Hyper-Raman scattering from vitreous boron oxide: coherent enhancement of the boson peak

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Hyper-Raman scattering spectra of vitreous B₂O₃ are reported and compared to Raman scattering results. The main features are indexed in terms of vibrations of structural units. Particular attention is given to the low frequency boson peak which is shown to relate to out-of-plane librations of B₂O₃ boroxol rings and BO₃ triangles. Its hyper-Raman strength is comparable to that of cooperative polar modes. It points to a sizeable coherent enhancement of the hyper-Raman signal compared to the Raman one. This is explained by the symmetry of the structural units.

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Most glasses exhibit at low frequencies ω a broad spectral component observed both in Raman scattering (RS) and inelastic neutron-scattering (INS). The reduced density of vibrational states, Z(ω)/ω², usually shows in that region a considerable excess of harmonic modes over the Debye level of sound waves. This is called the boson peak (BP). Although the nature of BP-vibrations remains much debated, it is generally accepted that it will be key to a real understanding of the glassy state. Lower frequencies being generally associated with larger objects, the BP should provide indirect structural information at distances of one to a few nm.

The structure of glasses at those scales is of considerable fundamental and practical interest, but it is generally not accessible to standard structural analysis tools. The nanoscale also corresponds to the size of crystal nuclei, so that phenomena at that scale are relevant to the glass formation itself. The slow progress in understanding the BP relates to the lack of experimental techniques to address the structural issues. For this reason, spectroscopies able to complement the information obtained with RS and INS are particularly valuable. Recently, hyper-Raman scattering (HRS) was found to be a powerful tool for the investigation of low ω excitations in vitreous silica, ν-SiO₂. These experiments confirmed previous measurements and simulations, indicating a large contribution of rigid SiO₄ tetrahedra librations in the BP of ν-SiO₂. This single example already demonstrates that the microscopic origin of the BP follows from the specific molecular structure of the glass.

Boron oxide is the second most important glass former after ν-SiO₂. Boron forms covalent bonds with oxygen, and ν-B₂O₃ is a network of oxygen-sharing BO₃ triangles. Three such triangles can associate to produce a planar supermolecular unit, the boroxol ring B₃O₃. The fraction of boron belonging to boroxol rings is difficult to ascertain from diffraction results alone. However, NMR as well as recent simulations of spectra have now confirmed that approximately 3 out of 4 borons belong to boroxol rings. Hence, the ratio in the number of rings and independent triangles is about 1/1. In this Letter, we report the first HRS results on ν-B₂O₃. We show that the HRS BP can be associated with out-of-plane librational motions of rigid rings and triangles. In addition, the HRS intensity of the BP is exceptionally high, of the same order as that of collective longitudinal optic (LO) and transverse optic (TO) polar excitations. This suggests that the coherence of the BP vibrations is quite extended in space. This coherence contributes much more effectively to HRS than to RS spectra for symmetry reasons that are explained below.

The HRS measurements were performed on a new spectrometer optimized for the study of liquids and disordered solids. It combines high luminosity with a favorable resolution and contrast, allowing to investigate low-frequency modes. The incident infrared radiation at λ=1064 nm is delivered by a Q-switched Nd:YAG laser, producing ~23 ns-long pulses of up to 70 kW peak power at 2.5 kHz repetition rate. These are focused with a f=3 cm lens, down to a beam waist in the sample of ~ 10 μm radius. The scattered light is collected with a f/1.8 aperture. The spectrum is analysed with a single grating monochromator and detected with a N₂-cooled CCD camera. Two gratings are available, with 600 or 1800 groves/mm. Using an entrance slit of 100 μm, this leads to instrumental full widths at half maximum of ~ 6 or ~ 2 cm⁻¹, respectively. The RS spectra shown for comparison were obtained with 514.5 nm excitation and analyzed with a Jobin-Yvon T64000 triple monochromator, operated in the macromode. The ν-B₂O₃ sample was prepared from isotopically pure (99.6%) B₂O₃ containing ~ 1 wt% moisture. The material was heated to 1100 °C in a platinum crucible, quenched on a heat conducting plate, and annealed at 571 °C for 200 hours. The sample was cut and dry-polished. The water content (0.8 mole %) was subsequently measured by IR-transmission of a thin slice as described in. The same sample, sealed in an optical silica cell containing silica gel, was used for RS and HRS measurements in 90°-scattering.

