Sub-picometer sensitivity and effect of anisotropic atomic vibrations on Ti $L_{2,3}$ -edge spectrum of SrTiO₃

Cite as: Appl. Phys. Lett. **119**, 232901 (2021); https://doi.org/10.1063/5.0068861 Submitted: 27 August 2021 • Accepted: 13 November 2021 • Published Online: 06 December 2021

🔟 Mitsutaka Haruta, 🔟 Takashi Nemoto and 🔟 Hiroki Kurata



ARTICLES YOU MAY BE INTERESTED IN

Electron orbital mapping of SrTiO₃ using electron energy-loss spectroscopy Applied Physics Letters **119**, 232902 (2021); https://doi.org/10.1063/5.0072190

Perspectives of solution epitaxially grown defect tolerant lead-halide-perovskites and leadchalcogenides

Applied Physics Letters 119, 230501 (2021); https://doi.org/10.1063/5.0068665

Perspectives on self-powered respiration sensor based on triboelectric nanogenerator Applied Physics Letters **119**, 230504 (2021); https://doi.org/10.1063/5.0071608





Shorten Setup Time Auto-Calibration More Qubits

Fully-integrated Quantum Control Stacks Ultrastable DC to 18.5 GHz Synchronized <<1 ns Ultralow noise



ious qubits

visit our website >



Appl. Phys. Lett. **119**, 232901 (2021); https://doi.org/10.1063/5.0068861 © 2021 Author(s).

Export Citatio

Tiow Onlin

Sub-picometer sensitivity and effect of anisotropic atomic vibrations on Ti *L*_{2,3}-edge spectrum of SrTiO₃ **5**

Cite as: Appl. Phys. Lett. **119**, 232901 (2021); doi: 10.1063/5.0068861 Submitted: 27 August 2021 · Accepted: 13 November 2021 · Published Online: 6 December 2021

Mitsutaka Haruta,ª) 🝺 Takashi Nemoto, 🝺 and Hiroki Kurata 🝺

AFFILIATIONS

Institute for Chemical Research, Kyoto University, 611-0011 Uji, Kyoto, Japan

^{a)}Author to whom correspondence should be addressed: haruta@eels.kuicr.kyoto-u.ac.jp

ABSTRACT

The effect of temperature on the electron energy-loss Ti $L_{2,3}$ -edge spectrum of SrTiO₃ was ascertained using monochromated scanning transmission electron microscopy. The results demonstrate that the spectrum is sensitive to structural changes involving volume expansion on the sub-picometer level, and the sensitivity is superior to that obtainable using conventional electron microscopy. Experimental spectra could be accurately reproduced by multiplet calculations that incorporated anisotropic atomic vibrations of oxygen atoms. This spectral technique could represent a powerful tool for investigating infinitesimal structural changes and atomic vibrations at local regions, such as interfaces.

Published under an exclusive license by AIP Publishing. https://doi.org/10.1063/5.0068861

The electron energy-loss near-edge structure (ELNES) in the core-electron excitation spectra obtained via electron energy-loss spectroscopy (EELS) and the equivalent x-ray absorption near-edge structure (XANES) in x-ray absorption spectroscopy (XAS) are powerful techniques that can be used to investigate the electronic structures of unoccupied bands. In particular, scanning transmission electron microscopy (STEM)-ELNES is widely used in the analysis of local electronic structures, such as those at interfaces¹ and surfaces.² STEM analyses performed in conjunction with a monochromated electron source can be used to investigate electronic structures and also atomic vibrations with high spatial resolution. However, most research concerning atomic vibrations has focused on phonon excitation spectra,^{3–6} and there has been minimal research using density functional theory (DFT) calculations to assess vibrational effects on the K-edge of the core-loss spectra of solid,⁷⁻¹¹ liquid,¹² and gas¹³ phases. In the case of solids, the effect of atomic vibrations appears as a small peak in the pre-edge regions of the K-edges for transition metals and can be interpreted as a forbidden transition due to symmetry breaking by atomic displacement.⁷⁻¹¹ In contrast, the experimental C and O K-edges of both liquid and gas represent the averages for various bond lengths as a consequence of molecular vibrations.^{12,13} Although vibrational effects on the $L_{2,3}$ -edge spectra of transition metals have long been known to contribute to spectral broadening,¹⁴ these effects have not been studied quantitatively in combination with simulations. Thermal vibrations are known to be highly correlated with various properties of crystalline solids, such as phase transitions, thermal expansion, bonding characteristics, and electrical and thermal conductivity. Therefore, it is important to be able to quantitatively determine the effect of thermal vibrations on the $L_{2,3}$ -edge spectra of transition metals.

