The Raman coupling coefficients of calcium and sodium silicate melts in high-frequency region – SiOT model study

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Abstract. The Raman coupling coefficient (CC), which was defined by Shuker and Gammon, of silicate melt in high-frequency region, is still an untouched subject but the key parameter for quantitatively processing the Raman spectra (RS) to achieve the abundance of microstructural units. In this paper, we present the results of a newly constructed model – SiOT model (Wu et al) about the Raman coupling coefficients of calcium and sodium silicate melts, especially in the high-frequency region. This new model combines classical MD simulation with decomposition of simulated configurations and vibrational analysis including Wilson’s GF matrix method, electro-optical parameter method (EOPM) and bond polarizability model (BPM). The displacement dependence of the cluster polarizability through the combination of EOPM and BPM connotes the description of the frequency dependence of CC. This allows us to make a direct comparison for the first time between the calculated VDOS (vibrational density of states) and RS within the entire frequency range. A strong conclusion was given that the partial VDOS, RS and CC are all the intrinsic properties of respective Q species, and the only variable inducing the change in total VDOS, RS and CC is the change of microstructure, i.e. the distribution of the Qi.

1. Instruction

In the past half century, great progress has been achieved in the RSI study of silicate glasses and melts, especially the high-temperature Raman spectra (HTRS) technique for the probing into the microstructure of molten silicates. \(^1\) But the quantitative analysis of Raman spectra (RS) \(^4\) in order to extract microstructural knowledge particularly the distribution of Q species (the Si-O tetrahedral units with i bridging oxygens), is still confronting many difficulties. One of the difficulties is the determination of Raman scattering coefficients, which are used to reduce the area fractions of characteristic peaks (located in high-frequency region) of Q species into the corresponding molar fractions. Mysen and Frantz \(^4\) have used NMR data of Stebbins \(^5\) in conjunction with their Raman data to compute the ratio of Raman scattering coefficients for Q and Q. Consequently, they used this ratio to deduce the distribution of Q species from the results of Gaussian deconvolution of high-frequency envelopes. You et al. \(^2\) also achieved two ratios of \(\theta_3/\theta_2\), \(\theta_1/\theta_2\) of the sodium disilicate melt with the reference of the inner standard of polycrystalline NaNO2 powder.

As we know, the disorder-induced broadening of peaks in RS corresponds to the frequency distribution in vibrational density of states (VDOS). In 1970, Shuker and Gammon \(^6\) defined a frequency-dependent coupling coefficient (CC) to correlate the Raman intensity and VDOS. After that, many researchers, such as Sen and Thorpe \(^7\), Achibat et al. \(^8\) and Ivanda et al. \(^9\), has tried to use this concept to interpret some Raman scattering properties of amorphous materials. Summarization of
the previous works, two common points can be achieved: 1) Almost all works were focused on the low-frequency region about the Boson peak; 2) In all subjects investigated, none but silica belongs to the silicate family. Meanwhile, the interpretation of medium- and high-frequency Raman peaks has also achieved great progress. But the CC that makes the shape of the Raman peaks in these two regions is still severely lack of comprehension.

It is known that the Raman scattering coefficient (not the CC) is a constant to connect the molar fraction with the area fraction of high-frequency characteristic band. That’s to say, the Raman scattering coefficient is essentially the integral mean of the CC in the high-frequency region. Thus, if we can understand the frequency dependence of CC, the Raman scattering coefficient is readily solved.

According to the original definition of VDOS: 6

\[ \rho(\nu) = \frac{dn}{d\nu} \]  \hspace{1cm} (1)

Where \( n \) is the number of the oscillators. \( \nu \) denotes vibrational energy level or frequency. As definition of Shuker and Gammon 6 and Achibat et al. 8, following equation was used to exhibit the relation of VDOS and other kinds of spectra:

\[ I(\nu, T) = C(\nu)\rho(\nu)(n(\nu, T)+1)/\nu \]  \hspace{1cm} (2)

Where, \( I(\nu, T) \) is the RS intensity. \( C(\nu) \) is the so-called coupling coefficient. \( n(\nu)+1 \) is the Bose-Einstein occupation factor for the Stokes Raman component. It was considered that INS might be used to give directly the measurement of VDOS. In fact, this is an approximation due to that the coupling constant of INS is not a constant but a slowly varying function of the frequency. In addition, so far the experiments were merely carried out for some simple compounds as SiO\(_2\) and so on 10-12. This situation promoted some researchers to develop the way of calculating VDOS. The computation methods they used and their principal results can be found from the review of Galeener etc. 13 and Zotov etc. 14.

