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Vibrational and structural properties of P_2O_5 glass: Advances from a combined modeling approach

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We present experimental measurements and *ab initio* simulations of the crystalline and amorphous phases of P₂O₅. The calculated Raman, infrared and vibrational density of states (VDOS) spectra are in excellent agreement with experimental measurements and contain the signatures of all the peculiar local structures of the amorphous phase, namely, bridging and non-bridging (double-bonded or terminal) oxygens, and tetrahedral PO₄ units associated with Q^2 , Q^3 , and Q^4 species (Q^n denotes the various types of PO_4 tetrahedra, with n the number of bridging oxygen atoms that connect the tetrahedra to the rest of the network). In order to reveal the internal structure of the vibrational spectrum, the characteristics of vibrational modes in different frequency ranges are investigated using a mode-projection approach at different symmetries based on the T_d symmetry group. In particular, the VDOS spectrum in the range from ~ 600 to 870 cm⁻¹ is dominated by bending (F_{2b}) motions related to bridging oxygen and phosphorus (~ 800 cm⁻¹ band) atoms, while the high frequency doublet zone (~ 870-1250 cm⁻¹) is associated mostly with the asymmetric (F_{2s}) and symmetric (A₁) stretching modes, and most prominent peaks around 1400 cm⁻¹ (exp. 1380 cm⁻¹) is mainly due to asymmetric stretching vibrations supported by double-bonded oxygen atoms. The lower frequency range below 600 cm⁻¹ is shown to arise from mixture of bending (E and F_{2b}) and rotation (F_1) modes. The scissors bending (E) and rotation (F_1) modes are well localized below 600 cm⁻¹, whereas the F_{2b} -bending modes spread further into the range ~ 600-870 cm⁻¹. The projections of the eigenmodes onto Q^2 , Q^3 , and Q^4 species yield well defined contributions at frequencies in striking correspondence to the positions of the Raman and infrared bands.

I. INTRODUCTION

The phosphate glass family exhibits many attractive properties depending on the glass composition. In particular, phosphate glasses possess excellent optical properties and ion exchangeability, and fiber drawing ability^{1,2}. Furthermore, phosphate glasses can sustain a high rare-earth ion loading enabling to produce compact laser sources and amplifiers in fiber form³. Not only that, at variance with silica-based glasses, phosphate glasses have suitable photodarkening properties^{4,5}. Despite the importance of P_2O_5 glasses in industry and nature, and the many theoretical and experimental studies of P_2O_5 phases⁶⁻¹³, spectroscopic observations pertinent to the optical and vibrational properties are few¹⁴⁻¹⁷. This may explain to some extent why no consensus exists yet about the structure and vibrations of pure P_2O_5 glass¹⁰. The power of Raman and infrared (IR) spectroscopies for investigating glasses has been recognized by many scientists. However, in order to exploit at their best these vibrational spectroscopies, it is necessary to possess a reliable theoretical modeling approach to correctly interpret the relevant features of the vibrational spectra. By contrast to our knowledge a modes assignment in vitreous P_2O_5 (v- P_2O_5) has been explored by numerical simulations for only specific cluster models^{14,15,17,18}. Essentially, it was implied that typical features of the Raman spectrum of $v-P_2O_5$ are three bands¹⁴⁻¹⁹: i) the phosphoryl stretch band, whose maximum is at $\sim 1380 \text{ cm}^{-1}$. ii) the symmetric stretch of bridging oxygen band at $\sim 640 \text{ cm}^{-1}$, and iii) the bending mode band appearing at a lower frequency range $300-500 \text{ cm}^{-1}$. However, the cluster model approach is hardly applicable in network glasses due to impossibility to account for the cooperative effects, the description of which requires more realistic glass models which allow for a proper treatment of longrange effects $^{20-26}$. Thus, till now there are no available theoretical investigations of vibrational spectra, relying on realistic models of $v-P_2O_5$ network, that can provide the attributions of vibrational modes.

In this paper, we generate realistic $v-P_2O_5$ models and present a comprehensive analysis of vibrational



Figure 1. (a) Elementary cell of o'– $P_2O_5^{27}$, (b) the network of v– P_2O_5 RMC1 model.



