Author Response to Reviews of

Lattice dielectric properties of rutile TiO_2: First-principles anharmonic self-consistent phonon study

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RC: ***Reviewer Comment***, AR: *Author Response*, □ Manuscript text

1. the First Referee

1.1. #1

RC: ***I understand the current method improves the phonon frequencies and linewidths significantly. How about the renormalization effect on eigenvectors? Take the phonon modes shown in Fig. 1 for example. How different are the eigenvectors obtained by harmonic calculations, SCPH, and SCPH+B, respectively?***

AR: First, in the current calculation, SCPH+B does not cause changes in eigenvectors because we do not include off-diagonal components of bubble self-energies. In the SCPH calculation, three E_u modes differ slightly from harmonic approximation, but at an almost negligible level. Renormalization of phonon eigenvectors is important when an imaginary phonon exists, but the influence is limited because rutile TiO_2 has no imaginary phonon.

1.2. #2

RC: ***In Table III, the harmonic B_{1u}^1 frequency by r^2SCAN agrees with the experiment much better than the anharmonic frequencies, no matter which method is used. This is also seen in the same optical branch along Gamma-M and Gamma-X in Fig. 3(a). Any idea why anharmonic frequencies agree with experiments worse than harmonic ones?***

AR: Because the Gruneisen parameter of this mode is positive, underestimating the lattice parameter leads to an overestimation of the frequency. From this point of view, it is natural that SCPH+B overestimates the frequency in the LDA. As for the r^2SCAN functional, we compared the potential energy surface of B_{1u}^1 phonon in Fig A1, which shows that the anharmonic calculation agrees better with DFT calculation than harmonic approximation. Deviation can be originated from DFT calculation itself, rather than our anharmonic calculation. Using more precise functional like hybrid functional can improve results.

1.3. #3

RC: ***In Fig. 3(b) and the first paragraph of Page 7, the authors indicated a generally good agreement between LDA and r^2SCAN phonon dispersions and LDAs overestimation of A_{2u} frequency due to its underestimation of volume (optimized at static zero pressure). I think it may be a better idea to compare LDA and r^2SCAN phonon dispersions at the same volume, say the experimental value, disregarding the calculated pressure. If that is the case, is LDA still good to use for vibrational properties calculations of TiO_2 and related materials?***

AR: When calculated with LDA using the r^2SCAN lattice constant, the $A_{2\mathrm{u}}$ mode becomes an imaginary phonon. If we use the experimental lattice constant, the frequency of the $A_{2\mathrm{u}}$ phonon is $146\,\mathrm{cm}^{-1}$, which is 15% smaller than the experimental value. These results indicate that there is strong volume dependence

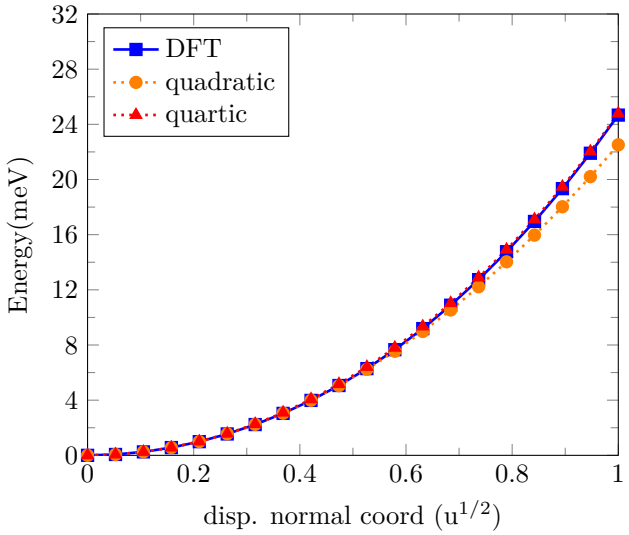

Figure A1: Frozen phonon potential (blue) of B_{1u} mode with x axis being the normal coordinate of B_{1u} phonon.

in the A_{2u} mode, and that r^{2}SCAN provides better results than LDA even if we use the experimental lattice constant.

1.4. #4

RC: ***In Table IV, except for the TO E_u^1 mode, the 4ph contribution to the rest of the phonon modes linewidth by the SCPH+B is not as significant as the bubble contribution, yet non-negligible. Whereas in the abstract, it is stated, We show that the four-phonon scattering process contributes as much as the third-order anharmonic term to phonon linewidths. Perhaps this statement can be improved.***

AR: The 4-ph contribution is as large as the bubble contribution only in TO E_u^1 and A_{2u} phonons. We've rewrited the statement to "We show that the four-phonon scattering process contributes as much as the third-order anharmonic term to phonon linewidths in some phonon modes."

2. the Second Referee

2.1. #1

RC: ***The temperature-dependent static dielectric constant in the x direction obtained by the SCPH+B method is in good agreement with the experimental data, while the difference in the z direction is very large (Fig. 5), which obviously should not be attributed to the bubble scattering. The authors need to discuss this issue.***

AR: Our calculation underestimates the static dielectric constant ϵ_0^z in low temperature. According to Eq. (3), the underestimation of ϵ_0^z is due to the overestimation of the frequency of A_{2u} phonon. The result indicate that our calculation overestimates the zero-point vibration in A_{2u} mode. Actually, Fig. A4 shows the large mode dependent contribution to the loop self-energy of A_{2u} phonon at 0 K. ($V(q = A_{2u}, -q = A_{2u}, q', -q')\frac{\hbar}{2\omega_{q'}}$) As shown in Fig. 4, our IFCs model reproduces the DFT calculations well, and the cause may lie in the DFT calculations.

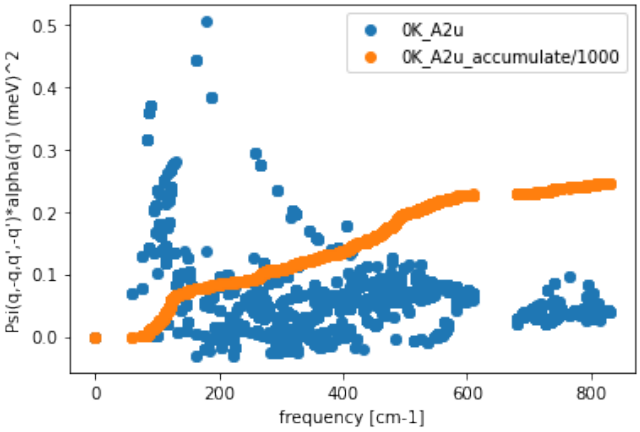

Figure A2: mode dependent contribution to the loop self-energy of A_{2u} phonon at 0 K. ($V(q = A_{2u}, -q = A_{2u}, q', -q') \frac{\hbar}{2\omega_{q'}}$

2.2. #2

RC: ***Although the SCPH+B is significant to correct the phonon frequency and phonon width for specific phonon modes, some typical modes, such as*** E_{3u} ***(***$26.5\,\mathrm{cm}^{-1}$***) and*** A_{2u} ***(***$16.2\,\mathrm{cm}^{-1}$***) listed in Table IV, have a larger deviation from experimental results (***$43.9\,\mathrm{cm}^{-1}$ ***and*** $46.4\,\mathrm{cm}^{-1}$***) compared with non-SC results (***$41.4\,\mathrm{cm}^{-1}$ ***and*** $30.4\,\mathrm{cm}^{-1}$***). Do phonon scattering processes beyond the bubble scattering play a major role?***

AR: Generally speaking, higher-order contribution is more important in the high frequency region such as LO E_{3u} and A_{2u} phonons. We could get better results by including higher-order diagrams, but higher-order calculations are difficult at this stage due to computational costs.

2.3. #3

RC: ***The contribution of the four-phonon scattering process to phonon linewidth is only significant for Eu1 and A2u modes. For other modes, however, the contribution of four-phonon scattering is much lower than the three-phonon scattering. Therefore, the statement of "We show that the four-phonon scattering process contributes as much as the third-order anharmonic term to phonon linewidths" in the abstract should be rewritten.***

AR: The 4-ph contribution is as large as the bubble contribution only in TO E_u^1 and A2u phonons. We've rewrited the statement to "We show that the four-phonon scattering process contributes as much as the third-order anharmonic term to phonon linewidths in some phonon modes."

2.4. #4

RC: ***Figure 3b demonstrates a good agreement between between LDA and*** r^2***SCAN throughout the Brillouin zone.The word "between" is repeated.***

AR: Thank you. I've corrected it.

3. the Third Referee

3.1. #1

RC: ***In Fig. 3(a), it looks like the harmonic (red) curve agrees better with experiment (orange dots). This is particularly clear with the lowest energy optical mode at the Gamma point. The authors instead write in the text: "The combination of the*** r^2***SCAN functional and the SCPH+B calculation agrees well with the experimental data", seemingly ignoring the better agreement with harmonic calculations for some modes? Along the same lines, from Table III a mixed picture emerges, where agreement with experiment is best for different combinations of theory depending on the mode. Can the authors comment on these points?***

AR: The Gruneisen parameter of this mode is positive, and underestimating the lattice parameter leads to an overestimation of the frequency. From this point of view, it is natural that SCPH+B overestimates the frequency in the LDA. As for the r^2SCAN functional, we compared the potential energy surface of B_{1u}^1 phonon in Fig. A3, which shows that the anharmonic calculation agrees better with DFT calculation than harmonic approximation. Deviation can be originated from DFT calculation itself, rather than our anharmonic calculation. Using more precise functional like hybrid functional can improve results.

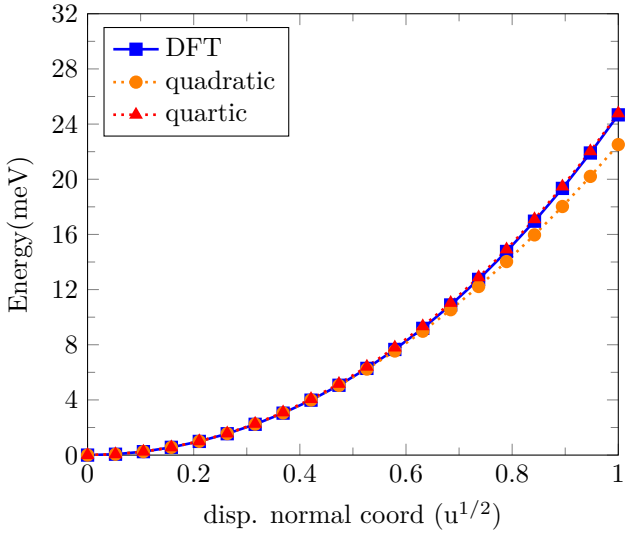

Figure A3: Frozen phonon potential (blue) of $B_{1\mathrm{u}}$ mode with x axis being the normal coordinate of $B_{1\mathrm{u}}$ phonon.

3.2. #2

RC: ***Can the authors speculate as to why the temperature dependence of*** ϵ_z ***is not well-reproduced in Fig. 5?***

AR: Our calculation underestimates the static dielectric constant ϵ_0^z in low temperature. According to Eq. (3), the underestimation of ϵ_0^z is due to the overestimation of the frequency of $A_{2\mathrm{u}}$, Fig. A4 shows the large mode dependent contribution to the loop self-energy of $A_{2\mathrm{u}}$ phonon at 0 K. ($V(q = A_{2u}, -q = A_{2u}, q', -q')\frac{\hbar}{2\omega_{q'}}$) As shown in Fig. 4, our IFCs model reproduces the DFT calculations well, and the cause may lie in the DFT calculations.

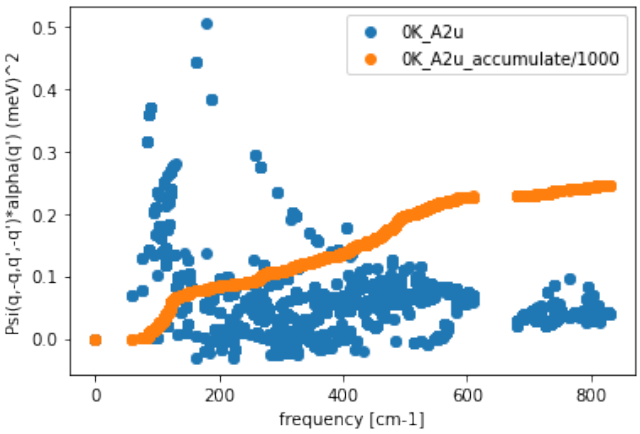

Figure A4: mode dependent contribution to the loop self-energy of A_{2u} phonon at 0 K. ($V(q = A_{2u}, -q = A_{2u}, q', -q') \frac{\hbar}{2\omega_{q'}}$

3.3. #3

RC: ***More generally, the authors show that four-phonon processes are important, sometimes comparable to three-phonon process. Based on this, could the authors justify stopping at four-phonon processes? What role could higher-order processes play?***

AR: Generally speaking, higher-order contribution is more important in high frequency region as in LO E_{3u} and A_{2u}. We guess that including higher-order correction can improve the results for lifetime of these two modes in Table IV, but higher-order calculations are difficult at the present stage due to computational costs. In facts, it is common to terminate the calculation at the fourth-order anharmonic term in many anharmonic phonon studies.