In the laboratory of the present authors, the HTRS technique was worked up for the microstructure study of molten silicates at the temperature up to 2000K. To facilitate the understanding of the recorded spectra, the computation of RS, VDOS and consequently corresponding CCs was progressed with a newly developed procedure 15.

This new procedure 15 is designed for the theoretical RS calculation of silicates, particularly for the glasses and melts. This procedure combined the classical MD simulation with Wilson’s GF matrix method, electro-optical parameter method (EOPM) and bond polarizability model (BPM). It can give not only the total but also the partial RS. In terms of the Raman intensity calculation, it can also give the results of VDOS and the corresponding CCs. The displacement dependence of the cluster polarizability through the combination of EOPM and BPM connotes the description of the frequency dependence of the CC.

2. Description of SioT model

The calculation procedure included five steps: 1) MD simulation with BMH potential; 2) Decomposition of the simulated configurations into five defined Q_i-species; 3) Eigen vibrational analysis of Q_i with Wilson’s GF matrix method to obtain the eigen frequencies and corresponding vibrational vectors; 4) Raman intensity calculation from the vibrational vectors obtained in previous step; 5) Accumulation of all data of frequencies and corresponding Raman intensities to form the final results, including total and partial RS and relevant VDOS. Following is the extending illumination of this procedure and the assessment of some parameters, and the detailed deduction and description of the formula in this procedure can be found in Ref. [15].

2.1. Sample selection and MD simulations

Two representative binary silicate groups of CaO-SiO\(_2\) and Na\(_2\)O-SiO\(_2\) were studied and for each group, 4 typical samples were selected as examples. The modified MOLDY program 16 was utilized for the MD simulations. Atomic numbers and composition for each sample are listed in the Table 1.
Because our focus is mainly on the medium- (400-800 cm\(^{-1}\)) and high-frequency (800-1200 cm\(^{-1}\)) regions, the atomic numbers were determined under the constraint of uniform number of \(Q_i\)-species, which indicates the uniform number of Si.

**Table 1.** The samples and particle numbers of simulated CaO-SiO\(_2\) and Na\(_2\)O-SiO\(_2\) systems.

| O/Si | CaO-SiO\(_2\) | Na\(_2\)O-SiO\(_2\) |
|------|---------------|---------------------|
|      | Sample | Ca | Si | O | \(\Sigma\) | Sample | Na | Si | O | \(\Sigma\) |
| 2.5  | Ca1     | 50 | 100| 250| 400   | Na1   | 100| 100| 250| 450   |
| 3    | Ca2     | 100| 100| 300| 500   | Na2   | 200| 100| 300| 600   |
| 3.5  | Ca3     | 150| 100| 350| 600   | Na3   | 300| 100| 350| 750   |
| 4    | Ca4     | 200| 100| 400| 700   | Na4   | 400| 100| 400| 900   |

Born-Mayer form potential was used in this MD simulation:

\[
u(r) = q_i q_j / r_{ij} + B_{ij} \exp\left(-r_{ij}/\rho_{ij}\right) \tag{3}\]

For three pairs of Si-Si, Si-O and O-O, the values of Matsumiya et al.\(^{17}\) were used, in which the two parameters of \(B_{ij}\) and \(\rho_{ij}\) were expressed as \(B_{ij} = \rho_{ij} = b_i b_j\); for the rest three pairs, applied were the values of Kieffer and Angell \(^{18}\), in which the parameter of \(B_{ij}\) was expressed as \(B_{ij} = 1 + q_i n_i + q_j n_j\), where \(n_i\) represents the number of out-shell electron in atom \(i\) and \(\rho_{ij}\) was maintained constant, 0.029 nm. All the parameters included in this potential were listed in Table 2 of Ref. \(^{15}\). Formal charges were used for each ion. Coulomb interactions were handled using the Ewald sum in three dimensions and the cut-off distances for the real- and reciprocal-space sum were adjusted according to the total number of sites and the volume. All ions were treated as rigid.

