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Adsorption dynamics of tetrahydrofuran on Si(0 0 1) studied by means of molecular beam techniques

M.A. Lipponer[a], M. Dürr[a,b,*], U. Höfer[a]

[a] Fachbereich Physik und Zentrum für Materialwissenschaften, Philipps-Universität, D-35032 Marburg, Germany
[b] Institut für Angewandte Physik, Justus-Liebig-Universität Giessen, D-35392 Giessen, Germany

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ABSTRACT

The reactivity of tetrahydrofuran (THF) on Si(0 0 1) was measured as a function of kinetic energy, surface temperature, and THF exposure. The initial sticking coefficient s_0 drops with increasing kinetic energy indicating an overall non-activated adsorption pathway. At constant kinetic energy, s_0 is insensitive on surface temperature T_S below 400 K but decreases with increasing T_S above 400 K. This behavior is quantitatively described using the Kisliuk model for molecules trapped in an intermediate adsorption state and discussed in the context of a datively bonded intermediate in the reaction channel.

1. Introduction

The reaction of organic molecules on semiconductor surfaces has attracted much interest in the recent past [1–7] and the adsorption properties of a large number of different organic molecules have been investigated [5]. The main focus of the experimental investigations lay on the adsorption configurations and mechanisms; in most cases the reaction was found to proceed via a metastable precursor or intermediate state. Information on the underlying potential energy curve can be obtained from experiments on the adsorption dynamics, however, such experiments were reported only for the most prominent systems, e. g., ethylene or acetylene on Si(0 0 1) [8–10]. It was shown that the adsorption dynamics of these overall non-activated reactions are governed by the presence of the intermediate state (Figure 1) which thus can be investigated in detail.

For molecules containing a heteroatom such as nitrogen or oxygen, this intermediate state involves lone pair electrons of the heteroatom and, in the case of Si(0 0 1), the empty dangling bond of the lower silicon atom of the silicon dimer, forming a so-called dative bond [11]. Most prominent examples are amines and alcohols. In the case of tertiary amines at low coverage, the dative bonded configuration is the final configuration since breaking the N—C bond is associated with a high activation barrier [12–14]; on the other hand the datively bonded intermediate of primary and secondary amines on Si(0 0 1) [11,15] as well as of alcohols on Si(0 0 1) [16–18] is short lived due to the low activation energy required for the proton transfer leading to the final configuration comprising a Si—N or Si—O and a Si—H bond. Most recently, we have shown that ethers, namely tetrahydrofuran (THF) and diethyl ether (Et_2O), also adsorb via a datively bonded intermediate state at the D_{down} state of the Si(0 0 1) surface [19,20] (Figure 1). At surface temperatures below 150 K, this intermediate was shown to be stable on the timescale of the experiments; at elevated surface temperature, one O—C bond of the ether group is cleaved leading to covalently bonded final configurations including Si—O and Si—C bonds. Ethers on Si(0 0 1) can therefore be seen as an ideal test system for the adsorption dynamics of reaction systems including a datively bonded intermediated state.

Here we present molecular beam experiments on the adsorption of THF on Si(0 0 1). With increasing beam energy, the initial sticking probability s_0 decreases monotonically, pointing toward an overall non-activated reaction channel. At constant beam energy, s_0 is constant at low temperature and decreases at elevated temperatures. We interpret this in the context of adsorption of THF via the datively bonded intermediate. Quantitative evaluation in the framework of the Kisliuk model, i.e., competition between conversion into the covalently bonded final state and desorption into the vacuum, reveals the difference between the energy barriers for these two channels, $\varepsilon_d - \varepsilon_a = 0.32$ eV (Figure 1). The coverage dependence of sticking probability and its change with surface temperature are interpreted in the framework of an extrinsic precursor state.

2. Methods

For the experiments, a four-stage molecular beam vacuum setup was used [21,22] with a base pressure of 3×10^{-11} mbar in the main

* Corresponding author at: Institut für Angewandte Physik, Justus-Liebig-Universität Giessen, D-35392 Giessen, Germany.
E-mail address: michael.duerr@ap.physik.uni-giessen.de (M. Dürr).

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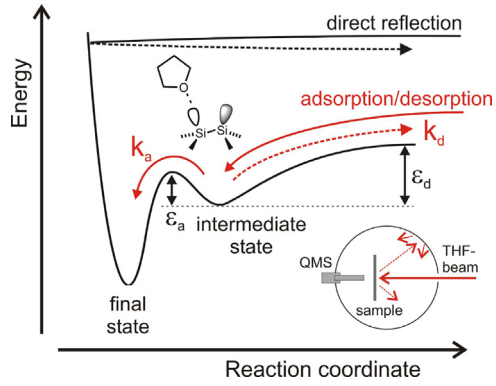

Figure 1. Schematic potential energy curve of a typical reaction pathway for organic molecules on semiconductor surfaces. The reaction is non-activated but exhibits an intermediate state; incoming molecules are either adsorbed in this intermediate or directly reflected. Molecules in the intermediate can either convert into the final state with rate k_a or desorb with rate k_d. Both direct reflection and desorption out of the intermediate contribute to the background pressure measured by a QMS in the main chamber (inset). In the case of THF on Si(0 0 1), the intermediate is formed by a dative bond between THF and Si(0 0 1) as sketched.

