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New features in the Raman spectrum of Silica:
Key-points in the improvement on structure knowledge

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This paper reports the evidence of new signatures in the low-frequency Raman spectrum of silica, obtained by very high signal-to-noise experiments. Two new Raman lines are observed at 295 and 380 cm$^{-1}$, and the presence of a third one at 245 cm$^{-1}$ is needed to account for the experimental spectra. The origin of these supplementary lines is discussed in terms of n-membered rings of [SiO$_4$]$^{2-}$ tetrahedral entities inside the glassy network.

Amorphous silica (SiO$_2$) is one beyond the most-well known materials, with interests going from a model compound in glass physics up to numerous industrial applications for optics and electronics. A huge number of papers devoted to it stands in the literature, in such a point that its structure and dynamics look well-known and are then used as reference for the study of more complex systems. Raman scattering investigations for instance are numerous and it is then difficult today to identify the first report on silica. The Raman spectrum of silica is today rather well understood since the works by Galeener and Lucovsky thirty years ago and confirmed by subsequent ab-initio calculations. The low-wavenumbers region of the silica Raman spectrum in the VV configuration polarization is usually decomposed as made of the boson peak at low wavenumbers (pointing around 50 cm$^{-1}$), a broad and asymmetric band at 450 cm$^{-1}$ assigned to $\delta_{\text{bend}}$ (SiOSi) bending vibrations (frequently referred as R-band), plus the D$_1$ and D$_2$ narrow peaks closed to 495 and 600 cm$^{-1}$. One widely accepted view of the structure of silica is a disordered more or less open network of corner-linked interconnected [SiO$_4$] tetrahedral entities. Such view intrinsically considers the existence of [SiO$_4$]$_2$ membered rings (hereafter denoted MR), and as an evidence, the so-called D$_3$ and D$_4$ peaks are now unambiguously assigned to respectively four-tetrahedral (4-MR) and three-tetrahedra membered rings (3-MR). The specific dynamics of these MR was recently observed by picosecond spectroscopy, that confirms the strong decoupling of these vibrations from the whole silica network. Nevertheless these assignments remain partially discussed, with possible mixed influence of 3-MR and 4-MR in the D$_1$ band and the absence of consensus in the estimation of rings population. Raman spectroscopy offers then a simple way to probe the statistics for 3 and 4-MR, and the greatest part of the literature devoted to rings statistics has focused on these small rings. However, the population of 3- and 4-MR is not dominant in silica compared to the whole MR distribution that can be obtained by molecular dynamics. Unfortunately, larger MR are rather hardly experimentally accessible, and very few knowledge is available on them apart from numerical approaches. In the literature one can found also some descriptions of the (SiOSi) bridges dynamic by force constant models. These rather simple models link vibrational spectroscopic data with the average angle $\theta$ and effective forces constant of (SiOSi). From considerations of these models, the Raman signatures of 5-MR and 6-MR larger rings are expected to be at lower wavenumbers than for small rings, i.e., in the R-band region. Besides, independently of any specific ring patterns consideration, three different spectral features were suggested to compose part of the isotropic R-band (symmetric stretching involving (SiOSi) bridges, $\delta_{\text{scis}}$ scissoring of [SiO$_4$]$_2$), and $\Delta_{\text{scis}}$ scissoring of the [SiO$_4$]$_2$-[Si$_4$] extended tetrahedron). Therefore, it is not surprising that the R-band is sometimes described as the superposition of several individual symmetric bands (see for instance), but the proposed decompositions remain a little bit ambiguous as different band combinations can reproduce the broad experimental asymmetric shape, due to lack of any pointed inflexion point on the rising edge between 200 and 400 cm$^{-1}$.
This short paper reports very high signal-to-noise Raman spectra of silica that highlights new structuring in the broad asymmetric 450 cm\(^{-1}\) R-band. These new features closed to 295 and 380 cm\(^{-1}\) are observed here for the first time in the nonetheless well know spectrum of silica. They arise owing to increase of the signal-to-noise ratio and have to be considered after a rigorous and exhaustive study, in order to exclude any instrumental origin. So, in the following, we present first the experimental condition leading to the new spectral features observation. Next, we introduce and illustrate in a short discussion, the relevant consequence of such observations in the study of vitreous silicates structure by mean of Raman spectroscopy.

Experiments were done on two spectrometers: a Renishaw Invia Reflex with a Leica DM 2500 microscope (simple spectrometer configuration), and a Jobin-Yvon T64000 (triple subtractive configuration), in macro configuration. Both systems are multichannel ones with CCD detectors. Different excitation laser wavelengths were used: 457, 514 (Ar\(^+\) lines) and 633 nm (He-Ne line). Measurements with the Leica microscope were done with two objectives in order to check the effect of numerical aperture and the subsequent changes in light polarization. The specificities of the experiments reported here are the very long acquisition times (up to 20 hours), in order to substantially increase the signal-to-noise ratio. As in this case the saturation limit of the CCD detector can be attained, measurements were performed in accumulation mode (several subsequent spectra of lower time, to keep beyond the saturation limit, which are added at the end of experiment). Silica samples were of Corning 7980 type. A test was done on a 7980 sample, thermally treated to change the fictive temperature (Corning 7980 \(T_f\) is 1040°C).

