

# Local atomic geometry and Ti 1s near-edge spectra in $\text{PbTiO}_3$ and $\text{SrTiO}_3$

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We study Ti 1s near-edge spectroscopy in  $\text{PbTiO}_3$  at various temperatures above and below its tetragonal-to-cubic phase transition, and in  $\text{SrTiO}_3$  at room temperature. *Ab initio* molecular dynamics (AIMD) runs on 80-atom supercells are used to determine the average internal coordinates and their fluctuations. We determine that one vector local order parameter is the dominant contributor to changes in spectral features: the displacement of the Ti ion with respect to its axial O neighbors in each Cartesian direction, as these displacements enhance the cross section for transitions to  $E_g$ -derived core-hole exciton levels. Using periodic five-atom structures whose relative Ti-O displacements match the root-mean-square values from the AIMD simulations, and core-hole Bethe-Salpeter equation (BSE) calculations, we quantitatively predict the respective Ti 1s near-edge spectra. Properly accounting for atomic fluctuations greatly improves the agreement between theoretical and experimental spectra. The evolution of relative strengths of spectral features vs temperature and electric field polarization vector are captured in considerable detail. This work shows that local structure can be characterized from first-principles sufficiently well to aid both the prediction and the interpretation of near-edge spectra.

## INTRODUCTION

Perovskite  $\text{ABO}_3$  compounds are a family of materials of technological interest, in part because of their usefulness as dielectric and piezoelectric materials. A variety of phase transitions are seen in perovskite oxides, from ferroelectric transitions in  $\text{BaTiO}_3$  and  $\text{PbTiO}_3$  to antiferrodistortive transitions in  $\text{SrTiO}_3$  and more complicated transitions in  $\text{CaTiO}_3$  and  $\text{PbZrO}_3$ . Additionally, *relaxor* behavior[1–3] (a broad, frequency-dependent dielectric maximum vs temperature, not associated with a paraelectric-ferroelectric phase transition) can occur in perovskite solid solutions such as  $\text{Pb}[\text{Mg}_{1/3}\text{Nb}_{2/3}]\text{O}_3$  (PMN).

Many of the practical properties of these materials are due to the displacement of ions in response to temperature, electric fields, stress, etc. Response functions can also be related to fluctuations and correlations of the ionic positions over time and/or space [4, 5]. To clarify structure-property relationships, it is therefore important to fully characterize the ionic positions as a function of temperature, etc., not only the average positions, but also their fluctuations around the average over time and/or unit cells. Such distributions can reveal interesting features that can dramatically affect a material’s properties, such as characteristic deviations of local structure from the average. While a difference between local atomic geometries and average properties is naturally expected in complex perovskites where different species occupy the same crystallographic site, pioneering work of Comes *et al.*[6] gave evidence that even simple perovskites such as  $\text{BaTiO}_3$  and  $\text{KNbO}_3$  in their cubic phases can exhibit correlated off-centering of their B ions (*e.g.*, Ti or Nb).

There are many theoretical methods to determine local atomic geometries in materials. Density-functional theory (DFT) ground-state calculations are direct, but are limited regarding the sizes of systems that can be treated. Also, DFT calculations are usually restricted to the zero-temperature case, and are subject to systematic error because of approximate treatments of exchange and correlation. To overcome the DFT zero-temperature problem, DFT-based *ab initio* molecular dynamics (AIMD) calculations allow finite-temperature fluctuations of ionic coordinates to be incorporated in the Born-Oppenheimer limit. However, the sizes of treatable systems may be even further restricted, and one must cover a sufficiently long simulation time to equilibrate to representative conditions at a given temperature. A molecular dynamics calculation that uses first-principles-based effective Hamiltonians or force-field models allows for effects involving greater length and time scales to be investigated, but its predictions are generally not as accurate as those obtained using AIMD.

There are also many experimental methods to determine local atomic geometry [7]. For example, x-ray absorption fine structure spectroscopies [near-edge x-ray absorption fine structure (NEXAFS), also known as x-ray absorption near-edge structure (XANES), and extended x-ray absorption fine structure (EXAFS)] can furnish a wealth of information via interference effects because of a core-level photoelectron’s multiple scattering from atomic sites [8]. Such core level spectroscopies are element-specific, and the excitonic “pre-edge” features (involving 1s-to-3d transitions from the ground state to a bound core-hole exciton state) are strongly affected by variations in the B-site (*e.g.*, Ti) position with respect to its nearest neighbors. As an example, this effect was pre-

viously demonstrated in strained, thin-film ferroelectric SrTiO<sub>3</sub> [9]. In that work, x-ray diffraction and DFT determination of the unit cell size and internal atomic coordinates agreed with respect to the detailed crystal structure, and theoretical and experimental NEXAFS calculations indicated similar degrees of Ti off-centering in the TiO<sub>6</sub> cages. Bulk calculations confirmed selection rules for excitation into  $T_{2g}$  and  $E_g$  core-hole exciton levels, and these rules were violated in a fashion that is consistent with average displacements and thermal fluctuations of the Ti coordinate relative to its O<sub>6</sub> cage.

