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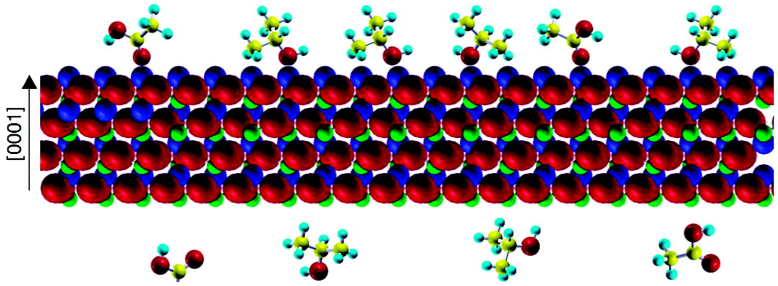

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Using Ferroelectric Poling to Change Adsorption on Oxide Surfaces

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Abstract: Adsorption has been invoked to explain many phenomena in ferroelectric materials including the unanticipated stability of ultrathin ferroelectric films; however, the intrinsic surface properties of ferroelectric oxides have been largely unexplored. Therefore, the effect of ferroelectric poling on the adsorption/desorption of two polar molecules, acetic acid and 2-propanol, and one nonpolar molecule, dodecane, on $LiNbO_3(0001)$ was compared. The two polar molecules were found to adsorb significantly more strongly on the positive surface. Temperature-programmed desorption (TPD) data yielded desorption pre-exponentials of the two polar molecules more than 11 orders of magnitude lower than expected. Ferroelectric materials are also intrinsically pyroelectric, and it is shown that the unusually low desorption pre-exponentials can be explained by temperature dependent heats of adsorption that result from changes in the surface dipole as the samples are heated. This conclusion was supported by dodecane adsorption/desorption, which was independent of polarity with normal desorption pre-exponentials. The differences between the polar and nonpolar molecules indicate that interactions between polar molecules and ferroelectric surfaces are dominated by electrostatics. It is shown that adsorption energy differences between positive and negative surfaces are large enough to switch the polarity of ferroelectric thin films.

1. Introduction

In analogy to ferromagnets, ferroelectric materials develop remnant macroscopic electric fields that can be switched by applying an external field.[1] This unique property has attracted interest in using ferroelectric oxides as gates in field effect transistors for nonvolatile memory and instant-on computing.[2−4] The magnitude of the field has also enabled new types of field effect devices, such as the superconducting switch where changing the polarization direction of a ferroelectric gate induces a normal to superconducting transition of an underlying thin film of a high-temperature superconductor.[5,6] The field, or alternatively spontaneous polarization, in ferroelectric materials is due to a lack of inversion symmetry along one crystallographic direction. As a result, ferroelectric surfaces are polar and are expected to have high surface energies.[7] Therefore, it has been suggested that, below a critical thickness, thin films of ferroelectric oxides would become paraelectric, thus limiting the ability to scale down ferroelectric devices.[8,9] Despite these expectations, it has been shown that $PbTiO_3$ films just three unit cells thick remain ferroelectric.[10] This paradox has been attributed to adsorption passivating the surface of the ferroelectric phase. Further, since opposite charges must be passivated on the positive and negative surfaces, it has been suggested that the poling direction of thin films should depend on the types of molecules in the surrounding ambient.[10] Thus, ferroelectric chemical sensors can be envisioned where adsorption switches the polarization of a thin ferroelectric gate of a field effect device. Alternatively, for thicker samples, it has been anticipated that it should be possible to switch adsorption and catalytic properties by applying an external field; some success in this area has been reported.[11,12] Despite the fundamental and practical implications of the surface chemistry of ferroelectric materials, there has been little detailed, fundamental experimental work in this area. In this paper, it will be shown that the adsorption strengths of polar molecules depend strongly on poling direction, and that desorption of polar molecules from ferroelectric surfaces is characterized by highly unusual desorption kinetics that can be associated with the pyroelectric behavior of ferroelectric materials.

