

Supporting Information for “Enhanced in-plane ferroelectricity, antiferroelectricity, and unconventional 2D emergent fermions in quadruple-layer XSbO₂ (X= Li, Na)”

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I. PHONON SPECTRA FOR DIFFERENT STRUCTURES OF QL-LiSbO₂

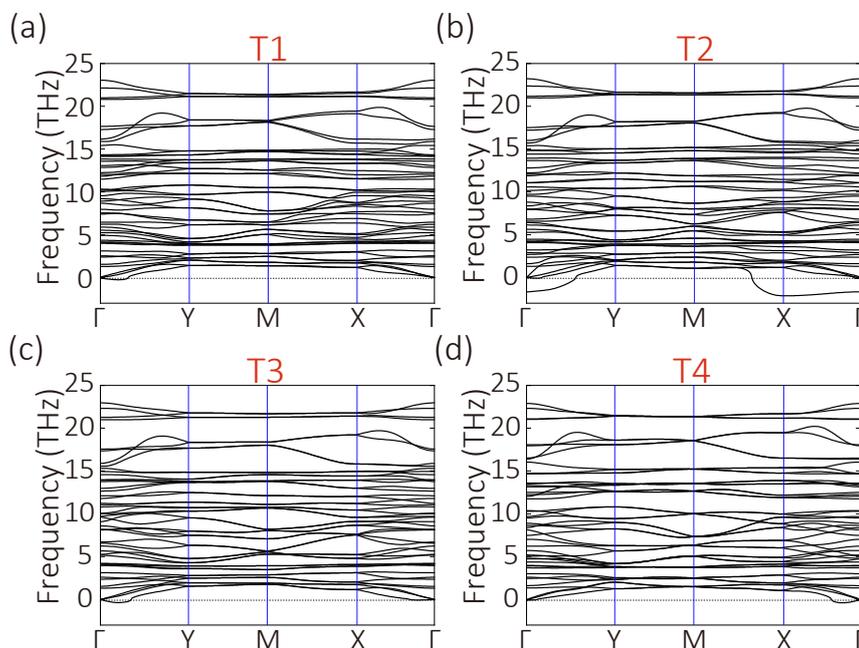


FIG. S1: Phonon spectra of QL-LiSbO₂ for (a) T1, (b) T2, (c) T3 and (d) T4 structures, respectively. There exists no imaginary frequency for the T1, T3 and T4 structures, but a pronounced soft optical phonon mode at X for the T2 structure.

II. PHONON SPECTRA FOR DIFFERENT STRUCTURES OF QL-NaSbO₂

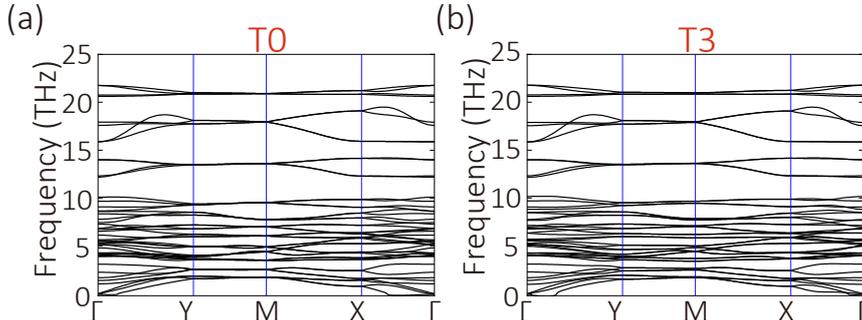


FIG. S2: Phonon spectra of QL-NaSbO₂ for (a) T0 and (b) T3 phases, respectively. There is no imaginary frequency for both the structures, indicating their dynamic stability.

III. ROOM-TEMPERATURE FERROELECTRICITY

Ab-initio molecular dynamics (AIMD) simulations are employed to study the robustness of ferroelectricity in T0 QL-XSbO₂, as usually applied to analyze the ferroelectric robustness in many 2D ferroelectric materials. Particularly, the polarization decreases as temperature increases because the polar distortion tends to be suppressed when approaching the phase transition temperature, at which the polarization value represents a sizable change. In other words, the preservation of spontaneous polarization during a sampled time range at a specific temperature definitely demonstrate the ferroelectric stability at this given temperature. The simulations are performed on a $4 \times 4 \times 1$ supercell at 300 K in the NVT ensemble, and is lasted for 2.5 ps with a 0.5 fs time resolution. The strength of spontaneous polarization can be represented by evaluating the average ionic displacement using $dy = \frac{1}{N} \sum_{i=0}^n (y_{X_i} - y_{O_i})$, where dy indicates the coordinate differences along the armchair direction between the nearest neighbor X (Li) and O ions, and N is the total number of ion pairs in the supercell. The results are shown in Fig. S3, we plot the averaged polarization $\langle P \rangle$ as a function of time t , which has been normalized with respect to $\langle P \rangle_{t=0} = P_S$. One finds that the averaged spontaneous polarization is maintained at 300 K, demonstrating the room-temperature ferroelectricity.

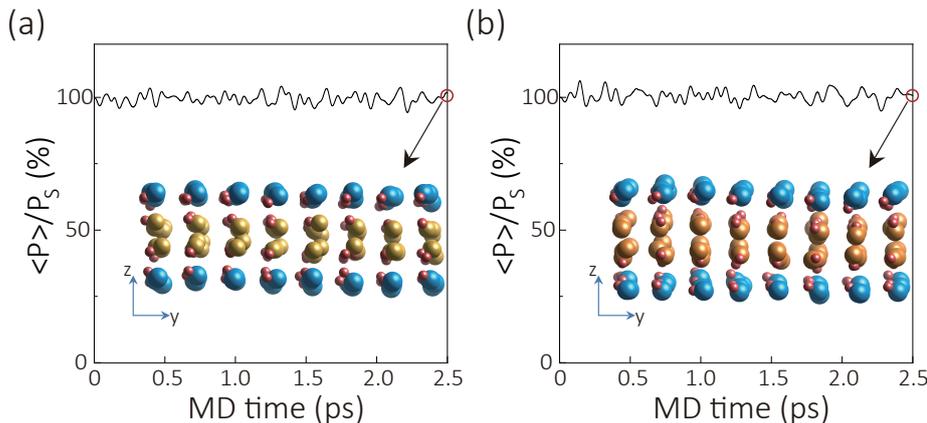


FIG. S3: Time dependence of averaged polarization obtained by the AIMD simulation for (a) T0 QL-LiSbO₂ and (b) T0 QL-NaSbO₂, respectively. The insets illustrate the snapshots of the corresponding geometric structures at 300 K after 2.5 ps.

IV. AIMD SIMULATIONS FOR THE METASTABLE PHASES OF QL-LiSbO₂

The temperature above which the metastable phases are stable depends on the barrier energy of their transition to other phases. A larger transition barrier usually suggests the stability at a higher temperature. To check the stability of metastable structures of QL-LiSbO₂ at room-temperature, we have performed the AIMD simulation at 300 K for T1 and T4 phases. The simulations are performed on a $4 \times 4 \times 1$ supercell at 300 K in the NVT ensemble, and is lasted for 8 ps with a 1.0 fs time step. The results are shown in Fig. S4. For T1 phase [see Fig. S4(a-b)], one observes that the averaged ionic displacement of LiO soon fades as the time increases, whereas that of SbO remains almost unchanged with opposite polarities in top and bottom SbO atomic layers. After 1 ps, the system has been transitioned to the AFE phase, i.e., T3 phase. In comparison, the averaged ionic displacement of LiO for T4 phase starts changing its sign initially, indicating the beginning of polarization reversal in LiO atomic layer. In the process, the averaged ionic displacement of SbO is preserved. At 2 ps, the polarization reversal of LiO atomic layer is finished, finally reaching a stable structure, i.e., the ground T0 phase [see Fig. S4(c-d)]. Therefore, these metastable T1 and T4 phases are unstable at room-temperature. Nevertheless, they might be able to persist their main structures at a lower temperature, as demonstrated by the MD results at 200 K (see Fig. S5).

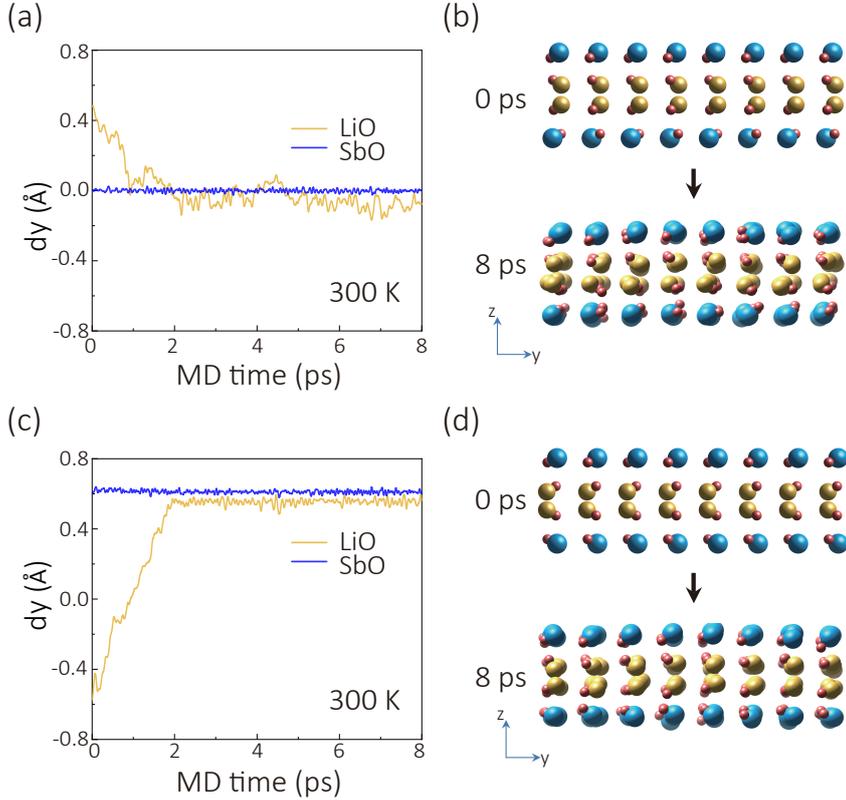


FIG. S4: Time dependence of averaged ionic displacement obtained by the AIMD simulation for (a) T1 and (c) T4 QL-LiSbO₂ at 300 K, respectively. Structure snapshots of the corresponding geometric structures at 300 K after 0 ps (top) and 8 ps (bottom) for (b) T1 and (d) T4 QL-LiSbO₂, respectively.

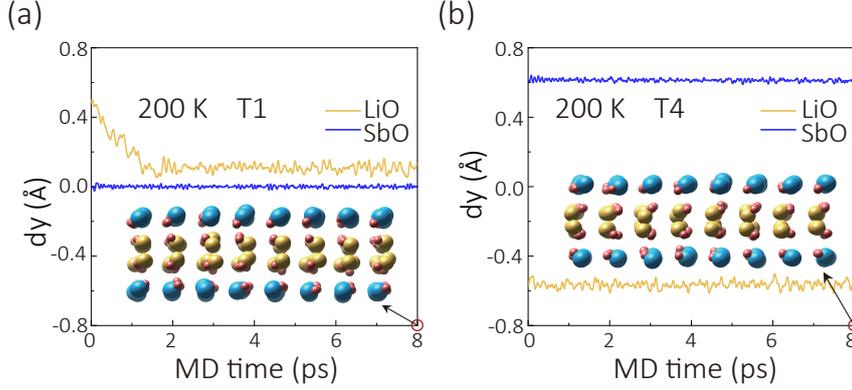


FIG. S5: Time dependence of averaged ionic displacement obtained by the AIMD simulation for (a) T1 and (c) T4 QL-LiSbO₂ at 200 K, respectively. The insets are the structure snapshots of the corresponding geometric structures at 200 K after 8 ps.

V. POSSIBLE KINETIC PATHWAY FOR POLARIZATION REVERSAL IN QL-XSbO₂

In order to obtain the lowest transition barrier to reverse the polarization in QL-LiSbO₂, we check the possible kinetic pathways during the reversal process. The results are illustrated in Fig. S6. One finds that both the overall activation barriers given by the two possible pathways are above 500 meV/u.c., which is larger than the value (469 meV/u.c.) in the main text.

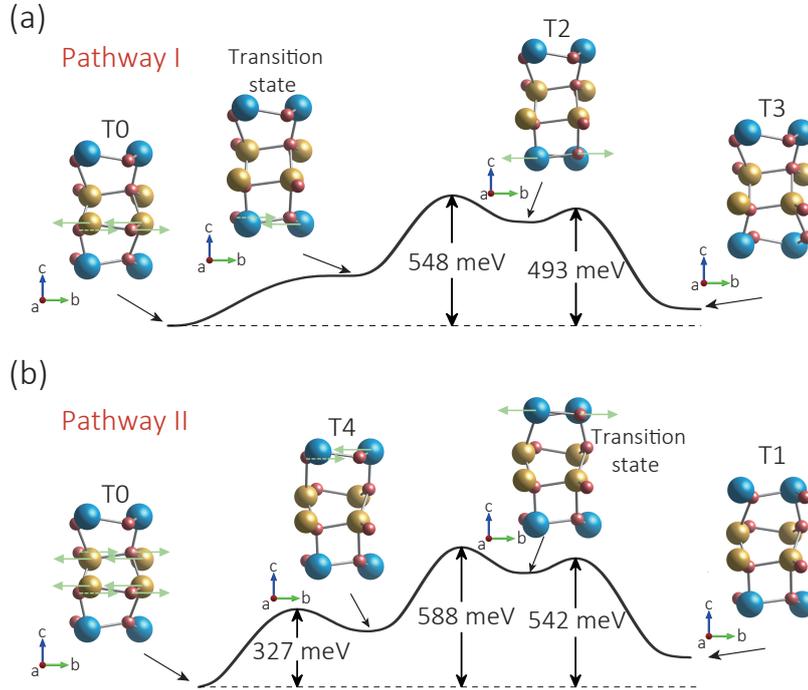


FIG. S6: Energy profile of the possible effective kinetic pathway for polarization reversal in QL-LiSbO₂. The lattice constants are fixed to the relaxed values of the FE T0 phase during this process. (a) Energy profile of transition from the ground FE T0 phase to the AFE T2 phase, which undergoes the unstable T2 phase. (b) Energy profile of transition from the ground FE T0 phase to the metastable FE T1 phase, during which the metastable FE T4 phase is undergone firstly. The green arrows attached to atoms refer to the directions of atomic motion.

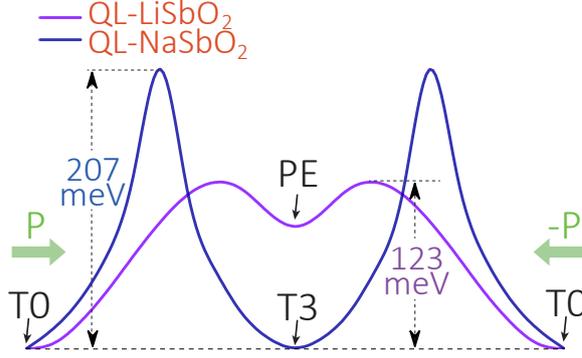


FIG. S7: Kinetics pathways of polarization reversal processes for T0 QL-XSbO₂, during which all the structural parameters are fully relaxed. The green arrows indicate the polarization orientations.

VI. BAND STRUCTURES FOR T0 AND T3 QL-NaSbO₂

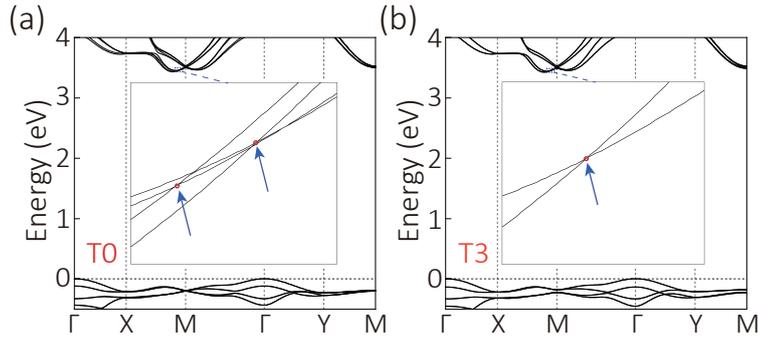


FIG. S8: Band structures with SOC considered for (a) T0 and (b) T3 QL-NaSbO₂, respectively. The zoomed-in images of low-energy spectrum around the crossing points are plotted in the inset, which indicate a 2D hourglass type-II NL for the T0 phase and a 2D type-II spin-orbit Dirac point for the T3 phase, respectively.

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