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Surface kinetics using line of sight techniques: the reaction of chloroform with Cu(111)

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The adsorption of chloroform ($CHCl_3$) on Cu(111) in the temperature range 100–480 K has been studied using line of sight sticking probability (LOSSP) measurements, line of sight temperature programmed desorption (LOSTPD), low energy electron diffraction (LEED), He I ultra-violet photoelectron spectroscopy (UPS) and work function measurements. Chloroform adsorbs molecularly at 100 K with a sticking probability of 0.98 ± 0.02, the monolayer reacting on heating to 170 K to form chemisorbed chlorine and adsorbed ethyne. The adsorbed ethyne desorbs at just above room temperature with first order kinetics, an activation energy of 77 ± 6 kJ mol^{-1} and a pre-exponential factor of $10^{11 \pm 1}$ s^{-1}. The sticking probability of chloroform on clean Cu(111) at 320 K is 0.23 ± 0.04, which corresponds to activated adsorption at zero coverage with an activation energy of 3.5 ± 0.7 kJ mol^{-1}. The initial sticking probability is found to increase slightly for temperatures above room temperature, and also for temperatures below room temperature, while the sticking probability at finite coverage is greatly increased by the presence of the dissociation product, ethyne, on the surface. These observations are explained in terms of activated adsorption at zero coverage which becomes non-activated at finite coverage due to attractive intermolecular interactions between adsorbed chloroform molecules, and adsorbed chloroform and ethyne molecules.

Introduction

Recently we have shown that the sticking probability (SP) of a species with a surface can be measured with an accuracy of ± 0.02 using a line of sight (LOS) method in which only those species originating from a well defined patch on the sample surface are detected by a quadrupole mass spectrometer, the LOSSP method.[1] Unlike the King and Wells method[2] for sticking probability measurements, the LOSSP technique does not require the generation of an incident molecular beam, the incident gas being fed into the vacuum chamber *via* a standard leak valve, and hence it can be implemented alongside other surface sensitive techniques in most UHV chambers without the need for extra pumping. The technique is best suited to sticking probability measurements for gases at room temperature, the King and Wells method being the preferred technique for surface dynamics studies in which the translational temperature of the gas exceeds room temperature. In its present form the LOSSP method is only applicable to gases having boiling points > 170 K (because a liquid nitrogen cooled shroud is used to cryopump all species not having line of sight trajectories to the mass spectrometer detector). In this paper we demonstrate how the sticking probability of a complex system, measured as a function of substrate temperature and adsorbate coverage, can be used not only to determine the activation energy for activated adsorption at zero coverage, but also to track how activated adsorption changes to non-activated adsorption, due to molecular interactions at the surface, as the coverage increases.

The system studied here is chloroform ($CHCl_3$) on Cu(111), where line of sight detection has been used to measure the sticking/reaction probability and the evolution of gaseous ethyne, C_2H_2, which is a product of the surface reaction. Line of sight detection was also used for monitoring temperature programmed desorption (LOSTPD) of the ethyne product, which remains adsorbed on the surface for reaction below room temperature. We find that at zero coverage chloroform undergoes activated dissociative adsorption, with an activation energy of 3.5 ± 0.7 kJ mol^{-1}. At higher coverages both physisorbed chloroform, and the decomposition product (adsorbed ethyne), increase the observed sticking/reaction probability by lowering the activation energy to adsorption, until it eventually drops below zero and the reaction becomes non-activated. He I ultra-violet photoelectron spectroscopy (UPS), work function measurement and low energy electron diffraction (LEED) were used to characterise the surfaces for adsorption between 100 K and 480 K.

Studies of halocarbons on well characterised surfaces, metals in particular, are rather extensive. For copper, mono-halogenated species[3,4] are the most, and dihalogenated species[5,6] the next most, widely studied compounds. However, studies of polychlorinated hydrocarbons on single crystals are rather sparse. Chloroform adsorption has been studied on graphite,[7] Si(100)[8] and Si(111),[9] amorphous and crystalline water ice on Pt(111),[10,11] calixarene layers[12] and Ag(111),[13,14] the present study being the first on copper. On Cu(111) alkyl halides, R–X, decompose by loss of the halogen (X) to form a chemisorbed halogen and an adsorbed alkyl radical.[3] Alkyl dihalides, X–C_2H_4–Y, decompose by the loss of both halogens (X and Y)[15,16] to form, not a di-radical, but ethene with a double bond, which is physisorbed to the surface (the reaction being more facile the heavier the halogens). It follows that chloroform might be expected to decompose by the loss of three chlorines, leaving the tri-radical CH. We show in this paper that this does indeed occur, the CH groups combining in pairs to produce ethyne, which is adsorbed to the surface. The nearest comparison we have for chloroform on Cu(111) is chloroform on Ag(111).[13,14] Silver, as expected, is less reactive

than copper and TPD studies of chloroform adsorption on the (111) surface have shown molecular adsorption and desorption without dissociation.[13]