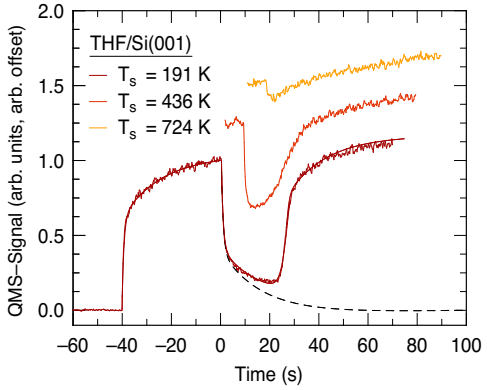

Figure 2. THF-pressure measured as a function of time for three different surface temperatures. For the 191-K-measurement, the molecular beam enters the main chamber at $t = -40$ s; at $t = 0$ s the shutter in front of the clean Si(0 0 1) sample is removed. A pronounced QMS-signal drop is observed which is correlated to the sticking coefficient s. Once the sample is saturated, the background pressure rises again ($t \approx 25$ s). The signal is influenced by the chamber response as observed when blocking the beam outside the main chamber (black dashed line). The solid line represents a fit to the data taking the chamber response into account. For details see main text.

chamber. The molecular beam was created via supersonic expansion from a continuous nozzle with an orifice diameter of 100 μm; the nozzle was located 30 cm from the sample, nozzle temperature was kept at room temperature for all experiments. In order to maintain a stable molecular flux during beam operation, a 5-l-container was filled with THF vapour from which the nozzle was supplied. When seeded-beam techniques were applied in order to increase the translational energy of the THF molecules in the beam, THF was mixed with helium in the 5-l-container. The velocity distribution of the THF molecules was determined by means of time-of-flight measurements, the speed ratio ranged from $S = 3$ for pure THF to $S = 11$ for seeded beams (compare Supplementary material); the flux of the pure THF beam was in the order of 10^{13} cm^{-2} s^{-1}. During beam operation with pure THF, typical background pressure in the main chamber was $\lesssim 1 \times 10^{-10}$ mbar. When using seeded beam techniques, the pressure increased up to 3×10^{-8} mbar due to a higher amount of helium in the beam.

Sample preparation was described in detail elsewhere [23]. In short, the Si(0 0 1) sample (11mm × 60mm) was prepared by removal of the native oxide layer via repetitive resistive heating to 1300 K. The sample temperature was measured using a thermocouple which was glued to the center of the rear side of the sample. After preparation, sharp peaks of the Si(0 0 1) 2×1 reconstruction where observed in the low energy electron diffraction pattern. No contamination was observed in X-ray photoelectron spectra when applying the identical preparation scheme in a different UHV chamber [19]. Between the adsorption experiments, the sample was cleaned by heating to 1100 K.

Sticking coefficients were measured following the method by King and Wells [24]: When the molecular beam enters the main chamber, it is first blocked by a non-reactive shutter in front of the sample surface (in the main chamber). The corresponding rise of the background pressure of THF (main fragment signal, $m/z = 42 \pm 2$) is recorded by a quadrupole mass spectrometer (QMS) which is placed in line with the molecular beam but which is blocked from the beam by the silicon sample. When opening the shutter, the silicon surface is exposed to the molecular beam and a drop in the QMS-signal is observed due to adsorption of THF on the surface (Figure 1, inset). As the sample is larger than the cross section of the molecular beam, in a first approximation the observed pressure drop is proportional to the sticking coefficient s. In the case of THF, however, the pressure change is superimposed by a non-instantaneous chamber response function which has to be taken into account for proper evaluation of the sticking probability on the silicon surface (see below). All measurements were performed under normal incidence of the molecular beam.

3. Results

Figure 2 shows the measured background pressure of THF in the vacuum chamber when exposing the silicon surface to the THF beam at three different surface temperatures T_S. Although the King-and-Wells experiment typically allows a straight forward evaluation of sticking probabilities, we will show that in the case of THF the measured QMS-signal is influenced by adsorption/desorption phenomena at the chamber walls and that the resulting chamber response function has to be taken into account for the determination of sticking probabilities. As an example, we discuss the observed QMS-signal of the 191-K-measurement in more detail: in that case, the beam entered the main chamber and hit the non-reactive shutter placed in front of the sample at $t = -40$ s. As the reactive sample surface is not yet involved, one would expect an almost instantaneous rise of the QMS-signal to the equilibrium signal given by the flux of the molecular beam and the pumping speed of the vacuum system. However, after an initial rise a rather slow increase of the QMS-signal is observed. At $t = 0$s, the clean sample surface was then exposed to the molecular beam and a pronounced signal drop is observed which is followed by a further, rather slow decrease of the QMS-signal. A very similar slow decrease of the signal (dashed line) is observed when we do not open the shutter in front of the sample surface but again block the beam outside the main chamber. Furthermore, the functional form of the decreasing signal strongly resembles the increasing signal after the beam is allowed to enter the main chamber. As a consequence, the measured QMS-signal is interpreted as a superposition of the pressure change induced by the reaction of THF molecules on the silicon surface and the rather slow chamber response function f_c [25], tentatively assigned to adsorption/desorption phenomena at chamber walls (including the cooled manipulator): when the beam enters the main chamber, molecules reflected from the shutter can stick at the chamber walls leading to a retarded increase of the QMS signal. On the other hand, when the beam hits the reactive sample and most of the molecules in the beam are adsorbed on the surface, desorption from the chamber walls can cause the retarded decrease of the QMS signal. In the further progress of