Activated associative desorption of C + O → CO from Ru(001) induced by femtosecond laser pulses

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Abstract. The femtosecond (fs)-laser-induced associative desorption of CO from a C/O coadsorbate on Ru(001) has been investigated. The recombination of the atomic reactants is found to originate predominantly from oxidation of isolated ‘reactive’ carbon atoms, whereas oxidation of surface carbon with carbon–carbon bonds is not observed. Due to the excess of oxygen atoms (C coverage in the few-percent range) the C_ads + O_ads → CO_gas formation exhibits first-order kinetics. For both excitation wavelengths 400 and 800 nm, a strongly nonlinear fluence (F) dependence of the CO desorption yield Y is observed with exponents n ≈ 4 in a power law parametrization Y ∝ ⟨F⟩^n. Furthermore, excitation with 400 nm pulses leads to a significantly higher desorption yield as compared to 800 nm laser light with cross sections and desorption probabilities for 400 and 800 nm excitation of σ_eff = 4.9 × 10^{-18} \text{cm}^2, P_{des} = 0.17 and σ_eff = 1.1 × 10^{-18} \text{cm}^2, P_{des} = 0.07, respectively, at an absorbed fluence of ⟨F⟩ = 170 \text{Jm}^{-2}. This wavelength dependence is attributed to the shorter optical penetration of 400 nm light in the Ru substrate leading to higher surface temperatures at the same absorbed energy rather than to nonthermalized hot electrons. In addition, two-pulse-correlation measurements show a full-width at half-maximum of ~20 ps excluding a purely electron-driven reaction mechanism, which should exhibit a subpicosecond response time. However, careful qualitative and quantitative analyses based on frictional modelling of

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the adsorbate–substrate coupling reveals that the C–O association reaction is mediated by both substrate phonons and electrons. The electronic, i.e. nonadiabatic contribution with a coupling constant of $\eta_{el} = 1/500 \text{fs}^{-1}$ is responsible for the ultrafast activation of the reaction found in the frictional modelling to occur within $\sim 1 \text{ps}$ after excitation. Similarities to the associative desorption of $\text{N}_2$ (isoelectronic with CO) from $\text{N}/\text{Ru}(001)$, a system for which density-functional calculations exist, can be drawn. Finally, the energy transfer to nuclear degrees of freedom during the C–O association process on the Ru(001) surface has been studied with time-of-flight measurements. The obtained translational energies expressed by $T_{\text{trans}} = \langle E_{\text{trans}} \rangle / 2k_B \approx 700 \text{ K}$ exhibit only a weak dependence on the absorbed laser fluence and are by a factor of $\sim 3$ lower than the calculated surface temperatures present after fs-laser excitation. Possible origins of this discrepancy, such as unequal energy partitioning between the molecular degrees of freedom or nonadiabatic damping, are discussed.

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1. Introduction

The interaction between and subsequently the reaction of atoms and molecules adsorbed on solid surfaces are of key interest for a variety of areas both in fundamental science as well as in technological applications such as heterogeneous catalysis, electrochemistry and corrosion [1]–[3]. Metals are often investigated as model substrates since the interaction of the adsorbed reaction partners with the substrate may cause a favourable energy landscape, e.g. a reduced reaction barrier as compared with the gas phase. Consequently, one of the major goals is to gain deeper insights into the dynamics and the underlying elementary processes of these reactions at surfaces on a microscopic level. To this end, it is highly desirable to obtain information on relevant timescales, i.e. times for bond fission and formation (femtoseconds, $1 \text{ fs} = 10^{-15} \text{ s}$). In addition, the appeal of surface photochemistry with ultrashort light pulses is that one can trigger the chemical transformation of the reactant and hence ‘switch on’ characteristic properties of the reaction system, e.g. the coupling between electronic and nuclear degrees of freedom, directly in
the time domain. The key questions one would like to address with investigations on ultrashort-laser-induced surface chemistry are the following; what is the driving force, the mechanism of a certain reaction pathway? And which are the timescales of energy flow from the initial, optical excitation to the reactants which undergo chemical and/or conformational changes?

Most studies on surface femtochemistry have addressed desorption of molecular adsorbates like NO or CO from transition metals (e.g. [4, 5]). But also associative desorption and reactions between molecules adsorbed on the surface have been investigated; a comprehensive list of the various reaction systems is given in [6]. Typical characteristics of this kind of chemistry are a nonlinear reaction yield dependence on the applied laser fluence, an ultrafast timescale of energy transfer from the substrate to the adsorbate as manifested in a two-pulse correlation of narrow (i.e. few picoseconds) width, pronounced isotope effects and high kinetic and/or vibrational state distributions of the desorbing particles. The general mechanism of all these reactions (with one exception, the desorption of molecularly bound CO from Ru(001) [7]), has been explained by nonadiabatic coupling between hot substrate electrons and nuclear degrees of freedom of the adsorbed reactants.

The present paper gives a comprehensive account on the associative CO desorption, \( \text{C}_{\text{ads}} + \text{O}_{\text{ads}} \rightarrow \text{CO}_{\text{gas}} \), from the Ru(001) surface. A rather broad two-pulse correlation is observed, which is usually thought to be indicative of adiabatic, i.e. phonon-mediated energy transfer between the substrate and the adsorbate [7, 8]. However, model calculations based on Kramers’ low-friction limit [9] show that the experimental findings can only be consistently explained in terms of absolute reaction rates if also nonadiabatic, i.e. substrate electron-mediated contributions are included. The C + O association from C/O/Ru(001) deserves attention since it can be regarded as a model system for studying activated associative desorption, with a significant barrier located in the vibrational channel [10] for the rather equally bound atomic reactant (both species, C and O, adsorb on threefold hcp hollow sites of the Ru(001) substrate with binding energies on the clean surface of 6.3 and 4.9 eV per C and O atom, respectively [10]–[13]).

