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## LETTER TO THE EDITOR

# Ion photon-stimulated desorption as a tool to monitor the physisorption to chemisorption transition of benzene on Si(111) $7 \times 7$

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## Abstract

We investigated the use of ion photodesorption as a tool to monitor the transition from the physisorbed to the chemisorbed state on a surface. The adsorption of benzene on Si(111)  $7 \times 7$  in the temperature range 40–300 K is chosen as a prototype. The  $D^+$  ion photodesorption yield was monitored as a function of temperature at various benzene exposures. Comparative measurements of the C 1s photoelectron yield in the same temperature range enable the physisorbed to chemisorbed state transition to be distinguished from that of the multilayer to the chemisorbed state. We find the onset at 110 K in the first case, and at 130–140 K in the second case. These results demonstrate that ion photodesorption is a potentially interesting method to identify physisorption to chemisorption transitions of adsorbed molecules on surfaces.

## 1. Introduction

Ion photon-stimulated desorption from adsorbed atoms and molecules on surfaces is a complex process involving a competition between desorption dynamics and the relaxation of the electronic excitations [1]. It follows that the ion photon-stimulated desorption intensity may strongly depend on the adsorption configuration of a given atom or molecule on a surface. Furthermore, ion photodesorption is usually only produced from species adsorbed on top of surface atoms rather than in subsurface sites. It follows that ion photodesorption is more

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sensitive to surface species than other methods such as electron photoemission. In recent years, these properties have been exploited to investigate how molecules adsorb on semiconductor surfaces [2–4]. However, there are still a number of problems to be investigated before ion photodesorption can be considered a versatile and universal method.

One of the puzzling problems we want to address here is whether ion photodesorption can significantly distinguish between physisorbed and chemisorbed species. Such transitions between the two states are important since the physisorbed species, though sometimes short lived at room temperature (RT), are often considered precursors for chemisorbed ones [5]. Other methods such as electron photoemission [6] or scanning tunnelling microscopy [7] can provide useful information on the physisorbed to the chemisorbed state transition, though ion photodesorption might be more surface and site specific. In principle, physisorbed species, being less electronically coupled to the surface than chemisorbed ones, might give rise to more intense ion photodesorption. However, this argument does not necessarily hold since, immediately after ionization and well before the ion desorption has occurred, the initially weakly bound physisorbed species may become strongly bound to the surface through the image state potential and/or the formation of new chemical bonds with the surface. On the other hand, the contribution of secondary electrons in promoting the desorption, especially above threshold, has to be taken into account.

As a consequence it is difficult to predict whether ion photodesorption can distinguish between physisorbed and chemisorbed species. The ideal system to answer this problem is an adsorbate that can easily undergo a transition from a physisorbed to a chemisorbed state. One could then monitor directly, without any possible artefact, the comparison between the ion photodesorption of physisorbed and chemisorbed species.

Here we present an ion photodesorption study of benzene on Si(111)  $7 \times 7$  as a function of temperature. This system satisfies many requirements for this kind of experiment. Benzene exists in either a physisorbed or chemisorbed state on Si(111)  $7 \times 7$ , the selection of state depending on the temperature [5]. Furthermore, it contains low-mass, i.e. hydrogen, atoms that are the best candidates for detecting an ion desorption process.

Information on benzene/Si(111)  $7 \times 7$  is available through valence band and core level photoemission [8, 9], HREELS [10, 11] and STM experiments [5, 7]. It was found that chemisorbed benzene is simultaneously di- $\sigma$  bonded on a surface adatom and rest atom at RT, and hence almost parallel to the surface. Furthermore, it displays a high surface mobility, attributed to the existence at RT of an easily accessible physisorbed state characterized by a high lateral mobility. Benzene in a physisorbed state on Si(111)  $7 \times 7$  was first revealed in a low-temperature [7] STM study, and it was recognized as the intrinsic precursor of a chemisorbed one, i.e. undergoing a transition on the same adsorption site. Benzene's electronic structure also allows a detailed study of the physisorbed versus chemisorbed state, due to the presence of a degenerate orbital in the former, whose degeneracy is removed in the latter. TPD and HREELS studies as well were performed at the temperature of coexistence of the chemisorbed and physisorbed benzene on Si(111)  $7 \times 7$ , revealing their simultaneous presence [11].

