Addendum and Erratum: Nature of vibrational excitations in vitreous silica [Phys. Rev. B **56**, 8605 (1997)]

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The aim of this paper is to clarify details of the projectional analysis for atomic vibrations in vitreous silica presented in a paper by Taraskin and Elliott [Phys. Rev. B **56**, 8605 (1997)]. The description of the stretching and bending modes has been discussed in detail while a description of the rotational modes and the procedure of their calculation have not been given in full detail. We specify the method for calculating the rotational modes omitted in the paper. We also correct a misprint in the expression for the $\mathbf{B}_2^{(E)}$ mode which, unfortunately, has been reproduced in the vibrational analysis of the E mode in some publications.

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The structure of vitreous SiO_2 may be described as a network of corner-sharing SiO_4 tetrahedra, XY_4 , or as being comprised of Si-O-Si or O-Si-O structural units, XY_2 . An ideal XY_4 tetrahedron belongs to the cubic point group T_d and its normal vibrational modes can be described in terms of symmetry coordinates transforming according to the irreducible representations of this group [1–3],

$$3F_2 + A_1 + E + F_1. \quad (1)$$

Similarly, the atomic vibrations of the Si-O-Si or O-Si-O units can be decomposed into irreducible representations of the orthorhombic point group C_{2v} of a symmetric XY_2 molecule [1–3],

$$3A_1 + A_2 + 3B_1 + 2B_2. \quad (2)$$

The symmetry modes F_2 (or T_2 in Ref. [4]), A_1 , and E for SiO_4 structural units, and A_1 and B_1 modes for Si-O-Si and O-Si-O units have been discussed in detail in Ref. [5] while a description of the rotational modes F_1 and B_2 and the procedure for their calculation have not been given in full detail. Below, we specify the method for calculating the rotational modes omitted in Ref. [5]. For a perfect SiO_4 structural unit, the rotations should be made around three fourfold rotation-reflection axes S_4 passing through the central silicon atom, [1,6] as shown in Fig. 1(a) (the red line represents one of the axes). The direction vectors for the rotation axes, $\mathbf{w}_k$ ($k = 1, 2, 3$), can be found in terms of position vectors of the oxygen atoms, $\mathbf{a}_{i'}$ ($i' = 1, \dots, 4$), as follows:

$$\mathbf{w}_1 = \mathbf{a}_1 + \mathbf{a}_2, \mathbf{w}_2 = \mathbf{a}_1 + \mathbf{a}_3, \mathbf{w}_3 = \mathbf{a}_1 + \mathbf{a}_4, \quad (3)$$

with the origin of the coordinate system fixed at the Si atom [see Fig. 1(b)]. The choice of the rotation axes for a *regular* tetrahedron given by Eq. (3) is unique due to the property, $\sum_{i'=1}^4 \mathbf{a}_{i'} = 0$.

In vitreous silica, the SiO_4 tetrahedra are distorted and this destroys the strict orthogonality of the rotation axes leading to some ambiguity in their choice. For example, axes (not necessarily mutually orthogonal) given by Eq. (3), in general, do not coincide with axes given by the same equations in which the vector $\mathbf{a}_1$ is replaced by $\mathbf{a}_2$ and $\mathbf{a}_2$ by $\mathbf{a}_1$. However, these distortions are not significant and average out when summing over many structural units, so that the sum of all contributions to the vibrational density of states (VDOS) corresponding to projections onto different symmetry modes including rotations practically coincide with the total VDOS obtained by numerical diagonalization of the dynamical matrix (see below).

In order to proceed with the projectional analysis, the symmetry displacement vector characterizing rotations of tetrahedra (F_1) can be defined as:

$$\mathbf{R}_k^{(F_1)} = \frac{1}{\sqrt{4}} \{0, \hat{\mathbf{r}}_{1k}, \hat{\mathbf{r}}_{2k}, \hat{\mathbf{r}}_{3k}, \hat{\mathbf{r}}_{4k}\}, \quad (4)$$

where

$$\hat{\mathbf{r}}_{i'k} = \frac{\mathbf{w}_k \times \mathbf{a}_{i'}}{|\mathbf{w}_k \times \mathbf{a}_{i'}|}. \quad (5)$$

FIG. 1. Graphical representation of a *regular* tetrahedral SiO_4 structural unit: (a) one of the rotation axes, $S_4(\mathbf{w}_1)$ (shown in red) with $\mathbf{w}_1 = \mathbf{a}_1 + \mathbf{a}_2$, goes through the origin (Si atom shown by the solid circle), i , connects two midpoints of edges 1–2 and 3–4 and thus belongs to the σ reflection plane (shaded in blue) which also contains a threefold axis C_3 [6]; (b) the position vectors $\mathbf{a}_{i'}$ of the oxygen atoms (open circles).

