Adsorption geometry of methyl chloride weakly interacting with Ag(111)

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Abstract
The adsorption structure of CH₃Cl on Ag(111) was investigated by temperature programmed desorption (TPD), infrared reflection-absorption spectroscopy (IRAS), and density functional theory (DFT) calculation. The saturation coverage of CH₃Cl at the first layer was estimated to be 0.22 ML by TPD spectra. In the IRAS spectra before the first layer was completed, a CH₃ asymmetric deformation mode was observed, while a CH₃ symmetric deformation mode and a CH₃ symmetric stretching mode were not observed. This result suggests that CH₃Cl at the first layer is almost parallel to the surface, which was confirmed by DFT calculations. In contrast, a CH₃Cl at the second layer was concluded to be inclined from the surface parallel.

1. Introduction

Much attention has been paid to the chemical patterning via the control of molecular adsorption [1–3]. In the chemical patterning, molecules are molecularly and uniformly adsorbed on a surface in the first step. Then, the surface is locally irradiated with photon or electron by a laser, a focused electron beam source, or a scanning tunneling microscope tip. The irradiation induces the dissociative adsorption of the molecules, which are stabilized on the surface [4–6]. The adsorption sites of the dissociated products depend on the adsorption sites and the orientation of the molecularly adsorbed molecules in the first step [7, 8]. Therefore, the understanding of the geometry of the molecularly adsorbed molecules is efficient for the control of the patterning of the dissociated products.

Methyl chloride (CH₃Cl) adsorbed on metal is a well-known system in which CH₃Cl is dissociated into CH₃ and Cl by photon or electron irradiation [9]. In the case of the photodissociation of CH₃Cl on metal, the process has been understood to be promoted by a hot-electron transferred from the metal substrate to the CH₃Cl [10–12]. An adsorbed CH₃Cl capture a hot electron in the anti-bonding σ*(C–Cl) orbital [13], which causes the C–Cl bond to be weakened. As the bond start dissociating, the excess electron becomes localized on the Cl atom, which is repelled by CH₃ and attracted to its image charge in the substrate.

The adsorbed structures of CH₃Cl have not been clarified on most of metal systems but on Pd(100) and Cu(410). In the former system, CH₃Cl at the first layer was concluded to stand up on the surface by the observation of a CH₃ symmetry stretching peak in IR spectra and fitting TPD spectra with a static dipole-dipole interaction model [14]. In the latter system, on the other hand, CH₃Cl was evaluated to attached Cl to the surface in a parallel position based on IR spectra [15].

In the present paper, we focus on CH₃Cl/Ag(111) system and aim to evaluate the adsorbed structures, because CH₃Cl/Ag is a potential system for chemical patterning. For example, since Cl adsorbed on Ag locally forms insulating AgCl, the dissociation of CH₃Cl on a Ag thin film [16] by scanning tunneling microscope forms a nanoscale circuit or waveguide. In addition, if the positions of dissociated CH₃ and Cl are simultaneously controlled, digital information can be included on the surface structure as reported on Si(100) [1].
The adsorbed structure was investigated by temperature programmed desorption (TPD), infrared reflection-absorption spectroscopy (IRAS), and density functional theory (DFT) calculation. The saturation coverage of CH$_3$Cl at the first layer was estimated to be 0.22 ML by TPD spectra. In IR spectra for the first layer, a CH$_3$ symmetric deformation mode and a CH$_3$ symmetric stretching mode was not observed, on the other hand, the CH$_3$ asymmetric deformation modes were observed. This suggested that CH$_3$Cl at the first layer adsorbed on Ag(111) was in an almost parallel position. The adsorbed geometry was reproduced by DFT calculations. In contrast, an additionally adsorbed CH$_3$Cl on the first layer was concluded to be inclined from the surface.