In the present work, we investigated the effects of atomic vibrations and thermal expansion on Ti $L_{2,3}$ -edge spectra by examining the temperature dependence of the Ti $L_{2,3}$ -edge spectrum of SrTiO₃. SrTiO₃ has a perovskite structure and has attracted significant attention because of its applications in oxide electronics, made possible as a consequence of the ideal cubic structure (perfect O_h symmetry) and physical properties of this compound. In particular, the oxygen atoms in SrTiO₃ have anisotropic temperature factors, such that the atomic vibrations along the Ti–O direction have a smaller amplitude than those in the Sr–O plane according to the ellipsoidal harmonic vibration approximation (Fig. 1). Conversely, the Sr and Ti atoms have isotropic temperature factors (Fig. 1). In the present work, we investigated the effects of atomic vibrations on Ti $L_{2,3}$ -edge spectra by performing crystal-field multiplet calculations that included thermal vibration effects.

In addition, SrTiO₃ is widely used as a substrate for the growth of epitaxial thin films of functional materials.^{15,16} The atomic and electronic structures at the interface regions of such films have been investigated using STEM–EELS.^{1,17} Because both the crystal structure and material properties of a transition metal thin film will be modified by minimal displacement of oxygen atoms at the interface,¹⁸ it is



FIG. 1. Graphical representation of atomic vibrations (at 99% probability) in SrTiO₃ at room temperature. Thermal factors are summarized in Table I.

important to investigate the sensitivity of the $L_{2,3}$ -edge to slight structural changes. Even a small structural change would be expected to modify the electronic structure of the material, and so, the ability to detect such changes in the electronic structure in the form of spectral variations would be very useful. Recently, our group demonstrated that local bond lengths in distorted FeO₆ octahedra can be extracted by analyzing Fe L_{2,3}-edge spectra acquired using monochromated STEM-EELS with atomic-level resolution, employing crystal field multiplet calculations.¹⁹ Thus, it is helpful to investigate the sensitivity of the L2.3-edge spectra of transition metal oxides to small structural changes. Because the lattice parameter of cubic SrTiO₃ is known to increase in a linear manner with the increasing temperature,²⁰ SrTiO₃ was determined to represent a suitable model for such analyses. In previous research, experiments with conventional cold field-emission gun STEM-EELS showed no changes in the Ti L2.3-edge spectrum of SrTiO₃ between 95 K and room temperature (300 K).²¹ In contrast, slight variations in the Ti L2,3-edge spectrum of BaTiO3 resulting from temperature-based phase transitions have been reported.² However, quantitative interpretations of spectral changes related to structural variations have not yet been discussed.

Electron energy-loss spectra were acquired in the STEM mode at 200 kV using a monochromated JEOL ARM200F analytical electron microscope equipped with a Gatan Quantum ERS spectrometer. During these analyses, the probe convergence semi-angle was 24.6 mrad and the EELS collection semi-angle was 57.3 mrad, while the practical energy resolution values were 0.2 and 0.15 eV when using a 1.3 μ m energy slit at energy dispersions of 0.05 and 0.01 eV/channel, respectively. The spectra were acquired in spectrum imaging mode, and the scanning regions were relatively wide (several tens of square nanometers). The spectra were captured with a short dwell time of 0.05 s and added according to a previously reported ultra-high-quality dark subtraction process²⁴ to avoid energy drift and to improve the signal-to-noise ratio. Thus, we obtained almost the same spectra at the same temperature apart from an extremely minimal amount of noise. Low-temperature spectra were obtained using a liquid-N2-cooled sample holder (Mel-Build), while high-temperature spectra were acquired using a heated tilting holder (JEOL, EM-31670SHTH).

