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Ab Initio Simulations of the (101) Surfaces of Potassium Dihydrogenphosphate (KDP)

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Abstract: We have used density functional calculations to examine the (101) surfaces of KDP, under vacuum, nitrogen, and aqueous conditions, and these simulations are found to agree well with nanoscale experimental studies demonstrating that the density functional calculations are providing a good description of the surfaces of this complex inorganic salt.

Wolfgang Pauli is famously quoted as suggesting “God made solids ... but surfaces were the work of the Devil”.¹ This statement reflects the immense difficulties faced by experimentalists when characterizing surfaces. As a result of this paucity of experimental data, computer simulations have been at the forefront of surface research. In the field of inorganic salts, one of the major triumphs was the prediction of extensive surface relaxation on the basal plane of alumina first by interatomic potential based calculations² and then by quantum mechanical simulations.^{3–5} These predictions were confirmed by experiment very much later.^{6,7} Similarly, good agreement has been obtained on the (001) surface of MgO. However, attention of the modeling community has turned to surfaces of complex salts, and yet to our knowledge there has been almost no direct validation of quantum mechanical simulations with experimental data for complex inorganic surfaces. This has been caused by both the lack of experimental data available, due to their nonconducting nature, and the complexity of the calculations. Recent advances in parallel efficiency and linear scaling algorithms now make it possible to simulate larger and more complex systems using quantum mechanics.⁸ KDP is an example of a complex inorganic solid, and the structure of the (101)

surface has been well characterized in a number of recent experimental studies.^{9–12}

There has only been a small number of ab initio molecular modeling studies reported for KDP. The bulk structure of KDP has been examined in several recent studies^{13–15} using density functional theory (DFT). The only reported theoretical study of the surfaces of KDP has been by Stack et al.¹⁶ They used DFT to study the (100) surface of KDP, in particular relating to the adsorbing/detaching of growth units. Surface X-ray diffraction (SXRD) studies have examined the relaxation of atoms on the (101) surfaces of KDP, under aqueous conditions.^{9,10} Recent SXRD studies on KDP surfaces in aqueous solution^{11,12} suggest that there are several icelike ordered water layers on the surface. Thus we have used DFT calculations to examine relaxations of the (101) surface of KDP and compared our results to these recent experimental studies.

At room temperature, KDP forms a paraelectric phase in the tetragonal *I42d* space group.¹⁷ KDP undergoes a phase transition at 122 K to a ferroelectric (FE) phase in the orthorhombic *Fdd2* space group.¹⁷ For easier comparison to the paraelectric phase, we used the body-centered *C_{2v}*¹⁹ I-setting space group as described by Baur.¹⁸

Density functional calculations on KDP were carried out using the SIESTA code.^{19,20} The generalized gradient approximation has been employed for all calculations, using the functional of Perdew, Burke, and Ernzerhof.²¹ Core electrons have been represented by norm-conserving pseudopotentials of the form proposed by Troullier and Martins.²²

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Table 1. Surface Energies for the Two Surface Terminations of the (101) Surface of KDP

surface termination	surface energy (J/m ²)
H ₂ PO ₄ ⁻	0.80
K ⁺	0.54

The valence electron configurations used were 1s¹, 2s²2p³, 2s²2p⁴, 3s²3p³, and 3p⁶4s¹ for H, N, O, P, and K, respectively. A double- ζ basis set with polarization functions was used for all atoms except oxygen, which had a triple- ζ basis set with polarization functions. The Brillouin zone was sampled using a $3 \times 3 \times 3$ Monkhorst-Pack \mathbf{k} -grid. The localized basis set in SIESTA consists of numerical atomic orbitals, which are radially confined to an extent that induces an energy shift in each orbital of 0.01 Ry. Hartree and exchange-correlation energies were evaluated on a uniform real space grid of points with a defined maximum kinetic energy of 200 Ry.

The bulk structure of KDP was relaxed at zero Kelvin, and then the (101) surface was generated using the GDIS program.²³ There are two possible ways to cut the (101) surface: one produces a cation (K⁺) terminated surface and the other produces a dihydrogenphosphate (H₂PO₄⁻) terminated surface. Surface slabs were created using a $1 \times 1 \times 4$ supercell, with a vacuum gap of approximately 26 Å. Relaxed surface configurations were generated by keeping the cell vectors fixed and only allowing the atom positions to relax, with calculations being run for both possible surface terminations. These calculations were then repeated using no vacuum gap. Surface energies were calculated for each surface termination using the following expression

$$E_{\text{surf}} = (E_{\text{slab}} - E_{\text{equiv bulk}})/2A$$

where E_{surf} is the surface energy, E_{slab} is the energy of the surface slab with a vacuum gap, $E_{\text{equiv bulk}}$ is the energy of the surface slab with no vacuum gap, and A is the surface area. E_{surf} is divided by two because each slab has two equivalent surfaces.