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FIG. 2. Graphical representation of an XY_2 structural unit. The direction vectors $\mathbf{w}_k$ for the rotation axes passing through the atom X (solid circle) are defined by the vector combinations [see Eq. (7)] of the position vectors $\mathbf{a}_{i'}$ for the atoms Y (open circles).

Similarly, for rotations of Si-O-Si or O-Si-O structural units, the symmetry (B_2) displacement vector can be defined as

$$\mathbf{R}_k^{(B_2)} = \frac{1}{\sqrt{2}} \{\hat{\mathbf{r}}_{1k}, \mathbf{0}, \hat{\mathbf{r}}_{2k}\}, \quad (6)$$

where $\hat{\mathbf{r}}_{i'k}$ are given by Eq. (5), and rotations are made around three orthogonal axes with the direction vectors

$$\mathbf{w}_1 = \mathbf{a}_1 - \mathbf{a}_2, \mathbf{w}_2 = \mathbf{a}_1 \times \mathbf{a}_2, \mathbf{w}_3 = \mathbf{w}_1 \times \mathbf{w}_2. \quad (7)$$

Here, the position vectors $\mathbf{a}_{i'}$ point to atoms Y with atom X being at the origin (see Fig. 2).

Finally, the projection of the j th displacement eigenvector $\mathbf{u}^j$ onto the rotation (around axis $\mathbf{w}_k$) displacement vector $\mathbf{R}_k$ ($\mathbf{R}_k^{(F_1)}$ or $\mathbf{R}_k^{(B_2)}$) is given by Eq. (21) in Ref. [5] which for rotations reads

$$r_{\mathbf{R}_k, i}^j = \sum_{i'(i)} \mathbf{u}_{i'}^j \cdot \mathbf{R}_{i'k}, \quad (8)$$

where the summation is taken over all atoms i' of a particular structural unit (i). The total contribution of the structural unit

FIG. 3. The partial VDOS for the projections onto the vibrations of SiO_4 structural units: A_1 symmetric stretching (solid red line), F_{2s} asymmetric stretching (dashed blue line), F_{2b} bending (dotted magenta line), E bending (dot-dashed green line), F_1 solid-unit rotations (double dot-dashed orange line), and their sum (brown dashed line) coinciding with the total VDOS (black solid line). The results are obtained for a model with 8232 atoms [7].

(i) to the rotational motion equals the sum of the squares of projections onto three axes, i.e., $\sum_{k=1}^3 (r_{\mathbf{R}_k, i}^j)^2$.

The expression for the $\mathbf{B}_2^{(E)}$ symmetry mode in Eq. (34) of the paper [5] contains a misprint. The correct expression reads

$$\mathbf{B}_2^{(E)} = B_2 \{ \mathbf{0}, (\hat{\mathbf{b}}_{13} - \hat{\mathbf{b}}_{14}), (-\hat{\mathbf{b}}_{23} + \hat{\mathbf{b}}_{24}), (\hat{\mathbf{b}}_{31} - \hat{\mathbf{b}}_{32}), (-\hat{\mathbf{b}}_{41} + \hat{\mathbf{b}}_{42}) \}. \quad (9)$$

In fact, the correct expression given by Eq. (9) has been used in the code for the calculation of the E bending component, the results of which are presented in Fig. 15 of Ref. [5]. In order to confirm this, we have repeated the projectional analysis of Ref. [5] for a larger model (8232 atoms [7]) of vitreous silica constructed by using the BKS potential [8] (see Fig. 3). We should mention that, unfortunately, the misprint in the expression for the $\mathbf{B}_2^{(E)}$ mode has been reproduced in the VDOS analysis of the E mode in some publications [9–12].

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