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(Invia spectrometer) were done with two objectives (x20 and x50) in order to check the effect of numerical aperture and the possible subsequent changes in light polarization (v) changes of size of sample (from thickness of 1cm to 1mm), to check any interference or reflection effect between opposite faces. All these check measurements (all done with very long acquisition times) have confirmed the spectrum of figure 1(a) with its bumps. To determine more precisely the bump positions, it is useful to see the derivative of the spectrum (Figure 1(b)), much more sensitive to small features. The derivation was performed by the algorithm comprised in Microcal OriginPro8.1 software, with a Savitzky-Golay smoothing. The maximum of a peak in the original curve corresponds in the derivative curve to a zero value, or crossing through the baseline in the case of a peak superimposed to a broader and more intense feature. The bumps positions can then be determined rather precisely from figure 1(b): ≈ 295 and ≈ 380 cm⁻¹, the uncertainty being about 5 cm⁻¹. Hereafter they will be called respectively D₃ and D₄ bands by analogy with the D₁ and D₂ bands.

Now that the presence of both D₃ ≈ 295 and D₄ ≈ 380 cm⁻¹ bands are established and even if to our knowledge, they were never reported explicitly before, one can remark that in some papers, the reported spectra have presumably exhibited them (13-14 for instance, among the most recent ones). Nevertheless, we underline that these features are very smooth compared to the underlying band and it was absolutely necessary to take specific acquisition times and to check for any possible artifact due to the experimental setup, as done in the present study. Above we have introduced that existence of numerous contributions to the Raman activity are expected in the R-band frequency region. Consequently, the possibility to fix the frequency of two of them has got considerable interest in the discussion of silicates structure.

In Figure 2, we present a new classic deconvolution of the spectrum. Generally, deconvolution results are dependent of the chosen band shapes and we have performed several tries. Figure 2 pictures one of these tries, where we have used a log normal shape for the boson peak, Lorentzian shapes for the D₁ and D₂ bands and Gaussian shapes for others. As one can see, additionally of the D₂ ≈ 605 cm⁻¹, D₁ ≈ 495 cm⁻¹, the ≈ 465 cm⁻¹ band (maximum of the R-band), the D₄ ≈ 380 cm⁻¹ new feature, the D₃ ≈ 295 cm⁻¹ new feature and the boson peak, a band closed to 245 cm⁻¹ is necessary in order to fit the full Raman activity in this wavenumbers region. In fact, this latter additional contribution is a common result of all the deconvolutions that we have performed (not shown here).

First, we note that these frequencies do not coincide with those of any of the natural SiO₂ crystalline polytypes (quartz, cristobalite, tridymite, stishovite, coesite) 15. Second, frequency of the δbend (SiOSi) bending dynamic was successfully connected to the value of (SiOSi) angle (θ) through simple effective force constant models 10, 11. Therefore, consideration of the D₁ and D₂ bands through these models assign them as δbend dynamic of (SiOSi) bridges with different θ. In fact, in the specific case of 3-MR and 4-MR, the (SiOSi) bridges forming the rings are vibrating in phase leading to a “breathing” dynamic of the rings poorly coupled with their environment. The 3- and 4-MR rings appear then obviously in the Raman spectrum despite their very small amount obtained from different calculations 7, 16; around one ring of each specie for more than 500 SiO₄ tetrahedra according to Umari et al 7. Then, if we consider, in one hand the (SiOSi) bridges in larger (n>=5) SiO₄ membered rings (hereafter denoted 5+MR) and, in other hand the widely observed and calculated θ distribution 7-18, one can assign part of the R-band to δbend...
dynamic of (SiOSi) bridges in 5+MR. Thus, the spectral signatures of larger rings are expected to be certainly broader than D1 and D2, and lying at lower wavenumbers than these lines. In fact, in many of the amorphous SiO2 calculated densities of states available in the literature (see for instance{16, 19, 7}), one can see peaks or clear shoulders lying in the wavenumbers range of those evidenced in the present paper. Obviously, calculated features of large structures such as 5+MR will exhibit lower linewidths than experimental ones, at least as the limited number of atoms in numerical approaches hardens a good description of coupling between different oscillators. Besides, we assume that the rest of the Raman activity comes from the scissoring modes introduced in ref 12. In order to illustrate the spectral consequence of the 0 distribution, in the following, we consider the (SiOSi) angle distribution calculated by Yuan et al.17. This calculation is consistent with NMR characterization of silica18 and gives (SiOSi) angle distribution centered at 147° with a full width at half maximum 23-30°. From the 0 distribution, the induced frequency distribution in the Raman signature of (SiOSi) δbend can be estimated by used of the Effective Force Constant model of Lucovsky10, with the limited frequency of the highest VV Raman doublet as frequency of the (SiOSi) asymmetric stretching that is also active in IR12. The distribution in frequency obtained is pictured by black crosses in Figure 2. In this calculation, the (SiOSi) δbend frequency for 0 = 147° is assumed to be at the 435 cm⁻¹ maximum. These assumption give an angle of ≈ 128° at the 3-MR frequency, consistent with others recent demonstrations20. One can see that above estimated δbend frequency distribution merges on both D1 ≈ 380 and ≈ 465 cm⁻¹ bands. Then, one of the most plausible structural elements that can be connected with them are effectively the 5+MR. In fact, one knows from molecular dynamics that the ring statistics in silica is dominated by such rings (between 5 and 10), whereas 3-MR and 4-MR, marginal in the statistics, appear obviously in the Raman spectrum due to their dynamic at the origin of sharp well-defined D1 and D2 bands. Besides, the lowest wavenumbers bands (≈ 245 cm⁻¹ and D3 ≈ 295 cm⁻¹) can thus be assigned to δwag and Δwag.

Above we have discussed a “classical deconvolution”. A rigorous discussion of the bands assignment containing band-shapes consideration needs to take also account of the Raman coupling parameter21 that was assumed to be mode and frequency dependent22. Such fine and complex discussion will be published elsewhere, being beyond the scope of this short paper where we essentially want to highlight the presence beyond doubt of two distinguishable new Raman spectral features in the R-band of silica: D1 ≈ 295 cm⁻¹ and D4 ≈ 380 cm⁻¹.

References