The use of $E_{\text{equiv bulk}}$, rather than an integer number of E_{bulk} , allows for maximum cancellation of errors relating to sampling and convergence for the different sized simulation cells. Two nitrogen molecules were added to the relaxed surface, and the system was relaxed to generate the nitrogenated surface configuration. A similar approach was taken to generate the hydrated surface configuration, by adding 12 water molecules onto the relaxed vacuum surfaces, and the system was then relaxed again.

The relaxed bulk structure for KDP matched closely to that from previous calculations, with the cell volume within 1.5% of the experimental value. Surface energies were calculated for each surface termination of the (101) surface, and the results are reported in Table 1. From the surface energy calculations, the cation (K⁺) terminated (101) surface appears significantly more stable than the H₂PO₄⁻ terminated surface. SXRD studies^{9,10} of KDP have experimentally determined that the (101) surface is indeed cation terminated.

The reason the cation terminated surface is the most stable can be rationalized in terms of the relative surface area of

Table 2. Translational Relaxations of Species at the (101) Surface of KDP

	translational relaxations (Å)	
	K ⁺	H ₂ PO ₄ ⁻
	Experimental Studies	
nitrogenated ^a	-0.13 ± 0.03	+0.12 ± 0.04
aqueous solution ^b	+0.10 ± 0.05	+0.04 ± 0.05
	Theoretical Calculations ^c	
vacuum	-0.25 (-0.27,-0.23)	+0.12 (+0.18,+0.06)
nitrogenated	-0.27 (-0.29,-0.25)	+0.14 (+0.06,+0.22)
hydrated	+0.14 (+0.17,+0.11)	+0.08 (0.00,+0.16)

^a Reference 12. ^b References 9 and 10. ^c The average relaxation is reported for the theoretical calculations, with actual relaxations reported in parentheses.

the two surface terminations. In a crystal with isotropic interactions, the surface energy is proportional to the surface area of the exposed surface. The greater the surface area, the more energy that is required to create it. Using the GDIS program,²³ we calculated the molecular surface (the surface defined by the van der Waals spheres of the surface atoms) of the two surface terminations. The reported areas were 114 Å² for the cation terminated surface and 157 Å² for the anion terminated surface. Thus if the interactions within the KDP crystal were isotropic, we expect the anion terminated surface to have a surface energy 1.37 times higher than the cation terminated surface. The calculated surface energy of the anion terminated face is actually 1.48 times higher, suggesting that this simple model is a good approximation. In short, the cation terminated surface is more stable because it is much less corrugated than the anion terminated surface.

The surface relaxations of the cation terminated surface of KDP was then measured. We used the approach taken in the experimental studies of de Vries et al.,⁹⁻¹⁰ where a H₂PO₄⁻ ion was treated essentially as a fixed group, and movements of the central atom in this group (phosphorus) were measured. The displacements of atoms (in the z direction) have been measured by comparing the positions in the relaxed and unrelaxed surfaces. These are reported in Table 2, with a negative (-) displacement referring to inward relaxation and a positive (+) displacement referring to an outward relaxation. Two relaxation values are reported for each particular surface species. This is because there are two symmetry independent H₂PO₄⁻ and K⁺ species on each surface, because of the hydrogen ordering in the orthorhombic phase at zero Kelvin. As the differences in interatomic distances between the orthorhombic and tetragonal phases are small, we believe that the average of our values should match closely with the experimental value, without recourse to the exceedingly compute expensive density functional molecular dynamics calculations that would be required to include the effect of temperature. The relaxed vacuum, nitrogenated, and hydrated (101) surfaces are illustrated in Figures 1-3, respectively.