Simulated Ti $L_{2,3}$ -edge spectra, including the thermal vibration effect, were generated using the multi-X crystal-field multiplet calculation code developed by Uldry and co-workers.²⁵ Because this code can also be applied to low-symmetry structures by placing charged particles at atomic positions, the atomic vibration effect could be

incorporated based on the displacements of each ion using the frozen phonon approximation.²⁶ First, a cluster of 613 ions was generated based on previously reported x-ray diffraction data.²⁰ This cluster size showed good convergence of the calculated multiplet levels. The individual displacements were generated independently using a Gaussian random distribution function. The mean square displacement, U, for individual atomic site (the so-called thermal factor) was used for the dispersion, σ^2 , in the Gaussian function. The calculated displacements were added to the equilibrium atomic positions. A simulated $L_{2,3}$ -edge spectrum reflecting a frozen phonon configuration was calculated. These processes were automatically repeated 10 000 times using the Python code (Fig. S1), after which all the spectra were averaged. The same final average spectrum generated using 10 000 different frozen phonon configurations could be obtained repeatedly. These calculations employed thermal factors determined by y-ray diffraction at room temperature,²⁷ while the high-temperature (1073 K) factors were simulated using the ALAMODE code^{28,29} (Fig. S2) because no experimental data were available. Table I summarizes the resulting unit-cell parameters and temperature factors at 293 and 1073 K. The scaling parameters were adjusted to fit the experimental L_3 -edge spectra because the simulated spectra did not include transitions to the 4s orbital or continuum states, and because the charge transfer effect was not correctly included. For these reasons, a large deviation between the simulated and experimental L_2 -edge spectra was observed. The core hole broadening was found to increase linearly from 0.2 to 0.7 eV between 458 and 468 eV.²² The input parameters for the multiX calculations are summarized in Table S1.

Figure 2(a) shows the temperature dependence of the Ti $L_{2,3}$ edge spectra acquired between 108 and 1073 K, where SrTiO₃ exhibits a perfect cubic structure. Each spectrum shows four main peaks that can be assigned to L_3 - t_{2g} , L_3 - e_g , L_2 - t_{2g} , and L_2 - e_g transitions according to crystal field theory in conjunction with a one-electron approximation. These demonstrate two primary changes in the L_3 -edge spectra as the temperature is varied, and similar changes are evident in the L2edge spectra (Fig. S3). Because we obtained reversible results by increasing and decreasing the temperature (Fig. S4) over the present temperature range, the contribution of Ti³⁺ ions¹⁷ due to the oxygen vacancy under a reducing atmosphere at high temperature appears to be negligible. One interesting feature of these data is that energy splitting between the t_{2g} and e_g peaks in the L_3 -edge spectra is evident [Figs. 2(a) and 2(b)], and Fig. 2(c) shows that the energy splitting decreases in a linear manner with the increasing temperature. Linear fitting established that the rate of decrease was 0.2 meV/K. This change in peak splitting can be attributed to a decrease in crystal field splitting due to isotropic volume expansion. This decrease in turn reflects a decrease in hybridization between the Ti t_{2g} or e_g orbitals and the O 2porbitals, which can be confirmed by variations in the intensities and

TABLE I. Lattice parameter a (Å) and temperature factor $U(Å^2)$ for SrTiO₃.^a

	а	Sr - U_iso	Ti-U _{iso}	O-U _{eq}	O- <i>U</i> ₁₁	O- <i>U</i> ₂₂
293 K ²⁷ 1073 K	3.905 3.938	0.00 577	0.00 395	0.00733	0.00 334	0.00 932

^a U_{11} and U_{22} correspond to the Ti–O direction and Sr–O plane, respectively. U_{iso} is the isotropic factor. U_{eo} is the isotopically transformed factor obtained using U_{11} and U_{22} .



FIG. 2. (a) Ti $L_{2,3}$ -edge spectra obtained at 105, 293, 373, 473, 573, 673, 773, 873, 973, and 1073 K. (b) Magnified portions of L_3 -edge spectra acquired at several temperatures. (c) Energy splitting between L_3 - t_{2g} and L_3 - e_g peaks as a function of temperature. Each error bar corresponds to the standard deviation (σ) of ten data points. (d) O K-edge spectra obtained at temperatures from 105 to 1073 K.