Lead titanate (PbTiO<sub>3</sub>) is a compound of interest, in part because it is an endmember of important solid solutions, such as lead-zirconium titanates (PZT). It has a single tetragonal/cubic transition at  $T = 763$  K, with the cubic phase existing at higher temperatures. At room temperature, the Ti 1s near-edge spectrum in PbTiO<sub>3</sub> features an  $E_g$  peak near 4970.5 eV that is strongly enhanced compared to the  $T_{2g}$  peak for x-ray photon electric field polarization along the tetragonal axis [9]. This is a hallmark signature of Ti off-centering relative to the surrounding O<sub>6</sub> octahedra in the tetragonal phase. However, the peak is still enhanced in the cubic phase above the transition temperature, whereas Bethe-Salpeter equation (BSE) calculations that assume only *average* cubic perovskite structure fail to predict this enhancement. Instead, thermal fluctuations must be taken into account [10]. Related EXAFS studies [11, 12] also indicate off-centering of Pb and Ti in PbTiO<sub>3</sub> above the transition temperature.

In this work, we combine AIMD and a BSE treatment of the Ti 1s near-edge spectrum in a fashion that addresses the thermal fluctuations. We find that the important fluctuations for a given temperature can be effectively reproduced by a single periodic five-atom cell. BSE calculations are performed using these cells and compared with measured spectra [10] to investigate the local structure in PbTiO<sub>3</sub> as a function of temperature and in SrTiO<sub>3</sub> at room temperature.

In what follows, we review the background and theoretical methodology (i.e., AIMD and BSE calculations). Aspects of measurements of experimental spectra to which we compare results are given in more detail elsewhere [10]. We then present our results, comparing calculated and measured spectra, and present our conclusions, primarily that our present accounting of ionic fluctuations greatly improves agreement between theoretical and measured spectra in the pre-edge region.

## BACKGROUND AND METHODOLOGY

### Underlying Physics

Let a Ti 1s electron’s coordinate relative to the nucleus be denoted by  $\mathbf{r}$ . Then the effective light-matter inter-

action operator responsible for a core excitation can be approximated as

$$\hat{O} \approx (\mathbf{e} \cdot \mathbf{r}) + \frac{i}{2}(\mathbf{e} \cdot \mathbf{r})(\mathbf{q} \cdot \mathbf{r}). \quad (1)$$

Here,  $\mathbf{e}$  is the photon’s electric-field polarization vector, and  $\mathbf{q}$  is its wave vector. Thus, the vectors  $\mathbf{q}$  and  $\mathbf{e}$  determine how the two terms respectively allow electric dipole (E1) and quadrupole (E2) transitions at the Ti 1s near-edge. As a consequence, a variety of experimental parameters can be varied to “tease out” and assign various spectral features, depending on the orientations of  $\mathbf{e}$  and  $\mathbf{q}$  relative to the crystallographic directions, as well as temperature, film thickness, polarization, strain and flexure. Near-edge spectra in SrTiO<sub>3</sub> and PbTiO<sub>3</sub> reveal electric-dipole and electric-quadrupole transitions to Ti 4p, 3d and mixed 4p-3d states. Weak, crystal-field-split “pre-edge” features are attributed to 1s→3d transitions and are small compared to the main “edge jump” at the onset of the Ti 4p continuum states around and above 4970 eV.

For octahedral Ti site symmetry, there are two leading pre-edge features, around 4968.5 eV and 4970.5 eV, because the  $T_{2g}$  and  $E_g$  orbitals are separated by the ligand-field splitting. These are understood as excitation to 3d level on the same site as the 1s hole, while the next features around 4974 eV could arise from excitation to 3d levels on nearby Ti sites because of hybridization with the on-site 4p states mediated by the O 2p states [10, 13]. In the presence of a Ti 1s core hole, an electron in any of the on-site orbitals would be bound to the Ti site, so that the electron-core hole pair constitutes a core-hole exciton. Pseudo Jahn-Teller splittings and site symmetry lower than cubic symmetry can split the otherwise threefold and twofold degeneracies further. The edge jump is chiefly due to the E1 term, which can greatly enhance pre-edge features when Ti-site inversion symmetry is broken. In that case, low lying Ti 4p-derived and 3d-derived  $E_g$  states, which are close in energy, mix, so that the latter become more strongly accessible via the E1 term. Otherwise, the E2 term alone can give rise to the weak pre-edge features. Selection rules imply that 3d lobes should have projections in the plane of  $\mathbf{e}$  and  $\mathbf{q}$  but not along either of these vectors. As an example, the antiferrodistortive tetragonal phase of SrTiO<sub>3</sub> should affect the E2 selection rules regarding observation of  $d_{xy}$ -derived vs  $d_{x^2-y^2}$ -derived exciton levels when  $\mathbf{e}$  and  $\mathbf{q}$  are both in the basal plane because of TiO<sub>6</sub> cage rotations. However, fluctuations of the cage rotational angles about their average values can be substantial, further weakening the selection rules. As examples of past work in the near-edge spectroscopy of simple perovskites, Ti off-centering in PbTiO<sub>3</sub> was analyzed by Vadrinskii *et al.* [10], and Ravel *et al.* [14], and Ti off-centering in SrTiO<sub>3</sub> by several groups [9, 15]. Other effects of symmetry were studied theoretically and exper-

imentally in non-perovskite compounds containing  $\text{TiO}_6$  cages, such as rutile and anatase [16–18].

