large displacements of the Si atoms against the BO atoms \cite{5,26}. The high-frequency modes correspond mainly to Si-BO and Si-NBO stretching motions \cite{5}.

In spite of the fact that the intensities of the CP low-frequency bands are slightly higher than the VFF ones, both approaches yield almost identical band positions and shapes. Larger discrepancies between the two VDOS are found in the mid- and the high-frequency ranges since the VFF mid-frequency bands are shifted to higher frequencies compared to the CP bands. Nevertheless the two approaches yield practically the same intensities (same number of vibrational modes). In the high-frequency range the shape of the vibrational bands is generally the same but the VFF bands are shifted to higher frequencies, have larger intensities and are more narrow. The latter effect may be attributed to the decrease of the standard deviation of the Si-O bond length distribution.

Unfortunately, to the best of our knowledge, there are no VDOS data for the NS4 glass measured by inelastic neutron scattering to compare with our calculations. Therefore we compare in Fig. 2 the calculated and experimentally reduced polarized (VV and
VH) Raman spectra. The polarization is VV if the electric fields of the incident and the scattered light are parallel and is VH when they are perpendicular. We recall that the so-called reduced spectrum is obtained by multiplying the experimental measured spectrum with the correction factor $\frac{\omega}{n(\omega) \cdot (\omega - \omega_0)^4}$ in order to have a temperature independent quantity ($n(\omega)$ is the Bose factor). The polarized Raman spectra were measured on doubly-polished glass plates in backscattering geometry using the 514.5 nm line of an Ar$^+$ laser and a XY triple spectrometer equipped with a liquid-nitrogen cooled CCD detector and confocal entrance optics with 300 s accumulation time per spectral window. The CCD spectra were binned with a step of 4 cm$^{-1}$. For the calculations of the theoretical spectra, the final spectra have been obtained by applying a uniform Gaussian broadening with full width at half maximum equal to 30 cm$^{-1}$ to the calculated Raman intensities. It should be noted that generally it is not possible to determine experimentally absolute Raman intensities. Therefore the VV spectra (Fig. 2a) were normalized so that the strongest peaks (at about 1100 cm$^{-1}$, and characterized by a small depolarization ratio $I_{VH}/I_{VV} \approx 0.07$) have the same maximum unit intensity, while the VH spectra (Fig. 2b), were normalized so that the strongest depolarized peaks at $\approx 800$ cm$^{-1}$ have the same intensity (with a depolarization ratio $I_{VH}/I_{VV} \approx 0.35$).

In the VV Raman spectra (Fig. 2a) we distinguish also three bands. The previous calculation [5] of the VV Raman spectra on NS4 glass models have assigned the low-frequency band at about 520 cm$^{-1}$ to symmetric bending of the Si-BO-Si linkages, the mid-frequency band at about 780 cm$^{-1}$ to the Si motions against the BO atoms and the high-frequency band at about 1100 cm$^{-1}$ with a shoulder at about 920 cm$^{-1}$ to the Si-NBO stretching motions.

For the position and the relative intensity of the low-frequency band, a good overall agreement between the experimental and the CP calculated curve is observed although, e.g., the width of the CP band is smaller and the shoulder in the experimental data at about 600 cm$^{-1}$ is not reproduced. The agreement between the low-frequency VFF band and the experimental spectrum is less good - the calculated VFF intensity is stronger and the maximum peak position is shifted to slightly higher frequencies. In other words, the VFF potential overestimates the amplitudes of the Si-BO-Si symmetric bending vibrations.

The intensity of the CP calculated mid-frequency band is in good agreement with the experiment but its position is shifted approximately 80 cm$^{-1}$ to lower frequencies. The shape of the VFF corresponding band is similar to the experimental one, but we note a smaller intensity and a slight shift to lower frequencies (see the inset in Fig. 2a).

Concerning the high-frequency band, we note that the position of the main peak is shifted approximately 20 cm$^{-1}$ downwards in the CP case and approximately 20 cm$^{-1}$ upwards in the VFF case indicating slightly weaker and slightly stronger Si-NBO interactions, respectively. Both approaches yield much stronger intensity for the 920 cm$^{-1}$
band which arises mainly from Si-NBO stretching vibrations in SiO$_4$ tetrahedra with 2 NBO per Si ($Q^2$ species) [5].