The impact of ferroelectric poling on the surface chemical properties of ferroelectric oxides was characterized by comparing temperature-programmed desorption (TPD) data for two polar molecules, acetic acid and 2-propanol, and one nonpolar

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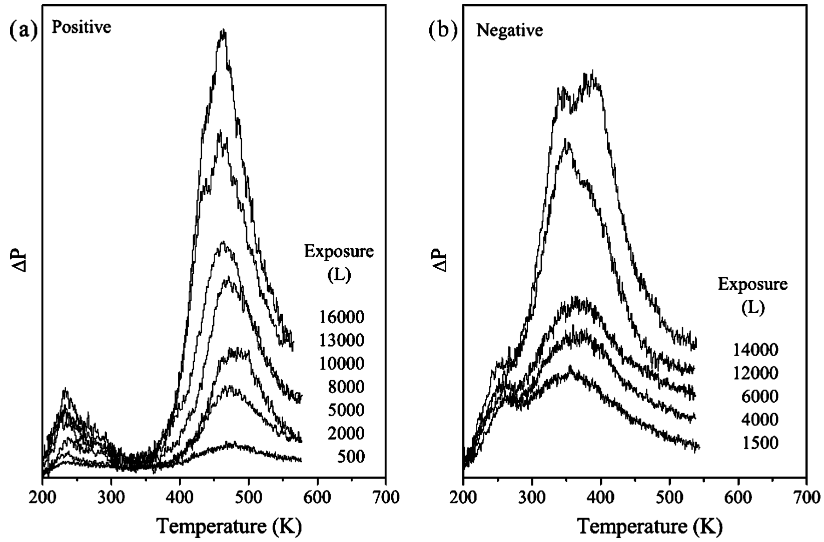

Figure 1. Temperature-programmed desorption curves for acetic acid on (a) positively and (b) negatively poled $LiNbO_3(0001)$ surfaces. The data were collected using a heating rate of 1 K/s while monitoring the signal at $m/q = 42$ (CH_2CO^+) for acetic acid. Acetic acid desorbs molecularly from both surfaces; however, the desorption peak temperature is ~101 K higher on the positive surface, indicating that acetic acid adsorbs more strongly on the positive surface.

molecule, dodecane, on $LiNbO_3(0001)$ surfaces. The $LiNbO_3$ structure closely resembles the corundum structure except with half of the cations Li and the other half Nb.[1] Below the 1470 K Curie temperature,[13] the cations segregate into Li and Nb planes in the [0001] direction, thus breaking the inversion symmetry of the corundum structure along [0001]. Although the clean, polar (0001) surfaces were expected to reconstruct, we recently showed that the positive and negative surfaces give only (1 × 1) surface diffraction patterns.[14] In addition, low-energy ion scattering from both surfaces was dominated by scattering from oxygen atoms.[14] These results were explained by an adatom/vacancy model in which oxygen anions adsorb on top of Nb cations on one side of the crystal, whereas anion vacancies are created on the opposite side.[14] Roughly one oxygen adatom (vacancy) per unit cell would cancel the divergent electrostatic surface energy of the polar orientation, accounting for the observed (1 × 1) periodicity. Meanwhile, the oxygen adatoms cover the Nb cations on one side of the crystal, yielding an essentially oxygen-terminated surface; the vacancies, on the other hand, expose Li cations that are difficult to detect with low-energy ion scattering. It will be shown that electrostatic interactions of the polar molecules with the ferroelectric surfaces are largely responsible for differences in adsorption strengths on the oppositely poled surfaces rather than structural differences between the two surfaces.

2. Experimental Section

Experimental details have been described in detail previously.[15] Briefly, experiments were performed using an ultrahigh vacuum (UHV) chamber equipped with a differentially pumped microwave electron cyclotron resonance plasma source (Tectra, Gen II Plasma Source), an X-ray source, a cylindrical mirror analyzer, and a quadrupole mass spectrometer. Samples were 8 mm× 6 mm× 0.5 mm thick plates of nearly stoichiometric $LiNbO_3$ obtained from Almaz Optics. The samples were polished on one side and were oriented to within 0.25° of (0001). The $+z$ direction was determined by sandwiching the crystals between Si electrodes and measuring the sign of the voltage deflection when the samples were mildly heated with a heat gun (ferroelectric materials develop a voltage when their temperature is changed due to the pyroelectric effect).[1] Samples were smoothed by annealing in flowing air at 1073 K for 5 h as described by Saito et al.[16] The temperature was measured using a chromel−alumel thermocouple attached to the front face of the sample using a ceramic adhesive. The primary contaminant on the surface visible with X-ray photoelectron spectroscopy after introduction into the UHV system was C, which was removed by heating the sample in an oxygen plasma at 575 K for 1 h.