Figure 1 shows polarized (VV) and depolarized (VH)
In a simplified model, triangles and rings can thus be decomposed into irreducible representations:

\[ \chi''(v) = \frac{I(\omega)}{(n+1)}. \]

\( I(\omega) \) is the spectral intensity and \( n \) the Bose factor. These HRS spectra were obtained using the 600 groves/mm grating. It is evident that there are many modes and that the RS and HRS spectra are remarkably dissimilar. However, one should note that the RS presentation zooms on small features, with the largest peak way off scale, while the HRS ordinate is adjusted to the dominant features, with the largest peak way off scale, while the HRS ordinate is adjusted to the dominant features, with small peaks mostly buried in the background.

The large number of modes is related to the simultaneous presence of BO3 triangles and B3O3 rings, nearly 1/1 ratio. We remark that the sum of one triangle plus one ring just amounts to two formula units 2(B2O3). In a simplified model, triangles and rings can thus be taken as the two building blocks. Both have rhombohedral D\(_{3h}\)-symmetry. Their vibrations are decomposed into irreducible representations:

\[
[1, 2] A'_1(R, HR) + [1, 2] A'_2(HR) + [2, 2] A''_1(IR, HR) + [3, 4] E'(IR, R, HR) + [1, 2] E''(R, HR).
\]

The figures within square brackets show the number of independent representations for triangles and rings, respectively, while the symbols in parentheses indicate activity in infrared (IR), Raman (R), or hyper-Raman (HR). The notation for the representations is that of [13].

The narrow peak at 808 cm\(^{-1}\) reaches over 50 in Fig. 1a, entirely dominating the VV-spectrum. This component has been indexed either as the \( A'_1 \) oxygen breathing of the boroxol rings, or as a correlated symmetric stretch motion of the O-atoms over the network [15].

\[
\delta p^{ζ,i} = \alpha^{ζ,i} \cdot E' + \beta^{ζ,i} \cdot E'E' + ... .
\]

The local field corrections are essential for quantitative results [17] but they should not affect our qualitative symmetry considerations.

Structural units that vibrate independently from each other, i.e. with random phases, scatter incoherently. The intensity is then just the sum of the individual intensities, \( \chi'' = \sum_1 \delta p^{ζ,i} \). This occurs in two important cases: i) for polar vibrations, which are the only ones compatible with a collective modulation of the average D\(_{3h}\)-glass symmetry [15]; ii) for external modes, in particular librations for which nearby units move together, leading to overall coherence.

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very regular boroxol units is able to produce the observed
narrow peak. This is now supported by a first-principle
analysis. The observed strong polarization just
indicates that the isotropic part, of trace $2(2\alpha_{zz}^\beta + \alpha_{xx}^\beta)$, is
much larger than the anisotropy $|\alpha_{xx}^\beta - \alpha_{zz}^\beta|$. From (1),
this vibration is equally active in HRS. In Fig. 1b, only
a relatively small peak is observed at the corresponding
frequency. It is shown in more details in the inset. The
modulation of $\beta$ by $\alpha_{1}^\prime$ leads to $\beta_{2xx}^\prime = -\beta_{2yy}^\prime$ with all
other combinations vanishing. In incoherent scattering,
this produces a depolarization ratio $I_{VH}/I_{VV} = 2/3$
[10], in excellent agreement with our observation. There
is no reason to believe that HRS would be particularly
small for this mode compared to RS. Rather, the com-
parative sizes of the 808 cm$^{-1}$ mode in HRS (Fig. 1a),
while corresponding features are not apparent in HRS
(Fig. 1b). We remark that all RS-active modes in (1)
are also HRS-active. Since the weak RS modes are just
not seen on the scale of our HRS spectra, we conclude
that many modes between 300 and 600 cm$^{-1}$ in RS (Fig. 1a),
are HRS-allowed. The isotropic HRS
tensor $\beta$ has components $\beta_{V}^{VV} = 3b$ and $\beta_{V}^{VV} = b$
[21]. The coupling of the LO-motions with the internal
Maxwell field produces the LO-TO splitting. The
tensor elements $b$ are distinct for TO and LO modes, $b_{TO}$ and $b_{LO}$ respectively, the latter being generally much
enhanced by the electro-optic coupling. In 90$^\circ$-scattering,
one finds that $I_{VV} \propto 9b_{V}^{2}$ while $I_{VH} \propto b_{V}^{2} + b_{V}^{2}$. From (1), the IR-active modes have $A_{2u}^\prime$ and $E'$
symmetries. The modes of $A_{2u}^\prime$-symmetry correspond to oppo-
site displacements of B and O along the $z$-axis. This
type of motion has a significantly lower restoring force
than the in-plane displacements of the $E'$-modes. Hence,
the group around 700 cm$^{-1}$ is assigned to the $A_{2u}^\prime$
internal modes. This double peak structure with maxima
located at $\sim 655$ and 717 cm$^{-1}$ in VV-scattering and previously
observed in IR-transmission [21], must be due to the separate activity of triangles and rings. The nar-
rowest peak at 717 cm$^{-1}$ in VV-scattering is assigned to the $A_{2u}^\prime$
Lo-motion, as confirmed by a first-principle calculation.
Regarding the VV and VH spectra, we find
for this peak a TO-LO splitting of $\sim 15 \pm 2$ cm$^{-1}$. This
is within the accuracy of the value $\sim 20$ cm$^{-1}$ reported
from IR-reflectivity [12].