However, most interest in the reaction dynamics of the C + O association originates from the fact that CO is isoelectronic with N\(_2\) and similar topologies of the potential energy surfaces (PESs) for activated processes like association and dissociation of these \( \pi \)-bonded molecules on d-band transition metals [14, 15] like ruthenium are expected. Furthermore, the associative desorption and dissociative adsorption of \( \text{N}_2 \) from Ru(001) have already been extensively studied both in theory and in experiments with nanosecond-laser excitation [16]–[21]. In particular, Diekhöner et al [16, 18] report on state-resolved experiments which reveal the rovibrational and translational energy of the \( \text{N}_2 \) molecules leaving the Ru(001) surface. The nascent \( \text{N}_2 \) are found to exhibit only little vibrational excitation despite the pronounced barrier along the vibrational coordinate. Nonadiabatic coupling of the nuclear motion to the substrate electrons was suggested to cause this finding [18]. Further support for this interpretation was gained when Luntz and Persson [19] calculated \( \textit{ab initio} \) electronic friction coefficients for the N + N/Ru(001) system, showing that nonadiabatic effects are indeed quite important during this surface reaction. The friction coefficients obtained for N/Ru(001) are about one order of magnitude larger than those for other reaction systems, e.g. the hot electron-mediated associative desorption of \( \text{H}_2 \) also from Ru(001) [22]. Thus, one might very well expect nonadiabatic effects to play a significant role also in the femtosecond (fs)-laser-induced associative desorption of CO from Ru(001).
2. Basic concepts

2.1. Surface femtochemistry

Surface femtochemistry, i.e. chemical reactions on an adsorbate-covered metal surface initiated by fs-laser excitation, can be viewed from a perspective of the energy flow [6]. The optical excitation energy of the ultrashort light pulse is deposited in the electronic subsystem of the metal substrate. The subsequent energy transfer to the adsorbate system involves coupling of electronic and nuclear degrees of freedom; (i) either directly via a nonadiabatic process into the adsorbate coordinate relevant to the reaction, or (ii) indirectly via first equilibration with the subsystem of lattice vibrations (phonons) of the substrate, i.e. electron–phonon coupling, which is then followed by adiabatic energy transfer to the reaction coordinate. A macroscopic description of the evolving dynamics of energy flow within the substrate is usually accomplished by the two-temperature model of coupled heat baths [23, 24], comprising the electron and phonon baths each characterized by its own temperature \( T_{el} \) and \( T_{ph} \), respectively. The coupling of the substrate’s subsystems, electrons and phonons, to the reactants in the adsorbate layer invokes either ‘desorption induced by multiple electronic transitions’ (DIMET) [25] or friction exerting fluctuating forces on the reactants [26]–[28]. In the latter case, frictional coefficients, the inverse of the energy coupling times, determine how fast energy is transferred between each subsystem of the substrate and the adsorbate system. Mathematically, based on a master equation formalism [26, 27], the evolution of the energy content of the adsorbate and in turn of the adsorbate temperature \( T_{ads} \) is represented by

\[
\frac{d}{dt} T_{ads} = \eta_{el} \left[ T_{el} - T_{ads} \right] + \eta_{ph} \left[ T_{ph} - T_{ads} \right],
\]

whereby the friction coefficients \( \eta_{el} \) and \( \eta_{ph} \), respectively, relate to the mass-independent coefficient \( \gamma \) via \( \eta = \gamma / m \). Note that \( \gamma \) fulfils a classical velocity-proportional friction relation \( F = -\gamma v \) [27]. With the temperature transients \( T_{el} \) and \( T_{ph} \) determined by the two-temperature model, the adsorbate temperature \( T_{ads} \) can be derived, which characterizes the amount of energy transferred to the adsorbate mode (usually considered as a one-dimensional (1D) problem) which is relevant to the reaction of interest. The time-dependent reaction rate \( R(t) \) in surface femtochemistry and, finally, for comparison with the experiment, the reaction yield \( Y = \int dt \ R(t) \) are discussed in more detail in the following subsection.

2.2. Desorption rates

Thermally activated desorption rates \( R \) are usually given by Arrhenius-type expressions

\[
R = v_0 \exp \left( -\frac{E_a}{k_B T} \right),
\]

where \( E_a \) is the barrier height and \( v_0 \) the so-called ‘attempt’ frequency, which generally is unknown \( \text{a priori} \). In a simple approach, \( v_0 \) is assumed to be the vibrational frequency of the adsorbed atoms perpendicular to the surface, which matches a considerable number of cases with \( v_0 \) between \( 10^{12} \) and \( 10^{13} \) s\(^{-1} \) for first-order desorption processes.

In transition state theory based on Eyring [29, 30], the concentration of the activated complex at the energy \( E_a \) higher than the initial adsorbate is given by [30]

\[
\sigma^+ = \sigma_{ads} \frac{f^+}{f_{ads}} \exp \left( -\frac{E_a}{k_B T} \right),
\]

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where $\sigma^\dagger$ and $\sigma_{\text{ads}}$ are the surface concentrations of the transition state and the adsorbate, respectively. The $f$s are the corresponding complete partition functions. With the reaction rate $R = \omega \sigma^\dagger$, whereby the reactants leave the activated complex at vibrational frequency $\omega$, one obtains the pre-exponential factor for a first-order desorption process in absolute terms as

$$v_0 = \sigma_{\text{ads}} \kappa \frac{k_B T}{h} \frac{f^\dagger}{f_{\text{ads}}},$$

(4)

with $f^\dagger = f^\dagger k_B T/(\hbar \omega)$ and the transmission factor $\kappa$. For the typical temperature range of 100–1000 K (i.e. $k_B T/\hbar \sim 10^{12}$ to $10^{13}$ s$^{-1}$), the usual values for $v_0$ are found (between $10^{12}$ and $10^{13}$ s$^{-1}$), if $\kappa \approx 1$ and $f^\dagger/f_{\text{ads}} \approx 1$.