### Ab initio molecular dynamics (AIMD) calculations

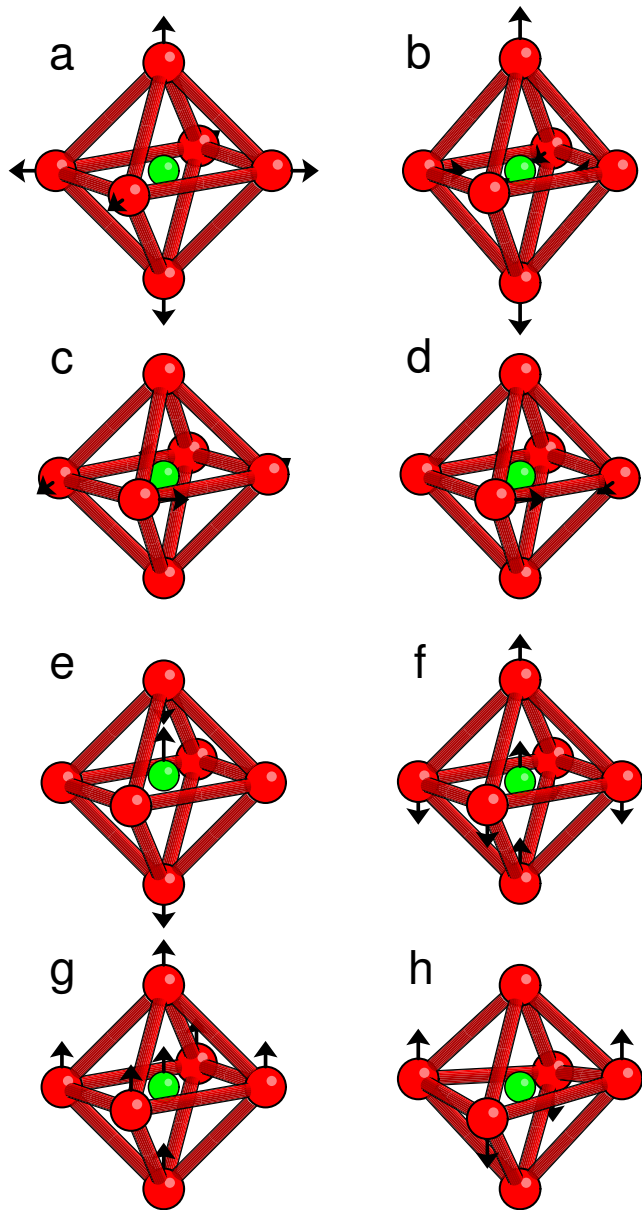


FIG. 1. One component of each irreducible representation for local  $\text{TiO}_6$  distortions in a cubic titanate perovskite: (a)  $a_{1g}$ ; (b)  $e_g(z)$ ; (c)  $t_{1g}(z)$ ; (d)  $t_{2g}(z)$ ; (e)  $t_{1u}^{(1)}(z)$ ; (f)  $t_{1u}^{(2)}(z)$ ; (g)  $t_{1u}^{(3)}(z)$ ; (h)  $t_{2u}(z)$ . Some “away-pointing” arrows are obscured.

From the theory in Sec. (A), the physics that dominates the Ti near-edge in  $\text{PbTiO}_3$  and  $\text{SrTiO}_3$  involves

Ti ions and their nearest O neighbors. The pertinent local environment thus features seven atoms: the Ti itself and an octahedron of six surrounding O ions. Under  $O_h$  symmetry, the 21 corresponding vibrational degrees of freedom transform into irreducible representations (irreps) as follows:  $a_{1g} + e_g + t_{1g} + t_{2g} + 3 t_{1u} + t_{2u}$ . One displacement pattern for each irrep is given in Fig. 1. and the corresponding normalized full displacement patterns are given in Supporting Information Table S1 (see <http://link.aps.org/supplemental/10.1103/PhysRevB.98.014111>). In the most important local displacement pattern in this work  $t_{1u}^{(1)}(z)$ , the central Ti ion moves proportionally to  $+(\sqrt{2/3})c$  along  $z$  and the the two neighboring O ions in the  $\pm z$  direction move proportionally to  $-(\sqrt{1/6})c$  along  $z$ , where  $c$  is the lattice parameter of the primitive five-atom perovskite cell along  $z$  (see Table I). For the corresponding  $t_{1u}^{(1)}(x)$  and  $t_{1u}^{(1)}(y)$  patterns,  $z$  is replaced by  $x$  ( $y$ ) and  $c$  is replaced by  $a$ . For simplicity, the same mode labels are used here for cubic and for tetragonal  $\text{PbTiO}_3$ ; tetragonal cell modes are identified with the cubic irrep from which they are derived.

Ab initio molecular dynamics [19] using DFT at the generalized-gradient-approximation (GGA) level with Hubbard  $U$  corrections was used to compute the time varying atomic coordinates,  $x_{\mu i}(t)$ . Here,  $t$  denotes time,  $\mu$  labels one of the above 21 local modes, and  $i$  the position (unit cell). Simulations were run for  $\text{PbTiO}_3$  at 300 K, 600 K, and 900 K. For all runs, we used 80-atom supercells with lattice vectors (0,2,2), (2,0,2), and (2,2,0) in terms of the lattice vectors of the corresponding 5-atom perovskite perovskite cell. The MD was run using the Vienna Ab initio Simulation Package (VASP) code [20, 21]. The simulation time step was 1.25 fs, and the total simulation time was 2.5 ps (2000 time steps). Langevin dynamics were used, with a frequency of 2 THz. The final runs were performed after a series of initialization runs totaling 2 ps. Such a simulation time is relatively short compared to other AIMD studies of  $\text{PbTiO}_3$  [22, 23], because we enforced high convergence with respect to k-points and plane-wave cutoff energy. Nevertheless, the 2.5 ps run is sufficient for convergence of atomic coordinate averages and fluctuations, as found by consistency of the results of the final run with those of the previous 1.25 ps initialization run.