The group centered around 1400 cm$^{-1}$ is due to modes
$E'$ active in IR, RS, and HRS. The main TO motion
produces the feature at 1260 cm$^{-1}$. Like for the breathing
mode, it is much better seen in RS than in HRS. It is
related to the boroxol rings [22]. The LO-TO splitting is
$\sim 290$ cm$^{-1}$ [12], and the corresponding LO peak is the
strongest feature in the VH-HRS spectrum. The entire
group is rather rich, with at least six peaks in the RS
spectra. This agrees qualitatively with the large number of
different modes of $E'$ symmetry in (1).

We are now equipped to discuss the nature of the
BP vibrations. Figure 2 shows in more details the $T$-
reduced HRS intensities, $I/(n+1)\omega$, obtained with the
1800 groves/mm grating. Since the BP is observed both in
RS and HRS, its symmetry must be either $A_{1}^\prime$, $E'$, or
$E''$. The breathing modes $A_{1}^\prime$ occur at higher frequencies,
such as 808 cm$^{-1}$ for the boroxols. The $E'$ modes, as just
shown, mostly belong to the high-frequency band around
1400 cm$^{-1}$. However, they do include relative transla-
tions that can be of rather low frequency and which, in
a collective model, must couple to rigid rotations. The
modes of symmetry $E''$ are precisely the out-of-plane ro-
tations. They include the librations of rigid triangles and
rings, plus an internal out-of-plane deformation mode of
rings that must be of higher frequency. The rigid libra-
tions, coupled to relative translations, remain the only
reasonable candidates for the BP. That the librations of
structural units produce the lowest frequency modes was
already noted for other glasses, e.g. $\nu$-SiO$_{2}$ [3, 6] or Se
[24]. The relative scattering strengths in Fig. 1 also sug-
gest a coherent contribution that greatly enhances the
HRS-signal of these rigid librations. This is further sup-
ported by the HRS depolarization ratio $I_{VH}/I_{VV}$ which
is 0.58 at the peak maximum in Fig. 2. This is signifi-
cantly smaller than the value 2/3 that applies to purely
incoherent scattering [16].

The coherent enhancement can be qualitatively under-
stood from the symmetry properties of the polarizabil-
ity and hyper-polarizability tensors. Equilateral trian-
FIG. 2: High resolution 90$^\circ$-scattering HRS spectra of $\nu$-B$_2$O$_3$
at low $\omega$. The inset compares the VH BP-spectra observed here in RS (dashed line) and HRS (solid line) with the total
$Z(\omega)/\omega^{2}$ obtained in INS at 330 K (dots) from [1].
angles are the basic D_{3h}-symmetry objects. Fig. 3a shows two triangles T_1 and T_2, where T_2 is derived from T_1 by a 180°-rotation. It is easy to see that the β-tensors of T_1 and T_2 are related by \( \beta^1 = -\beta^2 \). However, the linear polarizabilities are identical, \( \alpha^1 = \alpha^2 \). Now, suppose that these triangles share an apex that oscillates vertically, so that they librate by angles ±δφ, as drawn in Fig. 3b. The modulation of \( \beta^1 \) by +δφ is equal in sign and magnitude to that of \( \beta^2 \) by −δφ, so that the HRS dipole fluctuations of both triangles add coherently. On the contrary, the modulation of \( \alpha^1 \) by +δφ is opposite to that of \( \alpha^2 \) by −δφ, so that these cancel and there remains no coherent RS-contribution. This trend remains for out-of-plane librations of a connected set of triangles, also for non-planar arrangements: cancellations preferentially occur for \( \alpha \) rather than for \( \beta \). Fig. 3c illustrates in a simple planar case how this can be extended to boroxol rings. It shows two rings connected by a single B-O-B bridge. The angle of the external B-O-B bond is \( 135^\circ \). The relative rotation of the two boroxols by only \( \sim 15^\circ \) is sufficient to produce a \( \beta^2 \) significantly different from \( \beta^1 \), leading to a coherent HRS signal for the motion illustrated in Fig. 3c, while \( \alpha^2 = \alpha^1 \), cancelling the coherent RS response. A detailed calculation of the coherent enhancement would require a large simulation, far beyond the scope of this work. Indeed, reproducing correctly the RS and HRS boson-peak shapes and intensities is likely to be an exacting test of the simulated structure.