As an alternative to the transition state theory-based reaction rates by Eyring, Kramers used a classical Fokker–Planck equation and developed a diffusion model of chemical reaction in viscous media [9]. Thereby, the coupling between the reactants and the heat bath of the surrounding medium is represented by the friction coefficient $\eta$. Applied to surface reactions [31], an interpolation for the pre-exponential factor $\nu$ as a function of the coupling strength $\eta$ was gained [32]. Eyring’s case of $\nu(\eta) \approx \nu_0$ is only obtained for a certain intermediated $\eta$ range. For both very high and very low values of $\eta$ compared to the characteristic frequency $v_0$, the pre-exponentials $\nu(\eta)$ become much smaller than in Eyring’s case. In particular, in Kramers’ low-friction limit, for a parabolic potential, $\nu(\eta)$ can be given in exact terms as

$$\nu(\eta) = \eta \cdot \frac{E_a}{k_B T}, \quad \text{for} \quad \eta < v_0 \cdot \frac{k_B T}{E_a}.$$

(5)

Newns et al [27] showed that equation (5) remains valid also for transient temperatures $T = T(t)$ and thus the reaction rate $R$ of equation (2) becomes time-dependent

$$R(t) = \frac{\eta_{\text{eff}} E_a}{k_B} \int dt \frac{1}{T_{\text{ads}}(t)} e^{-E_a/k_B T_{\text{ads}}(t)},$$

(6)

with the time-dependent adsorbate temperature $T_{\text{ads}}(t)$. This transient reaction rate in Kramers’ low friction limit for an truncated harmonic oscillator has been frequently used in modelling surface femtochemistry processes mediated by hot substrate electrons, whereby the activation energy $E_a$ and the electronic coupling strength $\eta_{\text{el}}$ were taken as fit parameters to reproduce the reaction yield $Y$ measured in the experiment [6].

In the case of a reaction where the energy transfer into the adsorbate is due to coupling to electrons and phonons, as will be shown for the present associative CO desorption from Ru(001), the fit parameter set increases to $E_a$, $\eta_{\text{el}}$, $\eta_{\text{ph}}$, and $\eta_{\text{eff}}$. The latter is introduced according to Mathiessen’s rule in solid state physics which states that the inverse effective relaxation time of a system with different relaxation mechanisms is given by the sum of the individual inverse relaxation times [33]

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{el}}} + \frac{1}{\tau_{\text{ph}}} \quad \text{and} \quad \eta_{\text{eff}} = \eta_{\text{el}} + \eta_{\text{ph}}.$$

(7)

3. Experiment

As is imperative in all surface femtochemistry experiments with molecularly clean adsorbates on single-crystalline metal substrates [6, 34], the experiments on the fs-laser-induced CO associative desorption reported here were carried out under ultrahigh-vacuum (UHV)
conditions. The Ru(001) single-crystal is mounted on a liquid-nitrogen cooled cryostat in a UHV chamber (base pressure \( < 1 \times 10^{-10} \) mbar) which is equipped with standard surface science preparation and analysis tools [34, 35]. High-quality, i.e. high signal-to-noise thermal desorption (TD) spectra are obtained with a so-called ‘Feulner cup’ [36] quadrupole mass spectrometer (QMS). In order to investigate the recombinative desorption of CO from the Ru surface, both reactants, carbon and oxygen, have to adsorb atomically. This is achieved by first flashing the Ru(001) crystal with electron bombardment to 1530 K for 10 s. After cooling down to 500 K, ethylene is dosed via either a pinhole doser or a background leak valve. Subsequent heating to 650 K decomposes the adsorbed \( \text{C}_2\text{H}_4 \) [37, 38] and leads to formation of surface carbon. Finally, at a temperature of 400 K, 8 L (1 L = \( 1.3 \times 10^{-6} \) mbar s\(^{-1}\)) of oxygen are dosed, which result in a \((2 \times 1)\) saturation coverage of atomically bound oxygen [39]. Usually, the \(^{18}\text{O}\) isotope is used to minimize the background level in the QMS signal of the CO product mass. All experiments are performed at a sample temperature of 400 K, which is above the desorption temperature for molecularly adsorbed CO on a \((2 \times 1)\Omega/\text{Ru}(001)\) surface [39] and below that of thermal recombination of C and O, see figure 1(a). This additionally assures that the CO detected in the various experiments reported here indeed results from associative formation of CO molecules.