Figure 2. Q^n distribution of $v-P_2O_5$. Distributions are presented for RMC1/RMC2 models obtained by Kohara's RMC approach^{28,29}, and for CMD model obtained by Classical MD³⁰. Q^n species for PO₄ structural unit are shown schematically in the inset.

spectra based on *ab initio* simulations, mode-projection approach, and comparison with experimental measurements of vibrational spectra, that allows to perform a consistent modes assignment of the Raman, IR, and vibrational density of states (VDOS) spectra in v-P₂O₅.

II. SIMULATION METHODS AND STRUCTURAL PROPERTIES

The pure $v-P_2O_5$ network is expected to be comprised from tetrahedrons having three bridging oxygen bonds (P-O-P), which share a maximum of three of its corners with neighboring tetrahedra, while the fourth bond represents double-bonded (terminal) oxygen (P=O) unconnected to other tetrahedral units (see Fig. 1), i.e. $v-P_2O_5$ network contains Q³ tetrahedral units in terms of the Qspeciation^{6,31}, where Qⁿ denotes PO₄ tetrahedra with n number (between 2 and 4) of bridging P–O–P linkages per tetrahedron. Usually, Classical Molecular Dynamics (CMD) and Reverse Monte Carlo (RMC) approaches are applied to simulate glasses, and models generated by these approaches provide satisfactory agreement with experiments on structure factor. However, despite of many researches dedicated to $v-P_2O_5^{8,9,30,32-36}$, up to now it



Figure 3. Dependence of the neutron (a) and X-ray (b) static structure factor on magnitude of momentum transfer for $v-P_2O_5$. Models RMC1 (solid grey curve), RMC2 (dashed red curve), CMD (dotted blue curve); experimental data for neutron⁷ and X-ray⁸ (shaded dotted green curve).

was not possible to generate $v-P_2O_5$ models with more than 75% of Q^3 units. Recently, S. Kohara *et al.* have developed the hybrid RMC approach which opened the door to confidently treat glass systems providing new insights into structural properties^{28,29,37}. Owing to these advances, we generate three models with 112 atoms: two RMC models (hereafter labeled as RMC1 and RMC2) and one CMD model. RMC modeling is performed using the RMC++ $code^{28,29,37}$. The difference between the RMC1 and RMC2 models lies in the different constraints that were applied in RMC calculations. For the case of the RMC1 model, the constraints on the P–O connectivity are that 32 phosphorus atoms ought to be coordinated by one non-bridging (terminal) oxygen atom at 1.4–1.5 Å (totally 32 non-bridging oxygen atoms), and three bridging oxygen atoms at 1.5–1.7 Å (totally 48 bridging oxygen atoms), whereas, for the case of the RMC2 model, the constraint on coordinations is not applied. Atomic number density for P_2O_5 glasses is 0.0708 Å⁻³. The final RMC run is conducted under these constraints by fitting to both X-ray and neutron total structure factors $S(q)^8$. In particular, the structure of RMC1 and RMC2 have the highest proportions of Q^3 units ever reported, being 100% and 87.5%, respectively (see Fig. 2). Such a distribution plays an essential role in our research due to strong sensitivity of vibrational spectra to local symmetry. We follow Ref.³⁰ in order to generate CMD model, and the simulations are carried out with the help of LAMMPS $code^{38}$.

Figs. 3(a) and (b) show good agreement of the glass



Figure 4. Reduced Raman HH spectra of $o'-P_2O_5$: theory (solid red curve), experimental data by Meyer *et al.*³⁹ (solid grey curve), and experimental data by Voron'ko *et al.*⁴⁰ (solid black curve). A Gaussian broadening (8 cm⁻¹) is used for the theoretical curve.