**NPT** ensemble was used with a time step of 0.001 ps. The initial temperature was ideally 6000K for 2000 steps to relax the initial random configuration to overcome the energy barrier. Upon completion of the 6000K run, the system was quenched to the target temperature of 2000K for 8000 steps and then relaxed for another 10000 steps to achieve some structural properties, such as RDF. Finally, a 300,000 steps relaxation was continued to obtain 2500 stochastic configurations for the frequency and intensity calculations.

**2.2. Decomposition of configurations**

As shown in Fig.1, all Si atoms were coordinated by 4 O atoms. This has also been proven by Palin et al.\(^{19}\). Thus, all configurations similar to the snapshot in Fig.1.(a) were decomposed into five defined \(Q_i\)-species as shown in Fig.1.(b). From Fig.1.(b), the difference between \(Q_1-Q_4\) is very clear.

**Figure 1.** A random snapshot of the simulated configurations of sample Ca3 (a) and a fragment including \(Q_1-Q_4\) extracted from the selected snapshot. Blue ball: Ca; yellow: Si and red: O.
2.3. Eigen vibrational analysis of $Q_i$ structural units

For each $Q_i$ after decomposition of configurations, eigen vibrational analysis was carried out using the Wilson’s GF matrix method. Essentially, it is to solve the following secular equation:

$$[G F - \lambda E] = 0 \quad (4)$$

Where $G$ is the kinetic matrix; $F$ is the force constant matrix, or called potential matrix; $\lambda$ is the for-solving eigen value related directly with the eigen frequency $\nu$ following $\nu = \sqrt{\lambda/2\pi c}$; $E$ is the unit matrix.

In this work, the empirical two-body Born-Mayer potential $u(r_{ij})$, as shown in Eqn. (3) and used in the MD simulation, was also applied to result in the force constant. Namely, the $F$ matrix element $(f_{ij})$ is defined by the following equation

$$f_{ij} = \left( \frac{\partial^2 V}{\partial \tau_i \partial \tau_j} \right)_0 \quad (5)$$

Where the subscript 0 denotes the equilibrium position. $\tau_i$ represents the $i$th internal coordinates. $V$ is the sum of the two-body potentials $u(r_{ij})$ for each $Q_i$:

$$V = \sum_{i,j} u(r_{ij}) \quad (6)$$

2.4. Raman intensity calculation

The Raman intensity is relative rather than absolute. According to the Raman scattering theory, when a completely polarized incident beam with electric field vertical to the scattering plane irradiate the sample, the induced perpendicular and parallel scattering intensities can be expressed as

$$I_\perp = K'(\nu_0 \pm \nu_k)^4 (\alpha'_{yz})^2 Q_{0\perp}^2 \propto (\nu_0 \pm \nu_k)^4 (\alpha'_{yz})^2 Q_{0\perp}^2$$

$$I_\parallel = K'(\nu_0 \pm \nu_k)^4 (\alpha'_{zz})^2 Q_{0\parallel}^2 \propto (\nu_0 \pm \nu_k)^4 (\alpha'_{zz})^2 Q_{0\parallel}^2$$

Where, $\nu_0$ is frequency of incident and $\nu_k$ frequency of the $k$th normal mode. $Q_{0\parallel}$ is the vibrational vector for the $k$th mode. The rest polarizability derivatives of $\alpha'_{yz}$ and $\alpha'_{zz}$ can be calculated from

$$\alpha'_{yz} = \frac{\partial \alpha_{yz}}{\partial Q_{iz}} = \left[ 1 - e_{yz} \right] \left[ \frac{\partial \alpha_{yz}}{\partial q} - \frac{\partial \alpha_{yz}}{\partial q} \right] + \Xi_{yz} \cdot 1^{(1)}$$

$$\Xi_{yz} = \sqrt{2} \left[ \alpha_{yz} - \alpha_{zz} \right] E_{y2z} (E_{y2z} + E_{z2y}) (S^\perp \Delta \bar{E} \bar{A})$$