It is well known that the GGA gives a  $c/a$  ratio for  $\text{PbTiO}_3$  that is much larger than experiment [24]. We have found empirically that the PBEsol [25] GGA with a Hubbard correction of  $U = 2.3$  eV for oxygen p-states and an artificial pressure of  $-21$  kbar ( $-2.1$  GPa) reproduces low-temperature structures of other perovskite titanates such as  $\text{BaTiO}_3$ ,  $\text{CaTiO}_3$ , and  $\text{SrTiO}_3$  quite well, but the  $c/a$  ratio of  $\text{PbTiO}_3$  remains too high. (It has recently been suggested that the inclusion of van der Waals forces, neglected here, can strongly affect the calculated  $c/a$  ratio [26].) On the other hand, we find

TABLE I. Atomic displacements corresponding to unit amplitude of the  $t_{1u}^{(1)}(z)$  degree of freedom for the  $\text{TiO}_6$  cluster in a perovskite titanate. Entries that are zero are left blank. The unit-amplitude  $t_{1u}^{(1)}(x)$  and  $t_{1u}^{(1)}(y)$  displacement patterns can be found by cyclic permutation and by replacing the  $z$  direction 5-atom primitive perovskite cell lattice parameter  $c$  with the corresponding lattice parameter in the  $x$  or  $y$  direction. Atomic displacement patterns for the other  $\text{TiO}_6$  cluster degrees of freedom can be found in the Supporting Information Table S1 (see <http://link.aps.org/supplemental/10.1103/PhysRevB.98.014111>).

Ti			O <sub>+x</sub>			O <sub>-x</sub>			O <sub>+y</sub>			O <sub>-y</sub>			O <sub>+z</sub>			O <sub>-z</sub>		
$x$	$y$	$z$	$x$	$y$	$z$	$x$	$y$	$z$	$x$	$y$	$z$	$x$	$y$	$z$	$x$	$y$	$z$	$x$	$y$	$z$
		$(2/\sqrt{6})c$															$(-1/\sqrt{6})c$			$(-1/\sqrt{6})c$

TABLE II. Experimental lattice parameters for  $\text{SrTiO}_3$  and  $\text{PbTiO}_3$  [27, 28] used in this work (in Å).

	$\text{SrTiO}_3$		$\text{PbTiO}_3$		
$T(\text{K})$	293		300	600	900
$a$	3.9051		3.901	3.927	3.980
$c$	3.9051		4.157	4.099	3.980

that a room-temperature AIMD run for  $\text{PbTiO}_3$  with the above parameterization, and with the unit cell fixed at the experimental one, yields an average structure with ionic positions within 0.05 Å of the experimental values. Therefore, each AIMD run was performed with the primitive lattice parameters fixed at the experimental values at the corresponding temperature [27, 28]. The lattice constants used are presented in Table II.

Defining  $\langle Q \rangle_t$  as an average of quantity  $Q$  over time and  $\langle Q \rangle_i$  as an average over sites, we define the mode average of a local coordinate by its mean value, namely

$$\bar{x}_\mu = \langle \langle x_{\mu i}(t) \rangle_i \rangle_t, \quad (2)$$

and the root-mean-square local coordinate as

$$\sigma(\mu) = (\langle \langle x_{\mu i}^2(t) \rangle_i \rangle_t)^{1/2}. \quad (3)$$

We also define the time-and-space deviation of a coordinate from its mean value by  $x'_{\mu i}(t) = x_{\mu i}(t) - \bar{x}_\mu$ . Most of the mode averages  $\bar{x}_\mu$  are zero by symmetry. However, in the tetragonal  $\text{PbTiO}_3$  phase, the average amplitudes of the polar  $t_{1u}(z)$  modes are nonzero.

### Bethe-Salpeter equation (BSE) calculations

In Sec. (B), we describe the 21 degrees of freedom of a  $\text{TiO}_6$  unit, and how their averages and root-mean-squares were calculated via AIMD. Before discussing the details of our Bethe-Salpeter equation calculations, we determine which of these 21 degrees of freedom are important. Rigid translation of the  $\text{TiO}_6$  cage ( $t_{1u}^{(3)}$  modes) has no effect on the absorption spectrum, while rigid rotation ( $t_{1g}$ ) serves only to change the polarization selection

rules for E2 transitions. Of the remaining 15 degrees of freedom, isotropic breathing ( $a_{1g}$ ) has little impact on the spectrum, while the two  $e_g$  breathing modes are responsible for pseudo-Jahn-Teller splitting of the  $1s$ -to- $E_g$  peak [29, 30]. The  $t_{2g}$ ,  $t_{1u}^{(2)}$  and  $t_{2u}$  modes do not change Ti-O distances to first order. Thus, the set of three  $t_{1u}^{(1)}$  modes in which the Ti ion moves relative to its axial O neighbors are expected to dominate the near edge spectra. Furthermore, the spectra should be proportional to the square of the amplitude of the mode. Thus, averaging over unit cells, the expected spectra are equivalent to that for a single periodic five-atom cell where the amplitude of each component of the  $t_{1u}^{(1)}$  displacement pattern is equal to the corresponding root-mean square value over all cells. Explicit expressions for the effective atomic coordinates, valid for  $\text{ATiO}_3$  perovskites of cubic and tetragonal symmetry, are given in Table III. The  $A_z$  and  $O_z$  displacements in Table III under tetragonal symmetry are insignificant (for near-edge spectra purposes), but are set at their values determined from the average AIMD structure.