models with the experimental measurements of structure factor with neutron⁷ and X-ray⁸ diffraction, however, the RMC models give better agreement. One can note that for $q \leq 2.5$ Å⁻¹, i.e. corresponding to length scales beyond nearest neighbor distance, both neutron and X-ray S(q) show a kind of double peak at 1.3 and 2.3 Å⁻¹, which is not resolved by the CMD model, while to some extent it is resolved by both the RMC models. Moreover, RMC2 model counterintuitively seems to provide a slightly better agreement for $q \lesssim 2.5$ Å⁻¹ with experiments, despite it has Q^2 and Q^4 units⁸. Thus it appears evident that relying only on the structural information provided by the structural probes such as neutron and X-ray scattering, may constitute a severe limitation for an advanced modeling of pure $v-P_2O_5$. Crucial complementary information can however be obtained by means of vibrational spectroscopies. However, a detailed understanding of the vibrational spectra can only be achieved through accurate theoretical modeling. Such high level of accuracy requires for theoretical approaches which address directly the electronic structure. In this context, first-principles calculations based on density functional theory (DFT) are particularly appealing for the good compromise between accuracy and computational cost. All the calculations carried out in this work are based on the DFT. In particular, a generalised gradient approximation (GGA) [i.e. the Perdew-Burke-Ernzerhof functional] and local density approximation (LDA) exchange-correlation functional are adopted for the DFT calculations included in Ref.⁴¹. Norm-conserving Trouiller-Martins and Bachelet-Hamann-Schlüter pseudopotentials are used for O and P atoms, respectively^{42,43}. Kohn-Sham wavefunctions are expanded in a basis of plane waves up to a kinetic cutoff of 70 Ry. The wavefunctions are expanded at the sole gamma point of the Brillouin zone, as justified by the large size and the large band gap of our system. Geometry optimizations are obtained by means of a two-steps relaxation procedure (TSP): first a spin-polarized GGA

optimization, followed by a further LDA relaxation of the atomic structure. As the classical MD provides configurations that are slightly far from a DFT ground-state, a gradient-corrected functional is preferred in the firststep to accelerate the convergence of the algorithm. The second optimization step is required in view of an accurate calculation of vibrational modes, as LDA is known to reproduce vibrational frequencies in better agreement with experiments than $GGA^{13,44}$. In both optimization steps, the minimum is found by adopting a force threshold 0.0025 eV/Å, which allows for a proper harmonic treatment of the vibrational modes. When applied to the CMD model, the TSP provides a structure lower in energy by 0.03 eV/atom with respect to a direct LDA relaxation. The former TSP relaxed structure features a decrease by 3% of Q^2 and Q^4 units and an increase of 6% of Q^3 units with respect to the structure relaxed directly in LDA. In contrast, as far as concerns RMC1, which has only Q^3 units, the TSP relaxed structure is equivalent to a direct LDA relaxation (difference in energy < 0.0005 eV/atom) with no change in the network topology, i.e., in both cases, the relaxed structure consists of only Q^3 units. Calculation of the vibrational modes of relaxed CMD and RMC models are obtained by exploiting a linear response approach 45 . The codes used for the present calculations of structural and vibrational properties are freely available with the Quantum-Espresso pack age^{46} .

III. RESULTS AND DISCUSSION

First, we demonstrate the reliability of our DFT calculation scheme by calculating the Raman spectrum for a crystalline phase, o' $-P_2O_5^{27}$ (see Fig. 1). As we can see in Fig. 4, the theoretical Raman spectrum very closely resembles the experimental one. All signatures are reproduced including a fine structure at $100-550 \text{ cm}^{-1}$ frequency range. A small shift $\sim 1\%$ with respect to experimental data at higher frequencies represents the accuracy limit of the present DFT calculations in agreement with recent calculations in phosphosilicate $glasses^{13}$. Thus, we can rely on DFT approach to consider $v-P_2O_5$ vibrational spectra. In Fig. 5(a), we can see that all $v-P_2O_5$ models reproduce two main experimental Raman peaks (~ 640 and ~ 1380 cm⁻¹) and one moderate band at $\sim 800 \text{ cm}^{-1}$. However, only the RMC1 model resembles the experimental spectrum over all the range, while the CMD and RMC2 models produce quite strong additional features at high frequencies ($\sim 1000-1300 \text{ cm}^{-1}$) compared to the silent doublet [~950 and ~1150 cm⁻¹ (exp. ~ 920 and ~ 1110 cm⁻¹)]. Considering IR spectra in Fig. 5(b), we can mention that only the Model RMC1 provides very good agreement with experimental spectrum and reproduces all signatures ($\sim 450 \text{ cm}^{-1}$, $\sim 800 \text{ cm}^{-1}$, $\sim 950 \text{ cm}^{-1}$, $\sim 1100 \text{ cm}^{-1}$, and $\sim 1380 \text{ cm}^{-1}$), whereas the CMD and RMC2 models do not reproduce the peak position of the central band $\sim 800 \text{ cm}^{-1}$, de-



Figure 5. Vibrational spectra of $v-P_2O_5$. (a) Reduced Raman HH spectra with experiment by Mohmoh *et al.*¹⁶, (b) IR absorption spectra with experiment by Meyer *et al.*⁴⁷, (c) VDOS spectra with experiment (present work). In all panels: experiment (solid grey curve); models RMC1 (solid black curve), RMC2 (dashed red curve), and CMD (dot-dashed blue curve). A Gaussian broadening (20 cm⁻¹) is used for all theoretical curves.

form and shift the most strong $\sim 950 \text{ cm}^{-1}$ band, and generate additional features at high frequencies similarly to Raman spectra.