The calculated vacuum and nitrogenated surface trends match the experimental trend found under nitrogen conditions, with the K⁺ ion displacing toward the surface and the H₂PO₄⁻ displacing away from it. De Vries et al.¹⁰ have examined the surfaces of KDP under high vacuum, but the

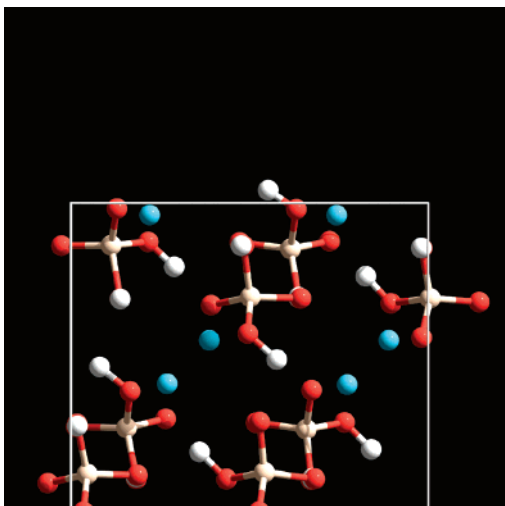


Figure 1. Relaxed vacuum (101) surface of KDP. Note: for this image and subsequent images, red = oxygen, orange = phosphorus, white = hydrogen, dark blue = nitrogen, and light blue = potassium.

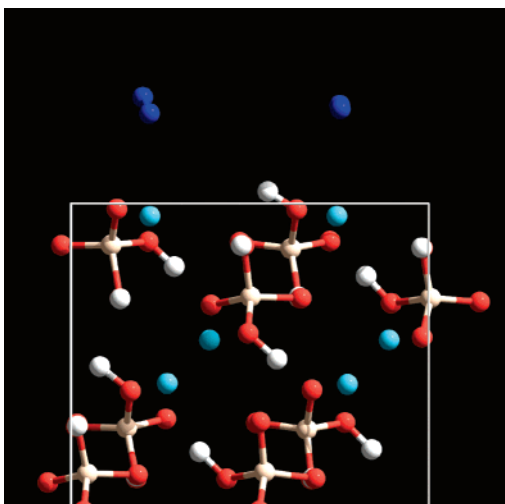


Figure 2. Relaxed nitrogenated (101) surface of KDP.

surface quality was found to change over time making it impossible to accurately determine the surface relaxation.

Comparing the experimental and nitrogenated surface relaxations, the magnitudes of relaxation compare favorably although vary slightly for K^+ , with calculations producing an relaxation of -0.27 \AA , while experiments reported a value of -0.13 \AA .

We then performed calculations on a hydrated surface of KDP, using explicit water molecules, to produce a surface that would closely match the aqueous conditions reported in experiments. For the hydrated surface, the calculated surface trend matches that found experimentally under aqueous conditions, with both the K^+ and $H_2PO_4^-$ ions having an outward relaxation. The magnitudes of relaxation are also quite similar, although slightly larger in the calculations. When we examined the hydrated surface, we found that there were a number of strong hydrogen bonds formed between the $H_2PO_4^-$ ions and the surface water molecules, with typical hydrogen bond lengths of $1.5\text{--}1.9 \text{ \AA}$. Density functional calculations are known to overestimate

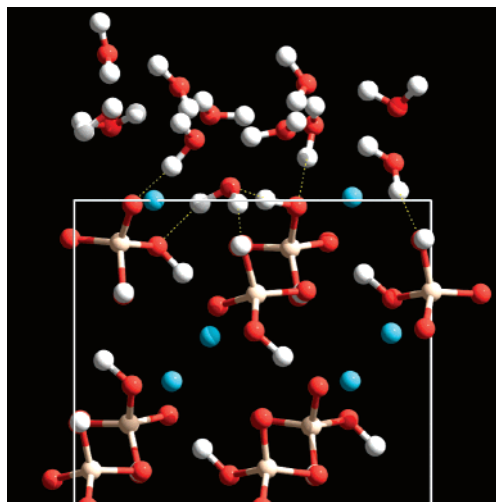


Figure 3. Relaxed hydrated (101) surface of KDP. Hydrogen bonds between water molecules and the surface are indicated with dashed lines.

the strength of hydrogen bonds,²⁴ so this could explain why the $H_2PO_4^-$ ions have a slightly larger outward relaxation in our calculations. There is potentially a range of configurations for water on the surface, and ideally molecular dynamics calculations should be run. However, for the present paper, we have examined two configurations and taken the lowest in energy (the energy difference was small). These calculations were carried out at zero Kelvin, while the experimental values are measured at room temperature. This could also account for some of the differences in magnitudes.

Overall, the good match between calculated and experimental results suggests that density functional calculations can provide accurate simulations of the structures of complex inorganic surfaces.

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