To laser-induce the \( \text{C}_{\text{ads}} + \text{O}_{\text{ads}} \rightarrow \text{CO}_{\text{gas}} \) reaction, fs-laser pulses of up to 4.5 mJ pulse energy and 130 fs in duration at centre wavelength of 800 nm from a high-power Ti : sapphire-based amplified laser system (Quantronix Titan II) are employed. The repetition rate is adjusted from 400 Hz down to 20 Hz using a pulse picker between the amplification stages; single-shot experiments were performed by the additional aid of a chopper and/or shutters. The pulse energy and hence the incident fluence can be varied by a half-wave plate in conjunction with a thin-film polarizer without adjusting the pump power to the multipass amplifier provided by Nd : YLF lasers, thus avoiding thermal effects which influence the beam diameter. The crucial parameter for nonlinear photoinduced processes as studied here is the absorbed laser fluence \( \langle F \rangle \) weighted with the respective yield [5, 7], which enables one to compare yield data obtained with different spatial laser beam profiles. To this end, a reference beam channel is used in which the beam profile is detected by a CCD camera at a position equivalent to the Ru sample. Possible self-focusing distortions imposed by the entrance window at high-laser fluences are also accounted for by placing a reference window with similar self-focusing behaviour into the reference pathway [7, 34, 35]. Yield fluctuations caused by shot-to-shot noise can be minimized by recording a decay curve of the desorption yield as a function of laser shot number within a series of pulses impinging on the same spot on the sample (see figure 3 further below).

4. Results and discussion

4.1. Thermal desorption spectroscopy (TDS)

Figure 1(a) shows a TD spectrum from a saturated CO layer on oxygen–carbon pre-covered O/C/Ru(001) surface. Desorption of the moleculely bound CO species occurs in the temperature range from 150 to 400 K. The main peaks, denoted \( \gamma_1 \) and \( \gamma_2 \), correspond to the two well-known binding states of CO molecules on a purely oxygen-covered Ru(001) with respective activation energies for desorption \( E_a \) of 0.5 and 0.9 eV [39, 40]. Apparently, the only small amount of adsorbed carbon in the coadsorbate system CO/O/C used here rendered the \((2 \times 1)\Omega\) structure on the Ru(001) surface largely unaffected.

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Figure 1. The TDS of CO from O/C/Ru(001). (a) TD from a pre-covered (2 x 1) \(^{18}\text{O}/\text{C}/\text{Ru}(001)\) surface saturated with C\(^{16}\text{O}\) yields two mass-28 features \(\gamma_1\) and \(\gamma_2\) which correspond to molecular CO (see text). In addition, the TD spectra of associatively desorbing CO from \(^{18}\text{O}/\text{C}/\text{Ru}(001)\) are shown as a function of carbon pre-coverage \(\theta_C\) (coverages given in panel (b)). Note that desorption of molecularly adsorbed CO occurs at distinct lower temperatures (\(\sim150–400\) K) than the associative formation of CO (distinguishable through isotope labelling) with desorption temperatures \(\geq450\) K. A second oxidation cycle, which does not yield any further CO desorption, ensures that all surface carbon oxidizes and desorbs during the first heating of the crystal. For comparison, the TD spectrum from a pure, i.e. without any atomic oxygen, CO saturation coverage (0.68 ML) is also displayed with its well-known two peaks \(\alpha_1\) and \(\alpha_2\), at \(\sim460\) and \(\sim400\) K, respectively. The heating rate for all TD spectra is \(\beta = 12\) K s\(^{-1}\). (b) \(\theta_C\)-coverage dependence of the double-peak structure of the associative CO desorption in detail with Gaussian fits to the TD spectra. Vertical lines indicate the dependence of the peak temperatures on \(\theta_C\) with LT and HT standing for low-temperature and high-temperature peaks, respectively. In the inset of (a), the areas of the Gaussian fits for the LT and HT peaks are plotted as a function of \(\theta_C\).

Also shown in figure 1(a) is the thermally induced associative CO desorption from \(^{18}\text{O}/\text{C}/\text{Ru}(001)\) for various carbon pre-coverages \(\theta_C\). In a temperature range from 450 to 750 K, a double-peak structure is observed for the associative CO desorption yield and is well reproduced by two Gaussian distributions. As detailed in panel (b) of figure 1, the maximum temperature \(T_{\text{max}}\) of the low-temperature (LT) peak remains basically constant at \(\sim560\) K as the carbon pre-coverage \(\theta_C\) (expressed in monolayers (ML), i.e. the ratio between...
carbon and ruthenium surface atoms) is increased from 0.003 to 0.14 ML. In contrast, $T_{\text{max}}$ of the high-temperature (HT) peak shifts with increasing $\theta_C$ approximately from 610 to 670 K. The constant peak temperature observed for the LT feature indicates a first-order reaction mechanism [41], although an associative desorption reaction generally is expected to be of second order. However, in the present case of low $\theta_C/\theta_O$ ratios, the carbon concentration alone is rate-limiting, since the oxygen ‘reservoir’ is virtually constant resulting in effectively first-order kinetics. Based on Redhead’s analysis of first order desorption [42], the activation energy $E_a$ can be obtained as a function of the pre-exponential factor $\nu$. For typical pre-factors on the order of $\nu \approx 10^{12} - 10^{13}$ s$^{-1}$ together with the experimental parameters of the CO TD spectra presented here ($T_{\text{max}} = 560$ K; heating rate $\beta = 12$ K s$^{-1}$), an activation energy of $E_a$ of $(1.5 \pm 0.1)$ eV is obtained for the C + O reaction from the LT peak.

In addition, the inset of figure 1(a) shows the integrated area of the two Gaussian distributions as a function of $\theta_C$. Increasing $\theta_C$ up to 0.08 ML leads to an almost equal increase of both contributions, whereas mainly the HT peak benefits from carbon coverages higher than $\theta_C = 0.08$ ML. The area rise of the LT peak appears to level off at higher $\theta_C$. As will be shown below, the carbon reactants forming the CO molecules of the LT peak in TD are also those which contribute to the fs-laser-induced CO desorption yield.