$$\alpha'_{zz} = \frac{\partial \alpha_{zz}}{\partial Q_{iz}} = \left( e_{zz} e_{zz} + e_{zz} e_{zz} \right) \left[ \frac{\partial \alpha_{zz}}{\partial q} - \frac{\partial \alpha_{zz}}{\partial q} \right] + \Xi_{zz} \cdot 1^{(1)}$$

$$\Xi_{zz} = \sqrt{2} \left[ \alpha_{zz} - \alpha_{zz} \right] (E_{zz} (E_{zz} + E_{zz}) + E_{zz} (E_{zz} + E_{zz})) (S^\perp \Delta \bar{E} \bar{A})$$

The description and expansion of all the terms in above two equations can be found in APPENDIX of Ref. [15]. Here, the deduction of Eqn.(8) was based on the three assumptions of bond polarizability model and29 and the third assumption, which defined a linear relationship of parallel and perpendicular parts of each bond polarizability with corresponded bond length, introduced four parameters of $\alpha^0_z$, $\alpha'_z$, $\alpha^0_y$, and $\alpha'_y$ for pre-evaluation in turn: $3.5\text{Å}^3$, $0.65\text{Å}^3$, $2.27\text{Å}^2$, and $0.64\text{Å}^2$.

2.5. Data accumulation to form the VDOS and RS

The data accumulation included two steps. Firstly, all the necessary data for the same kind of $Q_i$ were accumulated to form the corresponded partial spectrum; Secondly, the five partial spectra were overlapped to form the total spectra, including VDOS and RS. The only difference was that for VDOS
the necessary data were only frequencies for all normal modes and for RS the necessary data included frequencies as well as the corresponding Raman intensities.

3. VDOS and corresponded RS

Since VDOS represents the relative number of vibrational modes for each particular frequency, the information obtained from experiments is quite limited and often inadequate to provide precise identification of particular modes, just like the total VDOS in Fig.2. However, the present theoretical procedure can provide not only the total VDOS but also the partial VDOSs, which gives the detailed frequency dependence of the different vibrational modes for each \( Q_i \)-species.

Therefore, Fig. 2 exhibits the results of the partial and total VDOSs and RS, as well as the corresponding vibrational modes. All the vibrational modes are sorted into 6 kinds: SS for symmetrical stretching (of \( Q_i \) units as a whole); ASS antisymmetric stretching; SB symmetrical bending; ASB antisymmetric bending; SBB symmetrical bending of bridging oxygen; ASBB antisymmetric bending of bridging oxygen. In Fig. 2, all the partial VDOSs include three envelopes respectively located at low-, medium- and high-frequency regions. For the high-frequency envelope, two types of normal modes, SS and ASS, give the contribution and overlap each other. In these two modes, the stretching of \( O_{ab} \) is along the Si-O_{ab} bond while the stretching of \( O_b \) is parallel with the line connecting both terminal Si atoms of Si-O_{ab}-Si. For a fully symmetrical tetrahedron, as depicted in our point group analysis of these five kinds of \( Q_i \)-species, ASS mode is of threefold degeneracy and SS mode is nondegenerate. In the previous studies, we have pointed out that the characteristic bands for \( Q_2 \) should be not symmetrical because of the notable Raman intensities of antisymmetric stretching modes. From the partial VDOSs in Fig. 2, we found that the SS and ASS peaks for \( Q_2 \)-species were located farthest away with each other while for \( Q_3 \)- and \( Q_4 \)-species, the differentiation of SS and ASS modes becomes even impossible. Because of the least symmetry of \( Q_2 \) in five \( Q_i \)-species and consequently the least Raman intensity difference between SS and ASS modes, the phenomenon of some unknown little bands achieved after deconvolution of high-frequency envelope in experimental spectra can be fully explained and resolved. Moreover, the intensity of VDOS of \( Q_4 \) in this region has a similar magnitude to that in medium-frequency region, while the intensity of RS of \( Q_4 \) in high-frequency region is ignorable. This can be interpreted with the following CC. Similarly, two types of normal modes are located at the medium-frequency regions, SBB and ASBB.