2. Experimental

Experiments were performed in an ultrahigh-vacuum (UHV) chamber with a base pressure of 3 × 10$^{-8}$ Pa. The sample used in the present study was a Ag(111) surface (Surface Preparation Laboratory, 0.68 × 1.5 mm). The clean surface of Ag(111) was prepared by several cycle of Ne$^+$ sputtering (Ne 6.5 × 10$^{-3}$ Pa, 600 eV, 4 μA cm$^{-2}$, 30 min) and subsequent annealing at 720 K for 30 min. The sample cleanliness was confirmed by Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). The surface was exposed to high purity CH$_3$Cl at a typical sample temperature of 86 K. The coverage of CH$_3$Cl was evaluated from the area of TPD spectra. IRAS measurements were carried out with a Fourier transform infrared spectrometer with a liquid-nitrogen cooled MCT (HgCdTe) detector. The spectral resolution was set to be 4 cm$^{-1}$ and typically 512 × 4 scans were collected in the present experiments.

Stable adsorption structures were estimated by DFT calculation with PHASE/0 package developed by National Institute for Material Science. In the calculation, the generalized gradient approximation with Perdew-Burke-Ernzerhof, plane waves (225 Ry cutoff energy), projector augmented wave method, and a dispersion force adjustment were used. Ag(111) was modeled using the slab approach, where seven Ag layers of 2 × 2 supercell and a vacuum layer of 21.7 angstroms are repeated alternately. Surface Brillouin zone integration was performed using the special k-point sampling technique of tetrahedral (3 × 3 × 1) sampling meshes.

3. Result and discussion

Figure 1(a) shows TPD spectra for Ag(111) exposed to CH$_3$Cl. The desorption peak position was defined as the center of the temperatures at the half maximums because the upper half of the desorption peaks were almost symmetrical. As shown in figure 1(b), a single desorption peak (β) for CH$_3$Cl was grown at 123 K by up to 1 L (1.33 × 10$^{-4}$ Pa s) exposure with a gradual shift of the peak position. Then the exposure above 2 L grew a second peak (α) at around 116 K. The β peak and the α peak were assigned to be a monolayer peak and a multilayer peak, respectively, based on a previous study [20]. The desorption energy ($E_d$) for the β peak and the α peak were calculated to be 31 kJ mol$^{-1}$ and 29 kJ mol$^{-1}$, respectively, by Redhead method with an assumed frequency factor of 10$^{13}$ s$^{-1}$. As the exposure increased, the β peak grew and became saturated between the exposure of 1 L and 2 L. The saturated β peak was simulated by the spectrum for 1 L exposure, which was enlarged 1.5 times to fit the high-temperature side edge of the spectrum for 2 L exposure, as shown in the inset in figure 1(a). Next, the coverage of CH$_3$Cl at each exposure was estimated from the peak area of the TPD spectra as shown in figure 1(b).
The peak area was increased almost linearly as the increasing of the exposure. This suggests that the sticking probability of CH$_3$Cl is approximately constant on Ag$_{111}$ in spite of pre-adsorbed CH$_3$Cl. The saturation coverage of the $\beta$ peak, which was 1.5 times larger than the coverage of $2.0 \times 10^{14}$ cm$^{-2}$ for 1 L exposure, was then estimated to be $3.1 \times 10^{14}$ cm$^{-2}$. This coverage corresponds to 0.22 ML per Ag atoms on the surface. LEED patterns at each exposure showed no clear superstructures for the CH$_3$Cl exposures below 5 L.

The CH$_3$Cl exposure dependence of the IRAS spectra on Ag$_{111}$ at a temperature of 86 K is shown in figure 2. No peaks were observed at between 2800 cm$^{-1}$ to 3100 cm$^{-1}$ below a exposure of 2.0 L, while a peak was observed at 1444 cm$^{-1}$. On the other hand, a peak probably appeared at 2958 cm$^{-1}$ for the exposure of 3 L in addition to the peaks at 1344 cm$^{-1}$ and 1437 cm$^{-1}$. These peaks are listed up in table 1 with vibration modes for CH$_3$Cl in a gas phase and for adsorbed CH$_3$Cl on Pd$_{100}$ [14]. The comparison in table 1 assigned peaks at 1344 cm$^{-1}$, 1437 $\sim$ 1444 cm$^{-1}$, and 2958 cm$^{-1}$ to a CH$_3$ symmetric deformation mode $\delta_s$(CH$_3$), a CH$_3$ asymmetric deformation mode $\delta_a$(CH$_3$), and a CH$_3$ symmetric stretching mode $\nu_s$(CH$_3$), respectively.