Therefore, benzene on Si(111)  $7 \times 7$  seems to be well adapted to compare ion photodesorption between physisorbed and chemisorbed species.

## 2. Experimental details

The experiments were performed at the storage ring Super-ACO at the French synchrotron facility (LURE) in Orsay. The SA72 beam line was used in the energy range 150–800 eV. The total resolution (monochromator plus analyser) was 250 meV. The experiments were performed in a UHV chamber with a base pressure below  $1 \times 10^{-10}$  mbar. The analysis chamber was

equipped with a high-sensitivity quadrupole mass spectrometer for the desorption studies. In the photodesorption experiments the sample was rotated and oriented normal to the mass spectrometer. The Si(111) crystal was n-type phosphorus doped with  $1 \Omega \text{ cm}$  resistivity. The  $7 \times 7$  reconstruction of Si(111) was obtained by flashing the sample at  $1100^\circ\text{C}$  by direct heating. In the experiments deuterated benzene was used instead of benzene, in order to distinguish the  $\text{D}^+$  produced by photofragmentation from  $\text{H}^+$ , which is always detected under our experimental conditions. In order to reach the required low temperatures, the system was cooled with liquid helium.

The temperature ramp was achieved by pulsed direct heating of the silicon wafer, with a feedback system controlled through a thermocouple glued to the back of the sample. The signal (ion yield or photoemitted electron yield) was recorded during the heating pause. We performed the experiments at two heating rates, 0.1 and  $0.03 \text{ K s}^{-1}$ , in order to establish whether the transitions we observed were affected by artefacts induced by too fast a heating rate. Pulsed direct heating is preferable to the alternative method of simply stopping the cooling He flow, because it avoids possible evaporation from the cryostat and readsorption on the silicon sample. Furthermore the heating rate is more constant.

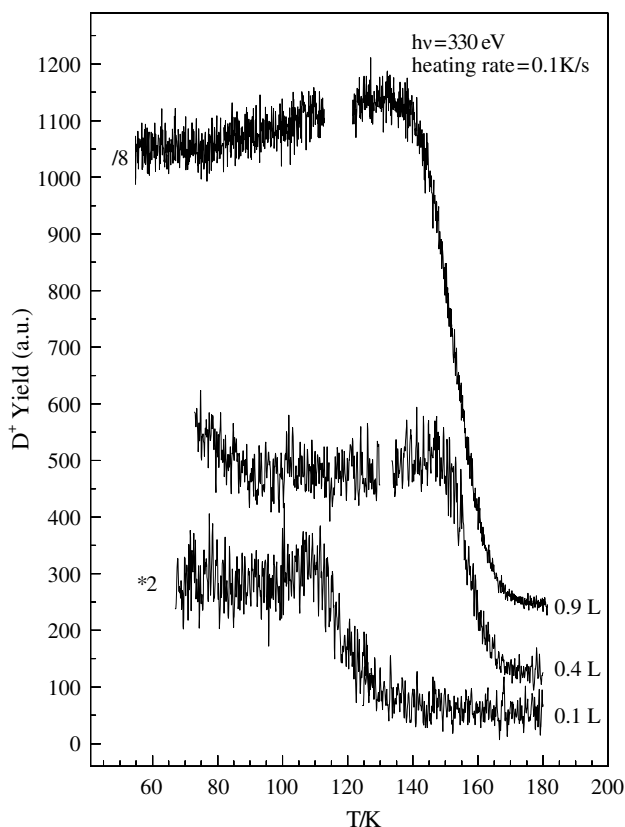
### 3. Results and discussion

We found that  $\text{D}^+$  is the only photodesorbed ion both at low (40–120 K) and at RT in the C 1s threshold energy range. In addition, we checked the desorption geometry by rotating the sample and we detected an ion yield only when the surface is perpendicular ( $\pm 5^\circ$ ) to the detection direction. Hence, we kept the geometry of the sample perpendicular to the quadrupole mass analyser. Furthermore, we chose to perform the temperature- and exposure-dependent experiments at 330 eV, i.e. well above the ionization threshold, in order to achieve the highest possible ion yield. In this way a lack of ion signal cannot be attributed to a low-yield process.

