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Comment

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Comment on Parts 1 and 2 of the Series "Electric Double Layer at the Rutile (110) Surface"

M. Předota*,†,‡ and L. Vlček§

Department of Medical Physics and Biophysics, University of South Bohemia, Jírovcova 24, České Budějovice 370 04, Czech Republic, Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 165 02 Prague, Czech Republic, and Department of Chemical Engineering, Vanderbilt University, Nashville, Tennessee 37235-1604

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We comment on an error in the real part of the Coulombic interaction (evaluated using the Ewald summation) between flexible atoms on a TiO_2 surface, that is, the mutual interaction of flexible bridging and terminal O and H atoms, and the interaction of these atoms with surface Ti and O atoms, which are kept rigid. This contribution to the intermolecular force acting on these atoms was by a factor of r_{ij} smaller compared to the correct value, where r_{ij} is the intermolecular distance. Due to internal dimensionless units, this factor was 0.31−4.0. The code used to produce the results published in refs 1 and 2 and appearing also in ref 3 was affected by this error. The error affects only simulations of the hydroxylated surfaces. The neutral nonhydroxylated surface features flexible bridging O atoms and the negatively charged nonhydroxylated surface features also flexible terminal OH groups; however, the mutual interactions of these groups are limited due to their large interatomic separations, and therefore, the error was negligible on these surfaces.

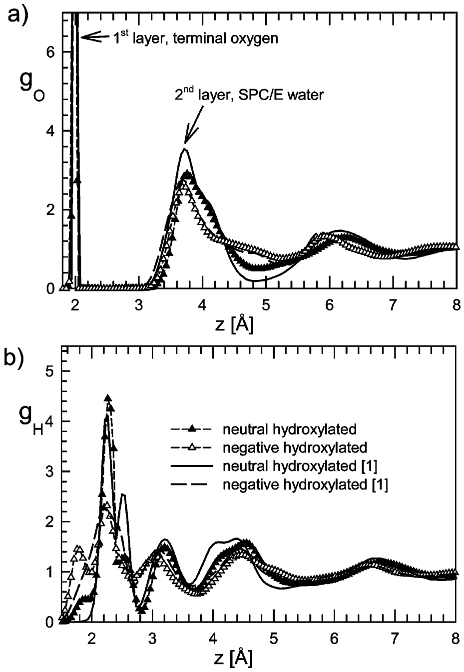

Figure 1. Axial density profiles of oxygen (top) and hydrogen (bottom) at neutral and negative hydroxylated surfaces. For comparison, the originally published curves, indicated by "[1]", are also shown.

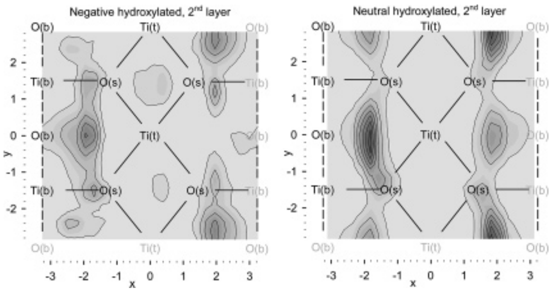

Figure 2. Contour plots of the lateral density profiles of water molecules in the second layer at the hydroxylated surface. Darker color means higher density.

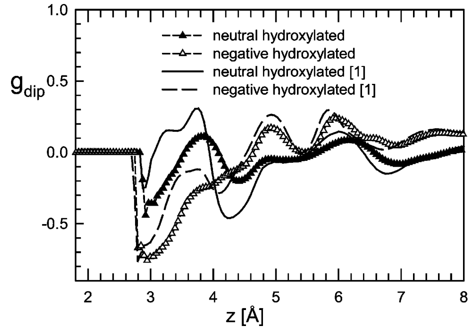

Figure 3. Average cosine of the dipole vector with the inward (pointing towards the bulk water) surface normal. For comparison, the originally published curves, indicated by "[1]", are also shown.