Adsorbates were exposed to the sample through a capillary array doser attached to a leak valve. The effective pressure in front of the doser was 80 times higher than the background pressure; all doses reported in this paper take this factor into account. Thermal desorption was performed line-of-sight with the sample positioned ~1 mm from the front of a cone fitted around the ionizer of the mass spectrometer. The mass spectrometer was differentially pumped by a 30 L/s ion pump and a non-evaporable getter pump rated at 70 L/s. The mass-to-charge ratios for the TPD runs were selected based on preliminary temperature-programmed mass spectra in which the complete mass spectra were repeatedly, rapidly collected while the sample temperature was ramped.

3. Results

The different interaction of polar molecules with the positive and negative surfaces of ferroelectric materials was revealed in TPD of acetic acid and 2-propanol from $LiNbO_3(0001)$. The molecules were exposed to the surface at ~190 K. Comparison of temperature-programmed mass spectra with mass spectra obtained when acetic acid and 2-propanol were leaked into the chamber revealed that desorption produced only the cracking fragments expected for acetic acid and 2-propanol in proportions consistent with molecular desorption. Therefore, neither molecule appreciably reacted with either $LiNbO_3(0001)$ surface. As shown in Figure 1a, acetic acid desorption from the positive surface was dominated by a peak at ~475 K; the weaker feature at ~240 K was attributed to desorption from the Ta wires on the sample holder. Meanwhile, the TPD results in Figure 1b

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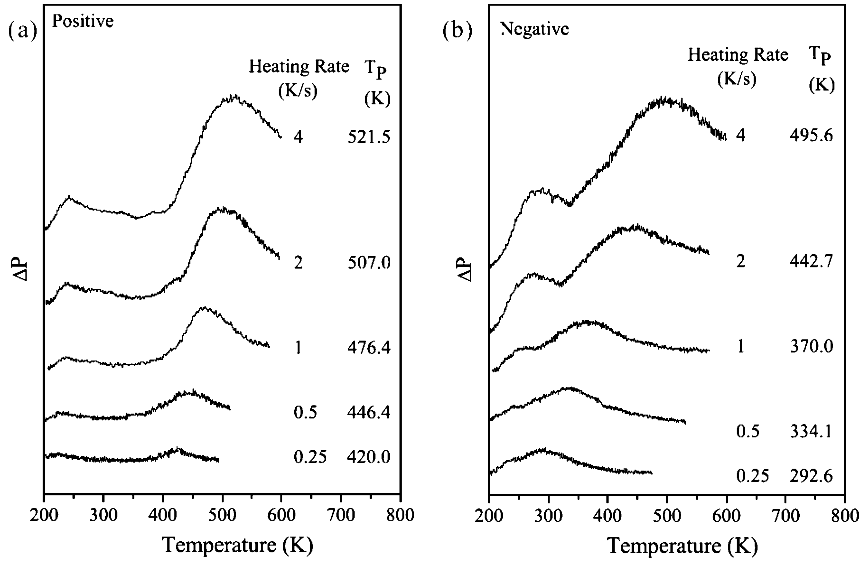

Figure 2. Comparison of acetic acid TPD curves recorded as a function of heating rate for (a) positively and (b) negatively poled $LiNbO_3(0001)$ surfaces. The acetic acid exposures were 8000 and 6000 L for the positively and negatively poled surfaces, respectively. The heating was stopped at ~600 K to prevent the severe desorption of Li_2O from the sample surface region.[14]