Experimental

The experiments were carried out in a UHV chamber which has already been described,[17] using equipment and methods for line of sight detection which have also already been described.[1,5,18] The sample was cleaned by argon ion bombardment (500 eV, 6 μA, 1000 s) , followed by annealing to 773 K, until low energy electron diffraction (LEED) and He I ultra-violet photoelectron spectroscopy (UPS) showed the surface to be clean and well ordered. [Note that the surface state and surface resonances in the UPS of Cu(111) are characteristic of the clean surface.[19] UP spectra were taken with the radiation incident at 45° to the normal with photoelectron detection at normal emission. The sample was biased to -9 V, so as to display the secondary electron cut-off clearly for work function measurements.
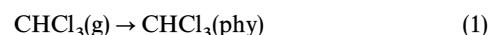
LOSSP measurements were taken using a quadrupole mass spectrometer (VG SX300, $m/z = 1$–300) modified to operate in pulse counting mode, surrounded by a liquid nitrogen cooled shroud. Chloroform (from Fisher Scientific, $>99\%$ purity), degassed by several freeze/pump/thaw cycles) was admitted to the chamber *via* a standard leak valve to a pressure of 2–10×10^{-8} mbar, whilst monitoring various masses for chloroform, ethyne, benzene and other hydrocarbons until saturation adsorption of the surface had occurred. Temperature programmed desorption was carried out using line of sight detection whilst applying a linear heating ramp of 0.88 K s^{-1} by radiative heating of the sample.
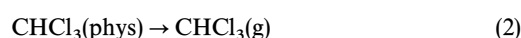
Results

LOSSP experiments were carried out at 99, 216, 320 and 480 K. Fig. 1 shows the results obtained for chloroform adsorption on Cu(111) at 320 K. On increasing the chloroform pressure from its background value of $\approx 2 \times 10^{-10}$ mbar to $\approx 4 \times 10^{-8}$ mbar, the intensity of molecular chloroform emanating from the surface, monitored using the CCl$_2^+$ peak ($m/z = 82$), underwent an immediate increase, indicating a sticking probability of less than 1. During the first ≈ 100 s of adsorption, the molecular chloroform signal decreased slightly in intensity, indicating a slight increase in sticking probability, after which the signal slowly increased, indicating a decreasing sticking probability, until saturation occurred (with $S = 0$) for adsorption times >500 s. A pulse of ethyne, monitored using

the C$_2$H$_2^+$ ion ($m/z = 26$) was observed to desorb ≈ 200 s after admission of the chloroform, while the other two masses, C$_2$H$_3^+$ ($m/z = 27$) a fragment from ethene and other higher mass hydrocarbons, and C$_6$H$_6^+$ ($m/z = 78$) for benzene, remained at their background levels throughout the adsorption. Note that the background level of ≈ 700 counts at $m/z = 27$ was due to the low mass wing of a large CO peak at $m/z = 28$, which is not pumped by the liquid nitrogen shroud. The saturated surface exhibited a bright, sharp, $(\sqrt{3} \times \sqrt{3})$R30° structure characteristic of chemisorbed chlorine on Cu(111).[20]
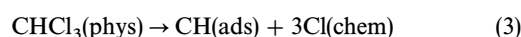
From these results we may deduce that ethyne is produced by the reaction of chloroform with the Cu(111) surface, as ethene would have produced a signal at $m/z = 27$ and any polymerisation of the ethyne to benzene would have produced a signal at $m/z = 78$. We also note that ethyne desorption is not prompt, but delayed until the chloroform adsorption is well advanced. The following reaction scheme (with rates v_i, accommodates these observations:
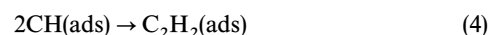
$$CHCl_3(g) \rightarrow CHCl_3(phy) \qquad (1)$$

$$v_1 = S_1 F_{in}$$

$$CHCl_3(phys) \rightarrow CHCl_3(g) \qquad (2)$$

$$v_2 = k_2[CHCl_3(phys)]$$

$$CHCl_3(phys) \rightarrow CH(ads) + 3Cl(chem) \qquad (3)$$

$$v_3 = k_3[CHCl_3(phys)]$$

$$2CH(ads) \rightarrow C_2H_2(ads) \qquad (4)$$

$$C_2H_2(ads) \rightarrow C_2H_2(g) \qquad (5)$$

This reaction scheme is discussed in more detail later, but it should be noted here that reaction (3) almost certainly consists of three individual steps in which chlorine atoms are sequentially lost, rather than a simultaneous loss of all three.