From Fig.2, we can summarize that: (1) the partial spectra (including partial VDOS and RS) of \( Q_0 \) have no peaks for the SBB or ASBB modes because this unit has no bridging oxygen; (2) the partial spectra of \( Q_1 \) have only one peak in the medium-frequency region corresponding to the SBB mode because \( Q_1 \) has only one bridging oxygen; (3) for any \( Q_i \), the partial spectra have similar line shape for different composition; (4) from \( Q_2 \) to \( Q_4 \), the intensities differ little between medium- and high-frequency peaks for VDOS, but greatly for the RS; (5) from \( Q_0 \) to \( Q_4 \), high-frequency peaks of partial RS become weaker but on the contrary for medium-frequency peaks under the condition of the same intensity of VDOS. All of these items, especially the fourth and fifth, are correlated with the action of the CCs.

Fig. 3 shows the deconvolution from the total spectra into partial spectra for both VDOS and RS, taking Na2 as example. We can found: (1) although the low-frequency peaks have great intensity for VDOS, but they generate very little signal in RS; (2) the antisymmetric modes, e.g. ASS and ASBB, has similar intensity with the corresponding symmetrical modes, e.g. SS and SBB, in VDOS, but their intensities of RS are much weaker than their counterparts. These can also be interpreted from the line shape of CCs.
Figure 2. Calculated partial and total VDOSs of 4 samples for each group.
4. Partial and total CCs

Fig. 4 shows the partial and total CCs of four calcium silicate melts. From it, although the line shape of total CCs varies greatly, the partial CCs have almost no change for different samples. First of all, the line shape of CC, whether partial or total, makes known that the CC acts as a function of the frequency. From the change of CC with the frequency, all the differences between the VDOS and RS can be interpreted. So, summarizing the above analysis gives us the first strong conclusion that the partial VDOS, RS and CC are all the intrinsic properties of respective $Q_i$, and the only variable inducing the change in total VDOS, RS and CC is the change of microstructure, i.e. the distribution of the $Q_i$.

Accompanying with the above conclusion, some other regulations can also be extracted from Fig. 4. Firstly, no peaks appear in the low-frequency region of all CCs. That is the reason why the strong peaks in VDOS generate very weak peaks in RS. In fact, the modes generating low-frequency peaks in VDOS are mainly bending of O-Si-O with little change of Si-O length. So, these kinds of vibrations can not induce very large variation of polarizability of structural units. Secondly, there is
almost no signal in the high-frequency region but a strong peak in medium-frequency region of partial CC of Q₄. Because amorphous SiO₂ is completely Q₄, the similarity of these calculated partial spectra of Q₄ to those of amorphous SiO₂ validates our model to some extent. Basically, the symmetric structures of four bridging oxygens account for this phenomenon because of the counteraction of both Si-O bonds in each Si-O₈-Si for the effect on polarizability. Thirdly, from Q₁ to Q₃, the uptrend of medium-frequency peaks accompanied with the downtrend of high-frequency peaks accounts for the similar trends of RS mentioned in section 3. Fourthly, comparing all the partial CCs with their corresponding VDOSs told us that the antisymmetric mode has very low CC relative to the high CC of symmetric modes except those of Q₂. That’s the reason why the characteristic bands of Q₂ is not symmetrical but the others are. Finally, all the results of this paper are only about two typical binary silicate melts, so the next step will be the extending of our model to other binary systems and ternary systems.

5. Conclusions

This paper applied our newly model for the study of VDOS, RS and most importantly CC for two typical groups, calcium and sodium silicate melts, with different compositions. Through careful analysis of partial and total VDOS, RS and CC, several important regulations have been achieved. Among those, the most important conclusion is that the partial VDOSs, RSs and CCs are all the intrinsic properties of respective Qᵢ, and the only variable inducing the change in total VDOS, RS and CC is the change of microstructure, i.e. the distribution of the Qᵢ.

Acknowledgements

This work is supported by the Chinese Natural Science Foundation under Grants Nos. 50504010, 40203001 and 50334040 and Shanghai Natural Science Foundation under Grants Nos. 04ZR14054 and Youth Foundation of Shanghai Educational Administration under Grants Nos. 04AC97. The MD simulations are performed with modified software of MOLDY.

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