splitting widths of the first and second peaks in the O K-edge spectra [Figs. 2(d) and S5]. Because the rate of an increase in the lattice parameter was found to be approximately 4×10^{-3} pm/K in a previous x-ray diffraction study,²⁰ the rate of energy splitting due to lattice expansion can be estimated to be 50 meV/pm. In the present work, a lattice expansion of 0.4 pm per 100 K produced a 20 meV decrease in energy splitting, meaning that examining Ti L2.3-edge spectra allow lattice expansion to be monitored with sub-picometer sensitivity. In the case of an electron microscopy image, the accuracy with which atomic displacement can be determined is on the order of only 5 pm.^{18,30} It should also be noted that, although sub-picometer lattice variations can, in principle, be detected by electron diffraction, the spatial resolution of this technique is poor. In contrast, STEM-EELS can acquire spectra with atomic-level resolution and so can be used to examine sub-picometer distortions at local regions, such as interfaces and surfaces.

A second feature is the increase in intensity on the low-energy side of the L_3 - e_g peak with the increasing temperature [Figs. 2(a) and 2(b)], such that the L_3 - e_g peak is asymmetric even at 293 K. The $L_{2,3}$ edge spectra of transition metals and the M4,5-edge spectra of rareearth metals are strongly affected by an atomic multiplet term because of localized electron-electron interactions.³¹ The blue line and the vertical lines at the base in Fig. 3(a) show the simulated spectrum, and the corresponding multiplet terms obtained from crystal-field multiplet calculations, respectively. Although the simulated spectrum roughly reproduces the experimental features, the L_3 - e_{σ} peak shows a symmetrical shape and so does not match the aforementioned experimental features. In fact, no multiplet term is observed on the slightly lowerenergy side of the L_3 - e_g peak, as shown in Fig. 3(a). According to crystal field multiplet theory, excitation from the d^0 ground state of a Ti⁴⁺ ion with O_h symmetry gives rise to seven $2p^53d^1$ final multiplet terms,¹⁴ as indicated by the vertical lines in Fig. 3(a). Thus, there is no reason for the spectral intensity to increase in the corresponding energy region as long as the O_h symmetry is maintained. In a previous report,¹⁴ the width of the L_3 - e_g peak was explained on the basis of dispersional and atomic vibrational broadening; the authors concluded that the latter contribution was the main factor. The dispersional broadening is due to the significant hybridization of the e_{g} state, which results in a larger bandwidth due to the solid effect. However, DFT calculations indicate that the increase in bandwidth due to thermal expansion should be small (Fig. S6). Thus, the possibility that ideal O_h symmetry was broken by thermal vibrations should be considered. According to the frozen phonon approximation,²⁶ the duration of the interaction between fast electrons and individual atoms in a crystal is much shorter than the vibration period of atoms. Similarly, according to the Franck-Condon principle, electronic transitions will be essentially instantaneous compared with the timescale of atomic vibrations.^{14,32} Thus, the experimental spectra should be considered as accumulations of spectra calculated on the basis of frozen phonon configurations of displaced atomic structures, meaning that they are so-called snapshots. Because the individual coordination structure in the frozen phonon configurations does not maintain O_h symmetry, additional multiplet terms would be generated. However, the vibration effects in the $L_{2,3}$ -edge spectrum have previously been treated simply using Lorentzian broadening for the four peaks in the calculated multiplet spectrum.¹⁴ Quantitative studies of spectral simulations that consider atomic vibrations have not been reported.

In the present work, we used the multiX code²⁵ to carry out crystal-field multiplet calculations that included the thermal vibration effect. The red and green lines in Fig. 3(a) indicate simulated spectra at 293 K that include isotropic and anisotropic atomic vibrations, respectively. Thermal vibration clearly increases the intensity at the low-energy side of the L_3 - e_g peak. In particular, whereas the spectrum that includes isotropic vibrations overestimates the corresponding intensity, the spectrum that includes anisotropic vibrations exhibits good agreement with the experimental spectrum. Figure 4(a) shows 10



FIG. 3. (a) Experimental and simulated Ti $L_{2,3}$ -edge spectra at 293 K. (b) Experimental and simulated Ti $L_{2,3}$ -edge spectra at 1073 K. In both (a) and (b), the black line shows the experimental spectrum, while the simulated spectra shown by the blue, red, and green lines correspond to those without thermal vibrations and with isotropic and anisotropic thermal vibrations, respectively.

