

Vibrational spectra of α -Ta₂O₅: A first-principles investigation

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We present a first-principles study of the vibrational spectra, i.e., vibrational density of states (VDOS) and infrared (IR) and Raman spectra, of amorphous tantalum (α -Ta₂O₅). Three model structures of up to 336 atoms in size have been generated by means of classical and *ab initio* molecular dynamics and subsequently used for a series of *ab initio* calculations of the vibrational modes and the relevant Raman and IR coupling tensors. For the assessment of size-dependent effects on the calculated vibrational spectra, we employed a machine-learned potential that enabled the calculation of the VDOS with *ab initio* accuracy for models containing up to a few thousand atoms. Raman and IR coupling tensors have been analyzed in a local reference frame, which provides direct insight into correlations with local structural parameters like the Ta–O–Ta angles and O–Ta bond lengths. Fair agreement is recorded with available experimental dielectric functions and Raman spectra for both the largest model structure and the fully *ab initio* generated model, in contrast with a third model, the Raman spectrum of which may appear to represent a structure approaching the onset of crystallization. In this study, we confirm that the vibrational modes above ~ 550 cm^{−1} consist mainly of Ta–O stretching motion of O atoms; meanwhile, Ta motion gives a major contribution to the VDOS only below ~ 200 cm^{−1}. The vibrational modes underlying the main Raman peak at ~ 670 cm^{−1} are related to Ta–O bond stretching motions, and a major contribution to the peak appears to come from twofold-coordinated O atoms, whereas the Raman weight of threefold-coordinated O atoms is maximized in the range ~ 500 – 550 cm^{−1}. Moreover, an analysis of the twofold-coordinated O contribution to the VDOS—resolved into rocking, bending, and stretching components—shows that, beyond ~ 550 cm^{−1}, the rocking and bending contributions vanish, leaving stretching as the dominant mode. Above 400 cm^{−1}, the contribution of threefold-coordinated O atoms to the VDOS is essentially given by an in-plane Ta–O stretching motion which exhibits maxima around 450 – 500 cm^{−1}, while oxygen out-of-plane motion is relevant mostly around 300 cm^{−1}. Finally, by means of further local projectional analysis, we infer that vibrational modes with frequencies above 550 cm^{−1} feature mostly asymmetric and symmetric stretching modes of TaO_{*n*} (*n* = 5, 6, 7) polyhedra. The latter decomposition allows us to explain the origin of the experimental Raman band above ~ 780 cm^{−1}.

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I. INTRODUCTION

Amorphous tantalum (α -Ta₂O₅) is a fascinating material belonging to the class of intermediate oxides [1,2], and unlike other oxide glasses such as amorphous silica (α -SiO₂), it cannot be obtained through a quench-from-the-melt procedure. Instead, high-quality amorphous tantalum is usually produced as thin films through physical vapor deposition techniques such as reactive magnetron sputtering or ion-beam sputtering (IBS). Nowadays, α -Ta₂O₅ is a material of paramount

technological relevance for electronics and microelectronics applications (e.g., RRAMs [3–5]), especially because of its large static dielectric constant (~ 25) and the considerably large electronic band gap (~ 5 eV). For instance, α -Ta₂O₅ thin films are employed as gate dielectrics in microelectronics due to their significantly higher dielectric constant than α -SiO₂, which enables larger capacitance at the same thickness. Although their leakage current may be generally higher than that of α -SiO₂, the enhanced capacitance allows improved device scaling and performance. Because of its high refractive index, low extinction coefficient (in the visible), and small thermo-optic coefficient, amorphous tantalum thin films have several applications in optics and photonics, ranging from the production of lenses and antireflection coatings for optical applications in the visible spectrum, near-ultraviolet (UV), and near-infrared (IR) to the production of microresonators [6–9]. Combined with other amorphous oxides, e.g., TiO₂, α -Ta₂O₅ thin films are used for the coatings of the test masses in the

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mirrors that make up the advanced LIGO and VIRGO interferometers [10]. Moreover, tantala-based materials constitute a class of promising candidates currently under investigation for future developments of gravitational wave detectors [11–13], and remarkable improvements have recently been obtained, e.g., by heat treatment above crystallization temperature [14–16].

Despite the tremendous technological importance of amorphous tantala, as illustrated by the applications mentioned above, its microscopic structure remains only partially understood. In contrast with bulk glasses—where a broader range of structural probes such as inelastic neutron scattering can be employed—the characterization of the microscopic structure of a -Ta₂O₅ films is constrained by the more limited set of available experimental techniques. As a result, current knowledge relies primarily on insights obtained from x-ray and nuclear magnetic resonance (NMR) investigations, which provide partial information on the short- and medium-range order in a -Ta₂O₅ [17,18]. The theoretical interpretation of the vibrational spectra of a -Ta₂O₅ has so far been largely confined to discussions of vibrational density of states (VDOS) bands and related properties [19–21]. In contrast, a detailed analysis and theoretical modeling of the IR and Raman spectra remain relatively unexplored, despite the widespread use of both spectroscopic techniques to investigate annealing effects, the onset of crystallization, doping effects, and pressure-induced amorphization [22–27]. Moreover, it is not yet clear what could be the fingerprints, if there are any, of structural units like the edge-sharing polyhedra (ESP) in the Raman spectra of amorphous tantala.

The Raman spectrum of a -Ta₂O₅ exhibits a prominent peak at ~ 670 cm⁻¹ together with minor features at ~ 220 – 240 cm⁻¹, ~ 500 cm⁻¹, and a broad band in the range 800 – 1000 cm⁻¹ [20,25,27–30]. The low-frequency part of the spectrum exhibits a sharp band peaking at about 70 cm⁻¹, in a frequency range which is typical for boson peaks in glasses [20,31–33]. Other minor features have occasionally been reported, e.g., around ~ 470 and ~ 620 cm⁻¹ and attributed to the presence of the substrate or to the optical system [28,34]. The Raman data collected with 785 nm laser by Favaro *et al.* (R1 region of Fig. 2(b) of Ref. [25]) show, beyond the main peak at ~ 670 cm⁻¹, a high-frequency doublet (~ 830 and ~ 935 cm⁻¹), unlikely related to the silica substrate, as the latter would give rise to peaks at 800 , 1065 , and 1200 cm⁻¹ [35]. Moreover, Raman spectra of a -Ta₂O₅ thin films grown on different substrates, e.g., silicon [30] and germanium [27], also may suggest the presence of two subbands possibly peaking at frequencies ~ 850 and ~ 940 cm⁻¹. In Ref. [20], based on classical molecular dynamics calculations [19], the main Raman peak was attributed to the bending and stretching motions of threefold coordinated oxygen atoms, yet we note that classical force fields cannot describe the vibrational properties of amorphous oxides, e.g., silica, with a good accuracy [36]. Hence, it is reasonable to assume that a similar limitation also occurs when trying to describe the vibrational modes of amorphous tantala, which is one of the motivations behind the present *ab initio* investigation of the vibrational spectra of a -Ta₂O₅.

As compared with Raman-based experimental studies, there are fewer IR-dedicated studies of a -Ta₂O₅ thin films;

we are aware of only two investigations where the complex dielectric function $\epsilon(\omega)$ has been measured [37,38]. The main peaks in the IR absorbance spectrum of a -Ta₂O₅ are located at ~ 630 – 640 cm⁻¹ and ~ 280 cm⁻¹, together with minor features at ~ 510 cm⁻¹ and with a broad shoulder extending from 800 to 1000 cm⁻¹ [2,39–41]. In Refs. [2,39], tentative assignments concerning the origin of the vibrational modes were done on the basis of analogies with V₂O₅ or using molecular models (e.g., WF₆, TaF₆). The assignments proposed in Ref. [39] attributed a strong role to the threefold-coordinated oxygen motion. Peaks/features at ~ 280 cm⁻¹ and in the range 500 – 650 cm⁻¹ were attributed to the stretching of Ta–O bonds of threefold-coordinated oxygen atoms [39], while minor features in the range ~ 800 – 900 cm⁻¹ (e.g., at 870 cm⁻¹ [40]) were ascribed to the Ta–O bond stretching of twofold-coordinated oxygen atoms [39,40].

In recent years, thanks to the continuous growth in the computational power of high-performance computing (HPC) facilities, *ab initio* calculations of vibrational spectra have become feasible for amorphous systems of up to several hundred atoms of size [21,31,42–44]. These investigations rely on established methods such as density functional perturbation theory [45] and the finite field approach [46,47], which have been developed over the past three decades and successfully applied, for example, to the study of Raman and IR spectra in various oxide glasses [31,43,48–53]. From such an amount of literature, it is nowadays possible to qualitatively infer common features which may be exhibited by the VDOS of amorphous oxide materials beyond the Debye regime and the boson peak range. For instance, whenever the majority of oxygen atoms are twofold coordinated (i.e., bridging O), a VDOS resembling the one of silica glass with three main bands [54], reflecting oxygen motion, could be expected. This is indeed the case for glassy GeO₂ and to some extent also P₂O₅, B₂O₃, and TeO₂ glasses, and so on [48,51–53]. By contrast, for amorphous materials like a -Al₂O₃, a -Ga₂O₃, and a -ZrO₂, where the majority of oxygen atoms are threefold coordinated, the VDOS becomes rather blurred [55–57], showing only two main oxygen subbands that then manifest into a camel-shaped IR ϵ_2 function [50]. Interestingly enough, glassy TeO₂ (g -TeO₂) shows a Raman spectrum [31,58] rather similar to the one recorded for a -Ta₂O₅ thin films, with a major peak at ~ 660 cm⁻¹, despite remarkable structural differences between g -TeO₂ and a -Ta₂O₅ [18,53]. Hence, first-sight analogies in the IR and Raman spectra of glasses must be taken with a caveat, and safely grounded assignments always require a dedicated combined structural-vibrational analysis [50,52,53]. Concerning *ab initio* investigations of the vibrational spectra in pure a -Ta₂O₅, apart from a very recent attempt to calculate the Raman spectrum with a Born-charges-based method [59], we are aware only of VDOS studies of tantala-alloyed systems such as Cu-doped Ta₂O₅ and ZrO₂-Ta₂O₅ [21,42] but none dedicated to the case of pure a -Ta₂O₅.

The present work on vibrational spectra of amorphous tantala is dedicated to the study of the oxygen motion part of the spectrum which reflects the variety of O local environments in the amorphous tantala. To acquire a sufficient variety of local O environments, we take advantage of three viable model structures of amorphous tantala generated by means of the

combined usage of classical molecular dynamics and *ab initio* approaches, including a fully *ab initio* generated model, with sizes up to 336 atoms. Size-dependent effects on the VDOS were then investigated using a machine-learned potential developed with the ALLEGRO package [60,61], which enabled the generation of models containing up to 3500 atoms and the calculation of the VDOS with *ab initio* accuracy. Although a deep study of the a -Ta₂O₅ structure is beyond the scope of the present work, a basic structural analysis has been included with the aim of giving a proper description of the main structural features of a -Ta₂O₅ and the O local environment. The comparison with the available experimental x-ray total correlation function allows us to discuss the reliability of our structural models of a -Ta₂O₅, validating our fully *ab initio* generated model. For the set of adopted models, we calculate vibrational spectra [VDOS, IR $\epsilon(\omega)$, and Raman] at *ab initio* level, which allows us to establish accurate assignments for the vibrational modes underlying the main peaks of the IR and Raman spectra. By means of projectional analysis, we show that stretching motion of twofold-coordinated O atoms dominates the VDOS above 550 cm⁻¹, and we infer that the asymmetric and symmetric stretching modes of TaO_{*n*} ($n = 5, 6, 7$) polyhedra could lead to a doublet in the vibrational spectra at frequencies above 800 cm⁻¹, which might suggest an assignment in terms of such modes for the high-frequency doublet resolved in the recent experimental Raman data at 785 nm of Favaro *et al.* [25]. Hence, our analysis substantially improves upon the assignments done in Ref. [20].