show that acetic acid desorption from the negative surface was dominated by a desorption peak centered at 370 K, ~100 K lower than the positive surface. On both surfaces, additional peaks began to appear at high exposures (>10 000 L). It has been shown that adjacent carboxylic acid groups adsorbed on metal oxide,[17] metal,[18] and graphite[19] surfaces form hydrogen bonds to one another that can lead to multiple desorption peaks at high coverages.[17] Thus, the coverage dependence, in particular the higher temperature peak seen on the negative surface near saturation, was attributed to attractive hydrogen bonding interactions as the adsorbed molecules moved closer together. The curves indicate that at 190 K relatively high exposures were required to saturate the surfaces, close to 10 000 L for the both the positive and negative surfaces. Although it was not possible to quantify the exact saturation coverage, the saturation coverage on the positive surface was roughly 20% higher than the negative surface. The initial sticking coefficient was estimated to be of the order 10^{-4} by assuming that one molecule adsorbs per surface unit cell at saturation on the positive surface. We recently reported very similar results for 2-propanol:[15] a 110 K higher desorption peak temperature for the positive surface, initial sticking coefficients on the order of 10^{-4}, and a 30% higher saturation coverage at 190 K for the positive surface; however, the coverage dependence was somewhat simpler for 2-propanol, which may reflect weaker hydrogen bonding interactions for the alcohol.

The desorption peak temperatures for the two polar molecules were over 100 K higher on the positive surface than on the negative surface, indicating much stronger adsorption on the positive surface. To quantify the difference in adsorption strength, TPD curves were recorded as a function of heating rate. Figure 2 shows a comparison of the heating rate dependence of the acetic acid TPD curves for the positive and negative surfaces. The desorption peaks shifted to higher temperatures, by 101 K for the positive surface and 203 K for the negative surface, as the heating rate was increased from 0.25 to 4 K/s. These shifts are much larger than expected or are generally observed.[20] For example, first-order desorption with a typical pre-exponential of 10^{13} s^{-1} and a 125 kJ/mol desorption activation energy would give a desorption peak temperature that shifts only from 440 K at 0.25 K/s to 480 K at 4 K/s. Still, the large shifts were not the result of experimental artifacts: the leading edges of the curves lie on top of each other, as would be expected. Rather, the unusually large dependence of the desorption peak temperature appears to reflect the intrinsic properties of how $LiNbO_3(0001)$ surfaces interact with polar molecules. A similarly strong dependence on heating rate was observed for 2-propanol.[15] In this case, the desorption peaks shifted to higher temperatures by 170 K for the positive surface and 219 K for the negative surface as the heating rate was increased from 0.25 to 4 K/s.

If the observed differences between the adsorption and desorption of 2-propanol and acetic acid from the positively and negatively poled $LiNbO_3(0001)$ surfaces are dominated by differences in electrostatic interactions between the molecules and the two surfaces, then adsorption of nonpolar molecules should be unaffected by the poling direction. Further, if the ferroelectric properties of $LiNbO_3$ play a role in the unusually strong peak temperature dependence on heating rate, then nonpolar molecules should display a normal temperature dependence. To test these ideas, the adsorption/desorption of dodecane on positively and negatively poled $LiNbO_3(0001)$ was studied using TPD. Comparison of temperature-programmed mass spectra with the expected cracking pattern for dodecane indicated that desorption was solely molecular. The results in Figure 3 show that dodecane adsorption/desorption from the two surfaces was in fact very similar. In both cases, two peaks can be seen: a peak at 253 K that saturates at ~40 L and a peak at 230 K that does not saturate. The position of the lower-temperature peak was consistent with multilayer desorption,[20] and so the peak at 253 K was assigned to the monolayer. The

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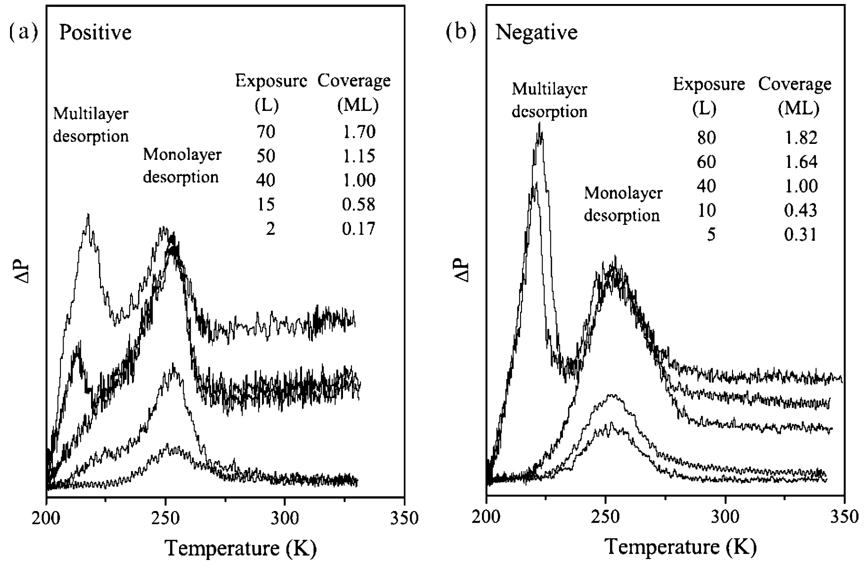