randomly selected spectra from 10 000 spectra generated for the anisotropic thermal vibration condition at 293 K. Figure 4(b) is the average spectrum with the bars that correspond to the standard deviation (σ) of 10000 data points. Although each individual spectrum exhibits quite different features reflecting the momentary distortion of octahedra due to atomic vibrations, the accumulated spectrum [Fig. 3(a)] does not demonstrate a significant change in splitting width; the main difference is observed at the low-energy side of the L_3 - e_g peak. Similar levels of agreement were obtained using the parameters determined by synchrotron x-ray diffraction³³ and ALAMODE calculations, while the spectrum generated using the results of laboratory x-ray experiments³⁴ showed a slight deviation (Fig. S7). Figure 3(b) presents the experimental and simulated spectra at 1073 K. The spectrum considering anisotropic vibrations agrees well with the experimental spectrum, whereas a discrepancy is clearly observed between the experimental spectrum and the calculated spectrum incorporating the effects of isotropic vibrations. These results suggest that thermal vibrations can



FIG. 4. (a) Randomly selected ten simulated Ti $L_{2,3}$ -edge spectra out of 10 000 spectra of the anisotropic thermal vibration condition at 293 K. (b) The average spectrum of 10 000 different frozen phonon configurations at 293 K. Each bar corresponds to the standard deviation (σ) of data points.

generate additional multiplet terms in $L_{2,3}$ -edge spectra because of the reduced symmetry.

In conclusion, we have demonstrated that the Ti $L_{2,3}$ -edge spectrum of SrTiO₃ is sensitive to structural changes at the sub-picometer level and is affected by anisotropic atomic vibrations. Simulated spectra, including the effects of anisotropic atomic vibrations based on crystal field multiplet theory, were found to agree well with experimental spectra. In the present research, the experimental spectrum was well reproduced by a simulation based on an ellipsoidal harmonic vibration approximation. However, in reality, SrTiO₃ exhibits anharmonic vibrations.³⁵ The good agreement between the experimental and simulation results obtained in the present study indicates that the effect of such anharmonic vibrations is likely weak in the case of SrTiO₃, although this factor may be important in other materials that exhibit a high degree of anharmonicity. Despite extensive research to date concerning the Ti L_{2,3}-edge spectrum of SrTiO₃, important information regarding local distortion and local atomic vibrations may be missing. Because the work reported herein demonstrates that an advanced monochromated electron source combined with STEM-EELS can achieve high-energy-resolution analysis on an atomic scale, further application of this technique in materials science should be possible. In particular, determination of the Debye-Waller factors for local regions is expected to be viable, based on fitting experimental spectra with calculated spectra.

See the supplementary material for details regarding the simulation parameters, a comparison of O K-edge data, DOS data, and simulated spectra using different experimental thermal factors estimated by various processes.

This work was supported by a Kakenhi Grant-in-Aid (No. 19H02597) from the Japan Society for the Promotion of Science (JSPS).

AUTHOR DECLARATIONS

Conflict of Interest

The authors declare no competing interest.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

- ¹N. Nakagawa, H. Y. Hwang, and D. A. Muller, Nat. Mater. 5, 204 (2006).
- ²G.-Z. Zhu, G. Radtke, and G. A. Botton, Nature **490**, 384 (2012).
- ³F. S. Hage, G. Radtke, D. M. Kepaptsoglou, M. Lazzeri, and Q. M. Ramasse, Science **367**, 1124 (2020).
- ⁴F. S. Hage, D. M. Kepaptsoglou, Q. M. Ramasse, and L. J. Allen, Phys. Rev. Lett. **122**, 016103 (2019).
- ⁵O. L. Krivanek, T. C. Lovejoy, N. Dellby, T. Aoki, R. W. Carpenter, P. Rez, E. Soignard, J. Zhu, P. E. Batson, M. J. Lagos, R. F. Egerton, and P. A. Crozier, Nature 514, 209 (2014).
- ⁶M. J. Lagos, A. Trügler, U. Hohenester, and P. E. Batson, Nature 543, 529 (2017).
- ⁷E. Cockayne, E. L. Shirley, B. Ravel, and J. C. Woicik, Phys. Rev. B **98**, 014111 (2018).
- ⁸O. Durmeyer, J. P. Kappler, E. Beaurepaire, J. M. Heintz, and M. Drillon, J. Phys.: Condens. Matter 2, 6127 (1990).
- ⁹A. L. Ankudinov and J. J. Rehr, Phys. Scr. 2005, 24.
- ¹⁰C. Brouder, D. Cabaret, A. Juhin, and P. Sainctavit, Phys. Rev. B **81**, 115125 (2010).
- ¹⁰D. Manuel, D. Cabaret, C. Brouder, P. Sainctavit, A. Bordage, and N. Trcera, Phys. Rev. B **85**, 224108 (2012).