In Fig. 5(c) we present the VDOS analysis. The experimental VDOS was obtained using the inelastic neutron scattering technique with experimental details as reported elsewhere⁴⁸. We can see that, apart from the very beginning, < 100 cm⁻¹ (boson peak area), and the double-bonded oxygen line, 1400 cm⁻¹ (exp. 1380 cm⁻¹), all models exhibit similar qualitative behavior and reproduce the main experimental features: i) mid-frequency bands at ~450 cm⁻¹, ~650 cm⁻¹ and ~800 cm⁻¹; ii) high-frequency bands at ~950 cm⁻¹, ~1150 cm⁻¹ and ~1380 cm⁻¹. The origin of slight shift of 1380 cm⁻¹ line is coming from the DFT calculation in the case of oxide glasses as mentioned above. A broad range of wavenumber used in the neutron experiments



Figure 6. The partial VDOS for Q^n species: (a) Model RMC1 vs. Model RMC2, (b) Model RMC1 vs. Model CMD. Q^n species for PO₄ structural unit are shown schematically in the inset. Note: the model RMC1 has 100% Q^3 units.

does not resolve accurately the boson peak area, however, it does not affect the present vibrational analysis. Despite the qualitative similarity of the simulation and experimental spectra, however, there are significant differences in the structure of simulation spectra. In particular, the CMD model shifts the high-frequency spectrum (~950 cm⁻¹ and ~1150 cm⁻¹) by ~100 cm⁻¹, essentially deforming it in relation to RMC and experimental spectra. In addition, the RMC2 model shifts the mid-frequency band ($\sim 650 \text{ cm}^{-1}$) and the high-frequency band (~1150 cm⁻¹). By contrast, a comparison of the experimental and *ab initio* RMC1 model VDOS spectra shows very good agreement over all the frequency range, reproducing the exact locations of all the main features. Thus, similarly to Raman and IR spectra, the CMD and RMC2 models deform VDOS spectra inducing additional features at high frequencies [see Fig. 5(c)]. In order to reveal these features, we decompose the VDOS spectra in terms of Q^n species by projecting vibrations onto corresponding Q^n structural units:

$$g(\nu) = \sum_{n=2}^{4} g_n(\nu) = \frac{1}{3N_{at}} \sum_n \sum_k \sum_{I_n} \left| \mathbf{e}_{I_n}^k \right|^2 \delta(\nu - \nu_k),$$
(1)

where the index k labeling the vibrational modes runs from 1 to $3N_{at}$, N_{at} is the total number of atoms in the models (112 atoms), \mathbf{e}^k and ν_k are eigenmodes and eigenfrequencies, the index I_n runs over the Q^n units,



Figure 7. The dependence of the participation ratio on frequency for RMC1 (violet circles), RMC2 (green circles) and CMD (blue circles) models.

and

$$\left|\mathbf{e}_{I_{n}}^{k}\right|^{2} = \left|\mathbf{e}_{P_{n}}^{k}\right|^{2} + \sum_{i_{TO} \in Q^{n}} \left|\mathbf{e}_{i_{TO}}^{k}\right|^{2} + \frac{1}{2} \sum_{i_{BO} \in Q^{n}} \left|\mathbf{e}_{i_{BO}}^{k}\right|^{2}, (2)$$

where P_n denotes phosphorus atoms belonging to I_n units, i_{BO} and i_{TO} enumerate bridging and terminal oxygen atoms within Q^n units. Figs. 5(c), 6(a) and 6(b) evidence clearly that the Q^2 and Q^4 units (in CMD and RMC2 models) deform VDOS spectra at ~ 600 - 1450 cm^{-1} and hence induce corresponding differences in Raman and IR spectra with respect to experimental measurements and RMC1 model. Thus, the RMC1 model, comprised from Q^3 units only, provides excellent agreement with all the experimental measurements and properly represents the structure of pure $v-P_2O_5$. The additional features at high frequency in all vibrational spectra are the signatures of Q^2 and Q^4 units in the network of CMD and RMC2 models (see Fig. 2), supporting previous experimental Raman studies¹⁹ on Na-doped P_2O_5 containing Q^2 units.