The measured sticking probability, defined as below in eqn. (6) where F_{in} is the incident chloroform flux, F_{out} is the exiting chloroform flux and hence $F_{in} - F_{out}$ is the flux that sticks, may be derived from Fig. 1 as follows. At time t after commencing adsorption, the applied chloroform pressure is P and the intensity of the molecular chloroform leaving the surface (F_{out}) is proportional to $(N - N_B)$, where N is the counts for CCl$_2^+$ and N_B the background counts at this mass (determined prior to starting the adsorption). The intensity of the incident flux of molecular chloroform (F_{in}) is equal to the flux exiting the surface when $S = 0$, and is hence proportional to $(N_0 - N_B)$ where N_0 is the counts for CCl$_2^+$ at saturation adsorption. As the applied pressure was not constant, these intensities were normalised by division by the applied pressure, measured using an ion gauge in the chamber, and the sticking probability calculated using

$$S = (F_{in} - F_{out})/F_{in}$$

$$= [(N_0 - N_B)/P - (N - N_B)/P]/(N_0 - N_B)/P \qquad (6)$$

The proportionality between fluxes and measured counts relies on the experimental geometry, and the angular distribution and translational temperature of the chloroform leaving the surface, remaining constant throughout the experiment.[1] The geometry was kept constant, and for chloroform which has resided in a physisorbed state prior to desorption and detection, it is reasonable to expect that it will have a cosine distribution of intensity and will have a translational temperature determined by the surface temperature. (A desorbing species in thermodynamic equilibrium with the same species adsorbing from the gas phase will have a cosine distribution.[21,22]) All sticking probability measurements were carried out at fixed temperature, and so all three conditions for proportionality were achieved.
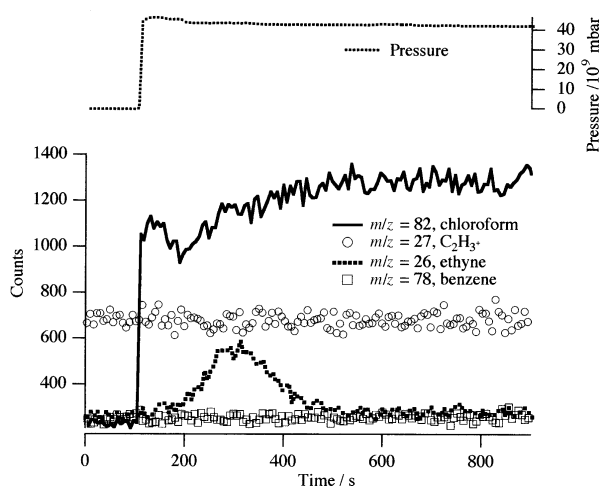

Fig. 1 Pressure, and line of sight mass spectrometer signals at $m/z = 26$ (C$_2$H$_2^+$), 27 (C$_2$H$_3^+$), 78 (C$_6$H$_6^+$) and 82 (CCl$_2^+$) for species leaving the sample surface during chloroform adsorption on clean Cu(111) at 320 K.

The exposure, E, at time t is given simply by $\int P(t)\,dt$, while the coverage of chloroform on the surface is $\int S(E)\,dE$. Plots of S and coverage *versus* exposure for adsorption at 320 K are shown in Fig. 2, which shows that the surface saturated at a coverage of $\approx 3 \times 10^{-6}$ mbar s. If we take the sensitivity of our (uncalibrated) ion gauge to chloroform as 3.34 (ref. 23) (where nitrogen has a value of 1), then the true surface coverage is $\approx 0.9 \times 10^{-6}$ mbar s, giving a value of $\approx 3.8 \times 10^{18}$ m^{-2} of chloroform molecules, or $\approx 1.2 \times 10^{19}$ m^{-2} of adsorbed chlorine atoms after dissociation. This last number should be compared with the expected chlorine atom coverage for a Cu(111)-$(\sqrt{3} \times \sqrt{3})R30°$ structure of 5.9×10^{18} m^{-2}. The values agree to within a factor of 2, which is as good as can be expected for a value based on an uncalibrated ion gauge reading. Three other points should also be noted. Firstly, approximately 10% of the full 2π steradians above the sample is blocked by the totally gas absorbing liquid nitrogen cryoshield, hence the applied gas pressure at the sample is only 90% of what it would be if the cryoshield were not there.[1] Secondly, the presence of the cryoshield in the vacuum chamber will generate an overall pressure differential between the sample position and the ion guage position (they were positioned in the same horizontal plane but ≈ 25 cm apart). Thirdly, the mass spectrometer measures number density, not flux, so a correction would need to be applied if gases of different temperatures were being directly compared.[1] All the measurements presented in this paper are relative, and at fixed geometry, and hence these effects need not be considered, except for the exposure calculation, where all three introduce
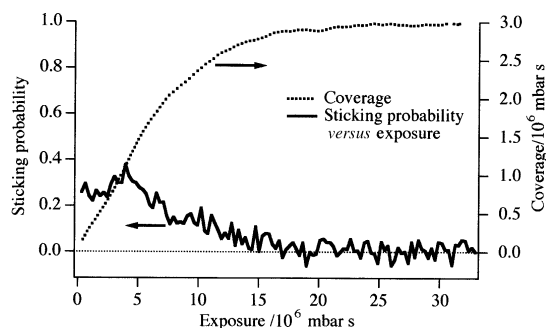
a systematic error, but a smaller one than that due to the calibration of the ion gauge itself.