Figure 3. Comparison of dodecane desorption from (a) positively and (b) negatively poled $LiNbO_3(0001)$ surfaces. The data were collected using a heating rate of 1 K/s while monitoring the mass spectrometer signal at $m/q = 43$ ($C_3H_7^+$) for dodecane. A monolayer (1 ML) was defined as the dodecane coverage when the TPD peak at 253 K saturated.

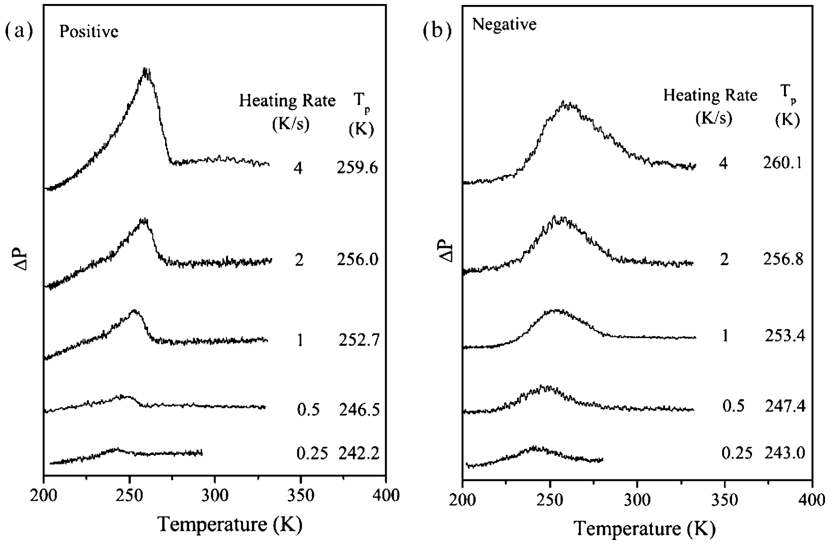

Figure 4. Dodecane TPD curves for different heating rates for (a) positively and (b) negatively poled $LiNbO_3(0001)$ surfaces at 1 ML dodecane coverage.

monolayer peak for the negative surface was slightly broader with a tail extending to ~285 K. The broader desorption peak on the negatively poled surface was also observed for acetic acid and 2-propanol. It could be due to a temperature gradient across the negative sample during heating. Unfortunately, the precision with which the insulating samples could be mounted cannot preclude temperature gradients, though repeating some of the runs after remounting the sample, did not narrow the peak. Nonetheless, it is clear that the peak positions for nonpolar dodecane were unaffected by ferroelectric poling. The effect of heating rate on dodecane desorption is illustrated in Figure 4. It is immediately obvious in Figure 4 that, in this case, when the heating rate was changed by a factor of 20, the peak temperature changed only modestly, by 17 K. This reinforces the conclusion that experimental artifacts were not responsible for the large changes seen for acetic acid and 2-propanol. More importantly, this finding links the unusually strong dependence on heating rate for acetic acid and 2-propanol to electrostatic interactions between the polar molecules and the ferroelectric surfaces.

Kinetic parameters for desorption can be obtained from the peak temperature dependence on heating rate. For all three of the molecules studied, the desorption peak temperatures did not shift with coverage until either multilayers formed in the case of dodecane or hydrogen bonding interactions became significant for acetic acid. A coverage-independent peak temperature is indicative of first-order desorption. For first-order desorption, the kinetic parameters can be obtained from the slope and intercept of a plot of the log of β/T_P^2 vs $1/T_P$ where β is the heating rate and T_p is the desorption peak temperature;[21] the slope corresponds to $-E/R$ and the intercept corresponds to $\nu R/E$ where R is the molar gas constant, ν is the desorption pre-exponential, and E is the desorption activation energy, or minus the heat of adsorption for nonactivated adsorption. Figure 5 shows the peak temperatures for acetic acid (Figure 2),