The change of the observed peaks as a function of the CH$_3$Cl exposure is explained as follows. In general, vibrational modes with a transition dipole moment parallel to a surface are not active for IR spectroscopy because the transition dipole moment is canceled by an induced dipole change on the surface. By contrast, if the transition dipole moment is inclined from the surface, the mode is active for IR spectroscopy. In observed IR spectra for 0.7 L, $\delta_a$(CH$_3$) at 1444 cm$^{-1}$ was observed, though $\delta_s$(CH$_3$) and $\nu_s$(CH$_3$) were not observed. The missing of $\delta_s$(CH$_3$) and $\nu_s$(CH$_3$) means that at least molecular axis of CH$_3$Cl at the first layer is almost parallel to the surface (Note that, for an isolated CH$_3$Cl molecule, the direction of the transition dipole moment for $\delta_s$(CH$_3$) and $\nu_s$(CH$_3$) are parallel to the molecular axis and those for $\delta_a$(CH$_3$) and $\nu_a$(CH$_3$) are perpendicular to the molecular axis). When the surface was exposed to CH$_3$Cl of 3.0 L, $\delta_s$(CH$_3$) and $\nu_a$(CH$_3$) appeared. This suggests that the molecular axis of CH$_3$Cl at the second layer is inclined from the surface.

### Table 1

| Gas/Pd(100) 1st layer | Experimental 0.7 L | Experimental 1 L | Experimental 2 L | Experimental 3 L | DFT 0.25 ML 0.50 ML |
|----------------------|-------------------|------------------|------------------|------------------|--------------------|
| $\delta_s$(CH$_3$)   | 1355              | 1330             | 1344             | 1333             | 1327, 1333         |
| $\delta_a$(CH$_3$)   | 1455              | 1426             | 1444             | 1437             | 1420, 1425, 1432   |
| $\nu_s$(CH$_3$)      | 2966              | 2927             | 2958             | 2879             | 2873, 2878, 2886   |
| $\nu_a$(CH$_3$)      | 3042              | 2972             | 2972             | 2972             | 2979, 2982         |

(see supplementary S1 is available online at stacks.iop.org/JPCO/2/075017/mmedia). The peak area was increased almost linearly as the increasing of the exposure. This suggests that the sticking probability of CH$_3$Cl is approximately constant on Ag$_{111}$ in spite of pre-adsorbed CH$_3$Cl. The saturation coverage of the $\beta$ peak, which was 1.5 times larger than the coverage of $2.0 \times 10^{14}$ cm$^{-2}$ for 1 L exposure, was then estimated to be $3.1 \times 10^{14}$ cm$^{-2}$. This coverage corresponds to 0.22 ML per Ag atoms on the surface. LEED patterns at each exposure showed no clear superstructures for the CH$_3$Cl exposures below 5 L.

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Possible stable structures for CH$_3$Cl of 0.25 ML on Ag(111), which corresponds to the saturation coverage for the $\beta$ peak in the TPD spectra, were calculated by the DFT method. A Cl atom in a CH$_3$Cl was put on an on-top site, a bridge site, and a follow site and the structure was then relaxed. There were found to be several metastable structures with a reference symmetry with respect to the molecular axis, in all of which CH$_3$Cl was almost parallel to the surface (see figure S2). At the experimental temperature of 86 K, an isolated adsorbed CH$_3$Cl can take all possible geometries above (see figure S2) by its rotations and diffusions on the surface. As a typical structure, we focus on the most stable one shown in figure 3(a). The distance between the Cl atom and the nearest neighbor Ag atom was 3.6 angstroms. The C atom was slightly farther away from the surface and the angles between the molecular axis and the surface plane were 10 degrees. The estimated adsorption energy ($E_{ad}$) was 30.66 kJ mol$^{-1}$, which was in good agreement with the $E_d$ of 31 kJ mol$^{-1}$ for the $\beta$ peak estimated from the TPD spectra.