Fig. 3C shows the sticking probability and the ethyne signal (after background subtraction) for adsorption at 320 K replotted as a function of coverage. The initial sticking probability is estimated to be 0.23 ± 0.04, and remains constant to a coverage of $\approx 0.75 \times 10^{-6}$ mbar s before rising slightly to 0.35 ± 0.03 at $\approx 1.2 \times 10^{-6}$ mbar s and then dropping to zero at saturation. Ethyne desorption is seen to occur towards the end of the chloroform adsorption and exhibits a completely different shape to the sticking probability curve.

Fig. 3D shows sticking probability and ethyne desorption *versus* coverage for adsorption at 480 K. The initial sticking probability is 0.26 ± 0.04, and remains constant to $\approx 0.9 \times 10^{-6}$ mbar s, after which it drops linearly to zero at saturation coverage. The ethyne desorption rate is seen to match the sticking probability behaviour very closely. The saturation coverage is apparently lower than for adsorption at 320 K, but the variation in saturation coverages was generally $\pm 0.5 \times 10^{-6}$ mbar s, so it is unclear whether this is a real effect of the elevated temperature.

Fig. 3B shows the results for adsorption below room temperature, 216 K. It is not clear how to extrapolate these data to zero coverage but if we assume that the sticking probability is level over the first 0.5×10^{-6} mbar s, then the initial sticking probability would be ≈ 0.35, rising to a value of ≈ 0.7 at a coverage of $\approx 2 \times 10^{-6}$ mbar s, after which it decreases to zero as the surface saturates. No desorption of ethyne was observed for 216 K adsorption. Fig. 3A shows the data obtained for adsorption at 99 K. The initial sticking probability is 0.98 ± 0.02, and remains at this value indefinitely as multilayers of chloroform ice form on the surface. No ethyne is desorbed at this temperature.

Fig. 4 shows the line of sight temperature programmed desorption (LOSTPD) data obtained for ethyne desorption using $m/z = 26$ and a heating rate of 0.88 K s^{-1}, starting from a chloroform saturated surface at 216 K (*i.e.* a single layer of dissociated chloroform, see below). No other species were observed to desorb. The desorption curve has been fitted using first order kinetics with an activation energy of 77 ± 6 kJ mol^{-1} and an assumed pre-exponential factor of $10^{11 \pm 1}$ s^{-1}. The error limits are derived from pairs of values of activation energy and pre-exponential factor that give equally good fits. For higher and lower values of the pre-exponential factor than these the simulated desorption curve becomes too
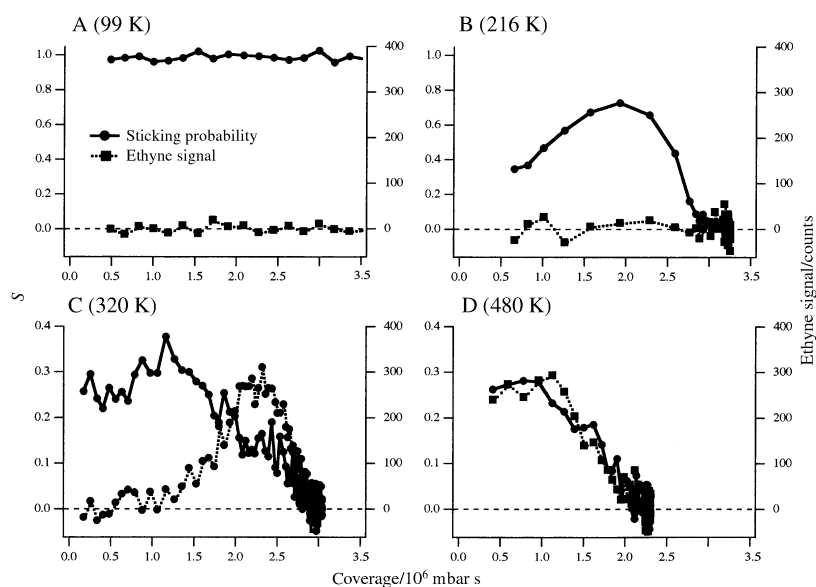

Fig. 2 Sticking probability and coverage (derived from the sticking probability) *versus* exposure to chloroform, for adsorption at 320 K.

Fig. 3 Sticking probabilities (left hand scales) and desorbed ethyne signal (right hand scales) *versus* coverage derived from the sticking probability curves, for chloroform adsorption at: A, 99 K; B, 216 K; C, 320 K; D, 480 K.
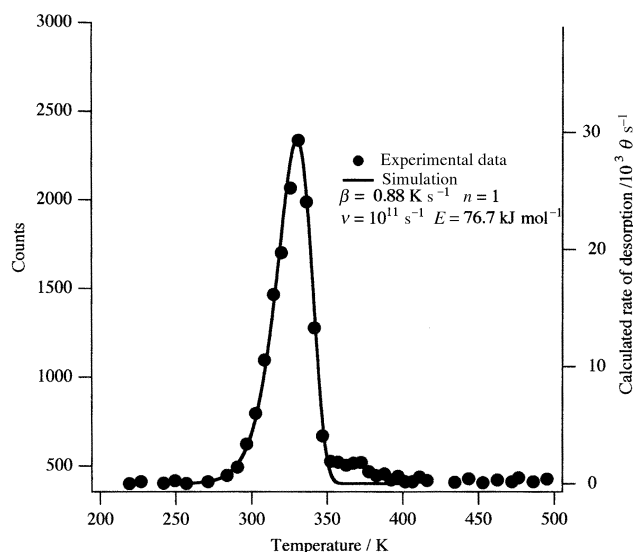
Fig. 4 Experimental data (left scale) and best fit (right scale) for temperature programmed desorption of ethyne from Cu(111) saturated with chloroform at 216 K. The ethyne is assumed to have an initial coverage of $\theta = 1$.