This paper is organized as follows. In Sec. II, we provide computational details of the present density functional theory (DFT)-based calculations of vibrational spectra (Sec. II), while the generation of the a -Ta₂O₅ models used for this study is outlined in Sec. II A. Details about the generation of the machine-learned potential used to discuss size-effects are given in Sec. II B. In Sec. III, we address structural properties; in Sec. III A, we analyze short- and medium-range orders using the Ta–O bond length and the x-ray total correlation function, which is used to validate our structures through comparison with available experimental data [18]. Moreover, in Sec. III B, we also discuss coordination numbers and amount of ESP, while the planarity of the OTa₃ units for threefold-coordinated oxygen atoms is analyzed in Sec. III C. Section IV is devoted to vibrational modes. We first consider the impact on vibrational frequencies due to the choice of the DFT setup and to size-effects, and next, we discuss the main bands of the VDOS of our models, particularly through decompositions in terms of oxygen rocking, bending, and stretching motions and in terms of local projections on A_1 and T modes of TaO_{*n*} polyhedra (Secs. IV A and IV B), while the localization of vibrational modes is investigated by means of the participation ratio in Sec. IV C. In Sec. V, we present results for the calculated and experimental IR dielectric functions and the static and high-frequency dielectric constants, and in Sec. V B, we provide an extended analysis of the dynamical Born charges. Section VI addresses the Raman spectra. We obtain Raman spectra for all our models and discuss the origin of the main Raman bands in terms of Ta, twofold-coordinated O, and threefold-coordinated O atom contributions (Sec. VI A). Moreover, in Sec. VI B, Raman derivative tensors of oxygen atoms are analyzed in terms of local struc-

tural parameters. The conclusions of this work are drawn in Sec. VII.

II. METHODS

All the IR and Raman spectra calculated for a -Ta₂O₅ in this work are based on DFT. Structural relaxations and vibrational modes (in the harmonic approximation) are obtained by employing the generalized gradient approximation (GGA), i.e., the Perdew-Burke-Ernzerhof (PBE) [62] functional and pseudopotentials from the standard solid-state pseudopotentials library optimized for precision or efficiency (SSSP) [63,64]. The Kohn-Sham wave functions are expanded in a basis of plane-waves up to a kinetic energy cutoff of 50 Ry at the sole Γ point of the Brillouin zone. For the electron density, a cutoff of 400 Ry was used, consistent with the SSSP prescriptions [64].

The structural models of a -Ta₂O₅ (described below) are relaxed by adopting force thresholds of 0.0014 eV/Å (or smaller), which allow for a proper harmonic treatment of the vibrational modes. We obtain the vibrational frequencies and eigenmodes by diagonalizing the dynamical matrix [49], which we calculate numerically from finite differences of atomic forces using atomic displacements of 0.1 Bohr. The high-frequency dielectric constant, the dynamical Born charges, and the Raman derivatives were obtained by means of the linear response based code *ph.x* (v. 7.2) of the QUANTUM ESPRESSO package [65]. Consistent with the current implementation [65], Raman (and IR) coupling tensors have been obtained by employing LDA-PZ norm-conserving pseudopotentials [66] with an adopted threshold for the self-consistent solution of the linear-response problem at most of 10⁻¹², whereas a smaller value 10⁻¹⁴ has always been used for the calculation of vibrational frequencies. Moreover, for the sole model III, we have also checked, by evaluating the derivatives of the dielectric polarizability tensor χ with respect to displacements via the finite-field approach [46,49] as it is implemented in the CP2K code [67], that the choice of the DFT flavor (LDA vs PBE) adopted to evaluate Raman coupling tensors does not substantially affect the shape of the calculated Raman spectrum (see Fig. S1(a) in the Supplemental Material [68]). In addition, the vibrational modes have been obtained under the constraint that the total force constants satisfy the acoustic sum rule to ensure that translational modes have zero frequency. For visualizing the structure and the vibrational modes of the amorphous tantala models, we employed XCRYSDEN visualization software [69].

A. Models generation details

In this study, we consider three plausible structural models of amorphous tantala [70] that are obtained by varying the generation procedure to enhance the variability in the tantalum and oxygen local environments. Two of these models, hereafter referred to as models I and II, containing 336 and 126 atoms, respectively, were generated [71] using classical molecular dynamics simulations via a quench-from-the-melt protocol, which is a commonly adopted generation procedure of a -Ta₂O₅ models [19,72–74], despite that Ta₂O₅ is not a glass former, as extensively discussed in Ref. [18]. The densities of model I (8.18 g/cm³) and model II (8.13 g/cm³)

were chosen consistently with reported values ($\sim 8.1 \text{ g/cm}^3$) previously obtained by employing the classical force field of Trinastic *et al.* [19,20]. The molecular dynamics simulations were performed with the LAMMPS code [75], employing the above-mentioned classical force field of Ref. [19]. The adopted quench rate is $\sim 10 \text{ K/ps}$ [19,20], from a high-temperature melt, with $T = 5000 \text{ K}$, and a total simulation time of 800 ps. The initial configurations were obtained from a $\beta\text{-Ta}_2\text{O}_5$ crystal cell by using a $3 \times 3 \times 2$ supercell (126 atoms) and a $4 \times 4 \times 3$ supercell (336 atoms). The third model, referred to as the full *ab initio* model (model III, containing 126 atoms), was generated using *ab initio* molecular dynamics via a melt-quench procedure, where a liquid of Ta_2O_5 was first equilibrated at 3000 K for 10 ps using the `pw.x` code and subsequently cooled below its melting point for a period of 20 ps. A thermostat with a stochastic-velocity rescaling was used [76]. The density of model III (7.5 g/cm^3) has been chosen within the range of experimental values ($7.30\text{--}7.68 \text{ g/cm}^3$) that have been measured in amorphous tantalum films.

The atomic positions of the models were then finally relaxed by first-principles using, for testing purposes, three different DFT flavors/setups: LDA-PZ [66], PBE-ONCV [77], and PBE-SSSP [63]. Subsequent calculations of the vibrational modes (see Fig. S1(b) in the Supplemental Material [68]) then allowed us to opt out for the PBE-SSSP setup, as explained in Sec. III B. A direct visualization [69] of the structure of model II shows a layering of the atoms and indicates that this model is reminiscent of a crystalline structure [78], as is also apparent from the structural analysis presented below. However, since amorphous models that exhibit crystalline features might be of interest in the context of describing the onset of crystallization [25], we estimate model II worth being included in the present analysis.

B. Size effects: Generation of larger models

To check how the VDOS depends on the size of the model (see Sec. IV), we have also generated a few tantalum models with sizes up to 3500 atoms using machine-learning force fields (MLFF). The interaction potential was obtained training an ALLEGRO model [60,61] on the DFT configurations taken from the molecular dynamics simulation which led to model III. The ALLEGRO model infers the energy contribution for each atom starting from the development of the local relative position vectors of the neighboring atoms until a cutoff radius $r_{\text{cut}} = 5 \text{ \AA}$, in terms of an expansion on Bessel's function (8 in our case) for the radial part and in terms of spherical harmonics (up to $l = 2$) for the angular part. The radial part is then expanded through multiplication with a matrix of free parameters to reach the dimension of the invariant number of features (64 in our case). During this operation, information on relative atomic species is also included. Two so-called interaction layers permit us to add information on relative bond directions which is first written, internally, in terms of 32 tensor features equivariant with respect to $O(3)$ transformations (i.e., rotations) and then collected on invariant scalars (64 in our case). These operations are performed by a multilayer perceptron (MLP) with Silu activation function. The weights are determined from the scalars of the previous layers

to be sensitive to local environment. Finally, a MLP gives the contribution of the atom-atom couple to the total energy. The adopted MLPs have one hidden layer with the same dimension of the input one. The final MLFF was then imported into the LAMMPS code.

We used the MLFF potential outlined above to generate large models of $\alpha\text{-Ta}_2\text{O}_5$. Specifically, we performed molecular dynamics melt-quench simulations, using the same protocol as employed to generate models I and II discussed in the previous sections. We started from $10 \times 10 \times 5$ and $7 \times 7 \times 4$ supercells of the $\beta\text{-Ta}_2\text{O}_3$ crystalline structure, resulting in 3500 and 1372 atom structures, respectively. We will refer to the two models as ML-3500 and ML-1372. We set the volumes of the supercells for the density to equal 7.89 g/cm^3 . These structures were used as the initial configuration for a melt-quench simulation. First, the liquid state was simulated for 200 ps. Then temperature was lowered to 1500 K in 200 ps. Finally, the structures have been relaxed to their equilibrium configurations with interatomic forces lower than $1 \text{ meV/\AA}$. For these ML models, we calculated the VDOSs (Sec. IV) via finite differences as described above for models I–III. The dynamical matrix was calculated through finite differences of atomic forces. For this task, atomic displacements of $10^{-2} \text{ \AA}$ were used. For testing purposes, we also relaxed the *ab initio* model III with our MLFF, keeping constant the simulation box and the density (hereafter named ML-126), and we obtained the vibrational modes and frequencies, fairly close to those calculated at *ab initio* level (Fig. S2 in the Supplemental Material [68]).

III. STRUCTURAL ANALYSIS

A. Total correlation function and bond lengths

In Fig. 1(a), we compare the x-ray total correlation function $T_X(r)$ as calculated for our models using the RINGS code [80] and as found in the experiment [18]. The first peak of $T_X(r)$ corresponds to the first peak of $g_{\text{OTa}}(r)$ [Fig. 1(b)] and is located at $\sim 1.9 \text{ \AA}$. The second and third peaks of $T_X(r)$ correspond to the first peaks in $g_{\text{OO}}(r)$ and $g_{\text{TaTa}}(r)$ and are found at $\sim 2.71, 3.26$, and $3.73 \text{ \AA}$, respectively [18]. Peaks located at close positions were also reported in the experimental $g(r)$ obtained by analyzing the selected area electron diffraction (SAED) patterns of the amorphous region [81]. Models I and III reasonably agree with the experimental data over all the reported lengths range. By contrast, the $T_X(r)$ of model II shows a strong peak at about $5.2 \text{ \AA}$, which is absent both in the experimental data and correlation functions of the other models. We attribute this peak to the occurrence in model II of atomic layers reminiscent of an orthorhombic tantalum phase, particularly to correlations due to Ta–Ta next-nearest-neighbor distances at $\sim 3.7\sqrt{2}$ i.e. about $5.2 \text{ \AA}$. We also note that the shoulder related to the edge-sharing structures in models I and II is located at a slightly larger distance ($\sim 3.36 \text{ \AA}$) with respect to the corresponding peak in model III ($3.26 \text{ \AA}$) which, for this model, is well separated from the main peak at $3.72 \text{ \AA}$.

In Fig. 1(b), we present the partial pair-correlation functions (PCFs), $g_{\text{OTa}}(r)$, $g_{\text{TaTa}}(r)$, and $g_{\text{OO}}(r)$, for model III. The corresponding PCFs for the other models exhibit qualitatively similar behavior (Figs. S3 and S4 in the

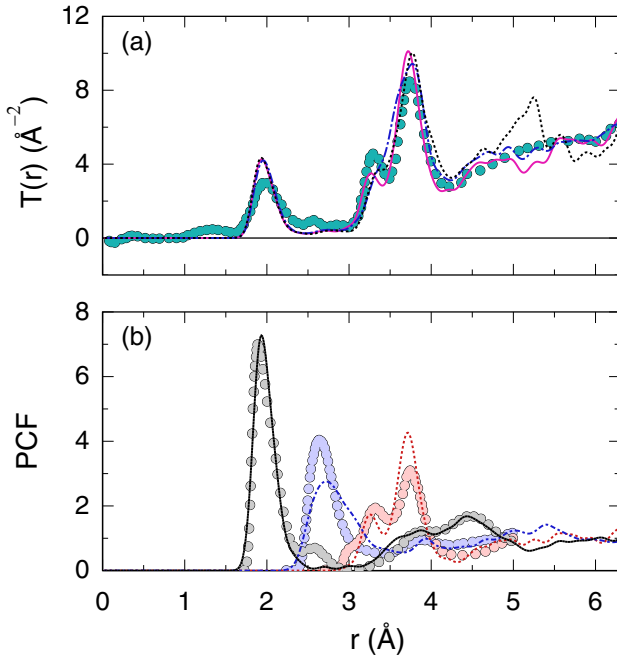


FIG. 1. (a) Theoretical x-ray total correlation function $T_X(r)$ as calculated for model I (dot-dashed/blue), model II (dotted/black), and model III (solid/violet). For comparison, the experimental $T_X(r)$ of Alderman *et al.* [18,79] is also shown (cyan discs). (b) Pair-correlation functions [80] $g_{TaO}(r)$ (solid/black), $g_{TaTa}(r)$ (dashed/red), and $g_{OO}(r)$ (dot-dashed/blue) of a -Ta₂O₅ as calculated for our *ab initio* model III and, respectively, as obtained from empirical potential structure refinement (EPSR) for Model-A in Alderman *et al.* [18,79] (light gray, pink and blue discs). A Gaussian broadening of 0.075 Å was applied to smooth the PCFs.

