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Hyper-Raman Scattering from Vitreous Boron Oxide: Coherent Enhancement of the Boson Peak

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Hyper-Raman scattering spectra of vitreous B_2O_3 are compared to Raman scattering ones. Particular attention is given to the low-frequency boson peak which relates to out-of-plane rigid librations of planar structural units, mostly boroxols. While the Raman strength can be accounted for by the motions of single units, the hyper-Raman signal exhibits a unequaled enhancement due to coherent librations of several boroxols. This important distinction is explained by the different symmetry properties of the polarizability and hyperpolarizability tensors of the structural units.

Hyper-Raman scattering (HRS) is a nonlinear spectroscopy in which two incident photons give one scattered photon with simultaneous creation or annihilation of one vibrational quantum in a material [1]. HRS obeys selection rules different from those of Raman scattering (RS). The scattering tensors have been tabulated for a variety of molecular symmetries [2]. In this Letter, we discuss HRS from the boson-peak (BP) vibrations of a glass. The BP is characterized by a reduced density of vibrational states, $Z(\omega)/\omega^2$, showing at low frequencies ω a considerable excess of harmonic modes over the Debye level of sound waves [3]. It has been observed by RS, e.g., in [4,5], or by inelastic neutron-scattering (INS), e.g., in [6,7], but only once by HRS [8]. In the latter study we found that, owing to its specific selection rules, HRS is a powerful tool to investigate the BP vibrations of vitreous silica, v-SiO_2. These experiments confirmed previous measurements [6] and simulations [9], indicating a large contribution of rigid SiO_4 tetrahedra librations, active in HRS but essentially inactive in RS. Here, we investigate another common glass, vitreous boron oxide, v-B_2O_3. In this case the BP is found to relate to rigid librations of flat structural units. Contrary to the SiO_4 librations, the latter motions are active both in RS and HRS. However, we observe that the HRS signal is considerably *enhanced* by the coherent librations of several nearby units, whereas this appears not to be the case in RS. The HRS intensity of the BP is of the same order as that of collective polar excitations. This suggests a coherence which extends in space. The sensitivity or insensitivity to coherence relates to the symmetries active in both spectroscopies. Information on the coherence is of particular value for the BP. Indeed, the BP being the lowest frequency optic vibration, it contains structural information at distances of one to a few nm. The structure of glasses at those scales is of considerable interest, but it is generally not accessible to standard structural analysis tools. We expect that the strength of HRS BP spectra will become an exacting test for simulations such as [10], ultimately leading to a better understanding of the medium to long range structure of glasses.

The HRS measurements were performed on a spectrometer optimized for such studies. It combines high luminosity with a favorable resolution and contrast, allowing to investigate low-frequency modes. The incident infrared radiation at $\lambda = 1064$ 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 analyzed with a single grating monochromator and detected with a N_2-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. RS spectra of the same sample were obtained with 514.5 nm excitation and analyzed with a Jobin-Yvon T64000 triple monochromator, operated in the macromode. The v-B_2O_3 sample was prepared from isotopically pure (99.6%) $^{11}B_2O_3$ 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 then cut and dry polished. The water content (0.8 mol%) was subsequently measured by infrared (IR) transmission of a thin slice [11]. The sample, sealed in an optical silica cell containing silica gel, was used at room temperature in 90° scattering.

B_2O_3 is the most important glass former after silica. The glass is a network of oxygen-sharing BO_3 triangles. Three triangles can associate to produce a planar supermolecular unit, the boroxol ring B_3O_3. The fraction of boroxol rings is difficult to ascertain from diffraction results alone [12]. However, NMR [13] and recent simulations [10] now confirmed that approximately 3 out of 4 borons belong to boroxols. Hence, the ratio in the number of rings and independent triangles is about $1/1$. The sum of one triangle plus one ring being $2(B_2O_3)$, in a simplified model triangles and rings in equal amounts can be taken as the two structural units. Both have D_{3h} symmetry. Their vibrations are decomposed into

$$[1,2]A_1'(R, HR) + [1,2]A_2'(HR) + [2,2]A_2''(IR, HR)$$
$$+ [3,4]E'(IR, R, HR) + [1,2]E''(R, HR). \quad (1)$$

The figures within square brackets show the number of irreducible 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 [14].

