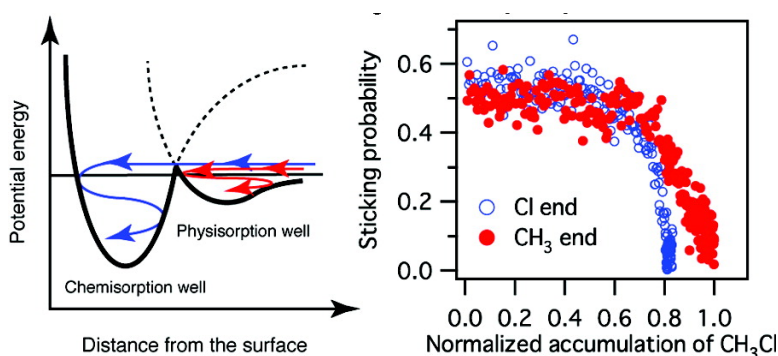


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Reaction-Path Selection with Molecular Orientation of CH₃Cl on Si{100}

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The dissociative adsorption of methyl chloride (CH₃Cl) on silicon (Si)^{1–4} is the first elementary step in silane formation.^{5,6} STM studies^{1,7} show that, for the dissociative adsorption of CH₃Cl on Si{100} at room temperature, the ratio of adsorbed Cl to CH₃ is 2:1. The deviation from the expected stoichiometric 1:1 ratio could be due to steric effects in the adsorption and, thus, hints at the possibility of controlling the final products by manipulating the orientation of the molecule colliding with the surface. A CH₃Cl molecule adsorbs dissociatively on Si{100} via precursor states,^{3,4,7} and it is usually expected that the molecular orientation effects would smear/average out. While steric effects (of reactants) have been reported in collision dynamics^{8–11} and reactions,^{12–15} in precursor-mediated adsorption on Si, for example, the role of the orientation of the incoming molecule remains unclear despite the demonstrated importance of steric effects on the *initial* CH₃Cl sticking probability ($S(t=0)$) on Si{100}.¹⁶

In this report, we present direct evidence of steric effects in the dissociative adsorption of CH₃Cl on Si{100}, as observed in the evolution of the coverage. The sticking probability (S) as a function of the amount of CH₃Cl ($\Theta(t)$) accumulated on the surface, where $\Theta(t) = F \int_0^t S(t') dt'$ with a constant beam flux of F , follows typical mobile precursor-mediated adsorption behavior. $S(\Theta(t))$ starts to decrease at a lower CH₃Cl accumulation for the Cl end collision than for the CH₃ end collision. Moreover, this steric effect depends on the surface temperature. On the basis of these data, we discuss the possibility that the orientation of the molecule, upon being trapped into a precursor state, may predetermine the following reaction path(s).

Experiments were performed with a molecular beam apparatus^{16,17} adapted for state selection and orientation of CH₃Cl and $S(t)$ determined with the King–Wells (KW) method.¹⁸ The base pressure of the surface-reaction analysis (SRA) chamber was below 1×10^{-8} Pa. A Si{100} sample (n-type, 0.01 Ω cm) was heated by passing a direct current and degassed overnight at 850 K at a pressure of 1×10^{-8} Pa. Finally, the sample was flashed to 1450 K several times and then cooled slowly from 1000 K to the experimental temperature. The sharp (2×1) reconstructed pattern was observed at room temperature by low-energy electron diffraction.

At a repetition rate of 60 Hz, the seeded molecular beam produces CH₃Cl pulses with durations of 0.2 ms fwhm. The CH₃Cl translational energy is 120 meV for CH₃Cl (25%) seeded in Ar. The angle of incidence is surface normal. The CH₃Cl beam is state selected with a $|J,K,M\rangle = |111\rangle$ rotational state by means of an electrostatic hexapole field^{19–22} (electronic and vibrational ground state). Since higher beam intensity is required for the whole range of the KW spectra, we remove the beam stop. As a result, the corresponding state purity of $|J,K,M\rangle = |111\rangle$ is less than 40%,