The LT-TDS feature is believed to originate from recombination events between reactive carbon and oxygen on adjacent sites, whereas the second order-like behaviour of the HT peak is suggested to be due to the onset of surface mobility of less reactive adsorbates at $\sim 650$ K giving rise to a reaction controlled by surface diffusion [43]. With a hopping rate of $10^5$ s$^{-1}$ at 400 K found for atomic oxygen on Ru(001) [44], it seems very likely that the surface mobility of the more strongly bound carbon species is the rate-limiting step governing the HT-TDS feature. This assumption is corroborated by experiments performed by Diekhöner et al [17, 45], who prepared atomically bound C on Ru(001) via dissociation of methane. This preparation procedure ensures that initially isolated carbon atoms are formed, which can be oxidized to CO and desorb at $\sim 570$ K. After annealing the carbon pre-covered Ru(001) surface at 660 K, the formation of a HT-TDS feature with a peak desorption temperature of $\sim 700$ K is observed [17]. It appears that due to the surface mobility of carbon more strongly bound C$_2$ structure are formed, which might also be present initially in a C/Ru(001)-preparation procedure based on ethylene decomposition as used in the present experiments.

Finally, since the reactivity for dissociation and association of $\pi$-bonded molecules on transition metal surfaces can be greatly enhanced by highly reactive sites, e.g. steps [46]–[48], a significant contribution from those sites to the CO recombination yield has to be excluded. Thus, the step density of the Ru(001) surface used here has been determined via a CO titration procedure according to [49] and a conservative upper bound of 1% step density is obtained. Indeed, as Zubkov et al showed in dissociation/recombination studies of CO on a stepped Ru(109) surface (10% step density), a significant amount of dissociated CO is obtained and desorbs recombinatively at $\sim 520$ K [50, 51]. However, the associative desorption reported here occurs at significantly higher temperatures (figure 1). Furthermore, the surface mobility of carbon, which is very low at $T = 520$ K, cannot account for the observed thermal CO desorption yield larger than 1% of a ML$^5$.

Note that especially in the fs-laser-induced CO association described further below the timescales of such reactions do not allow for any substantial diffusion events from terrace to step sites to contribute.
4.2. The fs-laser-induced reaction

All experiments using fs-laser excitation to induce the C + O recombination from Ru(001) have been performed at a base surface temperature of $T_S = 400$ K, which guarantees that no molecular CO is adsorbed on the surface and that the detected CO molecules indeed originate from associative desorption. In figure 2(a), the fs-laser-induced first-shot CO desorption yield is plotted as a function of the carbon coverage $\theta_C$ for fluences $\langle F \rangle = 140$ and 190 J m$^{-2}$ at 800 nm. For both fluences, the yield increases with $\theta_C$ and considerably levels off for $\theta_C > 0.05$ ML. This behaviour resembles the increase of the LT-TDS feature with $\theta_C$ (see inset of figure 1(a)) and suggests that the yield of the fs-laser-induced associative desorption of CO from O/C/Ru(001) results mainly from carbon species also responsible for the LT peak in the TD spectra. This is underlined in figure 2(b) where the laser-induced desorption yield is plotted against the area of the LT-TDS peak. Small deviations, especially at low coverages, most likely arise from difficulties in determining the correct ratio between the LT- and HT-TDS peaks in these overlapping TD features. In the remainder of this work, a constant carbon pre-coverage of $\theta_C \approx 0.04$ ML has been used in all other fs-laser experiments on CO association.

To quantify the efficiency of the laser-induced process, the CO desorption yield is measured in series of laser shots impinging the same spot on the adsorbate-covered Ru sample. That way, as shown in figure 3, the initial O/C coverage is gradually depleted depending on the absorbed laser fluence and obviously also on the excitation wavelength. With 400 nm pulses, the CO yield decays considerably faster than in the case of 800 nm excitation. For a quantitative evaluation of the reaction cross section, these decay curves due to multiple-pulse excitation need to be fitted to a functional relationship between remaining coverage and accumulated laser fluence. While for
Figure 3. Decay of the fs-laser-induced associative CO desorption yield from a O/C/Ru(001) surface with an initial carbon coverage $\theta_C = 0.04$ ML as a function of the laser shot number within a series of 100 pulses. Data sets for excitation with (a) 400 and (b) 800 nm laser light are shown for various fluences and offset for clarity. Note the considerably faster decay for excitation with 400 nm than 800 nm light at comparable absorbed fluence $\langle F \rangle$. The solid lines in black represent single-exponential fits to the experimental data. The red line in the lowest 400 nm panel shows an inverse power-law fit (as expected for a second-order process like an association reaction), however, which exhibits clear discrepancies from the experimental data.

an associative desorption process, naturally as a bimolecular reaction, the yield should follow an inverse power law (e.g. H + H association [35]), the desorption of a molecular entity exhibits first-order kinetics with a single-exponential decay (e.g. CO desorption [7]). However, as clearly demonstrated in the lower panel of figure 3(a), the association of C + O from Ru investigated here is only accurately described with first-order kinetics, which in turn is consistent with the observations for the LT peak in TD. Thus, the few-percent carbon concentration appears the rate-limiting step also in fs-laser-induced C + O association.

Following the evaluation of [7, 35, 52], an effective cross section for the associative CO desorption from Ru(001) $\sigma_{\text{eff}}$ can be derived. Values of $\sigma_{\text{eff}} = (4.9 \pm 0.3) \times 10^{-18}$ cm$^2$ and $(1.1 \pm 0.2) \times 10^{-18}$ cm$^2$ for 400 and 800 nm, respectively, are obtained. For comparison, typical cross sections for photon-induced desorption of neutrals from surfaces lie in the range from $10^{-18}$ to $10^{-20}$ cm$^2$ [53]. For the desorption of molecularly bound CO from Ru(001) at 800 nm, a $\sigma_{\text{eff}}$ value of $1.7 \times 10^{-18}$ cm$^2$ was reported for an absorbed fluence of $\langle F \rangle = 305$ J m$^{-2}$ [7]. However, these numbers have to be treated with care, since the absorbed fluences given in [7] extend well beyond 300 J m$^{-2}$, a range where ablation of the Ru crystal becomes highly probable.