Figure 1 shows polarized (VV) and depolarized (VH) HRS and RS susceptibilities $\chi'' = I(\omega)/(n + 1)$. $I(\omega)$ is the spectral intensity and n the Bose factor. The RS and HRS spectra are remarkably dissimilar. The indexing of their main features in terms of (1) is described elsewhere [15]. The RS VV spectrum (b) seems dominated by a narrow peak at 808 cm^{-1}, which, however, is so narrow that its integrated strength is comparable to other modes. This peak was already assigned either to a correlated symmetric stretch of all O atoms over the network [16], or to the A_1' oxygen breathing of boroxol rings [17]. If there would be overall coherent breathing, one would expect for steric reasons that adjacent units would vibrate in opposite phase, so that their contributions to RS would mostly cancel each other. Also, it hardly could explain a narrow peak. Instead, *independent* breathing of very regular boroxols does produce the observed peak, as shown in a first-principles analysis [10]. Although the same motion is active in HRS, it gives only a very small feature in (a). There is no reason to believe that HRS would be particu-

larly small for this mode compared to RS. Rather, the comparative sizes of the 808 cm^{-1} peaks in (a) and (b) is presumably a fair indication for the relative scale of these two plots. This is further supported by the observation of many modes between 300 and 600 cm^{-1} in RS on the expanded scale of (c), while the corresponding features are not apparent in (a), although all RS-active modes in (1) are also HRS active. Thus the three main groups in (a), E'', A_2'', and E', must all be strongly enhanced by *coherence*, while A_1' is not. The weaker modes in (c) relate to other internal vibrations of triangles and rings [18] scattering incoherently.

It is useful to describe the origin of scattering in some detail. In the molecular picture used for (1), light scattering results from the fluctuations of dipoles induced on all structural units by the applied optical field $\mathbf{E} \propto e^{-i\omega t}$. For structural unit i, the induced dipole can be written $\mathbf{p}^i = \boldsymbol{\alpha}^i \cdot \mathbf{E}_\ell + \boldsymbol{\beta}^i : \mathbf{E}_\ell \mathbf{E}_\ell + \cdots$, where $\boldsymbol{\alpha}^i$ and $\boldsymbol{\beta}^i$ are the first and second-order polarizability tensors, respectively, and $\mathbf{E}_\ell$ is the local field. In the molecular frame [19], the form of $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ is well known. For a symmetric top, $\boldsymbol{\alpha}$ is diagonal with $\alpha_{xx} = \alpha_{yy} \neq \alpha_{zz}$. For $\boldsymbol{\beta}$, we remark that both ω and 2ω are far from any material resonance in our experiment. In that case, $\boldsymbol{\beta}$ can be approximated as fully symmetric in all permutations of its three indices [1]. For D_{3h} symmetry, there remains just $\beta_{xxx} = -\beta_{xyy}$ with all other index combinations zero. In the laboratory frame, $\boldsymbol{\alpha}^i$ and $\boldsymbol{\beta}^i$ are just rotated from the molecular frame. It is the modulation of $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ by the normal modes, of amplitude $W^\zeta \propto e^{\mp i\omega_\zeta t}$ for mode ζ, which leads to the molecular Raman and hyper-Raman polarizability tensors, $\boldsymbol{\alpha}^\zeta$ and $\boldsymbol{\beta}^\zeta$, respectively. These are tabulated for all molecular symmetries, e.g., in [2]. In the laboratory frame, each rotated molecule i has then a fluctuating dipole shifted in frequency by $\pm\omega_\zeta$:

$$\delta\mathbf{p}^{\zeta,i} = \boldsymbol{\alpha}^{\zeta,i} \cdot \mathbf{E}_\ell + \boldsymbol{\beta}^{\zeta,i} : \mathbf{E}_\ell \mathbf{E}_\ell + \cdots. \quad (2)$$

The local field corrections are essential for quantitative results [20], but they should not affect qualitative symmetry considerations.

Structural units vibrating independently from each other, i.e., with random phases, scatter *incoherently*. The intensity is then the sum of the individual intensities, $\propto \sum_i |\delta\mathbf{p}^{\zeta,i}|^2$. This is expected for all nonpolar *internal* vibration modes in random media [2]. For example, for the breathing mode $\zeta \equiv A_1'$, the modulation of $\boldsymbol{\beta}$ leads to $\beta_{xxx}^\zeta = -\beta_{xyy}^\zeta$, with all other combinations vanishing [2]. In incoherent scattering, this produces a depolarization ratio $I_{VH}/I_{VV} = 2/3$ [2], as observed in the inset of Fig. 1(a).