After various benzene exposures (0.1, 0.4 and 0.9 L) and at low temperature (42 K), the  $\text{D}^+$  ion intensity was monitored as a function of increasing temperature (figure 1). The important feature in the curves of this figure is that they all show a drop in  $\text{D}^+$  yield as a function of temperature that we attribute to a change in the benzene adsorption configuration. The three plots are shifted vertically with respect to each other in order to avoid any overlap of the curves, but they all end up at the same  $\text{D}^+$  count rate after the transition. This suggests a common final adsorption state in the three cases. The low exposure curve (0.1 L) shows a decrease of  $\text{D}^+$  yield starting at 110 K. The higher exposure ones (0.4 and 0.9 L) show a delayed onset in the range 130–140 K. We tentatively assign the decrease in intensity in the 0.1 L curve of figure 1 to the transition from a physisorbed layer to a chemisorbed one and the decrease of the 0.4 and 0.9 L curves to the transition from multilayers to a chemisorbed monolayer. It is worth noticing that previously performed low-temperature TPD experiments of benzene on Si(111)  $7 \times 7$  also indicate 0.1 L as the limit for obtaining a physisorbed layer. In the multilayer case, we have a double effect. The transition of the first physisorbed layer is actually masked by the thermally induced desorption of the benzene multilayers on top of the first layer. The second process, however, occurs at higher temperatures and, as a consequence, the transition of the first physisorbed layer is not observable, because of all the overlayers still on top of it, providing an unaltered  $\text{D}^+$  yield.

The occurrence of the two transitions, i.e. the physisorption to chemisorption state transition and the multilayer desorption, can be confirmed through two different types of experiments.

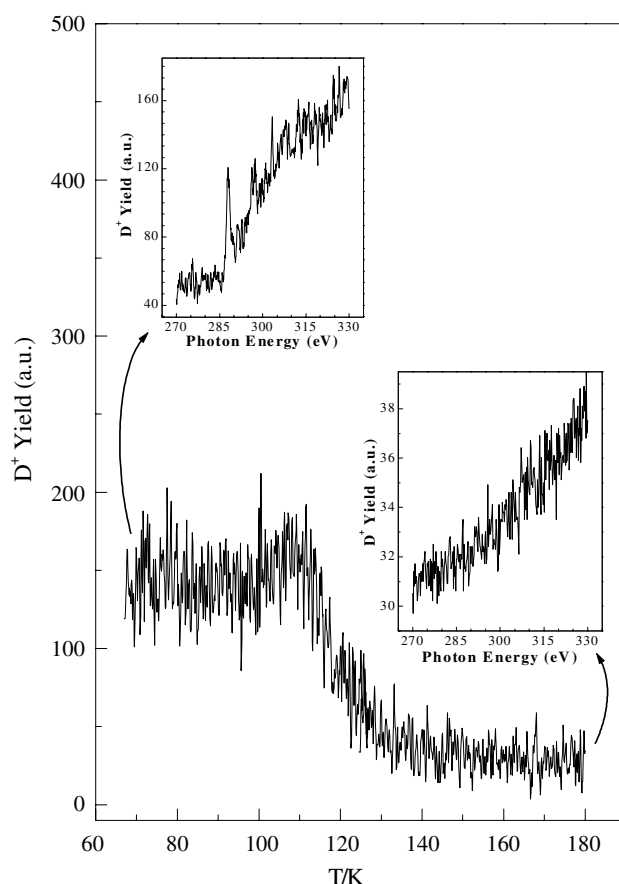
First of all, at the beginning and end of each temperature-dependent  $\text{D}^+$  monitoring we recorded the  $\text{D}^+$  photoexcitation spectra (i.e.  $\text{D}^+$  yield as a function of photon energy).



**Figure 1.**  $D^+$  yield as a function of temperature, for the three benzene exposures on Si(111)  $7 \times 7$ : 0.1, 0.4 and 0.9 L. The incident photon energy is 330 eV. The curves at higher exposures are artificially shifted upwards, though the final count rate is the same for all curves. The heating rate is  $0.1 \text{ K s}^{-1}$ .

The spectra of the low-temperature states are rather structured and show a good correspondence to the condensed benzene spectra collected by Menzel *et al* [12]. The photoexcitation spectra of the high-temperature state become structureless, as can be expected for a chemisorbed species in strong interaction with the surface. In figure 2 the  $D^+$  photoexcitation spectra before and after transition are reported for the physisorption case (0.1 L).