Previous researches based on specific cluster model^{14,15,17} were able to confidently assign only the high-frequency Raman and IR band 1380 cm^{-1} ascribing it to the motion of the double-bonded oxygens along the P=O bonds. Since high-frequency modes are quite localized (having participation ratio (PR) ~ 0.2 , see Fig. 7), cluster models 14,15,17 are capable to explain their nature. However, the medium-frequency range (~ 300 - 870 cm^{-1}) is characterized by quite strong cooperative effect (in fact modes are rather non-localized having PR ~ 0.5 , see Fig. 7) and cluster models can hardly be applied. We overcome the cluster model limitations by using the 112-atom models (RMC and CMD). To better understand the internal structure of vibrations, we perform a projection analysis in terms of the chemical species. In Fig. 8(a), VDOS spectrum projected onto species reveals a quite noticeable coupling of phosphorus and oxygens atoms at $\sim 600-870 \text{ cm}^{-1}$, uniform moderate presence of phosphorus motion at frequencies below $\sim 600 \text{ cm}^{-1}$, suppressed phosphorus activity at high fre-



Figure 8. (a) The partial VDOS for phosphorus (P) atoms (solid red line), terminal oxygen (TO) (dot-dashed green line) and bridging oxygen (BO) (dotted blue line) atoms compared to the total VDOS (solid black line). Inset schematically shows Q^3 –PO₄ structural unit. (b) Deconvolution of Raman HH spectrum with the same color code as in panel (a). Inset shows zoom of intensity multiplied by a factor of 40 for 700–1250 cm⁻¹ frequency region. (c) The partial VDOS for the projections onto the T_d-group symmetries: A₁ symmetric stretching (solid red line), F_{2s} asymmetric stretching (dashed blue line), F_{2b} bending (dotted magenta line), E bending (dotdashed green line), F₁ solid-unit rotations (double dot-dashed orange line). Inset schematically shows the relative atomic displacements of the T_d-group. The results are obtained for the Model RMC1.

quency doublet zone ($\sim 870-1250 \text{ cm}^{-1}$) with respect to the bridging oxygens, and considerable phosphorus gain at the narrow $\sim 1400 \text{ cm}^{-1}$ band. The doublet zone can be attributed mostly to the bridging oxygens, while the terminal oxygens only provide a negligible contribution. By contrast, the band $\sim 1400 \text{ cm}^{-1}$ (exp. 1380 cm⁻¹) is practically forbidden for the bridging oxygens, and mostly arising from terminal oxygen motions. Some very interesting Raman features relates to the frequency range between ~ 550 and 700 cm⁻¹ [see Fig. 5(a)], where a strong Raman enhancement is observed at ~610 cm⁻¹ (exp. 640 cm⁻¹). Umari and Pasquarello developed an approach for the decomposition of Raman spectra^{49,50}, however, their approach does not take into account the interference effect between specific groups of atoms or vibration, which does not provide the decomposition of the spectra in an additive manner. We adapt this approach to take into account the interference effect to decompose the Raman spectrum into partial contributions of specific groups of atoms, i.e. P, TO, BO (phosphorous, terminal- and bridging-oxygen atoms, see the legend in Fig. 8), so to fully represent the total spectrum (see Appendix A). In result, the Raman HH intensity is a sum of three terms:

$$\mathcal{I}(\nu) = \mathcal{I}_P(\nu) + \mathcal{I}_{TO}(\nu) + \mathcal{I}_{BO}(\nu).$$
(3)

By projecting VDOS onto phosphorous, terminal- and bridging-oxygen atoms, we can see that in the range \sim 550-700 cm⁻¹ bridging oxygen motions are major as compared with terminal oxygens [see Fig. 8(a)], however, the polarizability of terminal oxygens are much stronger than bridging oxygens, that leads to their predominance in producing the Raman 640 cm^{-1} band [see Fig. 8(b)], and this assignment disproves the previous band attribution^{14,16–18} ascribing mainly its origin to the symmetric stretching modes of bridging oxygens. Also, we indicate comparable contributions of bridging oxygen and phosphorus motions and quite moderate contributions of terminal oxygens at 700-870 cm⁻¹ band, however, the phosphorus atoms contribute lightly to the Raman $\sim 800 \text{ cm}^{-1}$ band [see inset in Fig. 8(b)], i.e. this Raman band is ascribed mainly to bridging oxygens. In the VDOS frequency range 100–550 $\rm cm^{-1}$ it is interesting to note that terminal oxygens make a larger contribution than bridging oxygens in the range $100-350 \text{ cm}^{-1}$, whereas the opposite is true in the range $350-550 \text{ cm}^{-1}$. It is also interesting to mention that Raman spectra appearing at $100-550 \text{ cm}^{-1}$ have a similar structure as VDOS, however the terminal oxygen contribution is decisive [see Fig. 8(b)] due to higher polarizability, and hence the Raman modes in the range $350-550 \text{ cm}^{-1}$ are not specifically related to bending modes of bridging oxy $gens^{14,16}$.