It is finally of interest to compare various BPs as illustrated in the inset of Fig. 2. The maximum of the HRS BP is at \( \Omega_{\text{BP}}^{\text{HRS}} \approx 23 \text{ cm}^{-1} \), while in RS we find \( \Omega_{\text{BP}}^{\text{RS}} \approx 26 \text{ cm}^{-1} \). In INS, also performed on a \(^{11}\)B_2O_3 sample, an out-of-phase (incoherent in our terms) contribution was separated from an in-phase one. The former matches quite well the RS BP, while the latter peaks at a much lower value \( \sim 16 \text{ cm}^{-1} \). The sum of these two components, shown in the inset, is positioned at \( \Omega_{\text{BP}}^{\text{INS}} \approx 19 \text{ cm}^{-1} \). That coherence lowers \( \Omega_{\text{BP}} \) is consistent with our finding on \( \Omega_{\text{BP}}^{\text{HRS}} \). However, INS detects in-phase displacements along a line joining neighbors [22], while the optical scattering should be more sensitive to rigid rotations. This could presumably explain the different coherent enhancements leading to \( \Omega_{\text{BP}}^{\text{HRS}} \neq \Omega_{\text{BP}}^{\text{RS}} \). Our analysis here, and in \( \gamma\)-SiO_2 [4], demonstrates that diverse spectroscopies project differently the BP-vibrations, leading to significant changes in BP shapes and positions. A discussion just in terms of a single light-to-vibration coupling coefficient \( C(\omega) \) is presumably too reductive to reflect the complexity of the real situation which involves librations vs. translations, coherence vs. incoherence, and unlike sensitivities of the various spectroscopies to the mode eigenvectors.

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![Diagram of triangles T1 and T2](image)

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[1] R. Shuker and R.W. Gammon, in *Light Scattering in Solids*, M. Balkanski, Ed. (Flammarion Science, Paris, 1971) p. 334.
[2] A. Brodin et al., Phys. Rev. B. 53, 11 511 (1996).
[3] U. Buchenau et al., Phys. Rev. B 34, 5665 (1986).
[4] D. Engberg et al., Phys. Rev. B. 58, 9087 (1998).
[5] *Amorphous Solids: Low-Temperature Properties*, ed. by W.A. Phillips (Springer, Berlin, 1981).
[6] B. Hehnen et al., Phys. Rev. Lett. 84, 5355 (2000).
[7] B. Guillot and Y. Guissani, Phys. Rev. Lett. 78, 2401 (1997); S.N. Taraskin and S.R. Elliott, Phys. Rev. B. 56, 8605 (1997).
[8] A.C. Hannon et al., J. Non-Cryst. Solids 177, 299 (1994).
[9] J.W. Zwanziger, Solid State NMR 27, 5 (2005).
[10] P. Umari and A. Pasquarello, Phys. Rev. Lett. 95, 137401 (2005).
[11] M.A. Ramos et al., J. Non-Cryst. Solids 221, 170 (1997).
[12] P.L. Galeener et al., Phys. Rev. B. 22, 3983 (1980).
[13] E.B. Wilson, Jr. et al., *Molecular Vibrations* (McGraw-Hill, New York, 1955).
[14] In the molecular-fixed reference frame, \( zis \parallel \) to the threefold axis and \( zis \parallel \) to one of the two-fold axes.
[15] V.N. Denisov et al., Phys. Rep. 151, 1 (1987).
[16] S.J. Cyvin et al., J. Chem. Phys. 43, 4083 (1965).
[17] R.W. Munn, J. Chem. Phys. 114, 5607 (2001).
[18] C.F. Windsied, Jr., and W.M. Risen, Jr., J. Non-Crys. Solids 48, 307 (1982).
[19] R.M. Martin and F.L. Galeener, Phys. Rev. B. 23, 3071 (1981).
[20] A.S. Tenney and J. Wong, J. Chem. Phys. 456, 5516 (1972).
[21] V.B. Podobedov, J. Raman Spectrosc. 27, 731 (1996).
[22] A. Pasquarello, private communication.
[23] A.K. Hassan et al., Phys. Rev. B. 45, 12 797 (1992).
[24] F.J. Bermejo, Phys. Rev. B. 49, 8689 (1994).
[25] D. Engberg et al., Phys. Rev. B. 59, 4053 (1999).