Second, we performed the same type of experiments by monitoring the C 1s photoelectron yield as a function of temperature in the same energy ranges. The reason for such an experiment is that the ion photodesorption yield is expected to be sensitive to both the adsorption state and the amount of species present on the surface, whereas the core photoemission yield depends only on the amount of species adsorbed on the surface and is hardly sensitive to the adsorption state. Therefore, if thermal desorption occurs, we should observe a parallel decrease in the C 1s electron emission intensity. At variance with this, a physisorbed to chemisorbed state transition should produce no change in the C 1s photoemission signal intensity. In figure 3, we have reported the C 1s photoelectron yield at the maximum peak, for the two exposures 0.1 and 0.4 L. The low-exposure C 1s intensity is totally unaffected by the phase transition, at variance with the higher exposure case where the C 1s signal shows a decrease of intensity in a temperature

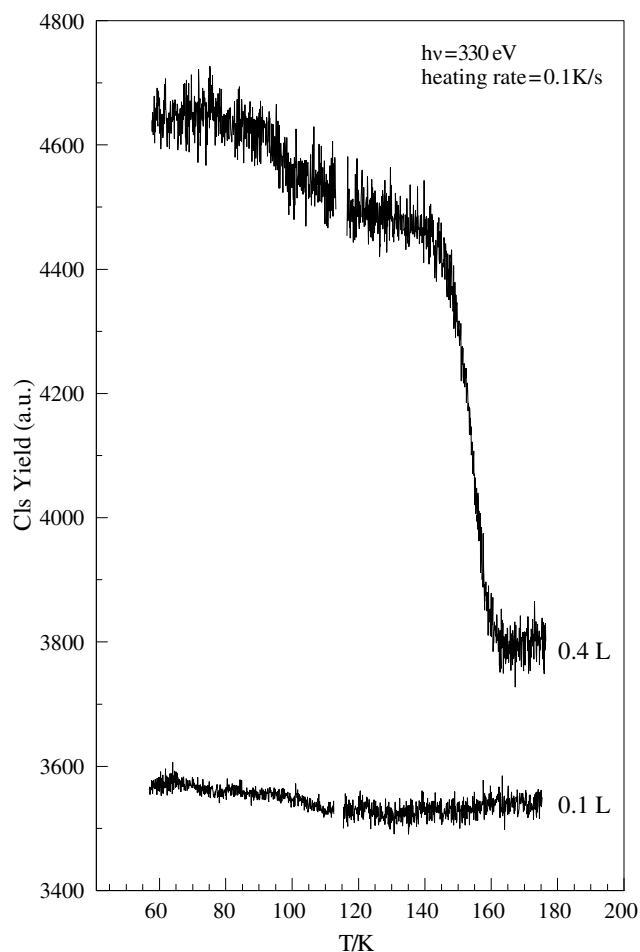


**Figure 2.** Photoexcitation spectra of 0.1 L benzene on Si(111)  $7 \times 7$  at the beginning of an experiment as a function of temperature, i.e. at 67 K, and at the end, i.e. at 180 K. The two spectra are significantly different in terms of ion yield and spectral structure, showing two different benzene adsorption states.

range perfectly consistent with that of the  $D^+$  yield decrease. This clearly confirms that the 0.1 L curve corresponds to the transition from a physisorbed to chemisorbed state whereas the 0.4 and 0.9 L curves correspond to the transition from multilayers to chemisorption. We note that, even by assuming a constant sticking coefficient equal to unity, it would have been very difficult to determine the benzene coverage only from the measured benzene exposure since the absolute values of this latter quantity are affected by many uncertainties.

We also checked whether the count rate could be restored upon re-cooling of the system, at any exposures. Once a transition has occurred, the initial count rate is never recovered; hence neither of the two observed processes is reversible.