- ¹²Y. Matsui, K. Seki, A. Hibara, and T. Mizoguchi, Sci. Rep. **3**, 3503 (2013).
- ¹³H. Katsukura, T. Miyata, M. Shirai, H. Matsumoto, and T. Mizoguchi, Sci. Rep. 7, 16434 (2017).
- ¹⁴F. M. F. De Groot, J. C. Fuggle, B. T. Thole, and G. A. Sawatzky, Phys. Rev. B 41, 928 (1990).
- ¹⁵A. Ohtomo and H. Y. Hwang, Nature **427**, 423 (2004).
- ¹⁶D. Kan, T. Terashima, R. Kanda, A. Masuno, K. Tanaka, S. Chu, H. Kan, A. Ishizumi, Y. Kanemitsu, Y. Shimakawa, and M. Takano, Nat. Mater. 4, 816 (2005).
- ¹⁷A. Ohtomo, D. A. Muller, J. L. Grazul, and H. Y. Hwang, Nature **419**, 378 (2002).
- ¹⁸D. Kan, R. Aso, R. Sato, M. Haruta, H. Kurata, and Y. Shimakawa, Nat. Mater. 15, 432 (2016).
- ¹⁹M. Haruta, A. Nii, Y. Hosaka, N. Ichikawa, T. Saito, Y. Shimakawa, and H. Kurata, Appl. Phys. Lett. **117**, 132902 (2020).
- ²⁰D. De Ligny and P. Richet, Phys. Rev. B 53, 3013 (1996).
- ²¹X. Rui and R. F. Klie, Appl. Phys. Lett. 114, 233101 (2019).
- ²²M. Bugnet, G. Radtke, S. Y. Woo, G. Zhu, and G. A. Botton, Phys. Rev. B 93, 020102(R) (2016).
- ²³G. Panchal, R. J. Choudhary, S. Yadav, and D. M. Phase, J. Appl. Phys. 125, 214102 (2019).
- ²⁴M. Haruta, Y. Fujiyoshi, T. Nemoto, A. Ishizuka, K. Ishizuka, and H. Kurata, Ultramicroscopy **207**, 112827 (2019).
- ²⁵A. Uldry, F. Vernay, and B. Delley, Phys. Rev. B **85**, 125133 (2012).
- ²⁶R. F. Loane, P. Xu, and J. Silcox, Acta Crystallogr., Sect. A 47, 267 (1991).
- ²⁷W. Jauch and M. Reehuis, Acta Crystallogr., Sect. A 61, 411 (2005).
- ²⁸T. Tadano, Y. Gohda, and S. Tsuneyuki, J. Phys.: Condens. Matter 26, 225402 (2014).
- ²⁹T. Tadano and S. Tsuneyuki, Phys. Rev. B **92**, 054301 (2015).
- ³⁰K. Kimoto, T. Asaka, X. Yu, T. Nagai, Y. Matsui, and K. Ishizuka, Ultramicroscopy 110, 778 (2010).
- ³¹F. D. Groot, Coord. Chem. Rev. **249**, 31 (2005).
- ³²C.-O. Almbladh and L. Hedin, in *Handbook on Synchrotron Radiation*. edited by E. E. Koch (North-Holland, Amsterdam, 1983), Vol. 1, p. 635.
- ³³E. N. Maslen, N. Spadaccini, T. Ito, F. Marumo, and Y. Satow, Acta Crystallogr. B51, 939 (1995).
- ³⁴Y. A. Abramov, V. G. Tsirelson, V. E. Zavodnik, S. A. Ivanov, and I. D. Brown, Acta Crystallogr. B51, 942 (1995).
- ³⁵Y.-N. Wu, W. A. Saidi, J. K. Wuenschell, T. Tadano, P. Ohodnicki, B. Chorpening, and Y. Duan, J. Phys. Chem. Lett. 11, 2518 (2020).