narrow and too broad, respectively, for a good fit. Close inspection of Fig. 4 shows that some desorption ($\approx 6\%$ of the total) occurred between 350 and 380 K. We are not sure what caused this feature, but it cannot be due to defects on the Cu(111) surface as a heavily argon ion bombarded surface showed no increase in this region when used in an identical adsorption/desorption experiment.

Fig. 5A shows the gas phase He I UP spectrum of chloroform, shifted by 6.25 eV in ionisation energy, while Fig. 5B shows the UP spectra taken as $CHCl_3$ adsorbed on a clean Cu(111) surface at 103 K. Clearly molecular adsorption of chloroform occurred, with three peaks growing at 5.6, 6.6 and 9.8 eV binding energy (BE), and a reduction in the substrate surface state at 0.2 eV and the surface resonances at 2.8 and 3.8 eV BE.[19] The total exposure, 2.64×10^{-6} mbar s, represents near completion of the first monolayer, as the sticking probability at 103 K is 1.0. The work function change during adsorption was small, decreasing by only 0.1 eV at completion of the first layer of molecular chloroform. This is a curious result, as chloroform has a permanent dipole of 1.01 D,[24] aligned along the 3-fold rotation axis of the molecule, and might be expected to significantly alter the work function of the surface. Such a

small work function change would be consistent with the molecule lying with the 3-fold rotation axis parallel to the copper surface, but further study is required to confirm or refute this supposition.

Fig. 6 shows what happened as the surface formed in Fig. 5B at 103 K was heated to successively higher temperatures, prior to cooling and measuring the UP spectrum. The molecular chloroform peaks decreased in intensity and by 163 K had been replaced by two peaks at 4.6 and 5.6 eV BE. These two peaks are characteristic of chemisorbed chlorine on Cu(111)[19] and show that the chloroform had almost completely dissociated by 163 K.

Fig. 7 shows the intensities of the 4.6 eV peak (due to chemisorbed chlorine) and the 9.8 eV peak (due to molecularly adsorbed chloroform) as well as the work function change (relative to the clean surface) measured during the heating experiments of Fig. 6. On heating the surface to 124 K the molecularly adsorbed chloroform began to decompose to chemisorbed chlorine and ethyne, the reaction being almost complete by 163 K, and complete by 173 K. Curiously, the work function only changed slightly up to a temperature of 133 K,

Fig. 6 Effect of heating the surface formed in Fig. 5 B to 133, 154, 163 and 303 K in vacuum. The 303 K spectrum has been displaced so that the 4.6 and 5.6 eV peaks due to chemisorbed chlorine are clearly visible.
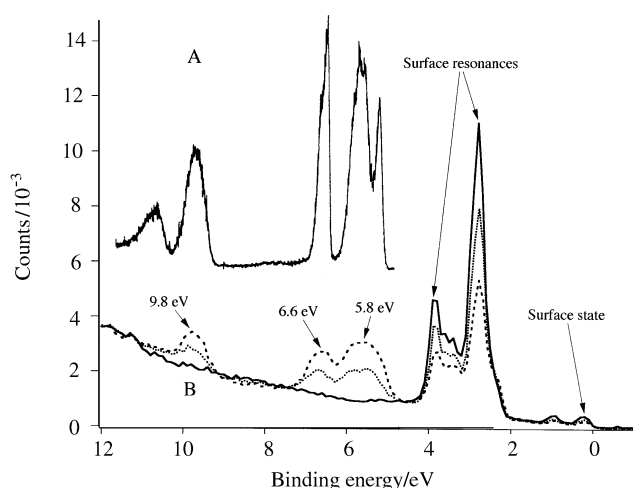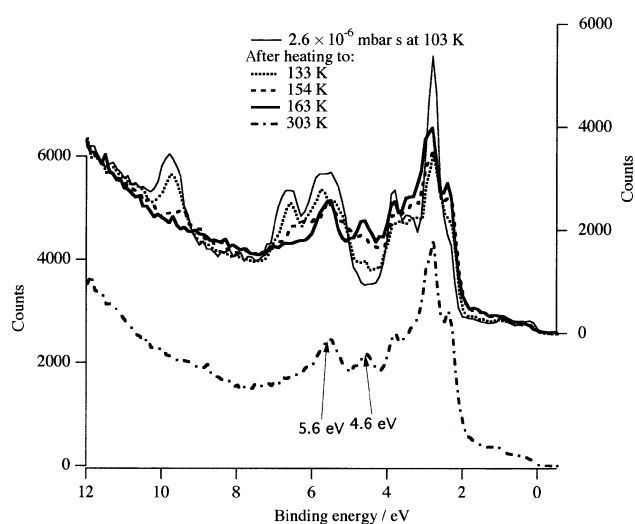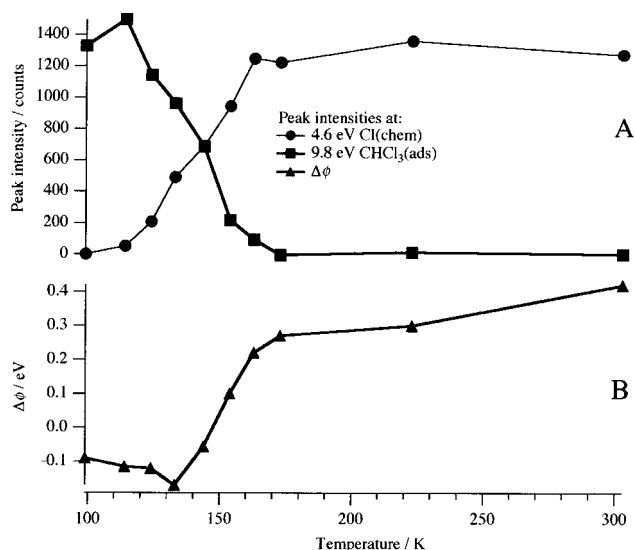