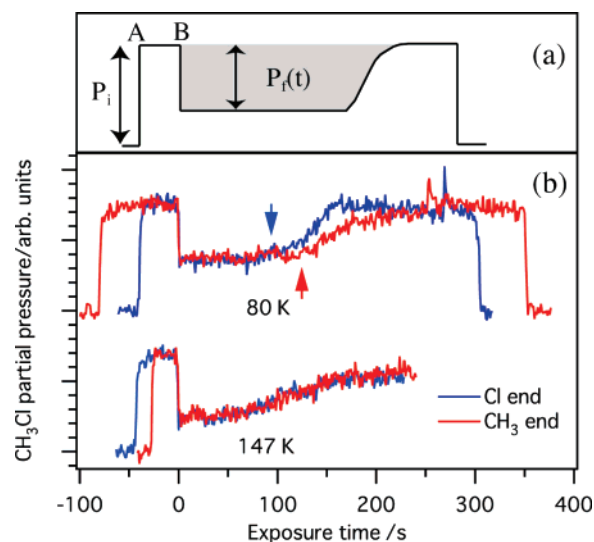


Figure 1. (a) Schematic KW spectrum. The gray area corresponds to the total accumulation of CH₃Cl on the surface. (b) Molecular orientation dependence of the KW spectra at 80 and 145 K.

estimated from the enhancement of the focused beam relative to the non-state-selected direct beam and the state purity of the focused beam determined from the focusing curve.¹⁷ The orientation of CH₃Cl molecules is constructed by a homogeneous orientation electric field in front of the Si surface.

At a hexapole voltage $V_0 = 0$, the CH₃Cl mass signal in the SRA chamber indicates a background in Figure 1a. With an applied V_0 corresponding to $|111\rangle$ and the beam stop removed at A, the CH₃Cl beam (with <40% in the $|111\rangle$ state) impinges a KW flag made of highly oriented pyrolytic graphite (HOPG), which is nonreactive to CH₃Cl at a room temperature, and we observe a sudden increase in the mass signal and keep a constant pressure (P_i). The experimental results are not affected by the difference in the pre-dose time (A–B) on HOPG in Figure 1a because of the low background pressure of $\sim 5 \times 10^{-8}$ Pa during the measurements. We then remove the HOPG flag at B ($t = 0$) and direct the state-selected beam onto the Si{100} surface. As a result of adsorption, the mass signal drops immediately from P_i to $P_i(t=0)$, and we can estimate $S(t)$ from $(P_i - P_i(t))/P_i$.

Figure 1b shows the orientation dependence of KW spectra for a 120 meV $|111\rangle$ beam incident on a clean Si{100} surface at 80 and 147 K. These KW spectra clearly show no molecular orientation dependence of $S(t=0)$, both at 80 and 147 K, as previous reports (using a pure $|111\rangle$ beam).¹⁶ After a period ($t \geq 0$) of nearly constant CH₃Cl pressure (a constant sticking probability) in the KW spectra, the pressure increases with increasing beam dose and finally reaches the same pressure as that with the beam on the HOPG. The molecular orientation dependence of the onset for the decrease

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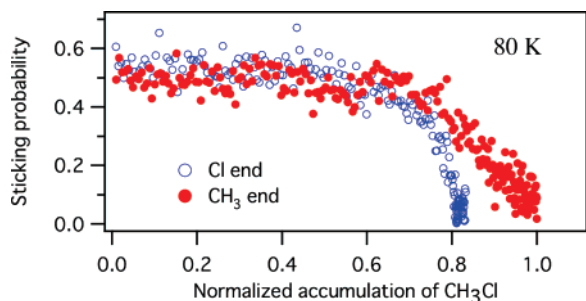


Figure 2. Molecular orientation dependence of the sticking probability S at 80 K. The accumulation of CH_3Cl is determined from the integration of KW spectra (see text) and normalized by the total CH_3 end accumulation (see the gray area in Figure 1a).

of $S(t)$ appears at ~ 80 K as indicated by arrows in Figure 1b. The earlier onset for the Cl end incidence relative to the CH_3 end incidence was reproducible for one set of experimental runs (Cl and CH_3 end) at constant beam intensity, although the absolute onset time depends on the incident beam intensity at each set of runs. The onset suggests the occupation of almost all available adsorption sites, and thus, the Cl end incidence saturates with less CH_3Cl accumulation than the CH_3 end incidence. Moreover, the total amount of CH_3Cl accumulated dissociatively or molecularly on the surface, corresponding to the gray area in Figure 1a, is larger for the CH_3 end than for Cl end. On the other hand, no molecular orientation dependence was found in the KW spectra at 147 K in Figure 1b.