Finally, we present *full* tetrahedral (T_d) symmetry group analysis^{20,21}, which have never been reported for ab initio glass models to date. In Fig. 8(c), the spectrum in the range from ~ 600 to 870 cm⁻¹ is dominated by bending (F_{2b}) motions related mostly to bridging oxygen and phosphorus ($\sim 800 \text{ cm}^{-1}$ band) atoms [see Fig. 8(a)], while the high frequency doublet zone ($\sim 870 1250 \text{ cm}^{-1}$) is associated mostly with the symmetric (A₁) and asymmetric (F_{2s}) stretching modes. One can note, that the Raman bands $\sim 870-1250 \text{ cm}^{-1}$ behave silently that complicates their accurate measurements and analysis, whereas IR spectrum shows strong resonances, especially at $\sim 950 \text{ cm}^{-1}$. Since the modes above $\sim 870 \text{ cm}^{-1}$ are quite spatially localized (PR ~ 0.2) that enables to infer information about intermediate range order (interbonding angle)⁵¹, and hence, in the case $v-P_2O_5$, the IR spectroscopy seems more preferred tool rather than Raman spectroscopy in this frequency range. The most prominent peak around 1400 cm⁻¹ (exp. 1380 cm⁻¹) is mainly due to asymmetric stretching vibrations of terminal oxygens, and its signatures are comparably strong in all vibrational spectra (see Fig. 5). The lower frequency range in VDOS below 600 cm^{-1} is shown to arise from mixture of bending (E and F_{2b}) and rotation (F₁) modes. However, the scissors bending (E) and rotation (F_1) modes are well localized below 600 cm^{-1} , whereas the F_{2b} -bending modes spread further into the range ~600- 870 cm^{-1} . The boson peak area, i.e. $< 100 \text{ cm}^{-1}$, is originating mostly from the rotation (F_1) modes similarly to $v-\mathrm{SiO}_2^{20,21}$. It should be noted that our mode-projection analysis can be applied for other point-symmetry groups. thus offering a powerful modes assignment tool, and hence unveils a more comprehensive methodology for studying vibrational properties in disordered systems.

IV. CONCLUSION

In conclusion, we presented a comprehensive analysis based on *ab initio* calculations and experimental measurements, which provides an assignment of the Raman, IR and VDOS spectra in v-P₂O₅ to vibrations of specific network structural units. Our analysis yields compelling evidence of the existence of only Q³ tetrahedral units in pure v-P₂O₅. It has been revealed in detail the internal structure of vibrations using a mode-projection analysis based on chemical species and T_d symmetry group. Thus, this work serves as an exemplary study of disordered material with complex bonding configurations, and the combined modeling approach based on RMC and DFT simulations with mode-projection analysis is very promising for further studies of amorphous materials.

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Appendix A: Raman decomposition

The Raman cross-section is calculated assuming nonresonant conditions in the Placzek approximation as described in a previous work²⁵ and given by (in esu units):

$$\mathcal{I}^{P}(\nu) = \frac{2\pi h}{\nu} \frac{\mathrm{g}(\nu) \left(\nu_{L} - \nu\right)^{4}}{V^{-1} c^{4}} \sum_{k} \mathcal{I}_{k} \delta(\nu - \nu_{k}), \quad (A1)$$

where the index k labeling the vibrational modes runs from 1 to $3N_{at}$, N_{at} is the total number of atoms in the models, ν_L is the frequency of the incoming photon, his the Planck constant, c is the speed of light, V is the volume of the scattering sample, $g(\nu) = n_B(\nu) + 1$, and $n_B(\nu)$ is the boson factor. In this work, we give the Raman intensities using the following reduced expression:

$$\mathcal{I}(\nu) = \nu \left(\nu_L - \nu\right)^{-4} g^{-1}(\nu) \mathcal{I}^P(\nu).$$
 (A2)