On the other hand, if several structural units vibrate with a fixed phase relationship, there is *coherent* scattering, and the intensity is $\propto |\sum_i \delta\mathbf{p}^{\zeta,i}|^2$. This occurs in two important cases: (i) for *polar* vibrations, which are the only HRS-active ones compatible with a collective modulation of the
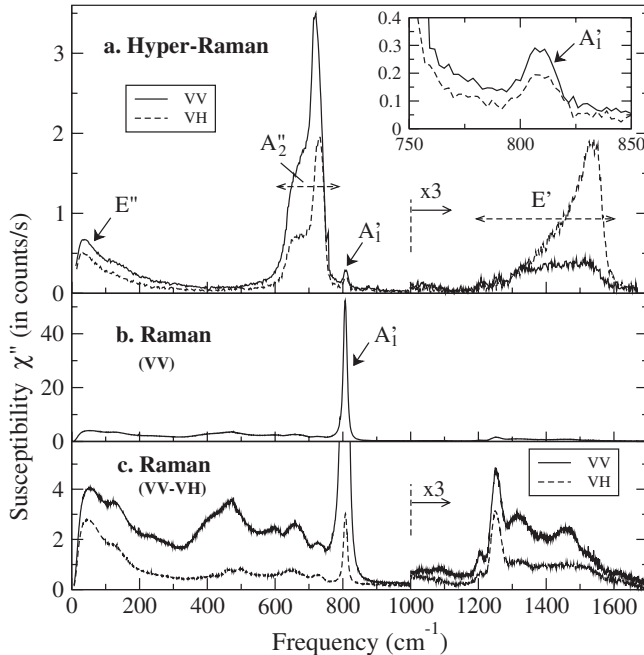

FIG. 1. Hyper-Raman (a) and Raman (b, c) susceptibility spectra of v-B_2O_3. The spectra in (a) were obtained using the 600 groves/mm grating. Above 1000 cm^{-1}, the ordinate in (a, c) is expanded by 3. The inset in (a) zooms on the HRS spectra of the 808 cm^{-1} mode.

average $D_{\infty h}$ glass symmetry [1]; (ii) for *external* modes, in particular, librations for which nearby units move together, leading to extended coherence. The groups around 700 and 1400 cm^{-1} are IR active [18] and belong to category (i). The modes A_2'' correspond to opposite out-of-plane displacements of B and O, which have a significantly lower restoring force than the in-plane displacements of E'. The coupling with the internal Maxwell field produces LO-TO splittings, and the frequencies are different for the different structural units, accounting for the complexity of these groups. These spectra depend on a predictable manner on the polarization and on the scattering geometry [1,15]. Of importance here is that the activity of these groups is considerably enhanced by collective effects [1].

Now consider the low-frequency BP vibrations. Figure 2 shows in more detail the temperature-reduced HRS intensities, $I/(n+1)\omega$, obtained with the 1800 groves/mm grating. Proceeding by elimination, out-of-plane rigid librations of structural units, coupled to their relative translations, remain as the only possibility to account for these modes which are not IR active [15]. It is already known that librations of structural units produce the lowest frequency modes in other glasses, e.g., v-SiO$_2$ [6,8] or Se [21]. The E'' modes are *external* vibrations of the structural units and they can thus exhibit coherent scattering of category (ii). However, the coherence seems to enhance much more the HRS signal than the RS one. To understand this, we remark that following (2) the quantities of interest in coherent scattering are $\sum_i \alpha^{\zeta,i}$ and $\sum_i \beta^{\zeta,i}$. Here, ζ is a particular mode belonging to the E'' group and the sum extends over units vibrating coherently in that mode. If N units vibrate in phase, one expects a signal $\propto N^2$.

Equilateral triangles are the basic D_{3h} symmetry objects. Figure 3(a) 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 $\pm\delta\phi$, as drawn in Fig. 3(b). The modulation of β^1 by $+\delta\phi$ is equal in sign and magnitude to that of β^2 by $-\delta\phi$, so that the HRS dipole fluctuations of both triangles add coherently. On the contrary, the modulation of α^1 by $+\delta\phi$ is opposite to that of α^2 by $-\delta\phi$, 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 nonplanar arrangements: cancellations preferentially occur for α rather than for β. Figure 3(c) 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° [10]. The relative rotation of the two boroxols by ~15° produces a β^2 significantly different from β^1, leading to a coherent HRS signal for the motion illustrated in Fig. 3(c), while $\alpha^2 = \alpha^1$, canceling the coherent RS response. A detailed calculation of the coherent enhancement would require a *large* simulation, far beyond the scope of this work. However, this symmetry argument explains how the HRS signal can be strongly enhanced by coherence, while the RS signal is not.