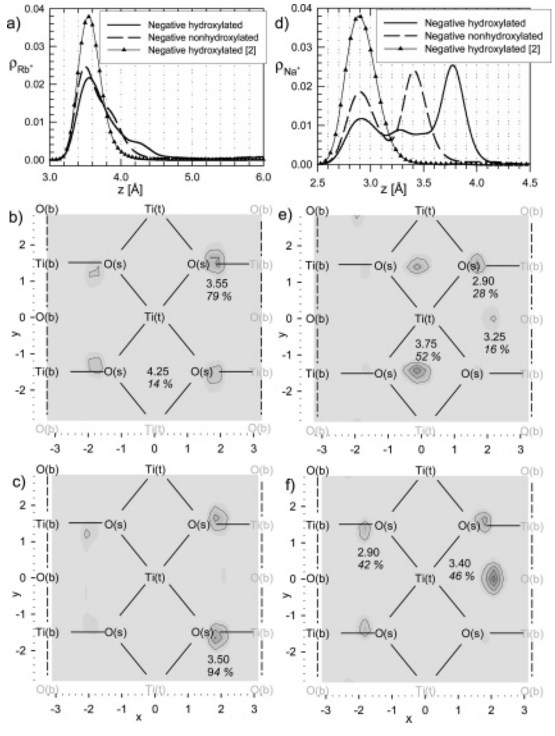

Figure 4. Adsorption of Rb^+ (left column) and Na^+ (right column): axial density profiles of cations for all negative surfaces (a and d) and lateral density profiles of cations at negative hydroxylated (b and e) and negative nonhydroxylated (c and f) surfaces. The labels on the lateral profiles indicate the height and occupancy of a particular adsorption site.

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* Corresponding author. E-mail: predota@icpf.cas.cz.
† University of South Bohemia.
‡ Academy of Sciences of the Czech Republic.
§ Vanderbilt University.

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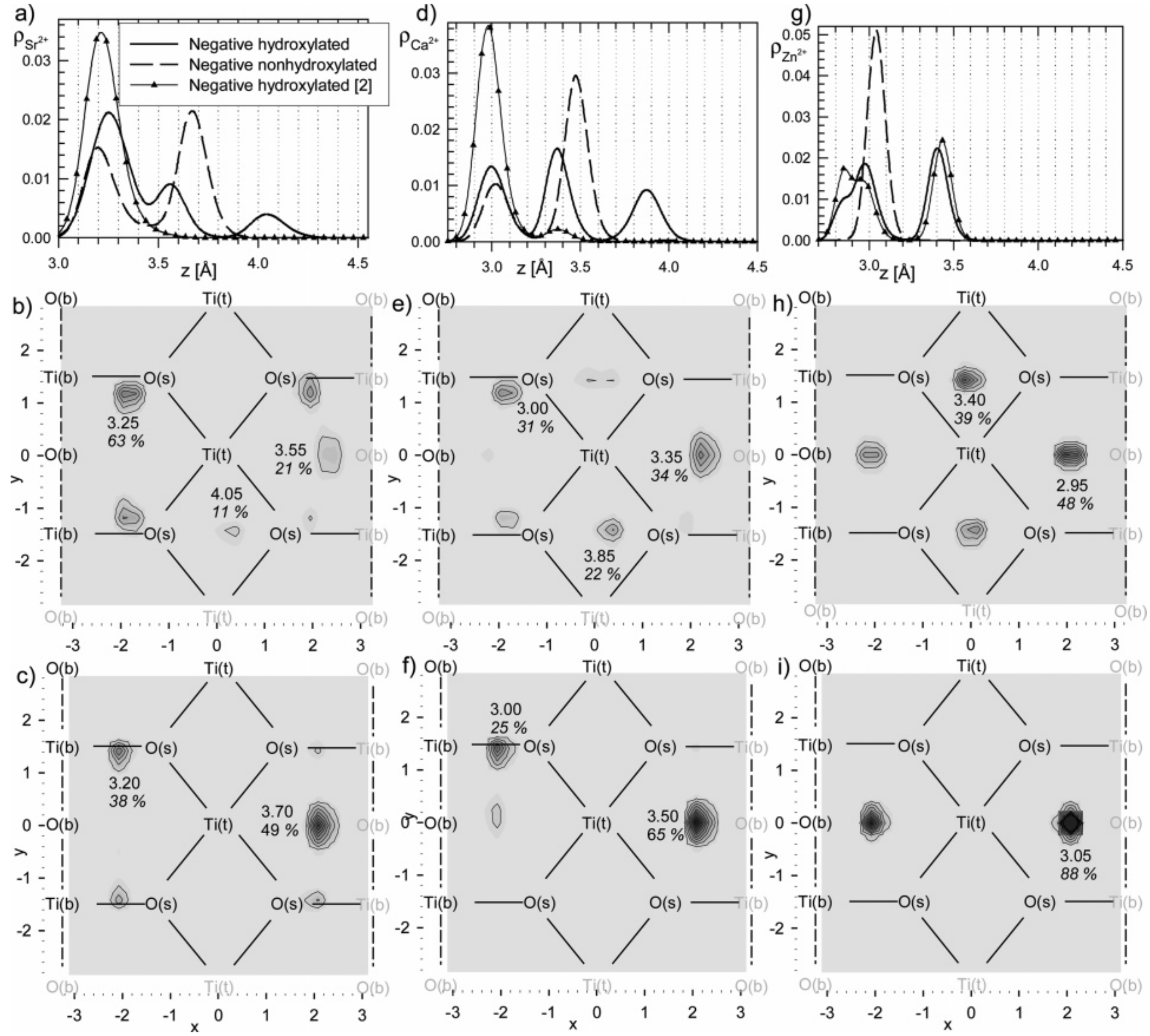