In the depolarized (VH) spectra, the calculated low-frequency bands seem to be correctly positioned (see Fig. 2b, where we have lopped off the top of the VH spectra in order to see the details of the spectra in the low- and mid-frequency ranges). Regarding the relative intensities, we note a good agreement for the CP band. In the mid-frequency range, the CP band is broadened and shifted to slightly lower frequencies, while the VFF band is shifted to slightly higher frequencies. In a previous calculation of the VH Raman spectra using a NS4 model generated by RMC simulations [5], the agreement was better in this frequency range. Since the mid-frequency band arises mainly from Si vibrations in $Q^4$—species [5], the differences between the present VFF calculation and the results presented in Ref. [5] are to be attributed to the different degree of polymerization of the corresponding models [5, 6].

In the high-frequency range (see the inset in Fig. 2b) the calculated depolarized Raman intensities are much weaker in both calculated spectra which indicates that the corresponding Si-O bending BPA parameters are too small.

4. Discussion

In order to understand the differences in the VDOS and Raman spectra computed within the CP and VFF approaches, we have analysed first the corresponding partial VDOS. The partial VDOS curves $g_\alpha(\omega)$ in Fig. 3 ($\alpha = \text{Si, BO, NBO, Na}$) have been defined as:

$$g_\alpha(\omega_p) = g(\omega_p) \sum_{i=1}^{N} |e_i(\omega_p)|^2 \quad (1)$$

where $e_i(\omega_p)$, $i = 1, \ldots, N$, are 3-component real space eigenvectors.

For the low-frequency bands, we have an overall good agreement between the CP and VFF partial VDOS. The band maxima positions for the Si (Fig. 3a), BO (Fig. 3b) and NBO (Fig. 3c) atoms are very close ($\pm 30 \text{ cm}^{-1}$). In this frequency range the NBO atoms participate mainly in O-Si-O bending vibrations [5]. The biggest intensity differences are observed in the BO (Fig. 3b) and Na (Fig. 3d) partial VDOS, which can explain the differences in the total VDOS in this frequency range.

As can be seen in Fig. 3d, both the CP and VFF calculations predict a dominant Na contribution only in the low-frequency range, but the VFF peak is shifted ($\approx 40 \text{ cm}^{-1}$) as a whole to lower frequencies. From a previous VFF analysis [5] of the vibrational characteristics of two NS4 structural models obtained by classical MD and RMC simulations, it followed that the Na motion dominated below $\approx 100 \text{ cm}^{-1}$. In the present VFF calculation, the Na contribution reaches a maximum at $\approx 170 \text{ cm}^{-1}$. Thus the Na-O
stretching force constants used in the present work describe better the Na-O motion than the force constants reported in Ref. [5].

At intermediate frequencies, the CP and the VFF partial VDOS for the Si, BO and NBO atoms have qualitatively the same shape but the ones for Si and BO are shifted to lower frequencies in the CP calculation (Fig. 3a and b). These shifts are similar to the observed shift of the mid-frequency band in the VV calculated using the CP eigenmodes. So it seems that the CP approach does not describe properly the vibrational dynamics of the Si and BO atoms in the mid-frequency range. Interestingly, the Si motions are enhanced in the CP calculation while the BO motions are enhanced in the VFF calculation.

In contrast to this, the partial VDOS show that in the high-frequency range all of the VFF partial VDOS bands are stronger and more narrow (especially for the BO and Si atoms) than the CP ones. This feature may be related to the stronger localization of the CP modes in this frequency range, as it will be discussed below.

As a first measure for the localization of the modes we consider the participation ratio \( p_c \) which, for a given eigenmode \( \omega_p \), is defined as follows [27]:

\[
p_c(\omega_p) = \left( \frac{\sum_{i=1}^{N} |u_i(\omega_p)|^2}{N \sum_{i=1}^{N} |u_i(\omega_p)|^4} \right)^{1/2},
\]

where \( u_i(\omega_p) = e_i(\omega_p)/\sqrt{M_i} \) is the atomic displacement of atom \( i \) in mode \( p \) and \( M_i \) is the mass of atom \( i \). The frequency dependences of the CP and VFF participation ratios are shown in Figs. 4a and 4c. As can be seen from Fig. 4a and 4c, the CP modes are generally more localized than the VFF ones, especially around 200 and above 900 cm\(^{-1}\). This is an interesting result which merits to be studied in more details. The localization is also enhanced near the edges of the three main VDOS bands for both the CP and the VFF participation ratios. These are the so-called band tails containing localized modes, which have been already observed for a larger NS4 glass models in Ref. [5], as well as for silica glass models [5, 10, 28]. In the CP case, these tails are more pronounced, in particular at the top of the lower band and on both sides of the high-frequency bands. The analysis of the frequency dependences of the vibrational correlation lengths \( L_c(\omega_p) \) which are plotted in Fig. 4b and 4d, confirms the localization of the high-frequency modes. The vibrational correlation length is defined as:

\[
L_c(\omega_p) = \sqrt{\frac{\sum_{i=1}^{N} |r_i - r_p|^2 |u_i(\omega_p)|^2}{\sum_{i=1}^{N} |u_i(\omega_p)|^2}}
\]

where \( r_i \) is the position of atom \( i \), \( r_p \) is the center of mode \( p \) displacements, defined as \( \sum_{i=1}^{N} r_i |u_i(\omega_p)|^2 \). In this sense, the vibrational correlation length [29, 30] is the standard deviation of \( r_p \), and gives a measure of the spatial localization of the vibrational modes.
by indicating that the amplitude of the atomic vibrations decreases significantly beyond this correlation length.

5. Conclusions

In this work, we have investigated some aspects of the vibrational dynamics of a model of sodium tetrasilicate glass, constructed by combined classical and Car-Parrinello molecular dynamics simulations. Its vibrational dynamics has been then studied using two different approaches - a first principles one and a classical valence force fields one. The valence force field serves as a natural approach to analyze the character of the vibrational modes in terms of simple motions like stretching, bending and rocking. Within the bond polarization approximation, we have calculated the polarized Raman spectra and compared with experimental Raman data.

The VDOS calculated by the two methods have very similar shape, especially for the low-frequency bands below 500 cm\(^{-1}\). In the high-frequency range, the VFF partial VDOS for the Si, BO and NBO atoms are shifted to higher frequencies and they are narrower. This may indicate that the potential VFF parameters have to be adjusted in order to better reproduce the CP vibrational characteristics of our NS4 model (an increasing number of low frequency modes, the position as well as the localization of the high frequency modes).

The comparison of the calculated and experimental VV Raman spectra shows that a good agreement between the relative intensities of the low- and high-frequency bands is achieved using the CP eigenmodes. This indicates that the corresponding BPA parameters are approximately correct and can be used for calculation of the VV Raman spectra of structural models of silicate glasses that are still too large to be fully treated \textit{ab initio}. However, despite the fact that the CP eigenvectors are calculated from first principles they do not reproduce well the position of the mid-frequency VV and VH Raman bands at around 780 cm\(^{-1}\). Additional improvement of the BPA parameters describing the high-frequency depolarized Raman bands is also necessary.

The analysis of the character of the vibrational modes shows that the localization of the CP vibrational modes is stronger than the one of the VFF modes, in particular on the high \(\omega\) side of the low-frequency band \((\approx 200\text{ cm}^{-1})\) and on both sides of the high-frequency bands.
Acknowledgments

We thank Magali Benoit for very interesting and stimulating discussions. Part of this was supported by the European Community’s Human Potential Program under contract HPRN-CT-2002-00307, DYGLAGEMEM. The financial support from the German Science Foundation under project SFB 408 for N. Zotov is kindly acknowledged. The \textit{ab initio} simulations have been performed on the IBM/SP3 at CINES, Montpellier, FRANCE.
References

[1] E. Courtens, M. Foret, B. Hehlen, R. Vacher, Solid State Commun. 117 (2001) 187.

[2] R. Dupree, D. Holland, P.W. McMillan, R.F. Pettifer, J. Non-Cryst. Sol. 68 (1984) 399;
J. F. Emerson, P.E. Stallworth, P.J. Bray, J. Non-Cryst. Sol. 113 (1989) 253;
G. H. Wolf, D.J. Durben, P. F. McMillan, J. Chem. Phys. 93 (1990) 2280;
H. Maekawa, T. Maekawa, K. Kawamura, T. Yokokawa, J. Non-Cryst. Sol. 127 (1991) 53;
J. Kümmelken, L. H. Merwin, A. Sebald, H. Keppler, J. Phys. Chem. 96 (1992) 6405;
N. Zotov, H. Keppler, A.C. Hannon, A.K. Soper, J. Non-Cryst. Sol. 202 (1996) 153.

[3] N. Zotov, H. Keppler, Phys. Chem. Minerals 26 (1998) 107.

[4] A. A. Tesar, A. K. Varshneya, J. Chem. Phys. 87 (1987) 2986;
C. Huang, A. N. Cormack, J. Chem. Phys. 93 (1990) 8180;
C. Huang, A. N. Cormack, J. Chem. Phys. 95 (1991) 3634;
J. Oviedo, F. Sanz, Phys. Rev. B 58 (1998) 9047;
E. Sunyer, P. Jund, R. Jullien, Phys. Rev. B 65 (2002) 214203;
X. Yuan, A.N. Cormack, J. Non-Cryst. Sol. 319 (2003) 31.

