Binding Energy and Dissociation Barrier: Experimental Determination of the Key Parameters of the Potential Energy Curve of Diethyl Ether on Si(001)

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Supporting Information

ABSTRACT: The key parameters of the potential energy curve of organic molecules on semiconductor surfaces, binding energy of the intermediate state and dissociation barrier, were experimentally investigated for the model system of diethyl ether (Et2O) on Si(001). Et2O adsors via a datively bonded intermediate from which it converts via ether cleavage into a covalently attached final state. This thermally activated conversion into the final state was followed in real-time by means of optical second-harmonic generation (SHG) at different temperatures and the associated energy barrier $\epsilon_d = 0.38 \pm 0.05$ eV and pre-exponential factor $\nu_d = 10^{12 \pm 3}$ s$^{-1}$ were determined. From molecular beam experiments on the initial sticking probability, the difference between the desorption energy $\epsilon_d$ and $\epsilon_f$ was extracted and thus the binding energy of the intermediate state was determined (0.62 ± 0.08 eV). The results are discussed in terms of general chemical trends as well as with respect to a wider applicability on adsorbate reactions on semiconductor surfaces.

The functionalization of semiconductor surfaces with organic molecules has attracted much interest, especially with respect to the challenges arising from the miniaturization in semiconductor device physics. On Si(001), adsorption of most organic molecules is controlled by an intermediate state; for various systems, this intermediate was observed by means of spectroscopic methods or scanning tunneling microscopy. However, experimental access to the main parameters of the underlying potential energy curve, especially to the barrier for conversion from the intermediate to the final state, is challenging: the experiment both has to be able to differentiate between the intermediate and final state as well as it has to be fast enough to follow the conversion between the two states in real-time.

In this Letter, we show that optical SHG can be employed for the determination of this conversion rate $k_a$ and, thus, the energy barrier $\epsilon_a$. For crystal structures with inversion symmetry, such as silicon, SHG is symmetry forbidden in the bulk and, thus, provides a background free, surface sensitive probe. The key for the present application is the sensitivity of SHG on the number of reacted Si dangling bond states, as this number typically changes from the intermediate to the final state. For example, the overall nonactivated adsorption of diethyl ether on Si(001) includes an intermediate with a dative bond between the molecule’s oxygen atom and the $D_{\text{Down}}$ state of the lower Si atom of the silicon dimer. Ether cleavage converts this intermediate into two covalently attached fragments of the former diethyl ether molecule on two neighbored dimer rows thus quenching two dangling bonds (inset Figure 1). We use this reaction as a prototype system for determining the energy barrier $\epsilon_a = 0.38 \pm 0.05$ eV and pre-exponential factor $\nu_a = 10^{12 \pm 1}$ s$^{-1}$ by means of SHG. We combine this measurement with a molecular beam experiment in order to also get access to the binding energy of the intermediate state. In the case of a barrierless adsorption channel from the gas phase into the intermediate state, the binding energy of the intermediate state is equal to the desorption barrier $\epsilon_d$ for desorption into the gas phase. By measuring the initial sticking coefficient as a function of surface temperature, the energy barrier difference $\epsilon_d - \epsilon_f = 0.24 \pm 0.03$ eV and thus $\epsilon_d = 0.62 \pm 0.08$ eV were determined. With $\nu_d/\nu_a = (7 \pm 3) \times 10^5$, the respective pre-exponential factor $\nu_d = 10^{12 \pm 3}$ s$^{-1}$ was deduced. Both $\nu_a$ and $\nu_d$ were found to be considerably lower than the typically assumed values of $10^{12}$ to $10^{13}$ s$^{-1}$; thus, the temperature-dependent rate measurements are necessary for an absolute determination of the energy barriers.