Separate quantitative evidence that the RS signal is essentially incoherent is available. We first remark that the BP strength in v-B$_2$O$_3$ is dominated by boroxols rather than by triangles. Indeed, we have observed that moderate substitution with alkali produces a sharp drop of the narrow 808 cm^{-1} RS peak, and thus in the density of boroxols. A simultaneous sharp drop in the BP occurs, showing the relation of the BP with the boroxols. Thus, one needs an estimate of the relative light-to-vibration RS coupling coefficients [4] of a lone boroxol for the A_1' and E'' groups. This can be taken from the first-principles calculation of RS on a sample of 160 atoms containing only 2 boroxols [10]. These calculations were performed both with all atoms active and with the boroxols silent [22]. The difference estimates the incoherent boroxol contribution.
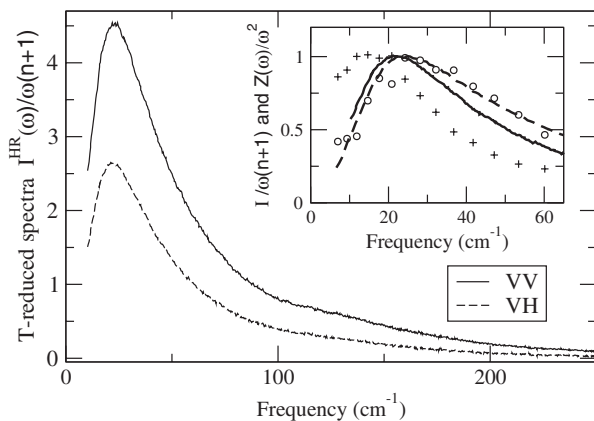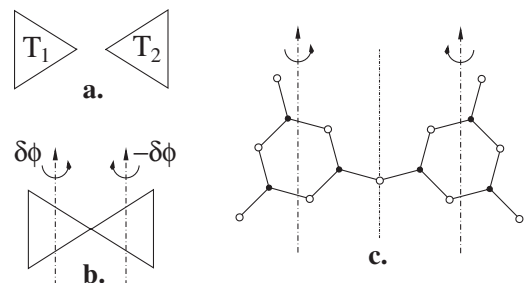

FIG. 2.   High resolution HRS spectra of the E'' group. The inset compares the VH BP observed here in RS (dashed line) and HRS (solid line) with the effective reduced density of states obtained in INS at 330 K from Fig. 11 of [7]: dots are for out-of-phase, and crosses for in-phase components (each scaled to its maximum).

FIG. 3.   (a) The relative position of two D_{3h} objects, T_1 and T_2, in a plane, (b) the joint libration of these rigid objects produced by a vertical displacement of a common apex, (c) the libration of two adjacent boroxols lying in a plane.

Comparing the scattered intensities of the groups A_1' and E'', we find that our experimental RS strength is consistent with the simulation. The uncertainty in the quantitative comparison is within a factor of 2. Hence, as done in [7], it is legitimate to compare the RS signal to the *out-of-phase* INS signal also expected to be essentially incoherent. These nicely superpose, as illustrated in the inset of Fig. 2.

On the other hand, one should not confuse the *in-phase* INS response with the coherent HRS signal. The former results from umklapp scattering of acoustic modes via the first sharp diffraction peak. It is essentially an *acoustic* signal which drops rapidly at high energies [7], above the Ioffe-Regel crossover of acoustic modes which occurs near the BP maximum [23]. For this reason this signal has the general shape of a BP, although it is *not* a BP: it does not result from a strong excess in the density of vibrational states, but rather from another neutron-scattering channel. Considering now the HRS signal, one should first note that one can speak of acoustic modes in a glass only to the extent that the medium can be approximated as centrosymmetric. However, in centrosymmetric media there is mutual exclusion between RS and HRS [1]. Since acoustic modes are active in RS, the HRS signal does not contain any genuine acoustic contribution. It is thus no surprise that the in-phase INS line shape and the HRS one do not coincide, as seen in the inset of Fig. 2. The fact that the HRS peak is at a frequency slightly lower than the RS one suggests that modes of larger than average N, which scatter more strongly in HRS, also have a lower than average frequency.

In conclusion, we have shown that the BP of v-B_2O_3 observed in HRS is considerably enhanced. N^2 is possibly as large as 50 if one assumes that the RS and HRS activities are comparable for both the A_1' and E'' groups. This large enhancement is explained by coherence in the librational motions of connected structural units. The size of N^2 suggests that as many as seven boroxols might librate coherently. A high *sensitivity to coherence* in the BP appears to be a unique property of HRS, not previously known. It can apply to many glasses. Indeed, it is generally true that the sign of $\boldsymbol{\beta}$ is reversed by inversion. Also, the lowest opticlike modes of many glasses are most likely related to rigid librations of connected units, as already shown for v-SiO_2 [6,8], Se [21], and here v-B_2O_3. Hence, following a reasoning similar to that developed above in connection with Fig. 3(b), the HRS BP signal must be particularly sensitive to coherence. In fact, we already have preliminary results on several other oxide glasses showing strong BPs and suggesting similar coherent enhancement. As coherence and the medium to long range structure are presumably related, such information should be of considerable value. In particular, attempts to use spectroscopic data to establish the structure of glasses should use the strength of observed HRS BPs as an essential input to validate simulated structures.

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