[5] N. Zotov, I. Ebbsjö, D. Timpel, H. Keppler, Phys. Rev. B 60 (1999) 6383.

[6] S. Ispas, M. Benoit, P. Jund, R. Jullien, Phys. Rev. B 64 (2001) 214206.

[7] S. Ispas, M. Benoit, P. Jund, R. Jullien, J. Non. Cryst. Sol. 307-310 (2002) 946.

[8] N. P. Bansal, R. H. Doremus, Handbook of Glass Properties, Academic Press, INC., New York (1986).

[9] M. Benoit, S. Ispas, P. Jund, R. Jullien, Eur. Phys. J. B 13 (2000) 631.

[10] M. Benoit, W. Kob, Eur. Phys. Lett. 60 (2002) 269.

[11] B.W. H. van Best, G.J. Kramer, R.A. van Santen, Phys. Rev. Lett. 64 (1990) 1955.

[12] J. Horbach, W. Kob, K. Binder, Chem. Geol. 174 (2001) 87.

[13] R. Car, M. Parrinello, Phys. Rev. Lett. 55 (1985) 2471.

[14] D. Marx, J. Hutter, in Modern Methods, Algorithms of Quantum Chemistry, ed. J. Grotendorst, Forschungszentrum Jülich, NIC Series, 1 (2000) 301.
[15] CPMD Version 3.3, J. Hutter, A. Alavi, T. Deutsch, M. Bernasconi, S. Goedecker, D. Marx, M. Tuckerman, M. Parrinello, MPI für Festkörperforschung, IBM Research (1995-1999).

[16] W. Kohn, L. Sham, Phys. Rev. A 140 (1965) 1133.

[17] A.D. Becke, Phys. Rev. A 38 (1988) 3098; C. Lee, W. Yang, R.G. Parr, Phys. Rev B 37 (1988) 785.

[18] G.B. Bachelet, D.R. Hamann, M. Schlüter, Phys. Rev. B 26 (1982) 4199.

[19] N. Trouiller, J.L Martins, Phys. Rev. B 43 (1991) 1993.

[20] N. Zotov, J. Phys.: Condens. Matter 14 (2002) 11655.

[21] B. Michailova, N. Zotov, M. Marinov, L. Konstantinov, J. Non-Cryst. Sol. 168 (1994) 265.

[22] R. Alben, D. Weaire, J.E. Smith Jr., M.M. Brodsky, Phys. Rev. B 11 (1975) 2271.

[23] R.J. Bell, D.C. Hibbins-Butler, J. Phys. C 9 (1976) 2955.

[24] P. Umari, A. Pasquarello, A. Dal Corso, Phys. Rev. B 63 (2001) 094305.

[25] A. Rahmani, M. Benoit, C. Benoit, arXiv: cond-mat/0306332, Phys. Rev. B (2003) in press.

[26] F.L. Galeener, A.E. Geissberger, Phys. Rev. B 27 (1983) 6199.

[27] R. J. Bell, Methods Comput. Phys. 15 (1976) 215.

[28] S.N. Taraskin, S.R. Elliott, Phys. Rev. B 56 (1997) 8605.

[29] M. Marinov, N. Zotov, Phys. Rev. B, 55 (1997) 2938.

[30] W. Jin, P. Vashishta, R.K. Kalia, J.P. Rino, Phys. Rev. B, 48 (1993) 9359.
FIGURE CAPTIONS

Figure 1: Vibrational densities of states of the *ab initio* NS4 glass model obtained within the Car-Parrinello *ab initio* approach (solid line) and within a classical valence forcefield approximation (dashed line).

Figure 2: Frequency dependence of the VV (a) and the VH (b) Raman intensities calculated within the bond-polarizability approximation using the CP eigenmodes (dotted lines) and the classical VFF eigenmodes (dashed lines). The solid lines are the experimental spectra.

Figure 3: Partial VDOS for Si (a), BO (b), NBO (c), and Na (d). The solid and dashed lines correspond to the CP and VFF calculations, respectively.

Figure 4: Frequency dependences of the participation $p_c$ and of the vibrational correlation length $L_c$ in the CP case (panels a and b) and in the VFF case (panels c and d). The horizontal lines at a height equal to 5.405 Å (i.e. half of our simulation box length) are drawn as a guide for the eye in order to estimate the number of the normal modes with correlation length smaller or bigger than this value.
Figure 1:
Figure 2:
Figure 3:
Figure 4: