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Supplementary Material for: DFT Molecular Dynamics and Free Energy Analysis of a Charge Density Wave Surface System

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I. DFT METHODS

Figure S1 shows the energy profile as a function of Δz for the transition path between the $2\sqrt{3}\times\sqrt{3}$ CDW distortion and the $\sqrt{3}\times\sqrt{3}$ geometry ($\Delta z = 0$), as calculated using the plane-waves code (QE) and the local-orbital code used in the DFT-MD simulations (FIREBALL: FB). In the FB calculations we have used the LDA exchange-correlation functional and norm-conserving pseudopotentials [1]. Although the exchange-correlation functionals used in FB and QE are different, the important point is that the code used in the DFT-MD simulations (FB) yields a good fitting to the QE results. We also mention that the FB energy profile in Figure S1 is obtained for the same unit-cell and k-point sampling as used in the DFT-MD simulations ($2\sqrt{3} \times 2\sqrt{3}$ unit-cell and (2×2) MP grid).

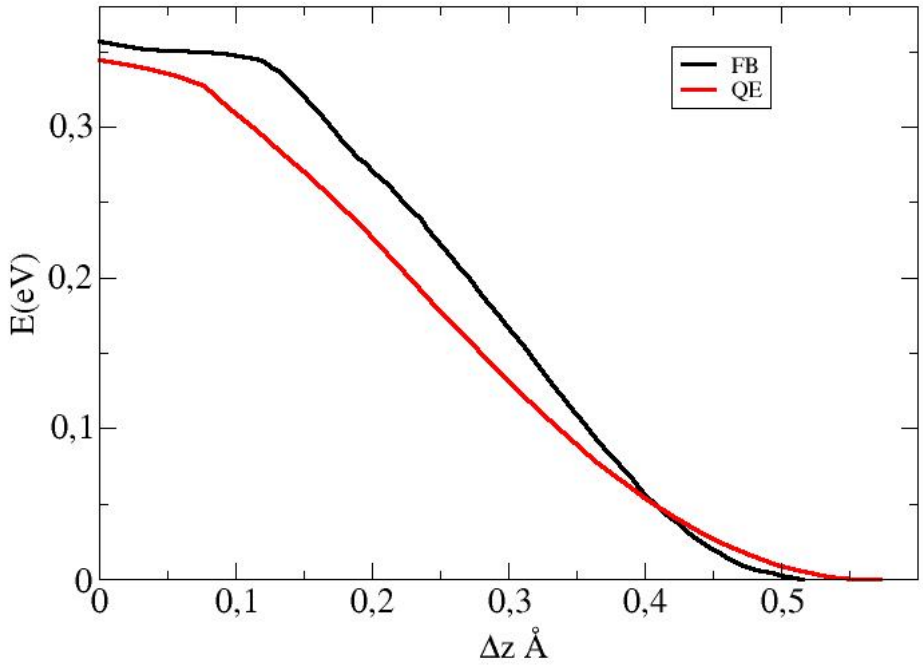

FIG. S1. Energy profile as function of Δz between the $\sqrt{3} \times \sqrt{3}$ geometry ($\Delta z = 0$) and the $2\sqrt{3} \times \sqrt{3}$ CDW geometry ($\Delta z \sim 0.5$ Å).

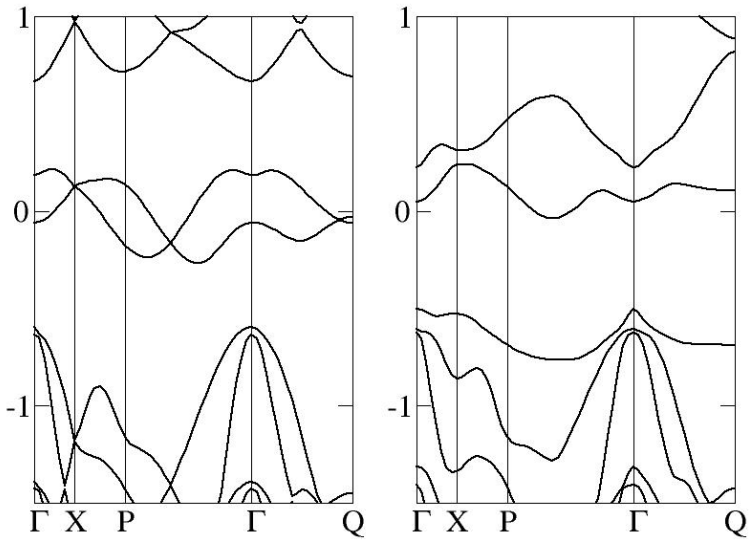

FIG. S2. Electronic energy bands (in eV) for the (a) K/Si(111):B-$\sqrt{3} \times \sqrt{3}$ and (b) $2\sqrt{3} \times \sqrt{3}$ surfaces, as calculated using the FIREBALL code.

Figure S2 shows the electronic energy bands for the $\sqrt{3} \times \sqrt{3}$ and (b) $2\sqrt{3} \times \sqrt{3}$ surfaces, as calculated using the FB code. A comparison of this figure with the bands calculated using QE (Figure 2 in the manuscript) shows a good agreement for the occupied bands (and also for the first unoccupied band). Notice that the calculation of total energies and forces in the DFT-MD simulations only depends on the occupied bands.

All these results show that the FB code yields an accurate description of the energetics associated with the CDW distortion, and thus can be used with confidence for the DFT-MD simulations and free energy calculations discussed in our work.

II. K DIFFUSION ON THE SURFACE

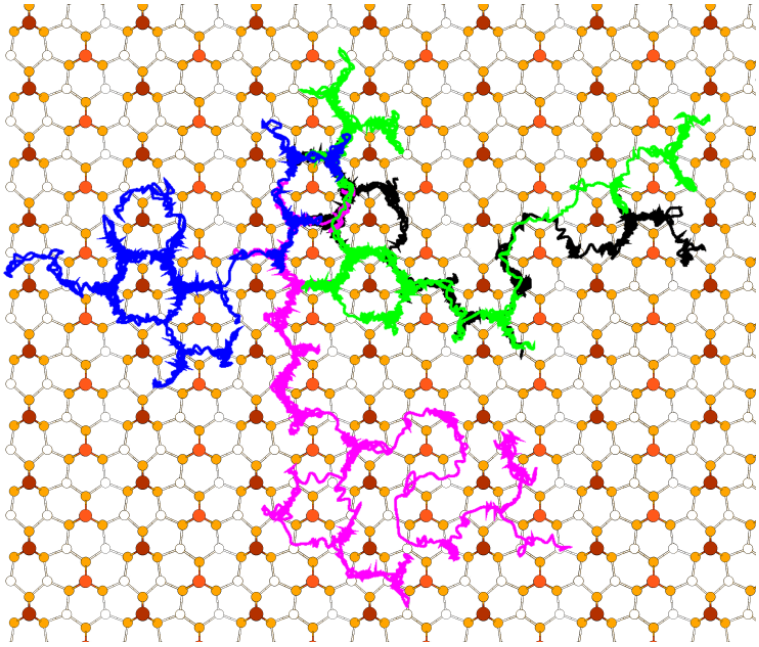

FIG. S3. Motion of the K atoms on the Si(111):B surface.

Figure S3 shows the motion of the 4 K atoms initially located in the central $2\sqrt{3} \times 2\sqrt{3}$-unit cell, for T = 450 K during $\sim$ 700 ps. The K atoms move on the surface along the lines of a honeycomb pattern, surrounding the Si adatoms. During the simulation time of $\sim$ 700 ps the 4 K atoms initially in the central unit-cell have moved several unit cells away from the central one. Although these simulations are performed using a periodic unit-cell (*i.e.* when one K atom is leaving the unit-cell in one side, another K atom is entering the unit-cell in the opposite side), this result is indicative of the important diffusive motion of the K atoms on this surface.

III. CALCULATION OF w_0 FROM THE DFT-MD SIMULATIONS

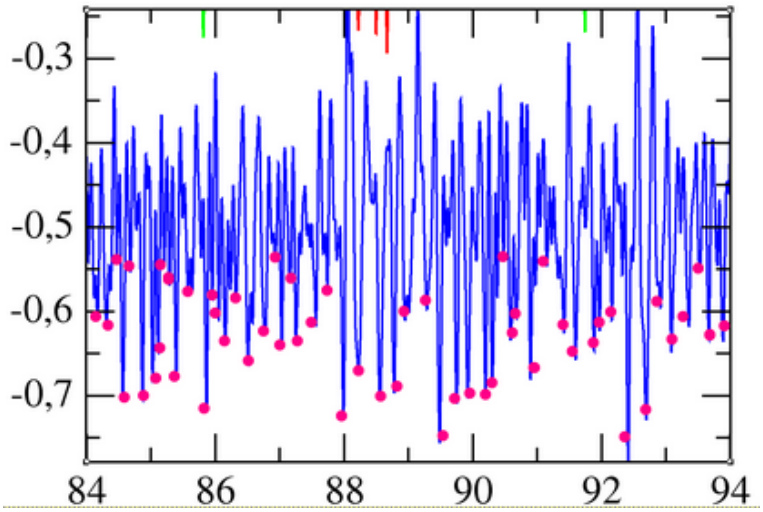

FIG. S4. Zoom of Figure 3(d) (T = 600K).

Figure S4 shows a zoom of Figure 3(d) (T = 600K) for the interval $t = [84, 94]$ ps showing the oscillations of $\beta(t)$. This figure illustrates the determination of the frequency w_0 in the Hubbard-Holstein hamiltonian from the DFT-MD simulations. The red dots indicate the different oscillations.

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[1] M. Fuchs and M. Scheffler, Comput. Phys. Commun. **119**, 67 (1999).