Supplemental Material [68]). The first peak of $g_{TaO}(r)$ is located at 1.93 Å and agrees closely with the experimental Ta–O bond length [18]. From a spherical integration of $g_{TaO}(r)$ up to its first minimum at ~ 2.6 Å, we derive an average coordination number of ~ 5.8 , consistent with the Ta coordination numbers in this model (Table I), which indicates a prevailing octahedral structural unit. The first peaks of $g_{TaTa}(r)$ correspond to Ta–Ta distances of 3.26 and 3.72 Å, respectively. These peaks reflect the Ta–Ta correlations occurring due to the presence of edge- and corner-sharing polyhedra, respectively. The first peak of $g_{OO}(r)$ corresponds to O–O distance of 2.72 Å, which roughly corresponds to the O–O distance in a TaO₆

TABLE I. Frequency (%) of coordination numbers of Ta and O atoms in the a -Ta₂O₅ models used in this study, obtained by directly counting the number of nearest neighbors within the Ta–O cutoff radius (2.6 Å). Experimental coordination frequencies, obtained from the ¹⁷O MAS NMR spectra of Ref. [17] are also given. The cutoff radius of $R_{cut} \simeq 2.6$ Å is used.

Coordination	Ta				O		
	4	5	6	7	2	3	4
Model I	–	27.1	57.3	15.6	65.0	34.6	0.4
Model II	–	22.2	66.7	11.1	64.4	35.6	–
Model III	–	38.9	50.0	11.1	71.1	28.9	–
Ref. [20]	0.5	28.5	69.4	1.6	69.6	30.1	–
Expt. [17]					57	43	–

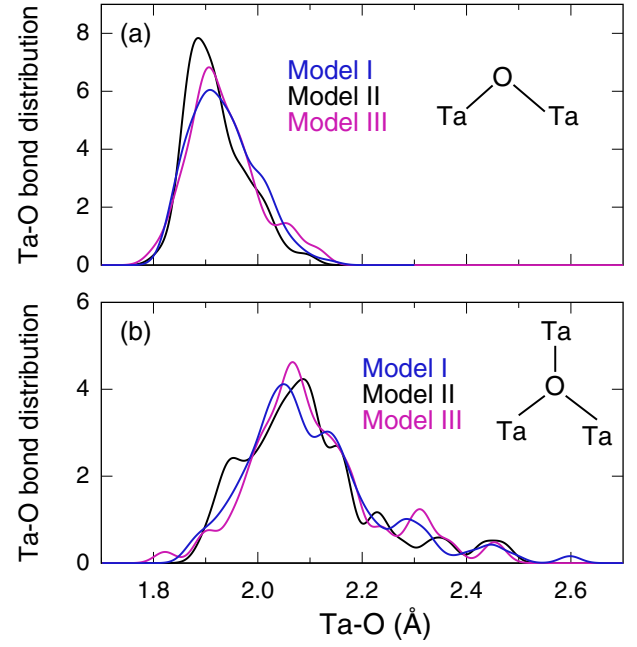


FIG. 2. (a) Distribution of Ta–O bonds as calculated for the twofold-coordinated oxygen atoms in our a -Ta₂O₅ models. (b) Distribution of Ta–O bonds as calculated for the threefold-coordinated oxygen atoms in our a -Ta₂O₅ models. Gaussian broadening of 0.02 Å is applied.

octahedron. In Fig. 2, we show the distributions of Ta–O bonds as calculated for twofold- and threefold-coordinated oxygen atoms in our models. The Ta–O bond distribution of twofold-coordinated oxygen (¹²¹O) atoms in models I and III has a peak at 1.91 Å, while in model II, it shows a peak at a smaller length of 1.89 Å. The full width at half maximum (FWHM) for model I is about twice the one of model II, and it is sensibly larger than in model III. For all our models, the distribution of Ta–O bonds for threefold-coordinated oxygen (¹³¹O) atoms, Fig. 2(b), is considerably larger than found for the ¹²¹O atoms in Fig. 2(a) and shows a peak at longer distance (~ 2.1 Å), reflecting a weaker Ta–O bond with respect to the one of ¹²¹O atoms.

B. Coordination numbers and ESP

Table I shows that oxygen atoms in our models I and II have similar Ta coordinations, i.e., the amount of ¹²¹O

TABLE II. Distribution of Ta atoms forming edge- and corner-sharing Ta polyhedra in our models. A cutoff of 2.6 Å is used to define atomic coordination.

Model	Edge-sharing (%)	Corner-sharing (%)
I	77	23
II	89	11
III	72	28

Distribution of corner-sharing Ta polyhedra		
Model	Pentahedra (%)	Octahedra (%)
I	64	36
II	100	0
III	60	40

and ^{13}O atoms is quite similar in the two models. However model II features a larger number of sixfold-coordinated tantalum (^{16}Ta) atoms with respect to model I, reflecting an enhanced similarity with the $\beta\text{-Ta}_2\text{O}_5$ structure, where 100% of Ta are sixfold coordinated. By contrast, model III shows the lowest amount of sixfold-coordinated Ta atoms and the largest amount of fivefold-coordinated tantalum (^{15}Ta) atoms among the three models, together with a slightly larger number of ^{12}O atoms. By comparing with NMR data, all our models considerably ($\sim 10\%$) overestimate the concentration of ^{12}O atoms and underestimate the concentration of ^{13}O atoms, yet we note that NMR estimates might suffer from errors up to 5% [50].

The structure of amorphous Ta_2O_5 is known to contain a considerable fraction of ESP as revealed by the x-ray pair distribution functions (PDFs) which show a hump at ~ 3.4 Å due to the Ta-Ta correlations ($\sim 20\%$) from ESP structures ([18,82] and Refs. therein). According to Prasai *et al.* [12], the amount of ESP might impact for the material mechanical dissipation in amorphous tantalum [83]. In fact, ESP could be associated with two-level systems (TLSs) that contribute to room-temperature mechanical loss [12]. In our models, O atoms associated with ESP, namely, those forming four-membered rings, are predominantly threefold coordinated. However, in model III, about 10% of the O atoms belonging to ESP exhibit twofold coordination. Despite this exception, the total number of O atoms participating in four-membered rings remains approximately equal to the number of threefold-coordinated O atoms.

In Table II, we give the amount of edge- and corner-sharing TaO_n polyhedra in our amorphous tantalum models. The vast majority of polyhedra (more than 70%) forms ESP, while the remaining Ta atoms form corner-sharing polyhedra. A further analysis reveals that most of the corner-sharing Ta polyhedra are Ta pentahedra. The overwhelming abundance of edge-sharing Ta polyhedra in model II (89%) reflects an amorphous structure exhibiting crystalline-like ordering. In models I and III, 85% and 80% of the sixfold-coordinated Ta atoms form ESP. None of the Ta atoms in our models are in a face-sharing polyhedron. The findings of Table II suggest that the fraction of penta-coordinated Ta atoms is indicative of the amount of corner-sharing polyhedra in $\alpha\text{-Ta}_2\text{O}_5$ so that a model structure containing a large number of penta-coordinated Ta atoms is likely to feature a high number of corner-sharing polyhedra.

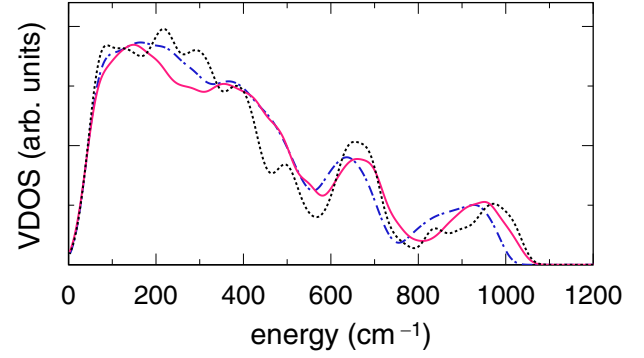


FIG. 3. VDOS of models I (dot-dashed), II (dotted), and III (solid) as calculated with the PBE-SSSP setup. A Gaussian broadening of 20 cm^{-1} is used.

Overall, Fig. 2 and Tables I and II highlight the significant diversity of local oxygen environments in our tantalum models.

C. Planarity of OTa_3 units

The threefold-coordinated O atoms are found to approximately lie on the plane of their three Ta nearest neighbors, forming what is here called an OTa_3 unit. To evaluate the planarity of these units, that in Sec. IV A allows us to distinguish between in-plane and out-of-plane O motion, we define the ratio π_d as obtained by dividing the sum over the three Ta-O-Ta angles by 360° , which at most equals 1 for an ideal planar unit. In model I, π_d , on average, is 0.983, comparable with the value found for the most planar OAl_3 units in amorphous alumina [50], and almost all (91.5%) of the OTa_3 units can be regarded as planar, i.e., they show $\pi_d \geq 0.95$, corresponding to a sum of Ta-O-Ta angles larger than 342° . In model II, all the OTa_3 units are planar with an average π_d of 0.997 that is consistent with the layering of its atomic structure and with the fact that, in the orthorhombic phase, $\pi_d = 1$. In model III, the vast majority (77%) of the OTa_3 units is planar, consistent with a slightly lower average planarity degree (0.970) than found for models I and II, thus suggesting a stronger amorphicity for the structure of model III with respect to the atomic structures of models I and II.

IV. VDOS

In Fig. 3, we show the VDOS, i.e., $\rho(\omega) = \sum_i \delta(\omega - \omega_i)$, where ω_i is the frequency of the i mode, as calculated for our models of $\alpha\text{-Ta}_2\text{O}_5$ using a PBE-SSSP setup. In Fig. S1(b) in the Supplemental Material [68], we also show the VDOS obtained for model III by changing the DFT setup. For model III, the choice of the PBE-SSSP setup results in improved agreement with the position of the main experimental Raman peak, overestimated by only 10 cm^{-1} (see also Sec. VI) with respect to the LDA-PZ and PBE-ONCV setups that underestimate it by $\sim 20\text{ cm}^{-1}$. Moreover, Fig. S1(b) in the Supplemental Material [68] indicates that the differences due to the DFT setup are really negligible up to $\sim 550\text{ cm}^{-1}$, while for higher frequencies, the impact of the DFT-setup choice can be mostly accounted for by a rigid shift that, as far as concerns the assignment of the main vibrational bands,

does not substantially affect the conclusions of the present work. We also note that vibrational frequencies of the main bands in the VDOSs calculated by using LDA-PZ and PBE-ONCV setups are very close (difference ~ 10 cm⁻¹), not only for model III (Fig. S1(b) in the Supplemental Material [68]) but also for model I (not shown). Three main broad bands could be distinguished in the VDOSs of all three models investigated here (Fig. 3): a first one extending from 0 up to ~ 550 cm⁻¹, a central one between ~ 550 and ~ 750 cm⁻¹, and a high-frequency band ~ 750 – 1100 cm⁻¹. The bands show model-dependent shifts (e.g., peaks of the central band are located at ~ 640 and 660 cm⁻¹ in models I and III, respectively) that may reflect the different O local environments in the models (see Fig. 2 and Table I). The VDOSs of models I and III are quite similar except for frequencies around ~ 200 – 250 and ~ 835 cm⁻¹, where the VDOS of model I (and that of model II) is slightly larger than the VDOS of model III. This could be understood as a consequence of the larger number of ¹⁸O atoms in model I (and model II) with respect to model III (Table I). As for the VDOS below ~ 250 cm⁻¹, we also remark on a smaller number of sixfold and sevenfold tantalum (¹⁸¹Ta) atoms in model III with respect to the other models, which affect the VDOS around 200 cm⁻¹ (Fig. S5 in the Supplemental Material [68]).

By comparing with the VDOS of Ref. [20], we note that, while the classical interaction potential developed by Trinastic *et al.* [19] allows us to generate reasonable amorphous structures (model I), it should not be used to calculate vibrational modes, especially in the range 600–1000 cm⁻¹, since it overemphasizes the weight of the ¹⁸O atoms [20], particularly of its out-of-plane motion that in our *ab initio* VDOS is negligible above ~ 500 cm⁻¹ (see Sec. IV A). Moreover, the VDOS obtained using the Trinastic classical force field [20,82] entirely fills the gap around ~ 750 cm⁻¹, separating the central band from the high-frequency stretching band which decays to zero ~ 50 cm⁻¹ earlier than in the *ab initio* VDOS [Fig. 4(a)]. In contrast, this gap remains clearly distinguishable in experimental Raman spectra [25,27,29] and is also evident in our *ab initio* calculated VDOSs (Fig. 3).

