Solubility mechanisms of H$_2$O in silicate melts at high pressures and temperatures: a Raman spectroscopic study: discussion

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In their paper on the solubility mechanism of H$_2$O in silicate melts at high pressures and high temperatures, Mysen et al. (1980) have used Raman spectroscopy to identify the molecular configurations present in quenched melts of compositions NaAlSi$_2$O$_6$, jadeite, and NaAlSi$_3$O$_8$, albite. They have used both H$_2$O and D$_2$O in various concentrations up to ~40 mole%. Any conclusions reached on the basis of these Raman studies strongly depend upon the band assignments made early in this paper. I would like to point out some errors in the assignments that affect the whole discussion that follows.

On page 903 it is stated with reference to a paper by Stolen and Walrafen (1976) that "Si-OH stretch vibrations are expected in the frequency region near 950 cm$^{-1}$." Shortly after it is said: "The analogous Si-OD bands are at frequencies that are lower than those of the OH vibrations by a factor of $\sqrt{2}$." This statement is inaccurate, because use of the factor $\sqrt{2}$ suggests that one simply takes the root of the mass ratio D/H for calculating the isotope shift factor for all normal modes which involve deuterium and hydrogen respectively.

Internal modes of the OH and OD group, where the O–H or O–D vibrate against each other, must be distinguished from other modes where the OH or OD group behave as an entity vibrating against, for instance, Si or Al.

The stretching frequency $\tilde{\nu}_{12}$ of an oscillator composed of two masses $m_1$ and $m_2$ depends upon (a) the force constant $K_{12}$ and (b) the reduced mass $\mu_{12}$:

$$\tilde{\nu}_{12} = \frac{1}{2 \pi c} \sqrt{\frac{K_{12}}{\mu_{12}}}$$  

where $c$ is the speed of light. The reduced mass is given by

$$\mu_{12} = \frac{m_1 \cdot m_2}{(m_1 + m_2)}$$

If we consider the O–H stretch vibration, i.e., the internal vibration of the O–H oscillator, equation 2 becomes

$$\mu_{\text{OH}} = \frac{16 \cdot 1}{(16 + 1)}$$  \hspace{1cm} (2a)

Correspondingly for the O–D stretch vibration we obtain

$$\mu_{\text{OD}} = \frac{16 \cdot 2}{(16 + 2)}$$  \hspace{1cm} (2b)

Assuming that the force constant for the OH bond is equal to that of the OD bond (which is correct within the limits of the zeropoint energy) we can use equation 1 to calculate the frequency shift factor for essentially "free" OH$^-$ and OD$^-$:

$$\tilde{\nu}_{\text{OD}} = \sqrt{\frac{\mu_{\text{OD}}}{\mu_{\text{OH}}}} = \sqrt{\frac{16 \cdot 2}{(16 + 2)}} = \sqrt{\frac{2 \cdot 17}{18}} = 1.37$$

This value is smaller than the root of the mass ratio D/H, $\sqrt{2}$ $\approx$ 1.41. The reason is that, when the H or D vibrates, the O is not at rest: it also vibrates and thus lowers the frequency of the internal O–H and O–D modes (Langer and Lattard, 1980).

However, on p. 903, Mysen et al. (1980) specifically refer to the Si–OH stretching band near 950 cm$^{-1}$; this band does not represent an internal O–H mode but an external one where the OH-group, mass 17, vibrates as a whole against the Si, mass 28. Correspondingly, in the Si–OD stretching mode the OD group vibrates against the Si. In order to indicate that the internal O–H and O–D vibrations are not excited, I propose to put these rigid entities OH$^-$ and OD$^-$ into parentheses: Si–(OH) and Si–(OD). If we calculate the reduced masses, we obtain: 28 · 17/(28 + 17) and 28 · 18/(28 + 18) respectively. The theoretical isotope shift factor thus becomes:
If the Si–(OH) stretch vibration occurs at about 950 cm\(^{-1}\) which is correct (Stolen and Walrafen, 1976), the Si–(OD) stretch vibration will not occur at a frequency lower than 933 cm\(^{-1}\). Coupling between Si and the other O\(^2-\) ligands may decrease this value slightly because in its vibrational motion the Si is not independent of the O\(^2-\) to which it is linked by rigid Si–O bonds. Hence, if the Si and the OH vibrate against each other, the Si partially drags along the other three oxygen. Thus, instead of calling the mass 28 for Si in equation 4, we have to choose an effective mass in order to take such coupling into account. For strong coupling the Si and its three oxygen ligands can be considered as a rigid entity: X–(OH), where X is equal to (–SiO\(_3\)). In this case the X–(OH) versus X–(OD) isotope shift factor becomes 1.023 which would bring the stretching band to 928 cm\(^{-1}\). If, as an extreme case, the (OH) and (OD) are allowed to vibrate against an infinitely large and rigid –Si–O–Si–frame, the Si(OD)/Si(OH) isotope shift factor becomes \(\sqrt{18/17} \approx 1.029\). This is the highest value allowed by theory. To assume for Si–(OD)/Si–(OH) modes an isotope shift factor in the vicinity of \(\sqrt{2}\) is a serious error.

By the same argument the statement made by Mysen et al. (1980) on p. 904 can be shown to be wrong: "We conclude, therefore, that the 880 cm\(^{-1}\) band cannot be assigned to Si–H, Si–D, Al–H, Al–D, Si–OH, Si–OD, Al–OH or Al–OD vibrations." The isotope shift factors for Al–(OH) versus Al–(OD) stretch vibrations fall into the range between 1.0175 and 1.029. For a band at 880 cm\(^{-1}\) the shifts will therefore be not more than 15–25 cm\(^{-1}\). Considering the broadness of the Raman bands shown in Figure 2 on p. 904 (Mysen et al., 1980), such a small shift cannot be ascertained. Hence, the 880 cm\(^{-1}\) band may well be due to an Al–(OH) vibration.

In order to arrive at a complete assignment of all vibrational bands, one would have to carry out a factor group analysis of all possible modes and use force fields to calculate the corresponding frequencies. Unfortunately, at present, silicate glasses are still far too complicated for such a rigorous treatment. In favorable cases isotope shift factors of deuteroylated versus hydroxylated samples can be useful, if the appropriate isotope shift factors for internal O–D/O–H and external X–(OD)/X–(OH) modes are used correctly.

Finally, I feel that Mysen et al. (1980) may be incorrect with regard to absence of molecular H\(_2\). They state, with reference to a paper by Lucovsky et al. (1979), "the presence of molecular H\(_2\) in the quenched Ab + H\(_2\)O melt is ruled out" (p. 905). First, the paper by Lucovsky et al. (1979) deals with H-doped silicon, the α-Si:H alloy, and does not mention molecular H\(_2\) at all. Second, the use of the expression "is ruled out" implies total absence of H\(_2\). However, Raman bands of H\(_2\) are weak. One generally needs, with large samples, the equivalent of one bar H\(_2\) pressure, \(=3 \times 10^5\) H\(_2\) per cm\(^3\), to obtain a detectable (H–H) Raman signal. The small size of the glass chips used by Mysen et al. (1980), \(\leq 1\) mm\(^3\), may have prevented the detection of H\(_2\) even in the mole % range.

References


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