Moreover, the original fluence values given in [7] extend well beyond 300 J m$^{-2}$, a range where ablation of the Ru crystal becomes highly probable.
Figure 4. Fluence dependence of the associative CO desorption yield $Y$ from C/O/Ru(001) after fs-laser excitation of the carbon pre-covered Ru surface with $\theta_C = 0.04$ ML. $Y$ is measured as a function of the absorbed fluence $\langle F \rangle$ for 400 and 800 nm excitation. Lines represent fits to a power law $Y \propto \langle F \rangle^n$.

of the obviously interchanged entities yields a more realistic $\sigma_{\text{eff}}$ of $8.6 \times 10^{-18}$ cm$^2$ at a fluence (now lowered) of $\langle F \rangle = 190$ J m$^{-2}$. Accordingly, it seems that the fs-laser-induced desorption of molecularly bound CO species is almost eight times more efficient than the recombinative desorption of the atomically bound counterparts reported in the present contribution. In addition, the CO association probability per pulse can be determined with the obtained effective cross sections via $P_{\text{des}} = \sigma_{\text{eff}} \langle F \rangle$. For an absorbed fluence $\langle F \rangle$ of $170$ J m$^{-2}$, desorption probabilities of 0.17 and 0.07 are obtained for excitation with 400 and 800 nm laser pulses, respectively. This means that approximately 0.7 and 0.3% of a ML CO are formed when a single laser pulse of the given fluence at 400/800 nm excites the O/C/Ru(001) surface at an initial coverage of $\theta_C = 0.04$ ML.

As already obvious from figures 2 and 3, the CO association yield strongly depends on the absorbed laser fluence $\langle F \rangle$. Figure 4 now plots the first-shot CO yield for 400 and 800 nm excitation as a function of $\langle F \rangle$ in the range from 100 to 200 J m$^{-2}$. For both wavelengths, a clearly nonlinear increase of the desorption yield $Y$ with increasing $\langle F \rangle$ is observed. A power-law parametrization $Y \propto \langle F \rangle^n$ fits the experimental data with virtually identical (within the error bars) exponents $n = 3.9 \pm 0.4$ and $4.3 \pm 0.2$ for 400 and 800 nm, respectively. Furthermore, figure 2 underlines the finding conveyed by the decay curves of figure 3(a) versus (b): excitation with 400 nm light leads to substantially higher reaction yields $Y$ than 800 nm excitation does at the same absorbed fluence.

Causes of this pronounced wavelength dependence of the fs-laser-induced CO association seen in the experiment might be twofold; (i) significant contributions of nonthermalized electrons immediately after photo-excitation and/or (ii) different depth profiles of the deposited laser pulse energy into the metal substrate. Figure 5(a) illustrates how a nascent nonthermalized
Figure 5. (a) Illustration of the wavelength-dependent nonequilibrium distribution directly after optical excitation of a metal with an ultrashort-laser pulse ($\Delta t = 0$). While for excitation with photon energy $h\nu_1$ a certain nonthermalized electron density is created (left panel), the excitation of identical fluence but with lower photon energies $h\nu_2 < h\nu_1$ leads to less energetic electrons (middle panel). Yet the high-energetic electrons after excitation with a shorter wavelength can couple more efficiently to certain unoccupied adsorbate resonances (e.g. the LUMO). This in turn may strongly influence the efficiency of a surface reaction. However, after electron thermalization (i.e. $\Delta t < \tau_{th}$), a hot electron distribution is obtained regardless of the initial excitation conditions (right panel). (b) Calculated surface temperatures as a function of time after fs-laser excitation obtained with the two-temperature model. At an absorbed fluence of $180 \text{ J/m}^2$, excitation with 400 as compared to 800 nm light leads to significantly higher electron and phonon temperatures, $T_{el}$ and $T_{ph}$, due to a shorter optical penetration depth for 400 nm light.
electron thermalization ($\Delta t > \tau_{\text{th}}$), right panel of figure 5(a)), the hot electron distribution of temperature $T_d > T_0$ (with $T_0$ being the substrate temperature before excitation) facilitates the relevant electronic transitions \textit{irrespective} the photon energy in the excitation step. On the other hand, in the case of significant contributions of nonthermalized electrons, a potential enhancement will result in less excitation steps required for the transfer of sufficient energy into the relevant reaction coordinate. Thus, a considerably smaller exponent $n$ for the power law describing the fluence dependence should be observed for excitation with more energetic photons. Indeed, such a behaviour was found in the O$_2$ desorption and CO oxidation after fs-laser irradiation of an O$_2$/CO/Pt(111) surface [54, 55]. The power-law exponents found in the experiments differed, for instance, in the case of O$_2$ desorption by almost a factor of two with the lower value for the 400 nm excitation instead of 800 nm [55]. In contrast, for the present case of the C + O association from Ru(001), the difference in the power-law exponent $n$ found between both excitation wavelengths (400 nm versus 800 nm) is largely negligible.