In our calculations, we chose to have the  $c$ -axis along the  $z$  direction. Two x-ray photon geometries were considered, corresponding to what was measured. One geometry had  $\mathbf{q} \parallel (-1, -1, 0)$  and  $\mathbf{e} \parallel (0, 0, 1)$ , and one geometry had  $\mathbf{q} \parallel (0, -1, 1)$  and  $\mathbf{e} \parallel (1, 0, 0)$ . Randomization of signs of displacements along each Cartesian direction was incorporated by averaging spectra with suitable variation of the signs of Cartesian components of  $\mathbf{q}$  and  $\mathbf{e}$ .

The x-ray absorption coefficient can be given as

$$\mu(E) = -\text{Im} \langle \Phi_0 | \hat{O}^\dagger \frac{1}{E + i\Gamma(E) - H} \hat{O} | \Phi_0 \rangle, \quad (4)$$

where  $\Phi_0$  denotes the ground state,  $\Gamma(E)$  accounts for lifetime damping of excited states, and  $H$  is the effective Hamiltonian for the electron core-hole pair's equation of motion, which is the Bethe-Salpeter equation. This Hamiltonian includes effects of the band structure, electron self-energy damping calculated as described elsewhere [31], core hole lifetime damping [32], and the very important screened electron-core hole interaction. The

TABLE III. Coordinates of 5-atom structures for use in the Bethe-Salpeter equations to compute near-edge spectra of cubic or tetragonal simple ATiO<sub>3</sub> perovskites, given root-mean-square fluctuations associated with the  $t_{1u}$  local coordinate (Table I). The origin is chosen such that the crystallographic average position of one O atom is (0.5, 0.5, 0.0).  $A_z$  and  $O_z$  coordinates are set at their average values.

$T=300$ K:			
Ion	$x$	$y$	$z$
A	0	0	$A_z$
Ti	$0.5 + (2/\sqrt{6}) \sigma(t_{1u}^{(1)}(x))$	$0.5 + (2/\sqrt{6}) \sigma(t_{1u}^{(1)}(y))$	$0.5 + (2/\sqrt{6}) \sigma(t_{1u}^{(1)}(z))$
O	$0.0 - (1/\sqrt{6}) \sigma(t_{1u}^{(1)}(x))$	0.5	$O_z$
O	0.5	$0.0 - (1/\sqrt{6}) \sigma(t_{1u}^{(1)}(y))$	$O_z$
O	0.5	0.5	$0.0 - (1/\sqrt{6}) \sigma(t_{1u}^{(1)}(z))$

Bethe-Salpeter equation solver is described by Vinson *et al.* [33], with various details regarding the calculation of matrix elements given elsewhere [34].

A precursor DFT calculation underlies the BSE calculation. This provides Bloch state wave functions and energies. We used a 200 Ry plane-wave cutoff. This was necessary to describe Ti 3s and 3p states well, while simultaneously having Ti 4s and 4p energies sufficiently accurate by virtue of a hard pseudopotential for Ti. Thus, we used He-like, Ne-like and Hg<sup>2+</sup>-like cores for Vanderbilt-type pseudopotentials [35] for O, Ti and Pb, respectively. We used the local-density approximation [36] with the Ceperley-Alder functional [37] as parameterized by Perdew and Zunger [38]. The self-consistent charge density was found using  $4 \times 4 \times 4$  Monkhorst-Pack grids [39].

The BSE calculation include 155 bands total and  $10 \times 10 \times 10$  grids. This was accelerated by use of optimized basis functions described by Prendergast and Louie [40], who improved upon earlier work [41]. The electron-core hole interaction was screened as described elsewhere [42]. For the electronic dielectric constant, we used  $\epsilon_\infty = 7.25$  at  $T = 300$  K,  $\epsilon_\infty = 7.60$  at  $T = 600$  K,  $\epsilon_\infty = 8.68$  at  $T = 900$  K, which averages the values of the three diagonal elements of the measured dielectric tensor at each temperature [43].

## RESULTS AND DISCUSSION

The average crystallographic structures found in the AIMD simulations are given in able IV, while the root mean square fluctuations of the important  $t_{1u}^{(1)}$  modes are given in Table V. An example of how the local  $t_{1u}^{(1)}(z)$  coordinate for one specific Ti ion varies over time for different temperatures is shown in Fig. 2. Normalization of the  $t_{1u}^{(1)}(z)$  displacement pattern (Table I) means that the displacement of the Ti relative to the neighboring oxygens in the  $\pm z$  directions is  $3/\sqrt{6} \times c$  times the amplitude

TABLE IV. Temperature-dependent average structure of PbTiO<sub>3</sub> from AIMD

$T=300$ K:			
Ion	$x$	$y$	$z$
Pb	0.0000	0.0000	0.1056
Ti	0.5000	0.5000	0.5709
O	0.0000	0.5000	0.4982
O	0.5000	0.0000	0.4982
O	0.5000	0.5000	0.0000

$T=600$ K:			
Ion	$x$	$y$	$z$
Pb	0.0000	0.0000	0.0739
Ti	0.5000	0.5000	0.5550
O	0.0000	0.5000	0.4993
O	0.5000	0.0000	0.4993
O	0.5000	0.5000	0.0000

$T=900$ K:			
Ion	$x$	$y$	$z$
Pb	0.0000	0.0000	0.0000
Ti	0.5000	0.5000	0.5000
O	0.0000	0.5000	0.5000
O	0.5000	0.0000	0.5000
O	0.5000	0.5000	0.0000

shown in this figure.