Figure 1 shows the results of a typical SHG experiment following the ether cleavage reaction in real-time. The
nonlinear optical response of the surface is characterized by the nonlinear susceptibility $\chi^{(2)}$, which is proportional to the square root of the measured SHG signal. For small surface coverage, $\chi^{(2)}$ depends linearly on the number of dangling bonds on the surface. In addition, $\chi^{(2)}$ changes as a function temperature. In Figure 1, $\chi^{(2)}$ is plotted as a function of time; prior to adsorption of Et$_2$O, the measured SHG signal and, thus, $\chi^{(2)}$ is constant. At $t = -155$ s, Et$_2$O was adsorbed in the datively bonded intermediate state at $T_s = 80$ K and quenches one dangling bond per adsorbed molecule; coverage was approximately 0.1 ML (1 ML equals one Et$_2$O molecule per silicon dimer). At $t = -22$ s, the surface temperature was increased to $T_s = 293$ K. Up to $t = 0$ s, the concomitant decrease of $\chi^{(2)}$ is dominated by the temperature dependence of the SHG signal. At $t = 0$ s, the final temperature is reached and for $t > 0$ s, the change in $\chi^{(2)}$ can be exclusively attributed to the conversion from the intermediate into the final state and the concomitant quenching of two dangling bond states. In order to compare different isothermal measurements, $\chi^{(2)}$ is normalized to $\Delta\chi_s^{(2)} = \chi^{(2)}(t = 0) - \chi^{(2)}_{\text{init}}$ and plotted in the form $\Delta\chi_s^{(2)}(t) = [\chi^{(2)}(t) - \chi^{(2)}_{\text{init}}]/\Delta\chi_s^{(2)}$, where $\chi^{(2)}(t)$ is the time dependent nonlinear susceptibility and $\chi^{(2)}_{\text{init}}$ is the nonlinear susceptibility when all adsorbates are converted into the final state. $\chi^{(2)}_{\text{init}}$ is obtained by heating the surface to temperatures slightly above 300 K (at $t = 670$ s in Figure 1) and again measuring the SHG signal at the temperature at which the reaction was followed (293 K at $t = 800$ s in Figure 1). In order to qualitatively compare the overall change in $\chi^{(2)}$ in Figure 1 the sample is further cooled down to 80 K at $t = 920$ s. As $\chi^{(2)}$ of a surface with still datively bonded molecules would return to the base level, the observed difference in $\chi^{(2)}$ can be directly attributed to the conversion from the intermediate into the final state.

For a quantitative analysis, the isothermal measurements are plotted on a logarithmic scale (Figure 2) and fitted with the exponential decay law $\Delta\chi^{(2)}(t) = \Delta\chi^{(2)}(t = 0)\exp(-k_s t)$ of a first order chemical reaction, with $k_s$ being the dissociation rate of Et$_2$O. The inset in Figure 2 shows the decay rates $k_s$ plotted as a function of inverse surface temperature. The data points are well described by the Arrhenius law $k_s(T_s) = A_s \exp(-\epsilon_a/k_B T_s)$ with activation energy $\epsilon_a = 0.38 \pm 0.05$ eV and pre-exponential factor $A_s = 10^{12} \text{ s}^{-1}$. In addition to random measurement errors, we take into account a possible systematic underestimation of $T_s$ by up to 10 K due to nonuniform laser-heating; in the given temperature regime this leads to the relatively high error bars.

Complementary information was obtained when measuring the initial sticking probabilities $s_0$ as a function of surface temperature $T_s$, which gives access to the difference between desorption and conversion barrier, $\epsilon_d - \epsilon_c$. In the left inset of Figure 3, two typical measurements following the King and Wells method are shown; in the case of the 171 K measurement, the molecular beam enters the main chamber at $t = -22$ s and is blocked by a nonreactive shutter, thus the background pressure $P_{\text{QMS}}(t)$ as measured by means of a QMS is used instead of the SHG signal. For details see main text and Supporting Information.
Within a Kisliuk plot (compare Supporting Information) from which \( \epsilon_d = \epsilon_a = 0.24 \pm 0.03 \text{ eV} \) and \( \nu_\text{d}/\nu_\text{a} = (7 \pm 3) \times 10^2 \) are deduced.

The experimental results are summarized in Figure 4. With \( \epsilon_a = 0.38 \pm 0.05 \text{ eV} \) \( (\nu_\text{d} = 10^{21.5} \text{ s}^{-1}) \) and \( \epsilon_d - \epsilon_a = 0.24 \pm 0.03 \text{ eV} \), the binding energy of the intermediate state can be deduced to \( \epsilon_d = 0.62 \pm 0.08 \text{ eV} \) \( (\nu_\text{d} = 10^{21.5} \text{ s}^{-1}) \) and thus the combination of both techniques determines the main parameters of the potential energy curve of the dative bonded \( \text{Et}_2\text{O} \) on Si(001). In the following, we will first discuss the binding energy of \( \text{Et}_2\text{O} \) with respect to other coordinatively bound organic molecules. Second, we will be focusing on the unusually low pre-exponential factors as well as having a short look on the kinetics of the ether cleavage reaction and its implications on the reaction mechanism. Finally, as we see SHG to be more generally applicable to the measurement of the reaction kinetics of organic molecules on semiconductor surfaces, we will review the method in more detail at the end of this section.

In a simple model, the dative bond strength \( \epsilon_d \) of heteroatoms on the Si(001) surface is expected to decrease with increasing electronegativity of the heteroatom, as also observed in DFT calculations. The presented results confirm this trend experimentally as \( \text{Et}_2\text{O} \) is more weakly bound on Si(001) than amines. For example, at low coverage trimethyl amine (TMA) desorbs intact from the surface as N–C cleavage is activated with respect to the molecule in the gas phase. In that case, the binding energy of the dative bonded TMA was directly determined by desorption experiments to be \( \epsilon_d = 1.1 \text{ eV} \), substantially higher than in the case of \( \text{Et}_2\text{O}/\text{Si}(001) \).