In an alternative scenario, the observed wavelength dependence might be explained by different optical properties of the Ru(001) substrate with respect to the two wavelengths applied. The penetration depth for 800 nm light is more than twice as large as for 400 nm light (16.2 nm versus 6.9 nm) [34], which means that the pulse energy of the shorter wavelength is absorbed closer to the surface of the metal substrate. Figure 5(b) depicts the calculated surface temperature transients for the electrons and phonons, $T_{\text{el}}$ and $T_{\text{ph}}$, after fs-laser excitation of the Ru(001) substrate with laser pulses of one and the same absorbed fluence of 180 J m$^{-2}$ for 400 and 800 nm, respectively. Significantly higher surface temperatures for both the electron and the phonon heat bath are obtained with excitation of shorter wavelength due to the differences in the optical penetration depths. Consequently, higher adsorbate temperatures $T_{\text{ads}}$ result in either of the basic reaction mechanisms driven by substrate electrons or phonons. The Arrhenius-like dependence of the reaction yield on $T_{\text{ads}}$ in turn boosts this difference between the two excitation wavelengths even further. We thus conclude that the observed enhancement of the associative CO desorption yield after excitation of the O/C/Ru(001) surface with 400 nm fs-laser pulses, compared to excitation with 800 nm pulses, in the present experiments originates from the different optical penetration depths and subsequently higher temperatures in the relevant heat baths. Contributions from nonthermalized electrons play—if anything—only a minor role.

As described above, in a substrate-mediated surface reaction, each of the substrate’s subsystems, electrons and phonons, can couple to the reactants in the adsorbate layer independently. The appropriate experimental approach to unambiguously distinguish a phonon- from an electron-mediated reaction mechanism is to measure the two-pulse correlation (2PC) of the reaction yield [56]. In such an experiment, two equally intense fs-laser pulses excite the sample with a variable time delay $\Delta t$ between them. The reaction yield is then detected as a function of $\Delta t$. Due to the typical nonlinear dependence of the reaction rate on the absorbed laser fluence (see figure 4), the width of the resulting yield correlation function critically depends on the excitation pathway. A narrow full width at half maximum (FWHM) of only a few picoseconds is a clear indication for the operation of a hot-electron, i.e. DIMET-like reaction mechanism, since only for pulse separations shorter than the electron–phonon equilibration time the electron temperature is greatly enhanced due to the combined effect of both excitation pulses. In contrast, a phonon-mediated process proceeds on a much slower timescale of tens of picoseconds due to the significantly longer energy storage time within the phonons compared to that of the electronic system and the slower coupling time from the phonon bath into the reaction coordinate.
Figure 6. Two-pulse correlation of the associative CO desorption yield from Ru(001) induced by 800 nm fs-laser pulses. As shown in the schematic in such a measurement, two pulses at variable time delay $\Delta t$ excite the adsorbate-covered surface, here with a absorbed fluence ratio of $55:45$ and total $\langle F \rangle$ of $170 \text{ J m}^{-2}$. Negative delays indicate the stronger pulse preceding the weaker one. A correlation FWHM of $\sim 20 \text{ ps}$ is obtained with lines as guide to the eye. The data point at $|\Delta t| = 1000 \text{ ps}$ is calculated for two pulses infinitely separated in time (see text). Note the logarithmic time axis in the main graph.

Figure 6 shows such a 2PC for the fs-laser-induced associative desorption of CO from O/C/Ru(001). A FWHM$_{2PC}$ of $\sim 20 \text{ ps}$ is found, which clearly rules out an exclusively electron-mediated reaction mechanism with an ultrafast coupling time shorter than the electron–phonon coupling of the Ru(001) substrate. ‘Slow’ electron-mediated reaction mechanisms with coupling times larger than the electron–phonon equilibration time cannot be resolved within a 2PC scheme, since after equilibration a differentiation between different heat baths of the substrate becomes invalid. Furthermore, the 2PC also reveals the exponent of the fluence dependence, since at large pulse–pulse delays $\Delta t$ the two pulses do not benefit from each other anymore and the measured yield is $Y \propto 2\langle F \rangle^n$. On the other hand, at $\Delta t = 0$, the yield corresponds to an excitation of twice the fluence of the individual pulse. Thus, the ratio between the yield of the peak and the wings gives the exponent of the fluence dependence via $Y(2\langle F \rangle)/[2Y(\langle F \rangle)] = 1/2 \times 2^n$. From the data of figure 6, an exponent of $n = 3.6$ is obtained, which is slightly lower than the $n = 4.3$ extracted from the 800 nm fluence dependence (figure 4). This deviation can be rationalized, since at the longest experimental delay $|\Delta t| = 250 \text{ ps}$ the surface temperatures (both $T_d$ and $T_{ph}$) have not yet fully relaxed to their initial values, rendering the denominator of the ratio slightly too large and, hence, the exponent $n$ too small.

Isotope effects are the second experimental observable of a surface reaction, which undoubtedly indicates the operation of an electron-driven mechanism. Unlike in a phonon-mediated process [57], a ratio of the reaction yield between isotopically substituted reactants different from unity is characteristic for a process involving electronic excitations, for example, in electron-stimulated desorption [58] as well as in surface femtochemistry [6], e.g. in the
CO oxidation [8] and H + H recombination [59] reactions both on Ru(001). However, in the present system of C + O association, both oxygen and carbon isotope substitution do not show any yield ratio significantly different from unity: \( Y^{(13}\text{C}^{16}\text{O})}/Y^{(13}\text{C}^{18}\text{O}) = 1.05 \pm 0.06 \) and \( Y^{(12}\text{C}^{18}\text{O})}/Y^{(13}\text{C}^{18}\text{O}) = 0.97 \pm 0.06 \). But one has to keep in mind the limited change in the reactants’ mass available, in particular, if the reduced mass of a certain molecular motion relevant for the reaction is involved. Quantitative details will be discussed further below.

