A. Multi-dimensional "first principle" theory for electron mediated associative desorption

In the following, the theoretical concept applied by Luntz et al. [Lun06] to investigate theoretically the fs-laser induced H_2 desorption from Ru(001) will be described. The outcome of these calculations is discussed in Section 3.4. Since the same theoretical approach has also been successfully applied investigating non-adiabatic effects in the associative desorption of N_2 from Ru(001) ([Lun05] and Section 4.1.1), the purpose of this section is to explain the concept in general. The peculiarities of the distinct adsorbate systems will be explicitly denoted, as soon as the generality is no longer valid.

The concept can be divided into three stages. A standard first principles density functional theory (DFT) calculation of the adsorbate-surface system is carried out to obtain the Kohn-Sham (KS) states and a multi-dimensional potential energy surface (PES) for the adsorbate at various positions. A friction coefficient is then obtained from the KS states and the PES. This friction coefficient provides a description of the average non-adiabatic energy transfer between the e-h pairs and the nuclear coordinates. Finally, a classical equation of motion considering non-adiabatic coupling is solved to obtain the trajectories for the desorbing particles. Thus, one has the possibility of developing a multidimensional dynamic model which describes associative desorption considering non-adiabatic coupling with *no* adjustable parameters.

Dynamical model

A schematic drawing of the dynamic model used to describe the hot-electron mediated associative desorption of diatomic molecules from the surface is depicted in Fig. A.1. It is based on molecular dynamics with electronic frictions in a manner originally proposed by Head-Gordon and Tully [Hea95]. The desorption is described by two molecular coordinates d and z, which are most relevant coordinates for an association/dissociation process [Dar95]. A fixed minimum energy path is implied for recombination and a fixed orientation of the molecule axis parallel to the surface throughout desorption. For the H/Ru(001) system. this assumption is additionally corroborated by the experimentally finding of "helicopter"-like molecular alignment of the desorbing hydrogen molecules (see Section 2.4.3 and Section 3.2.2). The third dimension is represented by a single Einstein phonon coordinate q, which couples the molecule to the lattice in the framework of the elastic recoil model [Han90].

Potential energy surface

The PESs are calculated employing a periodic DFT slab model. For the H/Ru(001) system, either four hydrogen atoms adsorb on a 2×2 Ru surface unit cell or 16 H adsorb on a 4×4

A. Multi-dimensional "first principle" theory for electron mediated associative desorption
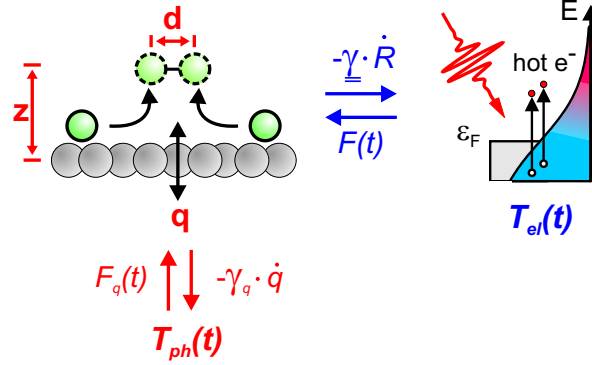

Figure A.1.: Schematic diagram of the 3D dynamic model used to describe hot electron induced associative desorption of a diatomic molecule.

Ru unit cell, representing a Ru(001) surface with a (1×1) hydrogen saturation coverage. For both geometries, six Ru layers and an equivalent seven layer vacuum region are applied. The outcome of these calculations is discussed in Section 3.1.1 and the obtained PES is depicted in Fig. 3.1(b). For the N_2/Ru(001) system, same-sized unit cells are considered, whereas only adsorption on a clean Ru(001) is taken into account. Further computational details can be found in [Lun06].

Friction coefficients

Elements of the friction tensor γ for each (d,z) of the corresponding PES points are calculated in a manner outlined in [Lun05]. The first principle expression for γ is based on work on vibrational damping of adsorbates [Hel84] and atomic adsorption [Tra03]. This procedures is based on DFT by evaluating the equation

$$\gamma_{ii} = 2\pi\hbar \sum_{\alpha,\beta} \left| \left\langle \psi_\alpha \left| \frac{\partial v}{\partial x_i} \right| \psi_\beta \right\rangle \right|^2 \delta\left(\epsilon_\alpha - \epsilon_F\right) \delta\left(\epsilon_\beta - \epsilon_F\right), \tag{A.1}$$

where ψ_j, ϵ_j are the Kohn-Sham orbitals and orbital energies respectively, $\partial v/\partial x_i$ is the derivative of the Kohn-Sham potential v with respect to the nuclear coordinate x_i and ϵ_F is the Fermi energy. Elements of γ along the reaction coordinate for desorption are discussed for H/Ru(001) in Section 3.4 and for N_2/Ru(001) in Section 4.1.1.

Langevin dynamics

The three dimensional classical equations of motion on the PES $V(d, z, q)$ are given by the following set of coupled differential equations

$$\mu\ddot{d} = -\frac{\partial V}{\partial d} - \gamma_{dd}\dot{d} - \gamma_{dz}\dot{z} + F_d(t), \tag{A.2a}$$

$$m\ddot{z} = -\frac{\partial V}{\partial z} - \gamma_{zz}\dot{z} - \gamma_{dz}\dot{d} + F_z(t), \tag{A.2b}$$

$$M_{\text{Ru}}\ddot{q} = -\frac{\partial V}{\partial q} - \gamma_q\dot{q} + F_q(t), \tag{A.2c}$$

where μ is the vibrational reduced mass, m is the molecular mass and M_{Ru} is the surface mass of a Ru atom. The molecular modes d and z are coupled to a thermalized electron distribution at temperature T_{el} via the frictional tensor γ_{ij} which causes damping and induces fluctuating forces $F_i(t)$, $(i = d,\, z)$ according to the second fluctuation dissipation theorem [Tul80]

$$\left\langle F_i(t)F_i(t')\right\rangle = 2k_B T_{\mathrm{el}}\gamma_{ii}\delta(t - t'). \tag{A.3}$$