Fig. 5 A, gas phase UP spectrum of chloroform (taken from ref. 25), shifted by 6.25 eV. B, UP spectra obtained for chloroform adsorption on clean Cu(111) at 103 K (full line), after exposures of 1.3×10^{-6} (short dotted lines) and 2.6×10^{-6} mbar s (longer dotted line).

Fig. 7 A, intensities of the peaks at 4.6 eV (due to chemisorbed chlorine) and 9.8 eV (due to molecularly adsorbed chloroform) in Fig. 6 as a function of annealing temperature. B, the work function change, relative to the clean surface, as a function of temperature.

at which point the decomposition was already almost half complete, and then underwent a rapid increase to $\Delta\phi = 0.27$ eV by 173 K. This lack of change in ϕ between 100 and 133 K, even though chemisorbed chlorine was being deposited on the surface, which should increase the work function appreciably, hints at complex interactions between the unreacted chloroform, and the chemisorbed chlorine and adsorbed ethyne products. For instance, a tendency for the work function of the surface to increase as chemisorbed chlorine is deposited could be countered by a reorientation of the remaining chloroform molecules such that the molecular dipole opposes the surface-chemisorbed chlorine dipole. The LOSSP and LOSTPD experiments above have shown that the ethyne formed by the decomposition cannot have desorbed at 173 K and this is confirmed by the behaviour of the $\Delta\phi$ plot which rises again to $\Delta\phi = -0.45$ eV as ethyne is desorbed on heating the surface to room temperature.

Clearly the UP spectrum for $T < 250$ K (see Fig. 4) must contain peaks due to ethyne adsorbed on the surface. Fig. 8C shows UP spectra obtained after heating a single layer of chloroform, adsorbed at 100 K, to 222 K (sufficient to completely decompose the chloroform and produce ethyne) and then to 350 K (sufficient to completely desorb the ethyne). Fig. 8B shows the difference spectrum obtained after subtracting the 350 K spectrum from the 222 K spectrum. The substrate d band and surface resonances are clearly seen as negative features, indicating that they had increased in intensity on desorbing the ethyne. A broad positive peak at 5.0 eV and a smaller positive peak at 8.9 eV are also visible and are thought to be due to ethyne adsorbed on the chlorine covered surface (both peaks were always visible in separate subtraction experiments). Fig. 8A shows the gas phase UP spectrum of ethyne, shifted by 7.7 eV in ionisation energy such that the $3\sigma_g$ (σ_{cc}) orbital in the gas phase spectrum matches the peak at 8.9 eV in the difference spectrum. This shift positions the $1\pi_u$ (π_{cc}) orbital of gas phase ethyne approximately 1 eV lower in binding energy than the 5.0 eV peak of the adsorbed ethyne in Fig. 8B. To a first approximation we would expect the shift in

binding energy of all the orbitals of ethyne, due to the work function and the presence of the surface, to be the same on passing from the gas phase to the adsorbed phase. It follows that as ethyne is expected to bond to the surface *via* the $1\pi_u$ orbitals, and as the adsorption energy is 77 kJ mol^{-1} (0.8 eV), we can identify most of this extra shift to higher binding energy for the $1\pi_u$ orbital as being due to chemical bonding to the surface. This confirms that ethyne is formed by the complete decomposition of chloroform at 173 K, but that it remains on the surface until desorbed at just above room temperature.