Finally, we checked whether any artefact could be introduced by the heating rate. Too fast a heating rate would induce an apparent transition at lower temperature while, conversely, the sample has already reached higher temperatures as an effect of the fast heating. Therefore, we repeated the experiments for a significantly lower heating rate ( $0.03 \text{ K s}^{-1}$  instead of  $0.1 \text{ K s}^{-1}$ ). The corresponding  $D^+$  yield curves are reported in figure 4. The transition of the 0.4 L curve is very similar to the corresponding one in figure 1. The transition of the 0.1 L curve extends over



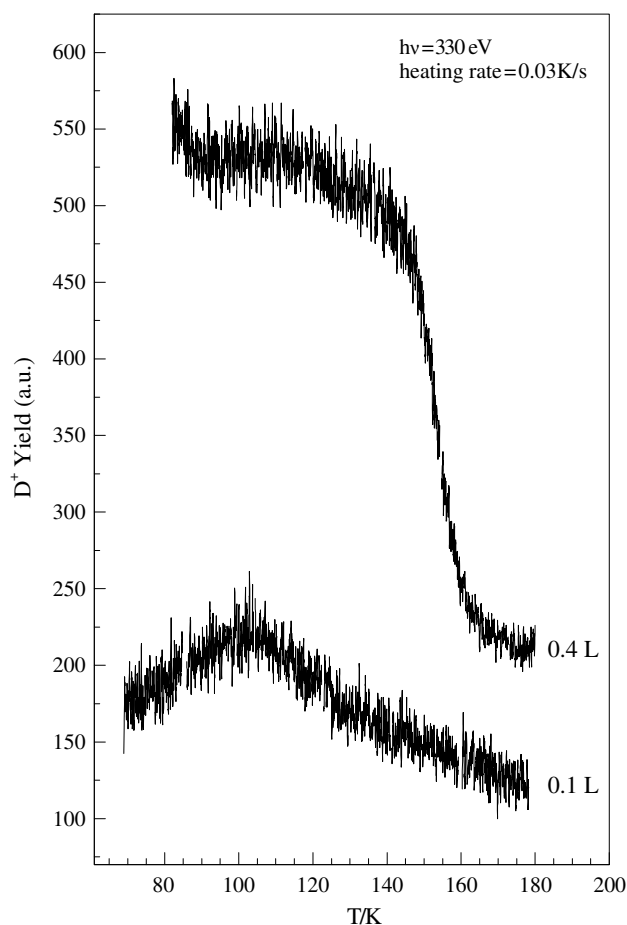
**Figure 3.** C 1s photoemission yield as a function of temperature for physisorbed benzene (0.1 L) and for benzene overlayers (0.4 L).

a larger temperature range than in figure 1, but the onset of the transition around 110 K is the same for the two heating rates. The count-rate increase below 100 K and the less pronounced decrease above 110 K of the 0.1 L curve in figure 4 as compared to figure 1 can be explained by undesirable readsorption of benzene molecules from the residual gas during the experiment.

The observed transition temperatures that we find here are systematically 30 K higher than what we have previously hypothesized [6]. However, this can be easily explained by the way we measured the temperature in the two types of experiments (i.e. the sample-holder temperature in [6] and the temperature of the back of the sample in this case). The transition temperatures measured here are believed to be more accurate than those previously measured.

#### 4. Conclusions

The main result of this study is that the physisorbed to chemisorbed state transition of benzene adsorbed on Si(111)  $7 \times 7$  induces a strong decrease in the ion photodesorption intensity. A detailed understanding of this effect is far beyond the scope of this paper since it would require



**Figure 4.** D<sup>+</sup> yield as a function of temperature for a heating rate of 0.03 K s<sup>-1</sup>, for physisorbed (0.1 L) and condensed benzene (0.4 L). The incident photon energy is 330 eV.

detailed knowledge of the ion photodesorption process itself, which is not accessible at the moment. However, this result has important consequences. It suggests that, immediately after photoionization, the benzene molecule, which was initially physisorbed, is still weakly interacting with the surface. The image state potential most probably increases the molecular ion–surface interaction by a few tens of electronvolts, but no chemical bond can be created before the ion desorption can occur. This indicates that the desorption of the D<sup>+</sup> fragment should be more rapid than any change in the adsorption geometry which would lead the ionized molecule into a possible more stable chemisorbed state. These results confirm that ion photodesorption is a suitable tool to monitor transitions from physisorbed to chemisorbed states. Further studies involving kinetic energy measurements of the photodesorbed ions could provide much other insight into such transitions of adsorbates on surfaces.

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