In this manner, Equation (A.3) and an analog version for the phonon coordinate q relate the substrate temperatures T_{el} and T_{ph} to the forces driving the molecular dynamics. fs-laser induced desorption is theoretically investigated by considering transient $T_{\mathrm{el}}(t)$ and $T_{\mathrm{ph}}(t)$, which are obtained from the two-temperature model (2TM) described in Section 1.2. Thermal desorption rates can be modeled by taking constant surface temperatures into account. Purely electron and purely phonon mediated reactions can be considered by setting either γ_{q} or γ_{ii} to zero. As can be seen from Eq. (A.2), electronic coupling is not only responsible for the energy transfer to and from the molecular coordinates, but also couples electronically d and z via γ_{dz}. The isotope effect discussed in Section 1.3.3 is also inherent in the present approach as obvious from the mass-dependent acceleration in Eq. (A.2).

A. Multi-dimensional "first principle" theory for electron mediated associative desorption

B. Estimation of the SFG data acquisition time for a direct investigation of the CO formation

Broadband IR-VIS sum-frequency generation is a well established spectroscopic method for the investigation of the internal stretch vibration of CO chemisorbed on Ru(001) [Bon00b, Hes00a, Hes00b, Bon01, Hes02, Bon04]. Time-resolved investigations of the dynamics of the the CO-stretch vibration [Hes00b, Bon01, Hes02] and the CO desorption [Bon00b, Hes02] have been performed. The sensitivity of this method is well suited to detect CO coverages lower than 0.001 ML [Hes00a] as can be seen from Fig. B.1.

The transient CO coverage formed during the associative desorption of CO from a O/C/Ru(001) surface due to the excitation with 800 nm fs-laser pulses leading to an absorbed fluence of $\langle F \rangle = 180\,\text{J/m}^2$ is $\approx 0.004\,\text{ML}$ as determined in Section 4.2.2. This means that a spectrum comparable to the red-marked in Fig. B.1 is expected. In the SFG technique, interference between different signal contribtutions is possible (see Section 2.4.4). For CO coverages where the contribution of the nonresonant background and the CO stretch exhibit comparable amplitude, the lineshape of the CO signal is distorted as shown in Fig. B.1. The wiggly shape
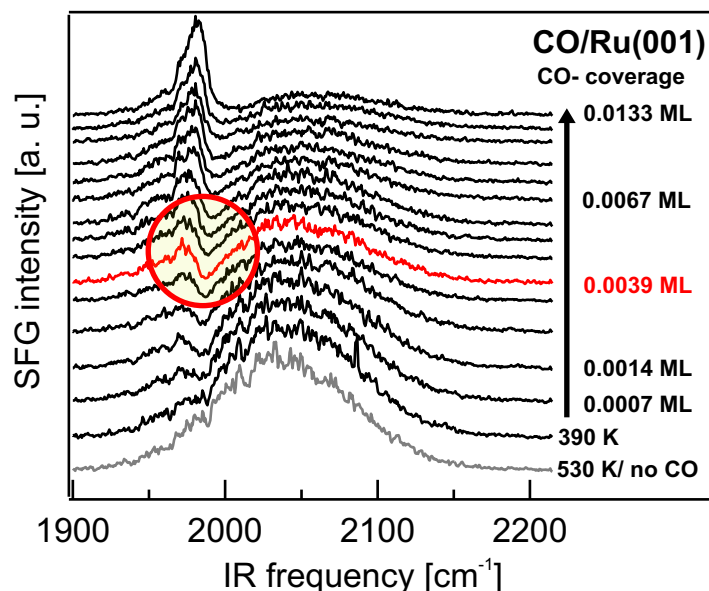

Figure B.1.: SFG spectra of the CO stretch of CO on Ru(001) as a function of coverage at a temperature of 390 K. Due to the high sensitivity of the method, CO coverages lower 0.001 ML are detectable. A transient coverage of $\approx 0.004\,\text{ML}$ is formed after fs-laser excitation of a O/C/Ru(001) surface with 800 nm laser pulses and an absorbed fluence of $\approx 180\,\text{J/m}^2$. The circle frames the contribution of the CO stretch to the overall SFG signal. Data taken from [Hes00a].

B. Estimation of the SFG data acquisition time for a direct investigation of the CO formation

of the CO signal for $\theta_{CO} \approx 0.004\,\mathrm{ML}$ is highlighted in Fig. B.1. This means that rather a distorted spectral contribution than a sharp CO resonance is expected.

The data acquisition time for the individual spectra of Fig. B.1 is ≈ 3 minutes [Hes01], which corresponds to 72 000 acquisitions for a system operating at 400 Hz as in the experiment. Concerning the fs-laser induced associative desorption of CO from O/C/Ru(001), the reaction yield decays to half the signal strength within the first 10 laser shots at corresponding fluence. Although the Ru(001) sample is scanned, an upper limit of independently irradiable 50 spots is found which results in 500 SFG spectrum acquisitions per scan and surface preparation. This means that almost 150 surface preparations are required to obtain a SFG spectra of comparable quality under the assumption that the detected SFG intensity is the same. The preparation and the scan over the surface involving the data acquisition as described in Section 2.5.2 last approximately one hour. This means that almost one week is required to obtain a spectrum for a single pump-probe delay exhibiting a signal to noise ratio as the spectra of Fig. B.1, if one only considers sample preparation and data acquisition.