Regarding size effects on the VDOS, Fig. 4 shows that the larger models obtained by employing the machine-learned potential (Sec. II B), ML-1372 and ML-3500, exhibit VDOS spectra that closely resemble those obtained from the *ab initio* model I (and model III; see Fig. 3). The main spectral features are reproduced well, both in terms of their positions and overall shapes. Increasing the model size primarily leads to a smoothing of the VDOS, while its overall profile remains essentially unchanged across the range of 126–3500 atoms. Nevertheless, the larger ML models display a broader and flatter distribution in the high-frequency stretching region (800–1000 cm⁻¹), whereas the *ab initio* VDOSs of models I–III exhibit a more pronounced maximum around 930–950 cm⁻¹. In addition, the gap near 750 cm⁻¹ becomes less distinct in the larger models, being partially filled as the system size increases although still clearly visible in the largest ML-3500 model. Given that size effects have only a limited impact on the shape and composition of the main vibrational bands, in the following, we further analyze the VDOS of tantalum by considering model I as our reference model.

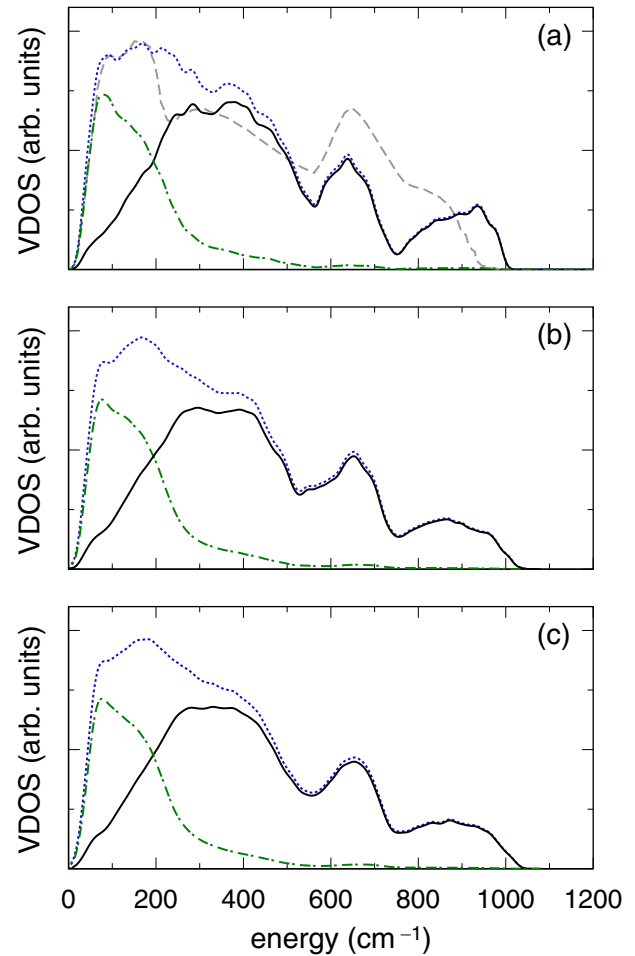


FIG. 4. VDOS calculated via an *ab initio* approach for (a) model I, and by means of machine-learned potential for the large size models (b) ML-1372 and (c) ML-3500. The total VDOS (dotted/blue) is decomposed in terms of Ta (dot-dashed/green) and O (solid) weights. A Gaussian broadening of 10 cm⁻¹ was applied. In (a), the VDOS obtained with the Trinastic potential [20] is also shown (dashed/gray).

A. VDOS decompositions by atomic species: Ta, ¹⁸O, and ¹⁸O contributions

In Fig. 4(a), we provide a decomposition of the VDOS in terms of Ta and O weights for model I (similar decompositions have been done also for the other models in Fig. S5 in the Supplemental Material [68]). Figure 4 shows that Ta motion is relevant for vibrational modes below ~ 200 cm⁻¹, while O motion gives the dominant contribution above ~ 250 cm⁻¹. In Figs. 5(a) and 5(b), we further decomposed O motion, both for ¹⁸O and ¹⁸O atoms, in terms of projections on stretching, rocking, and bending directions [20,84]. For ¹⁸O atoms, i.e., oxygen atoms of OTa₃ units, with the term rocking, we hereafter alternatively refer to the out-of-plane motion of ¹⁸O atoms, whereas stretching and bending directions refer to a basis for in-plane oxygen motion [50]. The decomposition shown in Fig. 5(a) indicates that rocking motion of ¹⁸O atoms is dominant up to ~ 300 cm⁻¹, with a peak at 245 cm⁻¹. Bending motion of ¹⁸O atoms is dominant in the range ~ 300 to ~ 520 cm⁻¹. Above ~ 520 cm⁻¹, stretching motions become

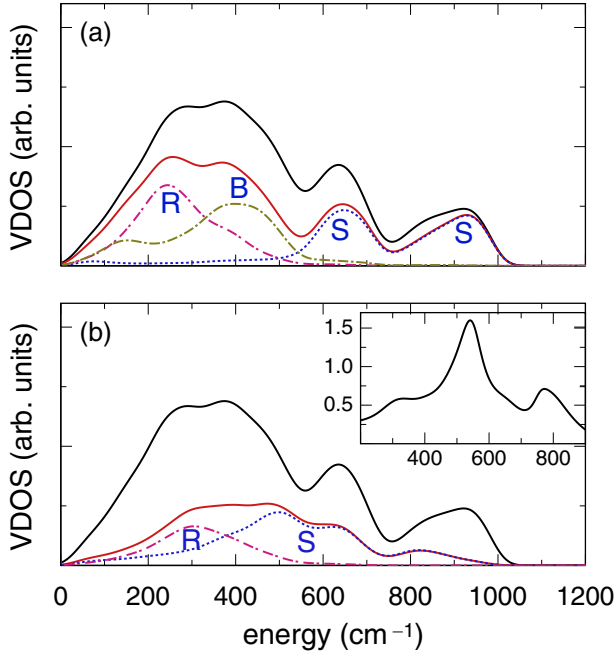


FIG. 5. Decomposition of the oxygen vibrational motion, in model I, into its projected components (a) bending (dot-dashed/green), rocking (dot-dashed/purple), and stretching (dotted/blue) for ^{12}O atoms, and (b) rocking (out-of-plane) and stretching for ^{13}O atoms. Inset: Ratio of the ^{13}O -to- ^{12}O contributions to the VDOS. A Gaussian broadening of 20 cm^{-1} is employed in all calculations. Decompositions for models II and III are included in Fig. S6 in the Supplemental Material [68].

dominant, with peaks at 650 and 930 cm^{-1} , while rocking motion completely disappears, and bending motion is very weak and fades away at $\sim 700\text{ cm}^{-1}$. The decomposition shown in Fig. 5(b) indicates that rocking motion of ^{13}O atoms has a maximum weight at $\sim 300\text{ cm}^{-1}$, while the stretching motion becomes dominant already above $\sim 400\text{ cm}^{-1}$, with a maximal contribution at $\sim 500\text{ cm}^{-1}$ and minor features at 650 and 830 cm^{-1} . The ratio between the total contributions of ^{13}O and ^{12}O atoms [inset of Fig. 5(b)] is maximal around 550 and 800 cm^{-1} , while at $\sim 650\text{ cm}^{-1}$, it is about 1:2, thus reflecting the relative ^{13}O -to- ^{12}O concentration ratio (Table I).

In their analysis, Damart *et al.* [20] indicated that, for ^{12}O atoms, rocking and bending motions are dominant/relevant in the range $\sim 200\text{--}600\text{ cm}^{-1}$, while stretching motions are dominant above $\sim 600\text{ cm}^{-1}$, yet due to the usage of a classical interaction potential, the decomposition is not so reliable as far as concerns the details in the intermediate range $200\text{--}600\text{ cm}^{-1}$. In fact, in contrast with Ref. [20], the central band around 660 cm^{-1} , in the *ab initio* calculations of Fig. 5(a), does not feature any relevant ^{12}O rocking contribution; meanwhile, in the O decomposition shown in Fig. 10 of Ref. [20], the rocking and bending of ^{12}O atoms extend up to $\sim 700\text{ cm}^{-1}$, with quite strong peaks at $620\text{--}630\text{ cm}^{-1}$. Furthermore, we also note that ^{13}O out-of-plane contribution to the VDOS in Ref. [20] is quite strong also above 600 cm^{-1} with a peak at $\sim 650\text{ cm}^{-1}$, in contrast with the result of Fig. 5(b) which indicates a negligible out-of-plane motion of ^{13}O atoms above $\sim 550\text{ cm}^{-1}$.

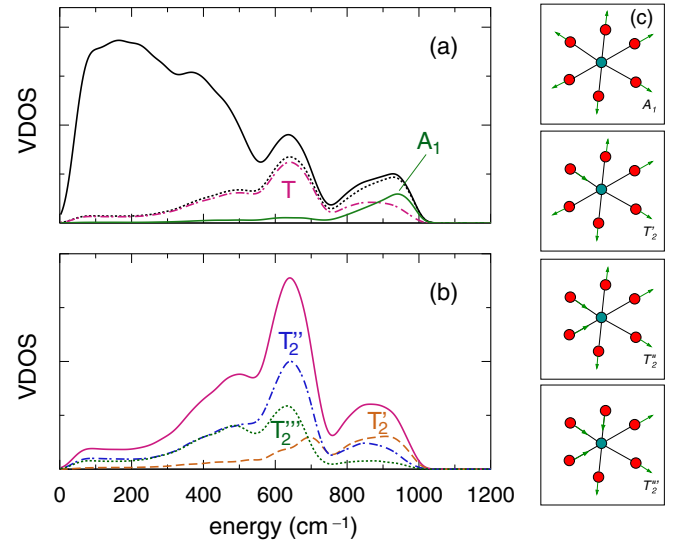


FIG. 6. (a) Contribution to the VDOS calculated for A_1 (solid/green) and T -like (dot-dashed/violet) modes of TaO_n polyhedra in model I (also see Appendix). For comparison of peak locations, the total VDOS (solid) and the sum of A_1 and T contributions (dotted) are also shown. (b) Further decomposition of T modes in terms of T_2' , T_2'' , and T_2''' modes. (c) Sketch of A_1 and T_2 modes used for projections illustrated, e.g., with TaO_6 polyhedra. A Gaussian broadening of 20 cm^{-1} is used.

B. Symmetric and antisymmetric stretchings of TaO_n polyhedra

In Fig. 6, we analyze the VDOS of model I in terms of local projection on A_1 modes, i.e., the symmetric stretching of TaO_n polyhedra, and T -like modes, i.e., the asymmetric stretchings [Fig. 6(c)] of TaO_n polyhedra (also see Appendix), where we follow an approach similar to the decomposition in A_1 and T_2 modes which was employed for the analysis of the high-frequency stretching doublet in silica [85]. The contribution of the A_1 mode shows a peak at $\sim 940\text{ cm}^{-1}$, while it is negligible below $\sim 750\text{ cm}^{-1}$. Similar decompositions have also been carried out for models II and III (Fig. S7 in the Supplemental Material [68]), where we observe minor frequency shifts ($\sim 25\text{ cm}^{-1}$) in the main peak positions that are also reported in Table III. These shifts may also reflect the slightly different Ta–O distributions among models (Fig. 2) that may lead to differences in the stretching frequencies (Fig. S8 in

TABLE III. Frequencies (cm^{-1}) of the main peaks as found by the decomposition of the VDOS in terms of local projections on A_1 and T_2'' modes of Ta polyhedra (Fig. 6) in our $\alpha\text{-Ta}_2\text{O}_5$ models. Δ indicates the frequency separation (cm^{-1}) between the A_1 and highest-frequency T_2'' peaks. Experimental data for the separation Δ as estimated from Raman experiments [25,27] are also reported.

	T_2''		A_1	Δ
Model I	640	850	940	90
Model II	647	840	974	134
Model III	675	874	960	86
Expt. [25]	670	830	935	105
Expt. [27]	670	850	940	90

the Supplemental Material [68]) as well as may reflect the differences in the TaO_n population between models (Table I).