$E_{ad}$ for the adsorbed structure shown in figure 3(a) without a dispersion force adjustment was calculated so that the contribution in $E_{ad}$ was evaluated. Without the dispersion force, $E_{ad}$ for CH$_3$Cl was calculated to be 4.0 kJ mol$^{-1}$ with the distance between the C atom in CH$_3$Cl and the surface of 4.0 angstroms. The $E_{ad}$ of 4.0 kJ mol$^{-1}$ was weak compared with $E_{ad}$ of 31 kJ mol$^{-1}$ calculated with the dispersion force. This means that the dispersion force is the dominant component for the adsorption of CH$_3$Cl on Ag(111). In the case of a CH$_4$ molecule, it interacts with metal substrates mainly with dispersion force and without static dipole-induced-dipole interaction because of the high symmetricity. The desorption temperature for CH$_4$ of 1.6 ML adsorbed on Pt(111) was 73 K [22], which is converted to $E_d$ of 19.4 kJ mol$^{-1}$ with the Redhead method. The difference in the $E_{ad}$’s calculated for 0.25 ML CH$_3$Cl with and without dispersion force was 26.66 kJ mol$^{-1}$, which is not far from the $E_d$ for CH$_3$Cl on Pt(111). This is consistent with that CH$_3$Cl at the first layer preferred the parallel geometry, which can increase the dispersion force interaction with the substrate.

Next, an additional CH$_3$Cl, whose molecular axis was aligned to be parallel to the molecular axis of a CH$_3$Cl at the first layer, was set 6 angstroms above the gap between CH$_3$Cl at the first layer. Then, the additional CH$_3$Cl was approached to the surface and the structure was relaxed. The converged structure was shown in figure 3(b). The additional CH$_3$Cl was coordinated to the CH$_3$Cl at the first layer in the twisted conformation. Calculated $E_{ad}$ for the additional CH$_3$Cl was 28.06 kJ mol$^{-1}$, which agreed with the experimental value of $E_d$ of 29 kJ mol$^{-1}$ for the $\alpha$ peak in the TPD spectra.

Vibrational modes for the structures shown in figures 3(a) and (b) and CH$_3$Cl in a gas phase were calculated as listed up in table 1. While the wavenumbers for the stretching modes were underestimated, the wavenumbers for the deformation modes agree with the experimental values within 20 cm$^{-1}$. The red shifts of the wavenumbers by the adsorption were also represented. For 0.25 ML, degenerate $\delta_{as}(CH_3)$ and $\nu_{as}(CH_3)$ in a gas phase were solved into two modes depending on the direction of the transition dipole moment with respect to the surface. For 0.50 ML, symmetric modes and asymmetric modes were divided into two and four modes, respectively, due to the CH$_3$Cl at the first layer and the second layer.

CH$_3$Cl at the first layer in a stable geometry shown in figure 3(a) can take three orientations I, II, and III denoted as arrows in figure 4. When CH$_3$Cl at the orientation of I, II, or III is dissociated by photon or electron irradiation, the Cl atom is probably adsorbed on an on-top site of 1, 2, or 3 shown in figure 4, respectively. As the orientation of the molecularly-adsorbed CH$_3$Cl can be controlled by the electric field by a STM tip, the adsorption sites 1, 2, and 3 for the Cl atom can also be selectable. That is, three bits of information can be stably recorded per one CH$_3$Cl molecule on the surface.

Figure 3. A stable structure for CH$_3$Cl of (a) 0.25 ML and (b) 0.50 ML on Ag(111).
4. Conclusion

We have investigated adsorbed structure of CH₃Cl on a Ag(111) surface. In IRAS spectra, a CH₃ symmetric deformation mode was not observed for CH₃Cl at the first layer on Ag(111) but for CH₃Cl at the second layer. This indicates that the first layer adsorbed in an almost parallel position with respect to the surface and the second layer was inclined from the surface. DFT calculations confirmed the parallel and the inclined geometry of CH₃Cl at the first layer and the second layer, respectively. The inclined CH₃Cl at the second layer formed a twisted dimer with CH₃Cl at the first layer.

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