A histogram of the amplitudes of the  $t_{1u}^{(1)}(z)$  fluctuations of *all* Ti atoms versus temperature is shown in Fig. 3. For  $T = 900$  K, we additionally show the histogram of displacements obtained by symmetrizing the data over  $\pm z$ . The asymmetry in the “raw” data is attributed to insufficient averaging time in the 2.5 ps AIMD run. Interestingly, at all temperatures investigated, the peak amplitude of the  $t_{1u}^{(1)}$  fluctuation is similar: about 0.1, or about a 0.5 Å relative displacement of Ti against

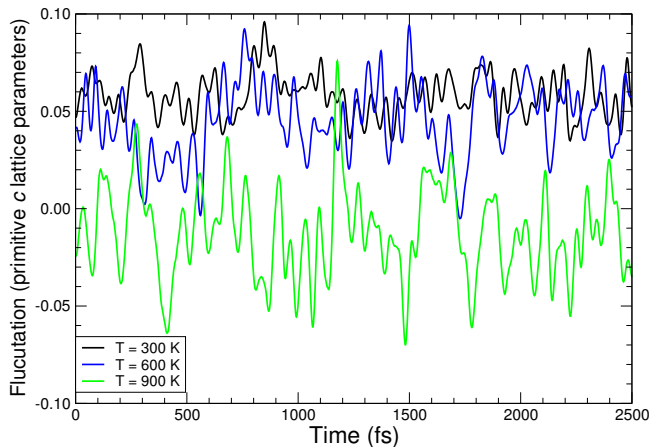


FIG. 2.  $t_{1u}^{(1)}(z)$  fluctuation of one Ti against its  $\pm z$  oxygen neighbors vs MD time, at different temperatures.

TABLE V. Root-mean-square fluctuations  $\sigma(\mu)$  of the  $t_{1u}^{(1)}$  modes of  $\text{PbTiO}_3$  as a function of temperature, as computed by *ab initio* molecular dynamics. Quantities in parentheses indicate one standard deviation uncertainty as calculated from five time averages. To convert into atomic displacements, multiply by the displacement patterns described in Table I. Root-mean-square fluctuations for the other modes as a function of temperature can be found in the Supporting Information Table S2 (see <http://link.aps.org/supplemental/10.1103/PhysRevB.98.014111>).

Mode $\mu$	$\sigma(\mu)$		
	300 K	600 K	900 K
$t_{1u}^{(1)}(x; y)$	0.0138(1)	0.0207(4)	0.0294(3)
$t_{1u}^{(1)}(z)$	0.0592(1)	0.0495(4)	0.0294(3)

O along the  $z$  direction.

There are two possibilities for the behavior in the cubic phase above the ferroelectric transition at  $T = 763$  K: if the amplitude peaks at zero, that indicates a displacive nature to the Ti off-centering in the ferroelectric transition; if the amplitude has two peaks at nonzero values, that indicates an order-disorder nature of Ti off-centering. Our present results for  $T = 900$  K can not clearly distinguish between the two cases. It would be useful to repeat the AIMD calculation for temperatures closer to the transition temperature, but the correlation length and time of the Ti off-centering fluctuation are expected to increase as the phase transition is approached[4, 44], requiring larger simulations cells and times for convergence. Our AIMD simulations used 80-atom cells. Classical molecular dynamics based on a bond-valence-sum model for  $\text{PbTiO}_3$  has recently been used to simulate cells with up to 2560 atoms[45]. Determining the fluctuations of the  $t_{1u}^{(1)}$  modes via the classical MD approach could help clarify to what extent the root-mean square local fluctuations are affected by longer-

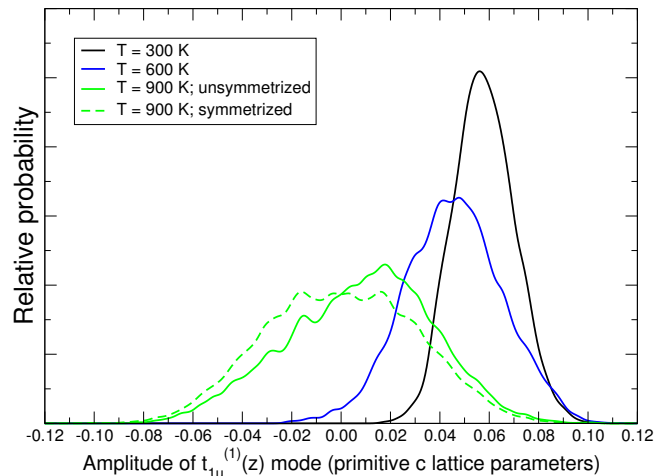


FIG. 3. Histograms of amplitude of  $t_{1u}^{(1)}(z)$  fluctuation of Ti ions against their  $\pm z$  O neighbors in  $\text{PbTiO}_3$  versus temperature, as calculated via *ab initio* molecular dynamics. The raw data for  $T = 900$  K is shown, as well as the data symmetrized about zero.

range correlations near the transition temperature.

Experimentally, near-edge measurements reported by Yoshiasa *et al.* [12] on a  $\text{PbTiO}_3$  powder sample show a nearly continuous evolution of the intensity of the  $E_g$ -derived peak near the transition temperature, suggesting a smooth trend for the root-mean-square Ti off-centering vs temperature, but measurement of a root-mean-square off-centering by itself does not show whether the underlying distribution has one peak or two. Other experimental[11] and computational[23] studies of  $\text{PbTiO}_3$  support an order-disorder nature of the phase transition in  $\text{PbTiO}_3$ . Neither of these studies measured precisely the same “local order parameter” as the AIMD calculations in this work. In light of our results, this raises the intriguing question of whether different possible local order parameters for the tetragonal-cubic transition in  $\text{PbTiO}_3$  could give different answers for the displacive vs order-disorder nature of the transition.