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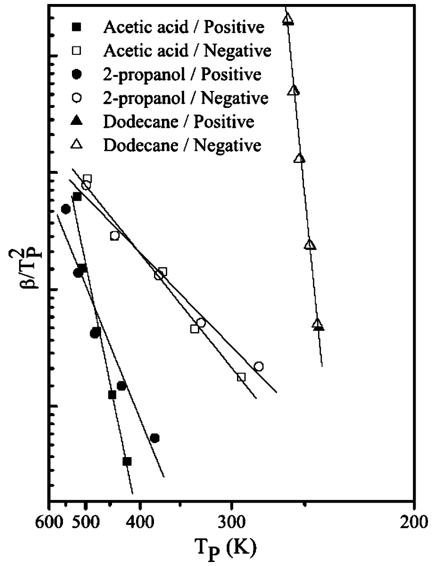

Figure 5. Log-scale plot of β/T_p^2 versus T_p for the desorption of acetic acid, 2-propanol, and dodecane from positively and negatively poled $LiNbO_3(0001)$ surfaces. The straight lines indicate linear fits that were used to estimate the desorption activation energies and pre-exponentials.

2-propanol,[15] and dodecane (Figure 4) plotted this way for the positively and negatively poled surfaces. The first thing to note in Figure 5 is that the points for dodecane on the positive and negative surfaces lie almost directly on top of each other, again illustrating that the poling direction does not affect the desorption of the nonpolar molecule. For dodecane, the slope indicates a desorption activation energy of 77.3 kJ/mol whereas the intercept yields a pre-exponential of 10^{15} s^{-1}. Although this pre-exponential is somewhat higher than the typically expected 10^{13} s^{-1},[21] the value is in accord with pre-exponentials observed for long chain alkanes on other surfaces.[20] The high pre-exponential has been attributed to an increase in configurational entropy in going from the adsorbed state to the transition state.[20] In contrast to dodecane, the data points for 2-propanol and acetic acid differ widely on the positive and negative surfaces. For both polar molecules, the slope is steeper for the positive surface, again indicating a higher desorption activation energy for polar molecules from the positive surface. Interestingly, for acetic acid, the intercepts suggest pre-exponentials of order 10^2 and 10^{-1} s^{-1} on the positive and negative surfaces, respectively. Meanwhile, for 2-propanol, the pre-exponentials are of the order 10^0 s^{-1} for the positive surface and 10^{-1} s^{-1} for the negative surface. These numbers are all more than *11 orders of magnitude smaller* than the typical value for small molecules.

4. Discussion

The normal pre-exponential for dodecane suggests that the unphysically low apparent desorption pre-exponentials for the polar molecules are related to how these molecules interact with ferroelectric surfaces. Determining the kinetic parameters from the variation in TPD peak temperature with heating rate relies on the assumption that the desorption activation energy is independent of temperature. Ferroelectric materials, however, are also pyroelectric;[22] that is, their spontaneous polarization decreases with increasing temperature.[23] The ferroelectric effect creates polar surfaces that would have divergent electrostatic surface energies in the absence of passivation.[24] Since stable (1 × 1) surfaces were observed prior to adsorption,[14] the surfaces must have been passivated during surface preparation by, for example, formation of oxygen anion vacancies on the negative side of the crystal and oxygen ad-anions on the positive side. As the samples are heated during TPD experiments, however, the spontaneous polarization decreases, resulting in surface charge densities in excess of those required to screen the field due to the bulk polarization. If relaxation is not instantaneous, an electric field will build up at the surface. This effect can be large. The spontaneous polarization of stoichiometric $LiNbO_3$ is 80 $\mu C/cm^2$ at room temperature,[25] suggesting a compensating charge density of 1.15 e/surface unit cell. If the compensating charges are within a few Ångstroms of the surface, the surface dipole will be ∼1 e Å. Although the $LiNbO_3$ pyroelectric coefficient is only -0.004 $\mu C/cm^2$ K,[23] the imbalance between the surface charges and the bulk polarization can rapidly create large surface dipoles: for the 0.5 mm thick samples used in this work, the increase in surface dipole would be 285 e Å/K if no relaxation took place. If acetic acid and 2-propanol adsorption are driven by their interactions with the surface dipole, then a temperature-dependent heat of adsorption, and thus desorption activation energy, would be expected. Using a linear relationship between the desorption activation energy and temperature as a first approximation, that is, $E = E_0 + \alpha(T - T_0)$ where T_0 is a reference temperature, E_0 is the desorption activation energy at T_0, and α is a proportionality constant, yields the following for the first-order desorption rate constant:

$$k = \nu \exp(-E/RT) = \nu \exp(-[E^0+\alpha(T-T^0)]/RT) = \nu \exp(-\alpha/Re-(E^0-\alpha T^0)/RT) = \nu_{\mathrm{eff}} \exp(-E^{\mathrm{eff}}/RT)$$

where ν_{eff} and E_{eff} are the effective desorption pre-exponential and activation energy observed in TPD experiments, respectively. Because the temperature dependence appears in the exponential, even a desorption activation energy that depends only weakly on temperature can give very low effective desorption pre-exponentials; for example, an activation energy that increases by 0.25 kJ/mol K is sufficient to decrease the pre-exponential by 13 orders of magnitude. Assuming a typical intrinsic pre-exponential of 10^{13} s^{-1},[21] the data in Figure 5 suggest that α is between 0.22 and 0.27 kJ/mol K for acetic acid on $LiNbO_3(0001)$ and between 0.25 and 0.27 kJ/mol K for 2-propanol on $LiNbO_3(0001)$. Setting T_0 to the starting temperature of the TPD ramp, 200 K, then suggests E_0 for acetic acid of 92 and 64 kJ/mol on positively and negatively poled $LiNbO_3(0001)$, respectively, and 73 and 62 kJ/mol for 2-propanol on the positively and negatively poled surfaces, respectively.

The strong influence of the pyroelectric effect on the desorption of the two polar molecules but not the nonpolar molecule indicates that adsorption of the polar molecules is largely driven by electrostatic interactions. This implies that the stronger adsorption of 2-propanol and acetic acid on the positively poled surface can be related to an adsorption geometry on the positive surface that allows a more favorable electrostatic interaction. Such a favorable geometry could be easily envi-

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sioned as one that places the negatively charged O atoms closest to the positive surface; however, the situation is complicated by the presence of compensating charges of opposite sign on the two surfaces and the temperature dependence of the surface dipole. We have begun to investigate the adsorption geometry in greater detail through theory.

The estimated differences between the heats of adsorption of the polar molecules on the positive and negative surfaces can be used to evaluate the feasibility of using ferroelectric thin films as chemical sensors. The energy barrier to switch a single domain ferroelectric thin film as a function of film thickness can be estimated from the coercive field, which gives the energy required to displace the charges, and the spontaneous polarization, which gives the number of charges that must be displaced per area. Near room temperature, the coercive field for stoichiometric $LiNbO_3$ is 50 kV/cm[22,25,26] and the spontaneous polarization is 80 μC/cm^2,[25] suggesting an energy barrier of 5.7 meV/nm. In comparison, assuming adsorption is unactivated, the TPD data suggest a 28 kJ/mol (0.29 eV) higher heat of adsorption of acetic acid on the positive surface and an 11 kJ/mol (0.11 eV) higher heat of adsorption of 2-propanol on the positive surface. If one molecule adsorbs per surface unit cell at saturation, then even the smaller energy difference for 2-propanol would be sufficient to switch a nearly 20 nm thick $LiNbO_3$ film from negative to positive.

5. Summary

The results revealed that the interaction of polar molecules with ferroelectric metal oxides is dominated by electrostatic interactions with the surface dipole. Although no reactions were observed, the adsorption of polar acetic acid and 2-propanol was significantly stronger on the positive surface than on the negative surface, whereas adsorption of nonpolar dodecane was insensitive to the poling direction. Moreover, TPD of polar molecules depended unusually strongly on the heating rate, yielding effective desorption pre-exponentials more than 11 orders of magnitude smaller than the typical value for small molecules. These unusual kinetics were associated with the pyroelectric effect causing the desorption energy barrier to increase by 0.2−0.3 kJ/mol K as the temperature increased. The differences in how strongly polar molecules interact with positively and negatively poled ferroelectric surfaces are sufficiently large to make chemical sensors based on adsorption-induced switching of ferroelectric thin films feasible.

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