Discussion

We now consider the reactions (1)–(5) proposed above in more detail. Reaction (1), with an inherent sticking probability of S_1, gives a rate of production of physisorbed chloroform of S_1F_{in}, where F_{in} is the incident flux of chloroform at the surface. Reaction (2) is simply desorption from the physisorbed state, while (3) is reaction between the physisorbed state and the copper surface to form chemisorbed chlorine and CH radicals. In reaction (4) the CH radicals combine together to form ethyne, which then desorbs from the surface in (5). Clearly it is possible that a radical chain mechanism could occur in which the CH radicals attack adsorbed $CHCl_3$ to form ethyne, but at this stage we shall keep the proposed kinetics simple.

For $T > 173$ K UPS data show that adsorbed $CHCl_3$ decomposes rapidly to chemisorbed chlorine and adsorbed ethyne, hence for $T > 173$ K reactions (3) and (4) are fast. For $T \geq 300$ K the physisorbed chloroform molecule in reactions (1), (2) and (3) may be regarded as a reactive intermediate of low surface concentration, allowing us to write

$$v_1 = v_2 + v_3 \qquad (7)$$

If we consider the surface at zero coverage, such that the concentrations of adsorbed ethyne and chemisorbed chlorine are zero, where the measured sticking probability, S takes the initial value S_0, we can write

$$S_0 = (F_{in} - F_{out})F_{in}$$
$$= (v_1 - v_2)/v_1 = v_3/v_1 = v_3/(v_2 + v_3) \qquad (8)$$
$$= k_3/(k_2 + k_3) \qquad (9)$$

where v_1 is equal to the net flux arriving at the surface, F_{in} (assuming $S_1 = 1$), and v_2 is the net flux leaving the surface, F_{out}. Depending on the relative sizes of k_2 and k_3 we have either activated or non-activated adsorption. If $k_3 > k_2$ the physisorbed molecule cracks in preference to desorbing molecularly and we have non-activated adsorption. If $k_3 < k_2$ the physisorbed molecule desorbs in preference to cracking and we have activated adsorption, which is the case here for chloroform on Cu(111). The measured sticking probability at zero coverage can now be written as

$$S_0 = k_3/(k_2 + k_3) \approx 1/[\exp(E_3 - E_2)/RT + 1] \qquad (10)$$

where $k_2 = A_2 \exp(-E_2/RT)$, $k_3 = A_3 \exp(-E_3/RT)$ and we have made the assumption that $A_2 \approx A_3$. Hence for activated adsorption E_3 is greater than E_2, see Fig. 9, and eqn. (10) provides a method of obtaining the barrier height, $E_3 - E_2$, above zero energy defined by gas phase chloroform an infinite distance from the surface. Inspection of eqn. (10) shows that for activated adsorption S_0 increases from zero at low temperatures to a value of 0.5 at high temperatures, whereas for non-activated adsorption S_0 is 1 at low temperatures and decreases to 0.5 at high temperatures. Both types of adsorption reach the same limiting value of $S_0 = 0.5$ at high temperature as the desorption and the dissociation channel become equal in probability. If $A_2 \neq A_3$ then $S_0 \neq 0.5$ at high temperature.
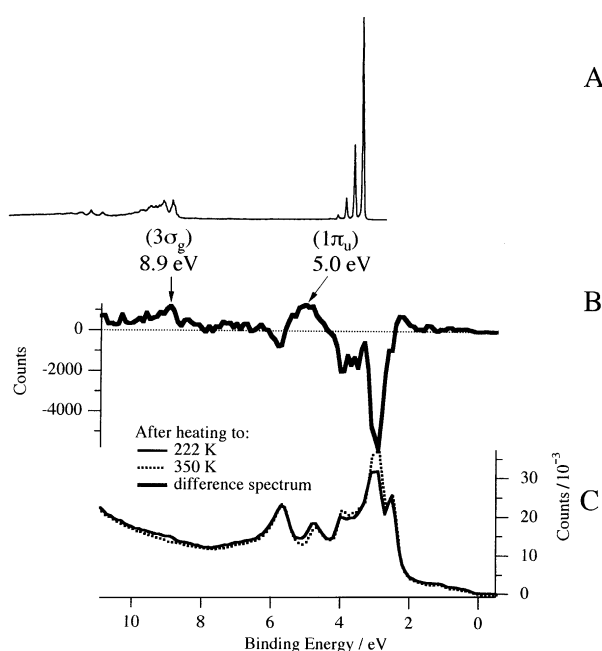

Fig. 8 A, gas phase UP spectrum of ethyne (taken from ref. 25), shifted by 7.7 eV so the $3\sigma_g$ peak matches the 8.9 eV peak for adsorbed ethyne in B. B, difference spectrum, representative of adsorbed ethyne, obtained by subtracting the 350K spectrum from the 222 K spectrum. C, UP spectra obtained after annealing a singe layer of chloroform on Cu(111) at 103 K to 222 K (forming chemisorbed chlorine with adsorbed ethyne) and 350 K (forming just chemisorbed chlorine).
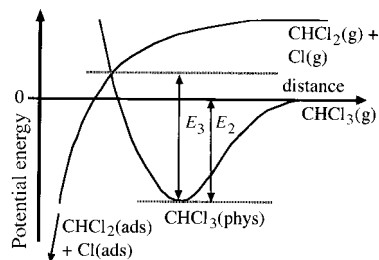
Fig. 9 Schematic showing how the potential energy curve of physisorbed chloroform at zero coverage crosses the curve for adsorption of $CHCl_2$ and Cl to give activated adsorption.