Plugging the AIMD fluctuations for  $\text{PbTiO}_3$  (Table V) into the general expression formula for the effective five-atom cell for BSE calculations (Table III), yields the temperature-dependent effective structures given in Table VI. Based on these effective structures, computed near-edge spectra for each x-ray photon geometry are presented in Fig. 4 for three temperatures for  $\text{PbTiO}_3$  and compared to measured spectra. The spectra are vertically offset for presentation, with the baseline indicated by a dashed line in each case. It should be noted that a rigid shift was required to energetically align the spectra, which is standard practice for calculated core excitation spectra. The peak that betrays the  $T_{2g}$ -derived core hole-exciton levels near 4968.5 eV shows minimal dependence on either temperature or x-ray photon geometry. On the other hand, the corresponding peak for  $E_g$ -

TABLE VI. Structures used in the Bethe-Salpeter equations to compute near-edge spectra in  $\text{PbTiO}_3$ . These are *not* the average crystallographic structures at the corresponding temperature, but are specifically created such that Ti is off-centered along each coordinate by the root mean square fluctuation as calculated by AIMD simulations.

$T=300$ K:			
Ion	$x$	$y$	$z$
Pb	0.0000	0.0000	0.1056
Ti	0.5113	0.5113	0.5483
O	0.9944	0.5000	0.4982
O	0.5000	0.9944	0.4982
O	0.5000	0.5000	0.9758

$T=600$ K:			
Ion	$x$	$y$	$z$
Pb	0.0000	0.0000	0.0739
Ti	0.5169	0.5169	0.5404
O	0.9915	0.5000	0.4993
O	0.5000	0.9915	0.4993
O	0.5000	0.5000	0.9798

$T=900$ K:			
Ion	$x$	$y$	$z$
Pb	0.0000	0.0000	0.0000
Ti	0.5240	0.5240	0.5240
O	0.9880	0.5000	0.5000
O	0.5000	0.9880	0.5000
O	0.5000	0.5000	0.9880

derived levels near 4970.5 eV shows a strong dependence on temperature. For  $\mathbf{e} \perp (001)$ , it grows in strength with temperature because of admixture of the Ti 4p and Ti  $3d_{x^2-y^2}$  levels because of fluctuations of the Ti  $x$ - and  $y$ -coordinates. However, this peak becomes particularly pronounced for  $\mathbf{e} \parallel (001)$  at temperatures below the transition temperature, when Ti off-centering is largest, especially at lower temperatures. A broad feature around 4974 eV appears to be enhanced along with the  $E_g$ -derived feature. Off-centering of the Ti affects hybridization of Ti 4p and O 2p states. In the unoccupied bands, there should be a node in such an antibonding state between the Ti and O atoms, and the weight of the Ti 4p state on the Ti site can be enhanced because of increasing localization arising from the node and fore-shortened bond length [10, 13].

In addition to  $\text{PbTiO}_3$ , we show results for  $\text{SrTiO}_3$  obtained at  $T = 293$  K [9]. In this case, the two x-ray photon geometries that were considered were (1.)  $\mathbf{q} \parallel (1, 1, 0)$  and  $\mathbf{e} \parallel (1, -1, 0)$ , and (2.)  $\mathbf{q} \parallel (1, 0, 0)$  and  $\mathbf{e} \parallel (0, 1, 0)$ . Naïvely, the first geometry should make transitions to Ti  $3d_{x^2-y^2}$ -derived core hole-exciton levels observable, though not transitions to Ti  $3d_{xy}$ -derived core hole-exciton levels. For the second geometry, ex-