The contribution of the T -like modes lead to peaks at about ~ 640 and ~ 860 cm⁻¹, with considerable intensity up to ~ 950 cm⁻¹. A further decomposition [Fig. 6(b)] indicates that contribution (T_2''') from sixfold and sevenfold Ta polyhedra is relevant only up to the main T peak, while it is rather negligible above ~ 750 cm⁻¹. The T_2'' component, besides providing the major contribution to the main peak at ~ 640 cm⁻¹, also features a high-frequency contribution peaking around 850 cm⁻¹ which is reflected in the shoulder at this frequency in the total T contribution and in the total oxygen VDOS [Fig. 6(a)]. The residual T_2' component features a peak at ~ 700 cm⁻¹; meanwhile, it marginally contributes to the main peak at ~ 640 cm⁻¹ and to the peak of the A₁ modes that are dominating around 940 cm⁻¹ [Fig. 6(a)].

Above ~ 750 cm⁻¹, the sum of the A₁ and T contributions recovers almost completely the total VDOS, here very well approximated by the oxygen VDOS [Fig. 4(a)], thus ruling out any other relevant contribution from other kinds of polyhedral modes. Furthermore, the decomposition clearly shows that the high-frequency peak of the VDOS at about 930 cm⁻¹ originates from A₁ modes. Above ~ 700 cm⁻¹, the frequency separation (~ 80 cm⁻¹) between the projection peaks on A₁ and T -like modes fairly corresponds to the experimental split (~ 90 cm⁻¹) between the two peaks of the high-frequency Raman doublet recently observed with a 785 nm laser by Favaro *et al.* [25] and as inferred from the line shape of the spectrum of Ref. [27] that shows a maximum ~ 850 cm⁻¹ and a shoulder at ~ 940 cm⁻¹. Incidentally, we note that, in glassy SiO₂, GeO₂, and P₂O₅, of which the networks are based on corner-sharing tetrahedra, high-frequency oxygen stretching doublets are also observed (see Refs. [48,49,52,85] and references therein).

C. Localization of vibrational modes

The localization of vibrational modes is analyzed by using the mode participation ratio [20,86]

$$\pi_j = \frac{1}{N} \frac{\left(\sum_{i=1}^N |\mathbf{u}_i^j|^2 \right)^2}{\sum_{i=1}^N |\mathbf{u}_i^j|^4}, \quad (1)$$

where N is the total number of atoms, $\mathbf{u}_i^j = \boldsymbol{\xi}_i^j / \sqrt{M_i}$ indicates the displacement of the i th atom with mass M_i , and $\boldsymbol{\xi}_i^j$ denotes the normalized vibrational (polarization) vectors of the j th mode [49]. The participation ratio as calculated for our models of a -Ta₂O₅ is shown in Fig. 7. An inspection of the participation ratio π_j allows us to distinguish the same vibrational bands that one can deduce from the VDOS decomposition of Figs. 4 and 5. A first band from 0 to 200 cm⁻¹ shows rather delocalized vibrational modes, with participation ratio values ranging from 0.3 to 0.6 (i.e., Tantalum band). Then π_j keeps a value around 0.3 until ~ 400 cm⁻¹ (oxygen rocking-bending band). Above ~ 500 cm⁻¹, the value of π_j falls down to 0.1 – 0.2 (oxygen stretching band), as a consequence of the higher spatial localization of Ta–O stretching motions, as also typically seen for the stretching bands in other oxides like SiO₂ and P₂O₅ above ~ 800 cm⁻¹ [52].

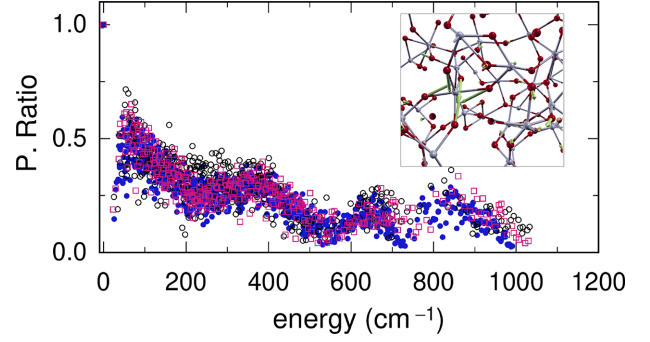


FIG. 7. Participation ratio as calculated for the vibrational modes of our a -Ta₂O₅ models [model I (blue discs), model II (circles), and model III (violet squares)]. Modes with participation ratio ~ 0.1 typically show a considerably large localization degree: For $\omega \sim 950$ cm⁻¹, the vibrational mode may be localized on one or two TaO_n polyhedra (green arrows, inset).

V. IR DIELECTRIC PROPERTIES

In this section, we examine the IR dielectric properties of a -Ta₂O₅. We begin by presenting the real $\epsilon_1(\omega)$ and imaginary $\epsilon_2(\omega)$ components of the dielectric function [49] as obtained from our tantalum models. The dielectric function $\epsilon(\omega)$ is a fundamental quantity for describing materials, as it governs their light transmission and absorption characteristics through the refractive index $n(\omega)$ and the extinction coefficient $k(\omega)$ [87]. We then analyze the key IR coupling tensors—namely, the oxygen and tantalum Born effective charges—by relating them to local geometric descriptors such as the Ta–O bond length and the Ta–O–Ta bond angle.

A. Dielectric function

The high-frequency dielectric tensor $\boldsymbol{\epsilon}_\infty$, as calculated by the linear response approach for models I, II, and III (Eq. S1 in the Supplemental Material [68]), can be regarded with a good approximation as isotropic, and so we introduce the high-frequency dielectric constant as $\epsilon_\infty = \text{Tr}(\boldsymbol{\epsilon}_\infty)/3$. In Table IV, we give the dielectric constants ϵ_∞ as calculated for all three models. For model III, we calculate 4.79 , which is in rather good agreement with the experiment [37]. Models I and II exhibit slightly larger values for ϵ_∞ . In model II, the anisotropy (i.e., the deviation from the average) can account for up to $\sim 8\%$ of the diagonal elements in $\boldsymbol{\epsilon}_\infty$, which is still

TABLE IV. Number of atoms N in the a -Ta₂O₅ model, calculated high-frequency dielectric constant ϵ_∞ and lattice contribution ϵ_{lat} to the static dielectric constant ϵ_0 , and sample density ρ (g/cm³). Experimental data for ϵ_∞ , ϵ_{lat} , and ρ are taken from Refs. [37] and [18], respectively.

	N	ϵ_∞	ϵ_{lat}	ϵ_0	ρ
Model I	336	5.33	25.91	31.24	8.18
Model II	126	5.24	38.61	43.85	8.13
Model III	126	4.79	20.56	25.35	7.50
Expt.		4.67	~ 18	~ 23 – 26	7.30–7.68

considerably smaller than typical values ($\sim 15\%$) obtained for δ_A and β -Ta₂O₅ phases [88].

The static dielectric constant ϵ_0 can be obtained by adding the lattice contribution ϵ_{lat} to the high-frequency dielectric constant $\epsilon_0 = \epsilon_{\text{lat}} + \epsilon_\infty$, where

$$\epsilon_{\text{lat}} = \frac{4\pi}{3\Omega} \sum_n \frac{|\mathcal{F}^n|^2}{\omega_n^2}, \quad (2)$$

and where Ω is the volume of the periodic simulation cell, and $\mathcal{F}^n$ is the oscillator strength of the mode ξ^n with frequency ω_n [49]: $\mathcal{F}_j^n = \sum_{lk} Z_{l,jk}^* \xi_{lk}^n / \sqrt{M_l}$, in which M_l is the mass of the l atom. The static dielectric constant calculated for our models I and III fairly agrees with the typical reported values of the experimental ϵ_0 for amorphous tantalum thin films that are ~ 23 – 26 [37,89,90]. For all the investigated α -Ta₂O₅ models, the lattice contribution is quite large, consistent with the experimental data reported for ϵ_0 and ϵ_∞ . Particularly ϵ_{lat} of model III shows a good agreement with the experimental data (~ 18); meanwhile, considerably larger values are obtained for model I (25.9) and II (38.6), quite close to the value corresponding to the annealed Ta₂O₅ film [37]. Comparison of the values calculated for models I and III allows us to estimate that a density variation of $\sim 10\%$ might slightly affect the high-frequency and static dielectric constant up to $\sim 10\%$. The latter, however, depends on the lattice contribution ϵ_{lat} , which is rather sensitive to the details of the VDOS [89] and hence also to the structure. In fact, despite that models I and II have similar densities, they exhibit considerably different ϵ_{lat} values.

The shape of the main bands in the calculated $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ spectra (Fig. 8) of both models I and III fairly reproduces the shape of experimental bands of the spectra obtained for magnetron sputtered thin films by Bright *et al.* [37] and Franke *et al.* [38], particularly for frequencies above ~ 250 cm⁻¹, i.e., in the oxygen motion region (see Fig. 4). Moreover, the calculated ϵ_2 values are also fairly consistent with the absorption spectra collected for IBS films [91]. Below ~ 250 cm⁻¹, both models I and II similarly overestimate the experimental ϵ_2 of Ref. [37], possibly indicating some analogy between these two models for the motion of the Ta sublattice. We note that, with respect to model III, both models I and II exhibit a larger number of sixfold- and sevenfold-coordinated Ta atoms which have larger Born charges with respect to fivefold Ta atoms (see the end of Sec. VB). The latter differences may also underlay the fact that ϵ_{lat} and $\epsilon_1(\omega)$ of model III are considerably smaller than the ones of the other two models (e.g., $\sim 20\%$ smaller than in model I) in the range 0 to ~ 200 cm⁻¹.

The $\epsilon_2(\omega)$ spectrum reported by Bright *et al.* [37] exhibits prominent maxima at ~ 250 , 505, 610, and 670 cm⁻¹, along with a weaker shoulder around 890 cm⁻¹. In comparison, the corresponding $\epsilon_2(\omega)$ spectrum of model III shows peaks at 295 and 495 cm⁻¹ (weak), a shoulder near 620 cm⁻¹, a pronounced maximum at 655 cm⁻¹, and a minor peak at ~ 935 cm⁻¹. The $\epsilon_2(\omega)$ of model I shows a similar sequence of peaks, and overall averaging ϵ_2 over models I and III would provide a fair approximation to the experimental one over all the range of frequencies. By contrast, $\epsilon_2(\omega)$ of model II shows very sharp and strong peaks at ~ 275 cm⁻¹, ~ 500 , and 685 cm⁻¹

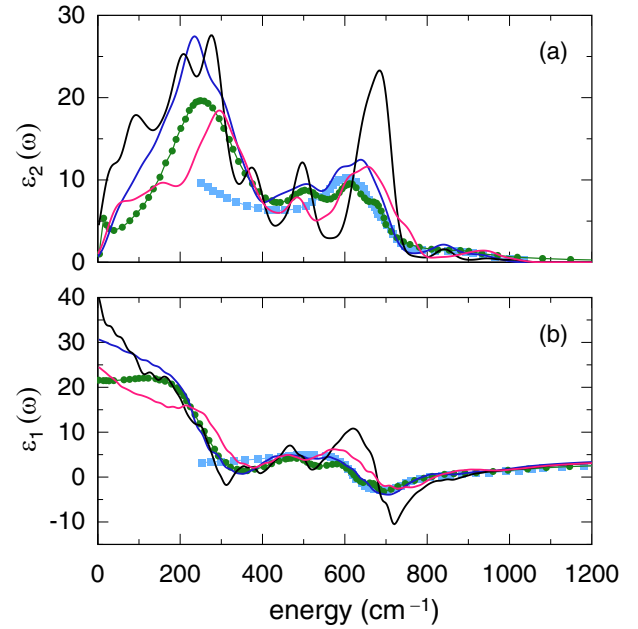


FIG. 8. (a) The imaginary part of the dielectric function $\epsilon_2(\omega)$ as calculated for model I (blue curve), model II (solid curve), and model III (violet curve). Experimental data are taken from Refs. [37,79] (green discs) and Ref. [38] (cyan squares). (b) Real part of the dielectric function $\epsilon_1(\omega)$ [the same notations as in (a)]. A Gaussian broadening of 20 cm⁻¹ is used in all calculations.