In experimental setups, it is customary to record the Raman spectra in the horizontal-horizontal (HH) configuration in which the polarization of the outgoing photons is respectively parallel to the ingoing photon polarization. Using the isotropy of disordered solids, we express the contribution of the kth mode \mathcal{I}_k to the HH-Raman spectra as

$$\mathcal{I}_{k}^{HH} = a_{k}^{2} + \frac{4}{45}b_{k}^{2}.$$
 (A3)

Below, we adapt the Umari and Pasquarello approach in Ref.⁴⁹ to take into account the interference effect and to additively decompose the Raman spectrum given by Eq. (A2) into partial contributions of specific groups of atoms $\{A_m\}(m = 1, 2, 3), A_m \in \{P, TO, BO\}$, i.e. $\mathcal{I}(\nu) = \sum_m \mathcal{I}_{A_m}(\nu)$. The Raman susceptibility tensors \mathcal{R}^k are given by

$$\mathcal{R}^{k} = \sum_{m} \mathcal{R}^{k}_{A_{m}} = \sum_{m} \left\{ \sqrt{V} \sum_{I \in A_{m}} \frac{\partial \chi}{\partial \mathbf{R}_{I}} \frac{\mathbf{e}_{I}^{k}}{\sqrt{M_{I}}} \right\}, \quad (A4)$$

where $\boldsymbol{\chi}$ is the electric polarizability tensor, the capital Latin index I runs over the atoms, \mathbf{R}_I and M_I are the

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position and the atomic mass of atom I, respectively. By using $\mathcal{R}_{A_m}^k$ we decompose a_k^2 and b_k^2 as follows

$$a_{k} = \sum_{m} a_{k,A_{m}} =$$
$$= \sum_{m} \left\{ \frac{1}{3} \sum_{i=1}^{3} \mathcal{R}_{ii,A_{m}}^{k} \right\} = \frac{1}{3} \sum_{i=1}^{3} \mathcal{R}_{ii}^{k}, \quad (A5)$$

$$a_k^2 = \sum_m \tilde{a}_{k,A_m}^2 = \sum_m \sum_{m'} a_{k,A_m} a_{k,A_{m'}}, \qquad (A6)$$

$$b_{k}^{2} = \sum_{i < j} \left\{ \frac{1}{2} \left(\mathcal{R}_{ii}^{k} - \mathcal{R}_{jj}^{k} \right)^{2} + 3 \left(\mathcal{R}_{ij}^{k} \right)^{2} \right\} =$$
$$= \sum_{i < j} \left(\gamma_{ij}^{k} \right)^{2} + \sum_{i < j} \left(\delta_{ij}^{k} \right)^{2} = \gamma_{k}^{2} + \delta_{k}^{2}, \quad (A7)$$

where γ_{ij}^k and δ_{ij}^k are represented as

$$\gamma_{ij}^{k} = \sum_{m} \gamma_{ij,A_{m}}^{k} = \sum_{m} \frac{1}{\sqrt{2}} \left(\mathcal{R}_{ii,A_{m}}^{k} - \mathcal{R}_{jj,A_{m}}^{k} \right), \quad (A8)$$

$$\delta_{ij}^k = \sum_m \delta_{ij,A_m}^k = \sum_m \sqrt{3}\mathcal{R}_{ij,A_m}^k, \qquad (A9)$$

and γ_k^2 and δ_k^2 are decomposed as

$$\gamma_k^2 = \sum_m \tilde{\gamma}_{k,A_m}^2 = \sum_m \sum_{i < j} \sum_{m'} \gamma_{ij,A_m}^k \gamma_{ij,A_{m'}}^k, \quad (A10)$$

$$\delta_k^2 = \sum_m \tilde{\delta}_{k,A_m}^2 = \sum_m \sum_{i < j} \sum_{m'} \delta_{ij,A_m}^k \delta_{ij,A_{m'}}^k.$$
(A11)

By using Eqs. (A5)–(A11) we decompose \mathcal{I}_{k}^{HH} as $\mathcal{I}_{k}^{HH} = \sum_{m} \mathcal{I}_{A_{m},k}^{HH}$, that allows to compute *m*th terms $\mathcal{I}_{A_{m}}(\nu)$ representing the total intensity $\mathcal{I}(\nu)$ given by Eqs. (A2) and (3).

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