Figure 2 shows the molecular orientation dependence of the sticking probability S as a function of the amount of accumulated CH_3Cl ($\Theta(t)$) calculated from the KW spectra at 80 K in Figure 1b. Here, $\Theta(t)$ is normalized using the total accumulation (the gray area in Figure 1a) for the CH_3 end incidence. $S(t=0)$ of ~ 0.5 for both ends is less than ~ 1.0 for the pure $|111\rangle$ state.¹⁶ This discrepancy is caused by the rotational-state dependence of the sticking probability. In a non-state-selected direct beam ($\sim 50\%$ of the beam), molecules with higher rotational states may reduce the sticking probability. The accumulation dependence of S tracks the typical textbook-like change for the mobile precursor-mediated adsorption.²³ It is demonstrated that the incoming molecular orientation plays an important role even at ~ 80 K where there is no observable $S(t=0)$ molecular orientation dependence.

It was reported in studies with high-resolution electron energy-loss spectroscopy³ that both molecularly physisorbed CH_3Cl and the dissociated species (CH_3 and Cl) exists at ~ 80 K. Thus, we may consider the observed molecular orientation effect at 80 K as caused by the bifurcation from a transiently trapped nonequilibrium state in the physisorption well into the final states of molecularly physisorbed and dissociatively chemisorbed states. For the CH_3 end collision, the interaction with the surface is always repulsive,^{24,25} and therefore, trapping into the stabilized physisorbed state is more probable than dissociative adsorption. In the physisorbed state, only one weakly bound adsorption site is occupied by a CH_3Cl molecule. On the other hand, for the Cl end collision, during the energy dissipation process, access to the dissociative state is more probable.^{1,16,24,25} As a result of dissociation, one or two chemisorption sites are occupied with dissociatively adsorbed species of CH_3 and Cl atoms. Therefore, even if $S(t)$ is the same for both Cl and CH_3 end incidences, the resulting surfaces could be quite different. The Cl end collision reaches saturation coverage with smaller $\text{CH}_3\text{-Cl}$ dose due to a higher occupation of the available sites via the dissociative adsorption, as compared to the CH_3 end collision. In

the physisorption, weakly bound CH_3Cl may be closely packed like on HOPG²⁶ and the expected occupation of the available sites per incident CH_3Cl molecule is smaller than in the dissociative adsorption. Thus, it is suggested that the molecular orientation dependence is caused by the route selection into the final destination of molecularly physisorption or dissociative adsorption during the trapping into the mobile precursor.

At a higher temperature of 147 K, there is no molecular orientation dependence in the KW spectra as shown in Figure 1b. According to the temperature-programmed desorption measurements,³ molecularly adsorbed CH_3Cl becomes unstable at 120 K. Therefore, it is expected that, at 147 K, some transiently trapped CH_3Cl , which will fall into the physisorption state at 80 K, are dissociated into CH_3 and Cl. As a result, the molecular orientation effect is smeared out. The slower saturation at 147 K relative to 80 K may be due to the increase in desorption from the transiently trapped states and/or occurrence of etching reactions.

In conclusion, we observed a molecular orientation effect in the uptake of CH_3Cl on $\text{Si}\{100\}$ at 80 K. This is caused by the orientation dependence of the reaction paths of CH_3Cl into the dissociative adsorption and the physisorption state. The reason for the ratio of 2:1 for $[\text{Cl}].[\text{CH}_3]$ remains unsolved. This will be our continuing future study.

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