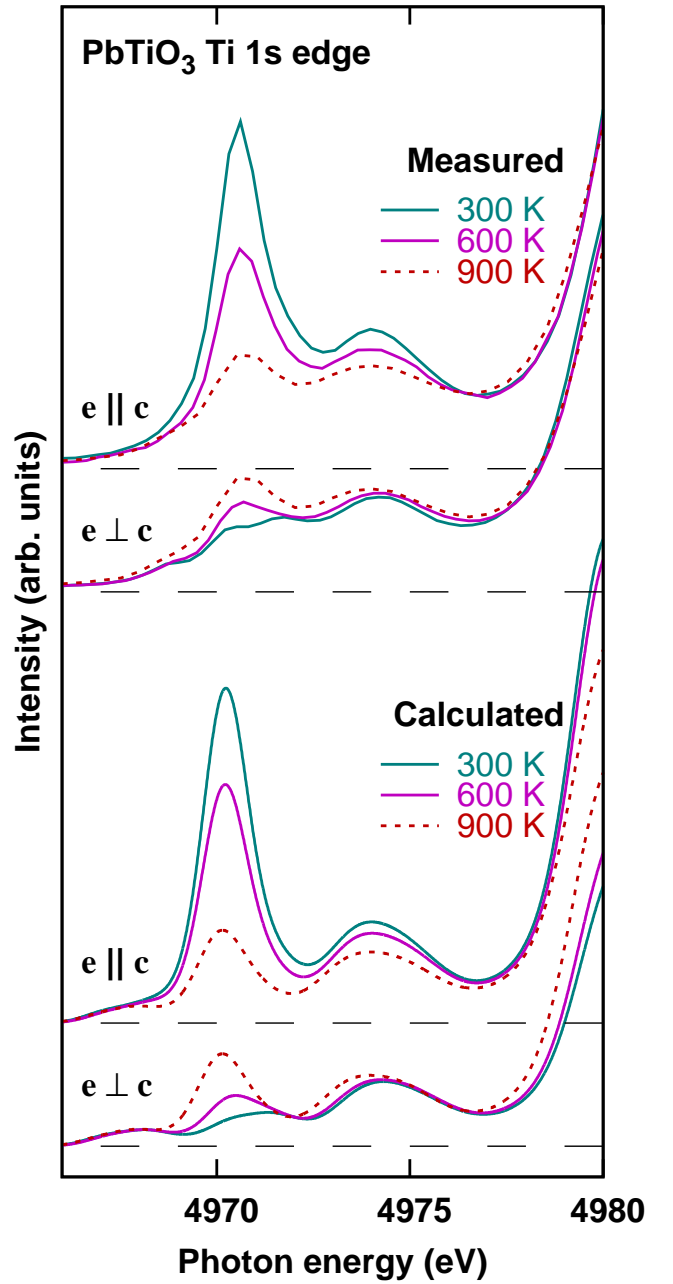


FIG. 4. Ti 1s near-edge spectrum emphasizing the pre-edge region for  $\text{PbTiO}_3$  at three temperatures, as measured and calculated.

actly the opposite should hold true. In fact, while the selection rule works nearly perfectly for the  $T_{2g}$ -derived peak, the  $E_g$ -derived peak is always visible with similar intensity in either case. We performed similar calculations in  $\text{SrTiO}_3$  as described for  $\text{PbTiO}_3$ . AIMD simulations  $\text{SrTiO}_3$  at room temperature give fluctuations  $\sigma(t_{1u}^{(1)}) = 0.0141$  along each Cartesian direction. The resulting spectra are shown in Fig. 5. Good agreement between the theoretical and experimental results is again observed, and the figure suggests similar breakdowns of



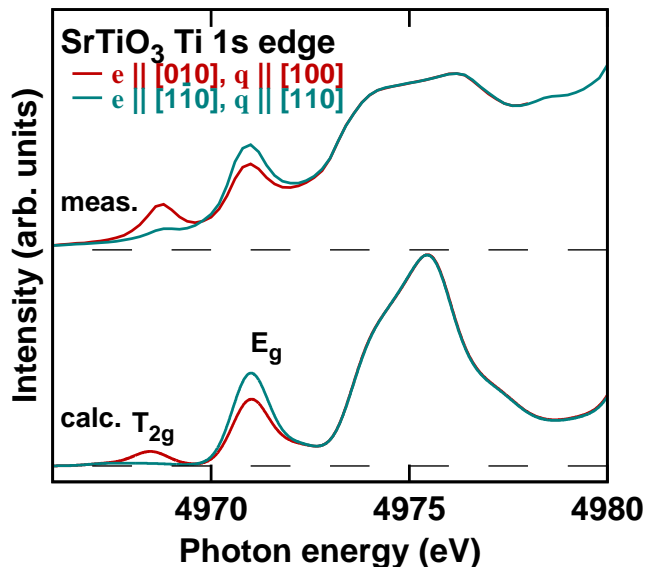


FIG. 5. Ti 1s near-edge spectrum emphasizing the pre-edge region for SrTiO<sub>3</sub> at 293 K, as measured and calculated.

selection rules being observed and calculated. Violations of selection rules have also been found that allow  $s \rightarrow s$  transitions in x-ray absorption because of lattice vibrations, which has been reported by others [46–49]. We also note that the exaggerated intensity of the features near 4975 eV in SrTiO<sub>3</sub> could result from the BSE calculations failure to account for charge-transfer processes that should appear like more effect screening of the Ti 1s hole when the excited core electrons leaves the Ti site [50].

## CONCLUSIONS

This work considers Ti 1s near-edge spectroscopic signatures of atomic displacement from those of the ideal perovskite structure in PbTiO<sub>3</sub> (and SrTiO<sub>3</sub>) for a variety of sample temperatures and experimental geometries. Using a combination of AIMD and BSE calculations, we have found that only one type of mode has a strong spectroscopic signature, namely the  $t_{1u}^{(1)}$  degrees of freedom involving the Ti<sup>4+</sup> moving relative to its axial O neighbors. This permits having the BSE calculations sample only a few frozen configurations of atomic coordinates to estimate effects on spectra accurately. To a good approximation, the strong peak around 4970.5 eV varies as the mean square displacement of this mode, and therefore does not vanish above the ferroelectric-paraelectric transition temperature, even though the average structure has Ti at the center of its oxygen cage.

Our results show that AIMD and BSE can be combined to successfully demonstrate the local fluctuations of Ti in PbTiO<sub>3</sub> and suggest that similar analysis could be fruitfully applied in other systems such as relaxors.

We have not attempted to consider cage-rotation effects at low temperature in SrTiO<sub>3</sub>. In that case, the associated modes could be both low-frequency and considerably more anharmonic, which might require extensions beyond the present analysis. In earlier work, a single, consistent picture could be constructed regarding crystal structure and local atom geometries based on several methods, including x-ray diffraction, x-ray absorption, density-functional theory calculations of ground state structures, and the degree and directionality of ferroelectric polarization and/or local off-centering in several perovskites [9, 51]. This work now incorporates molecular dynamics into the suite of collectively consistent and compatible methodologies in the same systems.

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