Figure 4. Potential energy curve of \( \text{Et}_2\text{O} \) on Si(001). The dative bonded intermediate state (1) is kinetically stabilized against the ether cleavage reaction by \( \epsilon_d = 0.38 \text{ eV} \) and is bonded with \( \epsilon_d = 0.62 \text{ eV} \) relative to the molecule in the gas phase.
photoelectron spectroscopy (XPS), infrared spectroscopy, or electron energy loss spectroscopy, as well as by STM. However, the typical time scale of these experiments is in the order of hundreds of seconds, which strongly limits the range of accessible reaction rates. As a consequence, available data either cover a limited temperature range or are restricted to the measurement of a single rate at a fixed temperature. An exception would be XPS using synchrotron radiation with increased photon flux; in that case one has to carefully exclude a possible influence of the intense X-ray radiation on the reaction or beam damage. On the other hand, SHG as an all-optical technique allows to follow surface reactions on a fast time scale without such restrictions and the need for a large-scale research facility. Its application to organic adsorbate systems benefits in particular from a clear correlation between the SHG signal and the reaction stage: most reactions of organic molecules with semiconductor surfaces are restricted to the dangling bonds, both in the intermediate and final state. Independent on the type of intermediate state, for example, involving a dative bond via lone pairs or \( \pi \)-electrons, the number of reacted dangling bonds will change from the intermediate to the final state. With the linear dependence of \( \chi^2 \) on the number of reacted dangling bond states, a linear relationship between the number of reacted molecules and \( \chi^2 \) can be expected to hold in such a situation. If no such simple relationship between the SHG signal and the number of reacted molecules exists, the method can still be employed when calibrating the SHG signal, for example, by means of XPS, as has been demonstrated in an early investigation of oxygen dissociation on Si(111).

In conclusion, the main parameters of the potential energy curve of an organic molecule on a semiconductor surface were experimentally determined. Temperature-dependent measurements of reaction rates by means of optical SHG were combined with molecular beam experiments to deduce both conversion barrier (\( \epsilon_c = 0.38 \pm 0.05 \text{ eV} \)) and binding energy (\( \epsilon_d = 0.62 \pm 0.08 \text{ eV} \)) of the intermediate state of diethyl ether on Si(001) as well as the respective pre-exponential factors (\( \nu_d = 10^{20.5} \text{ s}^{-1}, \nu_f = 10^{20.3} \text{ s}^{-1} \)). The energy barriers fit into trends based on general chemical considerations; the low values of \( \nu_d \) and \( \epsilon_d \) can be rationalized based on the relatively large number of degrees of freedom of the molecules in the intermediate state. Our results furthermore indicate that for this kind of systems temperature-dependent rate measurements are necessary for an absolute determination of energy barriers; optical SHG should allow for such measurements for a wider range of adsorbate systems.

**EXPERIMENTAL METHODS**

The optical SHG and molecular beam experiments were performed under ultrahigh vacuum conditions with a base pressure of 3 \( \times 10^{-11} \text{ mbar} \). The Si(001) surface was prepared by direct current heating up to 1500 K and slow cooling rates down to 80 K (1 K/s) resulting in a clean surface with clear 2 \( \times 1 \) surface reconstruction. The surface temperature was measured with a type K thermocouple glued to the rear side of the sample. The SHG measurements were performed with a Ti:sapphire oscillator with 60 fs pulse duration and 82 MHz repetition rate; the chopped 800 nm pulses were focused on the sample in s-polarization at an angle of incidence of 45\(^\circ\). The resulting absorbed power on the sample was 100 mW, the respective absorbed fluence was \( 6 \times 10^{-3} \text{ mJ/cm}^2 \). The values were chosen to keep cumulative laser-induced heating of the sample low (<10 K); transient surface heating induced by single laser pulses is negligible under the given conditions. The frequency doubled p-polarized light was separated from the fundamental using optical filters and detected using lock-in techniques; due to the two-domain structure of the Si(001) surface, the SHG intensity is isotropic with respect to the azimuthal angle of incidence. Sticking probabilities were measured in a four-stage molecular beam apparatus using the King and Wells method. The supersonic molecular beam (\( E_{\text{kin}} = 0.1 \text{ eV} \)) hit the silicon sample under normal incidence, the background pressure of Et_2O was monitored by a quadrupole mass spectrometer sensitive to the respective mass range.

**REFERENCES**


(13) As we also observe small changes in the SHG signal due to residual gas adsorption on time scales longer than 1000 s, the evaluation is restricted to surface temperatures above 220 K.