together with minor features, particularly weak peaks at ~ 840 and ~ 940 cm⁻¹ also visible in ϵ_2 of model I. However, the shape of $\epsilon_2(\omega)$ in model II, apart from the intensity of peaks, is still qualitatively similar to ϵ_2 of models I and III and rather different from ϵ_2 of annealed Ta₂O₅ films [37], which supports a prevalent amorphous character in model II, as far as concerns the vibrational spectra. Analogous considerations apply to the real part of the dielectric function $\epsilon_1(\omega)$ [Fig. 8(b)]. The calculated spectra for models I and III show good agreement with the experimental data above ~ 200 cm⁻¹, aside from minor shifts in the peak positions. In addition, the extinction coefficient $k(\omega)$ and refractive index $n(\omega)$ are compared with experimental results [16,37] in Fig. S9 in the Supplemental Material [68]. The $k(\omega)$ spectrum of model I closely matches the experimental data, while model III shows a comparable level of agreement, consistent with the behavior of its $\epsilon_2(\omega)$ in Fig. 8(a). Our VDOS analysis (Sec. IV A) suggests that, analogous to amorphous silica [49] and alumina [50], the broad band peaking at ~ 250 cm⁻¹ in the experimental $\epsilon_2(\omega)$ of Bright *et al.* [37] can be attributed mainly to the rocking motion of ¹²O atoms and to the out-of-plane motion of ¹³O atoms (together with a background of Ta motion). Here, ¹²O bending motion, in the range 350–450 cm⁻¹, does not lead to any visible feature in the infrared spectra, probably due to the large mixing with rocking and stretching motion also of the ¹³O atoms. The latter are likely to significantly contribute to the peak at ~ 500 cm⁻¹, as in all our models, the ¹³O contribution to the VDOS is maximal in the range 400–500 cm⁻¹. The ratio between the VDOS weight of ¹³O and ¹²O atoms exhibits a minimum around 700 cm⁻¹, and it is below ~ 0.5 above ~ 640 cm⁻¹, which is in contrast with the previous

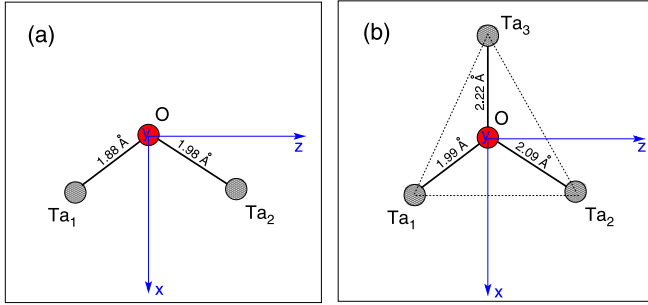


FIG. 9. Sketch of the local reference system (x, y, z) for the dynamical charges of (a) twofold-coordinated O atoms and (b) threefold-coordinated O atoms. y direction is normal to the plane containing (a) the Ta–O–Ta angle and (b) the three Ta neighbors. Ta atoms are ordered following increasing bond length, i.e., $OTa_1 < OTa_2 < OTa_3$. Average values of OTa_i are indicated in the figure.

attribution of the IR absorption peak at $\sim 640 \text{ cm}^{-1}$, specifically to the presence of OTa_3 units [22,39,40,92]. Moreover, the VDOS analysis of our α -Ta₂O₅ models, as well as the analysis of IR couplings presented in the next section, indicate that stretching modes of ^{12}O atoms dominate above $\sim 600 \text{ cm}^{-1}$, accounting for the experimental peak and shoulder at 610 and 670 cm^{-1} in $\epsilon_2(\omega)$ [37].

B. Born charges

The vast majority of O atoms in α -Ta₂O₅ is twofold coordinated with Ta atoms (about 70%, see Table I); hence, to analyze their Born charge tensors Z^* , it is convenient to introduce the following local reference frame [Fig. 9(a)]: The first basis vector is chosen along the bisector of the Ta–O–Ta angle (x direction, i.e., bending direction); the second basis vector is taken along the direction perpendicular to the plane on which the three Ta–O–Ta atoms lie (y direction or rocking direction); and the last one can be found by the cross-product of the first two basis vectors (z direction, i.e., stretching direction) and results to be along the Ta–Ta direction. In this local reference system, we calculate for the ^{12}O atoms in our models an average $\overline{Z^*}$ which is essentially diagonal, with negligible off-diagonal elements (~ 0.01) and with diagonal elements

$$\overline{Z_{xx}^*} = -1.29, \quad \overline{Z_{yy}^*} = -1.13, \quad \overline{Z_{zz}^*} = -5.57, \quad (3)$$

and corresponding to an isotropic Born charge of $\frac{1}{3}\text{Tr}(\overline{Z^*}) = -2.67$. The coupling along the stretching direction (i.e., $\overline{Z_{zz}^*}$) in Eq. (3) is more than four times larger than the coupling along bending or rocking directions, which further enhance the stretching character of the IR peaks in $\epsilon_2(\omega)$ and extinction/absorption spectra above 500 cm^{-1} . From Eq. (3), we also infer that the motion of the ^{12}O atoms along the Ta–Ta direction induces the largest modulation of the dipole moment. Furthermore, we remark on a similarity of Eq. (3) with the Born charges of bridging oxygen atoms in g -TeO₂ [53], where the stretching component of the Born charge is two to three times larger than for the other components.

For the analysis of the Born charge tensors Z^* of ^{13}O atoms, it is also convenient to introduce the following local

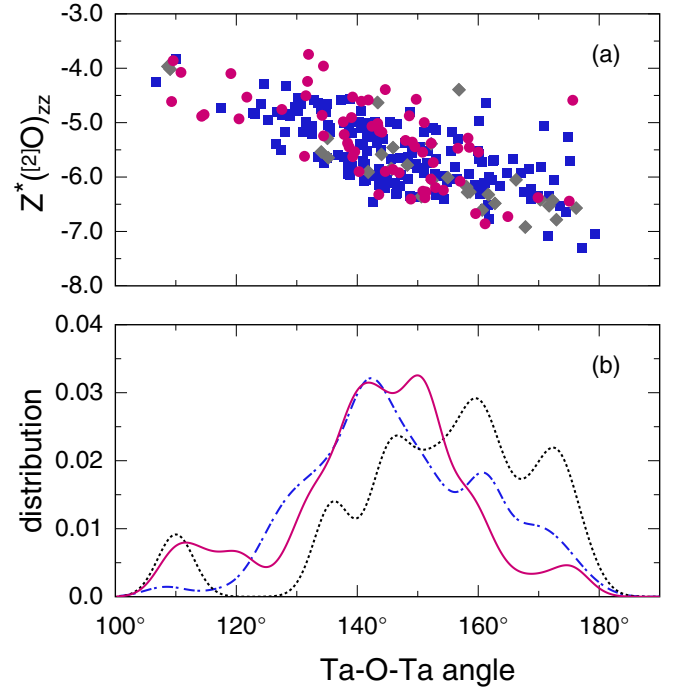


FIG. 10. (a) IR coupling along the stretching direction vs Ta–O–Ta angle as calculated for ^{12}O atoms in model I (blue squares), model II (gray diamonds), and model III (violet discs). (b) Distribution of Ta–O–Ta angles for ^{12}O atoms in models I (dot-dashed/blue), II (dotted/black), and III (solid/violet). A Gaussian broadening of 3° was used.

reference frame [Fig. 9(b)]: The first basis vector is chosen along the bisector of a Ta–Ta–Ta angle (x direction) of the triangle with the Ta neighbors at the vertices; the second basis vector is taken along the direction perpendicular to the plane defined by the three nearest neighbors Ta atoms (y direction); and the last one can be found by the cross-product of the first two basis vectors (z direction). In this local reference system, we calculate an average $\overline{Z^*}$ for the ^{13}O atoms

$$\overline{Z_{^{13}\text{O}}^*} = \begin{pmatrix} -3.00 & 0.00 & -0.24 \\ 0.00 & -1.21 & 0.00 \\ -0.24 & 0.00 & -3.75 \end{pmatrix}, \quad (4)$$

where the matrix entries exhibit std values up to ~ 0.5 .

Our calculated Born charges Eqs. (3) and (4) are rather similar to those reported by Clima *et al.* [88] for the δ_A crystalline phase, although the coupling along the stretching direction, for ^{12}O atoms, is in our case reduced by $\sim 20\%$ with respect to Ref. [88]. We also note that the ^{12}O atoms, in crystalline phases such as δ_A and β -Ta₂O₅, occupy inter-layer positions and show considerably large Ta–O–Ta angles ($\sim 160^\circ$). We found that the IR coupling along the stretching direction (z) becomes stronger with increasing Ta–O–Ta angle [see Fig. 10(a)]. Such a trend can indeed explain the $\sim 20\%$ smaller IR coupling [Eq. (3)] we calculated for amorphous tantalum, where the average Ta–O–Ta (for ^{12}O atoms) is about $\sim 145^\circ$ [see distribution for models I and III in Fig. 10(b)] with respect to the couplings previously reported for crystalline phases by Clima *et al.* [88].

The average Z^* for the Ta atoms is essentially isotropic, consistent with the fact that Ta atoms form highly coordinated polyhedra (i.e., pentahedra, hexahedra, and heptahedra). For the tantalum atoms in our models, we found an average isotropic Born charge $\frac{1}{3}\text{Tr}(Z^*) = 6.67$ with a std of 0.76. The large spread is due to occurrence of different kinds of Ta polyhedra.

In fact, the calculated average isotropic Born charges for Ta atoms with fivefold, sixfold, and sevenfold coordination are 5.93, 6.93, and 6.54, respectively. For sixfold-coordinated tantalum, the isotropic Born charge is slightly smaller than previously calculated for the β -Ta₂O₅ and δ -Ta₂O₅ crystalline phases [88], consistent with the remarks outlined above for the Born charges of the ¹⁸O atoms and with the existence of a Born charge neutrality rule [93].

VI. RAMAN SPECTRA

A. First-principles Raman spectra of α -Ta₂O₅

In a first-order Stokes Raman scattering process in a solid, an incident photon with frequency ω_L and polarization vector $\hat{\mathbf{e}}_L$ interacts with the lattice, resulting in the emission of a scattered photon with frequency ω_S and polarization $\hat{\mathbf{e}}_S$. The energy difference between the incident and scattered photons corresponds to the creation of a vibrational excitation of frequency $\hbar\omega_k = \hbar\omega_L - \hbar\omega_S$. The Raman cross-section [94], for $\hbar\omega_L$ smaller than the band gap of the material, as it is the case for visible light in α -Ta₂O₅, i.e., in nonresonant conditions, is given by

$$\frac{d^2\sigma}{d\Omega dE} = \frac{\omega_S^4 V}{(4\pi)^2 c^4} \sum_k |\hat{\mathbf{e}}_S \cdot \mathcal{R}^k \cdot \hat{\mathbf{e}}_L|^2 \frac{\hbar}{2\omega_k} \times [n_k + 1] \delta(E - \hbar\omega_k), \quad (5)$$

where V is the volume of the scattering sample, c is the speed of light, E is the exchanged energy, and $n_k = 1/(e^{\hbar\omega_k/k_B T} - 1)$ is the boson factor. Here, $\mathcal{R}^k$ are the Raman susceptibilities tensors [94] associated with the normal mode k ,

$$\mathcal{R}_{ij}^k = \sqrt{V} \sum_{I\ell} \frac{\partial \chi_{ij}}{\partial R_{I\ell}} \frac{\xi_{I\ell}^k}{\sqrt{M_I}}, \quad (6)$$

where $\frac{\partial \chi_{ij}}{\partial R_{I\ell}}$ are the derivatives of the dielectric polarizability tensor χ with respect to a displacement $R_{I\ell}$ of the atom I in direction ℓ . In the following, the latter derivatives multiplied by the cell volume V factor are also referred to as Raman derivative tensors:

$$V \frac{\partial \chi_{ij}}{\partial R_{I\ell}} = \frac{\partial^3 E_{\text{tot}}}{\partial \mathcal{E}_i \partial \mathcal{E}_j \partial R_{I\ell}}, \quad (7)$$

where E_{tot} and $\mathcal{E}_i$ indicate the DFT total energy and electric field components, respectively [49].