Figure 5. Adsorption of Sr^{2+} (left column), Ca^{2+} (middle column), and Zn^{2+} (right column): axial profiles for all negative surfaces (a, d, and g) and lateral profiles at negative hydroxylated (b, e, and h) and negative nonhydroxylated (c, f, and i) surfaces.

TABLE 1: Tetradentate (TD) and Bidentate (BD) Adsorption Sites of Ions as Observed in MD Simulations and X-ray Experiments

	adsorption site					
		MD hydroxylated		MD nonhydroxylated		X-ray[3]
ion	type	height, *z* (Å)	occupancy (%)	*z* (Å)	occupancy (%)	*z* (Å)
Rb^{+}	TD	3.55	79	3.50	58	3.44 ± 0.03
Rb^{+}	BD-BOTO	4.25	14[a]	3.90	36	*b*
Rb^{+}	BD-TOTO	4.25	14[a]	*b*	*b*	*b*
Na^{+}	TD	2.90	28	2.90	42	*c*
Na^{+}	BD-BOTO	3.25	16	3.40	46	*c*
Na^{+}	BD-TOTO	3.75	52	*b*	*b*	*c*
Sr^{2+}	TD	3.25	63	3.20	38	3.07 ± 0.07
Sr^{2+}	BD-BOTO	3.55	21	3.70	49	*b*
Sr^{2+}	BD-TOTO	4.05	11	*b*	*b*	*b*
Ca^{2+}	TD	3.00	31	3.00	25	*c*
Ca^{2+}	BD-BOTO	3.35	34	3.50	65	*c*
Ca^{2+}	BD-TOTO	3.85	22	*b*	*b*	*c*
Zn^{2+}	TD	*b*	*b*	*b*	*b*	*b*
Zn^{2+}	BD-BOTO	2.95	48	3.05	88	3.12 ± 0.14[d]
Zn^{2+}	BD-TOTO	3.40	39	*b*	*b*	2.6 ± 0.25

[a] Both BD-BOTO and BD-TOTO sites are present at the same height. [b] Site not observed by X-ray or MD. [c] Experimental data not available. [d] Site identified as monodentate adsorption to BO by X-ray standing wave measurements.

This error affected the axial density profile of H atoms along the surface normal direction at the hydroxylated surfaces (both neutral and charged), Figure 4 of ref 1, and average dipole orientation, Figure 6 of ref 1; see Figures 1−3. The effect on the oxygen axial density profiles is much smaller but still observable. The effect on the electrostatic properties, Figure 7 of ref 1, is hardly noticeable and therefore is not shown.

The error also affected the derived distribution of ions at hydroxylated surfaces. Its effect is minor on Rb^+ and Zn^{2+} ions; however, for Na^+, Ca^{2+}, and Sr^{2+}, the adsorption is significantly altered, with adsorption at sites not originally observed for the hydroxylated surface. The axial and lateral density profiles of cations are given in Figures 4 and 5, correcting Figures 2, 4, and 5 of ref 2. The axial profiles at both hydroxylated and nonhydroxylated surfaces are given, with the incorrect previously published data for hydroxylated surfaces indicated as “hydroxylated [2]” for comparison. The lateral density profiles are shown for the corrected negative hydroxylated surface and the negative nonhydroxylated surface. The data for the latter surface are identical to those published previously. The comparison of adsorption results on both types of surfaces shows that after correction the adsorption patterns on both types of surfaces are more similar than previously reported. Comparison of the derived ion distributions for Zn^{2+} and Sr^{2+} for both surfaces with X-ray determined ion locations[3] suggests that the hydroxylated surface remains the more realistic model of the actual rutile surface. The difference between the two surfaces results in different coverages of various adsorption sites rather then their positions, as given in Table 1 and Figures 4 and 5. The sites are identified as the tetradentate site (TD), the bidentate site between bridging (BO) and terminal (TO) oxygen atoms (BD-BOTO), the bidentate site between two TO atoms (BD-TOTO), and the bidentate site between two BO atoms (BD-BOBO). The occupancy is calculated as the percentage of adsorbed ions in a given adsorption site relative to the number of ions in the region 0−7 Å from the rutile surface.

The results in ref 4 were obtained with the corrected code.

References and Notes

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