Using a value of $E_3 - E_2 = 3.5$ (± 0.7) kJ mol^{-1} we obtain theory values for S_0 of 0.13 ± 0.04, 0.21 ± 0.04 and 0.29 ± 0.04 for 216, 320 and 480 K respectively. The last two agree reasonably well with the measured values of 0.23 ± 0.04 and 0.26 ± 0.04, but the measured value of 0.35 for 216 K is significantly higher than the theory value of 0.13. We suggest that at the higher temperatures of 320–480 K physisorbed chloroform is dispersed across the surface as individual molecules, and thus E_2 is the activation energy for desorption of a single isolated molecule on the Cu(111) surface. However, at 216 K, at the lowest initial coverages obtainable in our experiment, the chloroform has already formed clusters on the surface in which there are attractive interactions between the molecules. Such attractive interactions between adsorbed species will lower one or possibly both of the curves in Fig. 9, causing the crossing point to move towards zero energy, and hence increasing the sticking probability. If we use the experimental value of S_0 at 216 K in eqn. (10) we obtain $E_3 - E_2 = 1.1$ kJ mol^{-1}, which is lower than the zero coverage value for 320–480 K. This supposition is consistent with the annealing experiments carried out on a monolayer of chloroform adsorbed molecularly at 100 K. It was found that the monolayer did not desorb molecularly, but cracked on the surface. Such behaviour is indicative of a non-activated adsorption process, and shows that for the monolayer covered surface, the crossing point of the two curves in Fig. 9 has moved below zero, making the process non-activated adsorption with dissociation rather than molecular desorption the dominant process.

If we now consider the ethyne desorption profile *versus* coverage for adsorption at 480 K, Fig. 3D, we find that it matches the sticking probability in shape. This means that, for each chloroform molecule adsorbed, an ethyne molecule is promptly desorbed. It follows that the sticking probability at 480 K is that for chloroform on a surface consisting of an increasing coverage of chemisorbed chlorine. For adsorption at 320 K, Fig. 3C, desorption of ethyne is delayed until almost half coverage. It is noticeable that this adsorbed ethyne has the effect of increasing the sticking probability during the first half of the adsorption. The effect is even more pronounced at 216 K, Fig. 3B, where all the ethyne product is retained by the surface, and the sticking probability soars to 0.7. These results may again be rationalised using attractive interactions between molecules. If physisorbed chloroform, or possibly the initial dissociation products, $CHCl_2(ads)$ and Cl(chem), or both, are stabilised by the presence of ethyne on the surface, it will again cause, the crossing point of the two curves in Fig. 9 to move towards zero, and eventually go below it, making the adsorption process non-activated and increasing the sticking probability above 0.5. Clearly the true interaction potential will be multidimensional, but for the results presented here a simple one dimensional potential is sufficient.

For adsorption at 100 K the measured sticking probability was 1.0. At this temperature reaction (1) is the only observable reaction, reactions (2)–(5) being too slow to be observable, and hence we are simply trapping intact chloroform molecules

on the surface. The observed sticking probability is therefore the same as the intrinsic sticking probability of reaction (1), S_1. As multilayer adsorption can occur at this temperature, the sticking probability remains at 1 indefinitely.

Summary

Chloroform adsorbs molecularly on Cu(111) at 100 K with a sticking probability of 1. On heating the monolayer surface formed at 100 K to 170 K, the chloroform reacts to form chemisorbed chlorine and adsorbed ethyne. On further heating, the ethyne product desorbs at just above room temperature with first order kinetics, an activation energy of 77 ± 6 kJ mol^{-1} and a pre-exponential factor of $10^{11 \pm 1}$ s^{-1}, leaving a $(\sqrt{3} \times \sqrt{3})$R30°-Cl surface. Chloroform adsorption on clean Cu(111) at room temperature and above is activated, with an activation energy of 3.5 ± 0.7 kJ mol^{-1} at zero coverage, with a sticking probability of 0.23 ± 0.04 at 320 K. For chloroform adsorption below room temperature the initial sticking probability is higher than expected and this is thought to be due to clustering of the adsorbed chloroform under the action of intermolecular attractive interactions, which causes the adsorption process to become less activated and hence increases the sticking probability. For situations where the ethyne product remains on the surface during chloroform adsorption, the sticking probability increases to greater than 0.5. This is thought to be due to attractive interactions between the adsorbed ethyne and the physisorbed chloroform, the effect of which is to convert the activated adsorption process at zero coverage into a non-activated process at finite coverage.

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