Raman spectra of disordered materials are usually recorded in configurations in which the polarizations of incoming and outgoing photons are either parallel (HH) or perpendicular (HV) [94]. Sometimes Raman intensity is unpolarized detected which, for the typical case of a linearly polarized incident light, corresponds to summing up HH and HV intensities. By omitting the thermal dependence in Eq. (5), the experimental Raman cross-section can be expressed in a

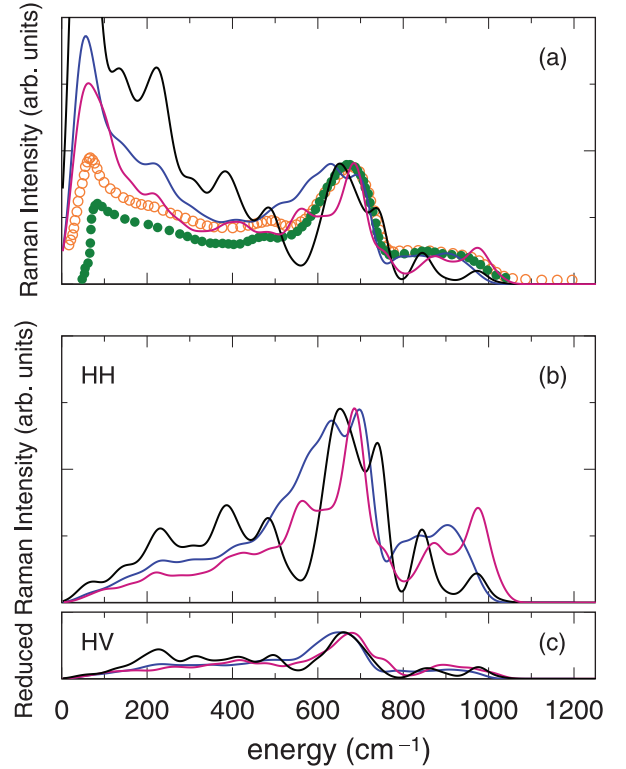


FIG. 11. (a) Calculated unpolarized Raman spectra of model I (blue), model II (black), and model III (purple) at room temperature compared [79] with the experimental Raman spectrum of Ref. [27] of α -Ta₂O₅ films grown on germanium substrate (discs/green) and Ref. [24] on silica substrate (circles/orange). Also shown are reduced Raman spectra for (b) HH and (c) HV polarizations, as calculated for model I (blue), model II (black), and model III (purple). All spectra have been rescaled to match the main peak ($\sim 670 \text{ cm}^{-1}$) height. A Gaussian broadening of 20 cm^{-1} is used.

reduced form

$$\left. \frac{d^2\sigma}{d\Omega dE} \right|_{\text{red}} \sim \sum_k |\hat{\mathbf{e}}_S \cdot \mathcal{R}^k \cdot \hat{\mathbf{e}}_L|^2 \delta(E - \hbar\omega_k). \quad (8)$$

For disordered solids, due to their peculiar isotropic nature, an average over all possible orientations [87,95] must then be performed for the Raman tensors in Eq. (8). This average, for the k mode, can be expressed by means of the trace a and the anisotropy τ of the tensor $\mathcal{R}_{ij}$, i.e., $\tau^2 = [(\mathcal{R}_{11} - \mathcal{R}_{22})^2 + (\mathcal{R}_{22} - \mathcal{R}_{33})^2 + (\mathcal{R}_{33} - \mathcal{R}_{11})^2 + 6(\mathcal{R}_{11}^2 + \mathcal{R}_{22}^2 + \mathcal{R}_{33}^2)]/2$, so that the intensity of the HH and HV Raman line can be calculated as $I_{\text{HH}} = a^2 + 4\tau^2/45$ and $I_{\text{HV}} = 3\tau^2/45$.

In Fig. 11(a), we show the unpolarized Raman spectra as calculated for our models at room temperature and compared with the experimental spectra of Refs. [24,27]. We note that, for all the models, the HV spectrum [Fig. 11(c)] only constitutes a minor fraction of the HH reduced Raman intensity [Fig. 11(b)] with a main peak in the range $640\text{--}680 \text{ cm}^{-1}$, so that the unpolarized spectrum can be regarded as dominated by the HH component. The Raman spectrum of model I [Fig. 11(a)] exhibits a strong boson-enhanced peak at $\sim 60 \text{ cm}^{-1}$, common to all models, along

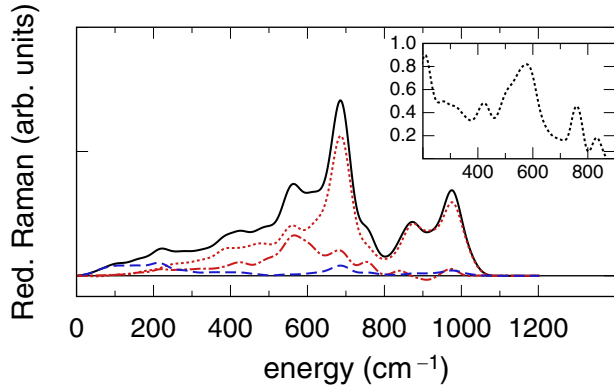


FIG. 12. Decomposition via the approach (additive) [52] of the reduced (HH) Raman intensity, as calculated for model III, in terms of ^{21}O atom (red/dotted), ^{31}O atom (red/dot-dashed), and Ta atom (blue/dashed) contributions. Inset: Ratio of the ^{31}O and ^{21}O atom contributions. A Gaussian broadening of 20 cm^{-1} was applied.

with a broad band between 600 and 700 cm^{-1} characterized by a doublet at 630 and 690 cm^{-1} . Additional weaker features appear at ~ 520 , ~ 840 , and $\sim 900\text{ cm}^{-1}$. In contrast, model II shows several relatively sharp peaks at 222 , 382 , 485 , 650 (dominant), 740 (strong), 844 , and 972 cm^{-1} , which may be reminiscent of a low-temperature β phase [27,96]. In fact, the unpolarized Raman spectrum of a crystalline β -Ta₂O₅ powder sample [27] shows strong peaks at ~ 630 , 705 (sharp), ~ 850 , and a broad feature at $\sim 500\text{ cm}^{-1}$. The HH Raman spectrum of the fully *ab initio* generated model III [Fig. 11(b)] displays a main peak at $\sim 685\text{ cm}^{-1}$ and a doublet at ~ 870 and 970 cm^{-1} plus some minor features at ~ 410 and $\sim 560\text{ cm}^{-1}$. Altogether, the Raman spectrum of model III provides the best frequency position and shape agreement among the three models [Fig. 11(a)], with the main peak of the experimental Raman spectrum [25,27,28]. Notably, the shift of the main Raman peak position between models II and III [Fig. 11(a)] resembles the shift observed between the R2 and R1 regions in Favaro *et al.* [25]. Moreover, the Raman spectrum of the R2 (crystalline grain) region shows peaks rather well corresponding to those of the calculated spectrum of model II (Fig. S10 in the Supplemental Material [68]).

The peak at $\sim 970\text{ cm}^{-1}$ in the HH spectrum of model III (and similar at ~ 905 and 970 cm^{-1} for models I and II) can be ascribed to the A_1 symmetry stretching motion of TaO_{*n*} polyhedra (see Fig. 6) which is reminiscent of analogous peaks in silica and P₂O₅ glasses [52,54]). The peak at $\sim 870\text{ cm}^{-1}$ and the main peak at $\sim 680\text{ cm}^{-1}$ arise, as suggested by Fig. 6 and Fig. S7 in the Supplemental Material [68], from the asymmetric stretching motion of TaO_{*n*} polyhedra. We note that the polarization ratio, i.e., the ratio between the HV and HH intensities is particularly low (~ 0.1 – 0.2) in the range 800 – 950 cm^{-1} , (i.e., in correspondence with the A_1 band) for our models III and I, while for model II, it is lightly larger ~ 0.2 – 0.3 , which is still considerably smaller than evaluated at the oxygen stretching band in other oxide glasses like silica (~ 0.6 – 0.7).

In Fig. 12, we decompose the Raman spectrum of model III into partial contributions of specific groups of atoms (Ta, ^{21}O , and ^{31}O atoms) by following the approach developed

in Ref. [52]. Similar decompositions for models I and II are given in Fig. S11 in the Supplemental Material [68]. Figure 12 indicates that the most interesting features of the HH Raman spectrum in the range 600 – 1000 cm^{-1} arise mainly from the motion of the ^{21}O atoms. The contribution of ^{31}O atoms to the main Raman peak appears to be quite limited ($\sim 20\%$ of the contribution of ^{21}O atoms); meanwhile, the Ta weight is practically negligible above $\sim 250\text{ cm}^{-1}$. This result closely mirrors the VDOS decomposition of Figs. 5(b) and 5(c) where, at $\sim 670\text{ cm}^{-1}$, the contribution of ^{21}O atoms is approximately twice that of ^{31}O atoms. However, the contribution of ^{21}O atoms to the main Raman peak (Fig. 12) is further amplified due to their stronger average coupling with stretching motions than ^{31}O atoms (see Sec. VIB). The contribution of the ^{31}O atoms is maximized in the ~ 500 – 550 cm^{-1} range (Fig. 12), accounting also for the shoulder observed around $\sim 520\text{ cm}^{-1}$ in the HH spectrum of model I (Fig. S11(a) in the Supplemental Material [68]). This broad feature could also be reminiscent of the broad peak at $\sim 480\text{ cm}^{-1}$ [27]. The decomposition of the HH Raman spectrum of model II is quite diverse since the contribution of ^{31}O atoms is remarkably stronger in the range from ~ 400 to 650 cm^{-1} (Fig. S11(b) in the Supplemental Material [68]), which reflects a substantial difference between the vibrational modes of models I and III, on one side, and of model II on the other side. The differences observed—especially in the oxygen stretching frequency region—between the calculated Raman spectra of our tantalum models not only mirror the variations previously discussed for the VDOS but also highlight the sensitivity of the oxygen Raman coupling tensors (see Sec. VIB) to changes in Ta and O coordination environments as well as to variations in Ta–O bond lengths and Ta–O–Ta angle distributions across the models.

Despite the considerably high amount of Ta atoms forming ESP (Sec. IIIB), we did not find any feature in the vibrational spectra that, analogous to the case of the Raman doublet in glassy GeSe₂ [97], could evidently be related to ESP, apart from those related to the ^{31}O atoms, the amount of which, however, reflects quite well the content of ESP. In light of the present investigation, only the vibrational features related to ^{31}O atoms, particularly the Raman band peaking at $\sim 550\text{ cm}^{-1}$ (Fig. 12) in model III and the shoulder at 520 cm^{-1} in model I (Fig. S11(a) in the Supplemental Material [68]), could constitute an indicator of the presence of ESP.

B. Raman coupling tensors

1. Twofold-coordinated O atoms

For model I, the Raman derivative tensors averaged over ^{21}O atoms and expressed in the reference frame defined in Sec. VB, i.e., $[(\partial\chi/\partial x), (\partial\chi/\partial y), (\partial\chi/\partial z)]$, are (in Bohr²):

$$\begin{pmatrix} -15.3 & 0.3 & 2.8 \\ 0.3 & -9.6 & -0.1 \\ 2.8 & -0.1 & -7.1 \end{pmatrix}, \begin{pmatrix} 0.5 & -2.0 & 0.0 \\ -2.0 & -0.3 & 3.1 \\ 0.0 & 3.1 & 0.2 \end{pmatrix}, \begin{pmatrix} 9.3 & -0.4 & 10.5 \\ -0.4 & 9.3 & -0.1 \\ 10.5 & -0.1 & 38.9 \end{pmatrix}. \quad (9)$$

Similar average tensors are found for the ^{21}O atoms in models II and III. The standard deviations are rather large ($\sim 5\text{ Bohr}^2$) for all elements of the matrices in Eq. (9) and

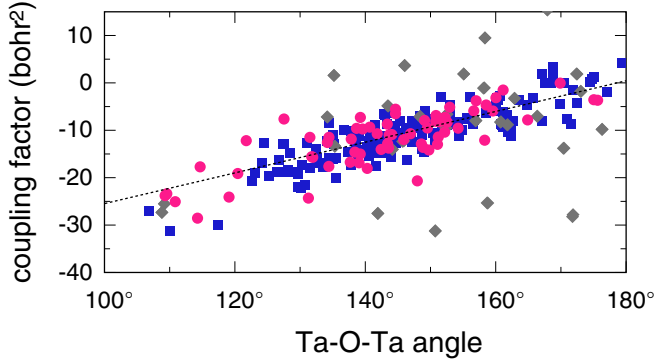


FIG. 13. Raman coupling factors f_I^b for bending modes vs Ta–O–Ta angle, calculated for ^{12}O atoms in model I (blue squares), model II (gray diamonds), and model III (violet discs). A linear fit (dashed line) of all data is given as a guide for the eye.

especially for the diagonal elements of $(\partial\chi/\partial z)$. The structure of the matrices in Eq. (9) is reminiscent of the one prescribed by the local symmetry model [98] for oxygen atoms in SiO_2 polymorphs, i.e., for oxygen atoms at the vertices of corner-sharing tetrahedra. In silica [98], the $\partial\chi/\partial x$ is a diagonal matrix described by three parameters, while only one parameter is required for describing either $\partial\chi/\partial y$ or $\partial\chi/\partial z$ for a total of five parameters. At variance, Eq. (9) indicates that other parameters are necessary in Ta_2O_5 polymorphs, particularly for describing the quite large diagonal terms of $(\partial\chi/\partial z)$ on which the Raman intensity of stretching bands depends. This is a huge difference with respect to silica where $\text{Tr}(\partial\chi/\partial z)$ is, both on average and for each oxygen atom, considerably smaller (around 5% and almost always below 10%) with respect to $\text{Tr}(\partial\chi/\partial x)$ [49].

Since the relevant coupling tensor $\partial\chi/\partial\mathbf{R}$ associated with the oxygen bending motions of ^{12}O atoms is rather isotropic, the anisotropy τ [87,95] leads to a contribution to the HH Raman intensity similar to the isotropic part a , i.e., $I_{\text{HH}} = a^2 + 4\tau^2/45 \propto a^2$, so that a volume-free scalar coupling factor can be defined for each O atom [49]

$$f_I^b = \frac{1}{3}V \text{Tr} \left(\sum_k \frac{\partial\chi}{\partial R_{Ik}} \mathbf{e}_{Ik}^b \right), \quad (10)$$

where $\mathbf{e}^b$ corresponds to the bisector direction of the Ta–O–Ta unit to which the ^{12}O atom belongs. Figure 13 shows the correlation between the calculated coupling factors f_I^b and the Ta–O–Ta bond angle for our three models. All models consistently exhibit a similar dependence, which is analogous to the angular dependence found in $v\text{-SiO}_2$ and $v\text{-GeO}_2$ [48,49], although data of model II are considerably more scattered than found for models I and III. The larger spreading of data recorded for model II can be ascribed to the occurrence of interlayer and intralayer ^{12}O atoms, as it happens in crystalline structures, together with a wide variety of Ta–O–Ta angles as typical of amorphous structures.

To describe the Raman intensity arising because of stretching motion of ^{12}O atoms, it is convenient to introduce,

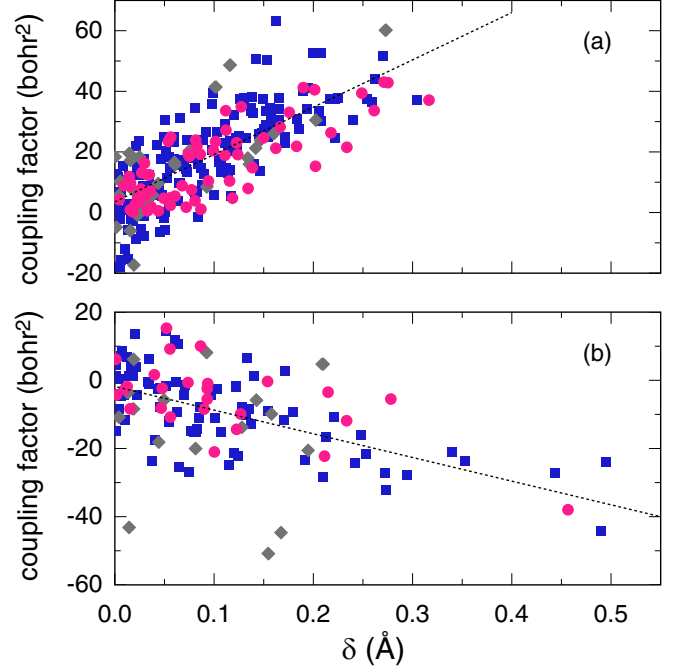


FIG. 14. (a) Raman coupling factors f_I^s for stretching modes vs $\delta = \text{OTa}_2 - \text{OTa}_1$ calculated for (a) twofold-coordinated O atoms and (b) threefold-coordinated O atoms in model I (blue squares), model II (gray diamonds), and model III (violet discs). In both panels (a) and (b), a linear fit (dashed line) of all data is given as a guide for the eye. For defining δ in (a) and (b), the local reference systems of Figs. 9(a) and 9(b) are used, respectively.

analogous to Eq. (10), another coupling factor

$$f_I^s = \frac{1}{3}V \text{Tr} \left(\sum_k \frac{\partial\chi}{\partial R_{Ik}} \mathbf{e}_{Ik}^s \right), \quad (11)$$

where $\mathbf{e}^s$ corresponds to the Ta–Ta direction of the Ta–O–Ta unit to which the ^{12}O atom belongs. Figure 14(a) shows the correlation between the calculated coupling factors f_I^s and the bond length asymmetry parameter $\delta = \text{OTa}_2 - \text{OTa}_1$, expressing the difference in length between the two O–Ta bonds formed by the ^{12}O atoms [δ is positive in the chosen reference system (Fig. 9)]. The parameter δ can reach relatively large values in amorphous tantalum, up to ~ 0.3 Å, which is approximately an order of magnitude larger than those reported for other amorphous oxides, such as silica [49]. All models in Fig. 14(a) consistently exhibit a similar trend, which reflects the analogous trend displayed by the dominant term in the sum of Eq. (11), i.e., $(\partial\chi/\partial z)_{33}$. Equation (9) and Fig. 14(a) show that the absolute values of the Raman coupling factor for stretching modes is, on average, about two to three times larger than that for bending modes. Unlike what is observed in other amorphous oxides such as SiO_2 or P_2O_5 , this difference in Ta_2O_5 polymorphs results in more intense Raman stretching bands compared with bending bands.

2. Threefold-coordinated O and Ta atoms

For model I, the Raman derivative tensors averaged over ^{13}O atoms and expressed in the reference frame defined in Sec. VB and shown in Fig. 9, i.e.,

$[(\partial\chi/\partial x), (\partial\chi/\partial y), (\partial\chi/\partial z)]$ are (in Bohr²)

$$\begin{pmatrix} 25.2 & 0.0 & -0.5 \\ 0.0 & 8.1 & 0.4 \\ -0.5 & 0.4 & -8.4 \end{pmatrix}, \begin{pmatrix} 1.1 & 2.2 & 0.3 \\ 2.2 & 0.9 & -1.7 \\ 0.3 & -1.7 & -0.2 \end{pmatrix}, \begin{pmatrix} -7.4 & 0.1 & -18.3 \\ 0.1 & -6.0 & -0.9 \\ -18.3 & -0.9 & -13.4 \end{pmatrix}. \quad (12)$$

Similar average tensors are obtained also for the ¹³O atoms in models II and III. Although diagonal values, e.g., $(\partial\chi/\partial z)_{33}$, in the matrices of Eq. (12) sometimes may be considerably smaller than in Eq. (9), all matrix elements show quite large fluctuations which may suggest the presence of underlying correlations with structural parameters. For instance, in Fig. 14(b), the coupling factor f_I^s shows a linear trend vs the parameter $\delta = \text{OTa}_2 - \text{OTa}_1$, analogous to the trend shown in Fig. 14(a) for ¹²O atoms.

Concerning Ta atoms, as they belong to highly coordinated TaO_{*n*} ($n = 5, 6, 7$) polyhedra, it is not convenient to define a local reference system to express the $[(\partial\chi/\partial x), (\partial\chi/\partial y), (\partial\chi/\partial z)]$ as done above for ¹²O and ¹³O atoms. Hence, we have just analyzed for each Ta atom its Raman derivatives in terms of the square root of the quadratic invariant $T_1 = T_{iik}T_{ppk}$ [99] that can be defined for a Cartesian tensor T_{ijk} of rank 3, as those implicitly defined for each atom I in Eq. (7). For ¹⁵¹Ta, ¹⁶¹Ta, and ¹⁷¹Ta atoms in our models, we found an average $\sqrt{T_1}$ of 101.3 (std of 41.7), 128.2 (std of 35.9), and 85.7 (std of 25.9) Bohr², respectively. As a term of comparison, we remark that the T_1 quadratic invariant calculated for twofold-coordinated oxygen atoms using Eq. (9) leads to a value $\sqrt{T_1} = 68.2$ Bohr² just slightly smaller than those calculated on average for tantalum atoms.

VII. CONCLUSIONS

In this work, we present a first-principles study of the vibrational properties—VDOS, IR, and Raman spectra—of three a -Ta₂O₅ model structures containing up to several hundred atoms. The models are first validated against experimental x-ray total correlation functions. The calculated vibrational spectra are then compared with available experimental dielectric and Raman data, showing overall good agreement for both the largest model and the fully *ab initio* generated structure. In contrast, the third model appears more representative of a tantalum structure at the onset of crystallization. Moreover, by employing a machine-learned potential that enabled the calculation of the VDOS with *ab initio* accuracy for models containing up to a few thousand atoms, we could assess size-dependent effects and further establish the reliability of the *ab initio* calculated VDOSs of our models.

The IR and Raman coupling tensors of oxygen atoms have here been analyzed in a local reference frame, which has allowed us to reveal the correlations with local structural parameters like the Ta–O–Ta angles and O–Ta bond lengths that are underlying the bending and stretching coupling factors. Moreover, the analysis of the Born charges and Raman derivative tensors of twofold-coordinated O atoms highlights the stronger coupling (about four and two times larger, respectively) with oxygen stretching motion with respect to oxygen bending motion. The relative strength is then reflected in the considerably larger Raman intensity of stretching bands with respect to the bending bands. This fact leads, for a -Ta₂O₅, to a

main Raman band originating from oxygen stretching motion, at variance with the Raman spectra of other oxide glasses like a -SiO₂ and a -P₂O₅, where the main Raman bands are related to oxygen bending motion.

Furthermore, by decomposing the HH Raman spectrum in terms of ¹²O, ¹³O, and Ta atom components, the main Raman peak at ~ 670 cm^{−1} (and similarly the features in $\epsilon_2(\omega)$ at ~ 610 and ~ 670 cm^{−1}) is shown to be predominantly contributed by ¹²O atoms, owing to their larger VDOS weight and their stronger Raman stretching coupling compared with ¹³O atoms. The latter appear to contribute to the Raman intensity mostly around ~ 500 – 550 cm^{−1} and hence may underlay features visible in the experimental spectra around ~ 500 cm^{−1}.

Finally, by projecting the vibrational modes onto local A_1 and T -like modes of TaO_{*n*} polyhedra, we show that the high-frequency region (≥ 750 cm^{−1}) of the *ab initio* calculated VDOS of our tantalum models is dominated by symmetric and asymmetric stretching vibrations of TaO_{*n*} ($n = 5, 6, 7$) polyhedra. This finding echoes the vibrational-mode decomposition that underlies the high-frequency doublets observed in a -SiO₂ [100] and a -P₂O₅ [52].

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

APPENDIX: PROJECTIONS ON A_1 AND T MODES

The local projections on A_1 and T modes have been obtained by assuming that the Ta contribution is negligible in the high-frequency part of the VDOS (above 750 cm^{−1}). Moreover, from Fig. 5, we may expect, starting from $\omega_n \sim 550$ cm^{−1}, each O atom to show displacements $\mathbf{u}_o = \xi_o^n$ only along stretching direction $\mathbf{u}_o \sim u_o \mathbf{e}_s$ (which for twofold O atoms, considering the typical Ta–O–Ta angle $\sim 145^\circ$, is also rather close to the bond O–Ta direction $\mathbf{e}_{\text{Ta-O}}$). Under the previous assumptions, we can define the contribution to the VDOS from the A_1 mode of the oxygen atoms o nearest neighbors of the I tantalum polyhedron as

$$\rho_{A_1}^I(\omega) = \sum_{o \in I} \sum_k \zeta_o(\mathbf{u}_o^k \cdot \mathbf{e}_{\text{Ta-O}})^2 \delta(\omega - \omega_k), \quad (A1)$$

where $\zeta_o = 1/\mathcal{C}_o$ is the weighting factor given by reciprocal of the coordination $\mathcal{C}_o$ of the oxygen atoms o and that avoids a double (or triple) counting of the oxygen o when summing over the polyhedron index I . Moreover, a condition to Eq. (A1) must be added that the displacements $\mathbf{u}_o$ occur for all the o oxygen neighbors with the same orientation (i.e., all outward or inward with respect to the central Ta atom). If at least one $\mathbf{u}_o$ displacement has a different orientation with

respect to the orientation of the displacements of the other oxygen atoms, then the Ta polyhedron undergoes a motion according to a T -like mode (Fig. 6). Hence, for the high-frequency part of the VDOS, we can recover approximately (within $\sim 5\%$) the total VDOS as

$$\rho(\omega) \approx \sum_I \rho_{A_I}^I(\omega) + \sum_I \rho_T^I(\omega). \quad (\text{A2})$$

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