To characterize the energy release into the reaction products, the translational energy of the desorbing CO molecules along the surface normal is measured. The recorded time-of-flight (TOF) spectra for various absorbed fluences \( F \) of laser pulses at 400 and 800 nm are depicted in figure 7. The experimental data are well reproduced by single modified Maxwell–Boltzmann distributions, which suggests that the desorption process occurs via a single reaction channel and allows to characterize the experimental data with a single temperature \( T_{\text{trans}} = \langle E \rangle/2k_B \). The flight times of the CO molecules induced both with 400 nm (figure 7(a)) and 800 nm (figure 7(b)) pulses decrease only moderately with increasing laser fluence. The measured \( T_{\text{trans}} \) range from 600 to 860 K. Slightly higher translational temperatures \( T_{\text{trans}} \) are obtained with 400 nm as compared to 800 nm excitation due to the higher surface temperatures resulting from the shorter optical penetration depth for 400 nm pulses (see above). Figure 7(c) plots these translational temperatures together with the so-called rate-weighted adsorbate temperature \( T_{\text{ads}}^{\text{RW}} \) as a function of the absorbed laser fluence \( F \). \( T_{\text{ads}}^{\text{RW}} \) is defined as \( T_{\text{ads}}^{\text{RW}} = \int_0^\infty T_{\text{ads}} R(t) \, dt / \int_0^\infty R(t) \, dt \) with \( T_{\text{ads}} \) and \( R(t) \) as the adsorbate temperature and rate, respectively, obtained from the friction model [27, 28], and it may be rationalized that this temperature describes the energy content relevant to the reaction in a more representative way due to the weighting procedure than just the mere maximum of the temperature transient \( T_{\text{ads}}(t) \) [60]. As seen from figure 7(c), \( T_{\text{ads}}^{\text{RW}} \) reproduces the trend of the fluence-dependent translational energies of the nascent CO molecules quite well, however, the absolute values are by a factor of 3 larger than \( T_{\text{trans}} \). Possible origins for this deviation are discussed in the following.

So far, no information is available on the energy transfer during reaction into internal (i.e. vibrational and rotational) degrees of freedom of the nascent CO molecule and how the multidimensional PESs governing the C + O association influence the overall energy partitioning between internal and external degrees of freedom. One might expect that due to the location of the barrier along the vibrational coordinate, excitation of the interatomic distance \( d \) will facilitate the CO associative desorption more than does excitation of the distance coordinate \( z \) between the C–O and the Ru surface. It is interesting to note that for the related associative desorption of \( \text{N}_2 \) from Ru induced with ns laser pulses, only very little vibrational excitation of the desorbing \( \text{N}_2 \) molecules was found [18], in total \( \sim 1/3 \) of the barrier height of 2–3 eV [16, 61] is transferred to molecular degrees of freedom (in this case, translational excitation). This means that for \( \text{N} + \text{N} \) roughly \( 2/3 \) of the desorption energy is lost to the surface in desorption. These findings imply strong vibrational quenching (cooling) in reactive trajectories passing the barrier and consequently were taken as (indirect) evidence for strong nonadiabatic coupling in the \( \text{N}_2 \) desorption process. This has been further supported by density functional theory (DFT)-based multidimensional friction calculations by Luntz and Persson [19]. However, one has to keep in mind that this vibrational damping of the nascent \( \text{N}_2 \) molecule relates to locations on the ground state PES beyond the transition state, whereas the nonadiabatic coupling in the excitation step of the fs-laser induced CO association corresponds to the ascending side of the desorption barrier.
One further possible origin of the weak fluence dependence of the translational energy of the desorbing CO molecules relies on peculiarities of the ground state PES for the C/O/Ru(001) system (similar to N/Ru(001)). A deep molecular adsorption well of $\sim$1 eV exists, where the CO is molecularly bound in an upright configuration [39, 40]. As a consequence, the
nascent CO molecule might be trapped (and at least partially thermalized) or scattered at this chemisorption well losing memory of the initial activation step. Such a scenario is supported in experiments by Diekhöner et al [17] where the thermally induced associative desorption of CO from Ru(001) yielded translational energies of the desorbing product molecules similar to those in the fs-laser induced reaction reported here.

Finally, potentially incomplete thermal equilibration of the departing CO molecules with the Ru substrate, in principle, could also cause rather low translational energies. Indeed, the values for $T_{\text{trans}}$ derived from the TOF spectra of $\sim 700 \text{ K}$ (for 800 nm excitation, see figure 7) are considerably lower than the modelled maximum phonon temperature of the Ru substrate $T_{\text{ph}} \approx 1500 \text{ K}$ (as figure 9 will show further below). Such behaviour might originate from dynamical cooling effects, which describe the insufficient energy transfer between adsorbate and substrate during the interaction time [62]. Consequently, systems exhibiting dynamical cooling should also show a significant decrease of the sticking probability of impinging particles with increasing particle energy. However, this is not observed for CO/Ru(001) where the initial sticking coefficient only falls off slightly from 1.0 to 0.6 for kinetic energies of the impinging molecules in the range of 0.09–2.0 eV [63]. Therefore, the dynamical cooling in the fs-laser-induced desorption of molecularly bound CO from Ru(001) invoked by Funk et al [7] needs to be treated with care. Figure 7(c) plots these translational temperatures of the desorbing CO from a CO-saturation covered Ru(001) surface at an initial temperature $T_S = 100 \text{ K}$. Taking into account the lower base temperature in the latter experiment, it appears that both the associative CO desorption and the desorption of molecularly bound CO species exhibit similar translational excitation if initiated with fs-laser pulses. For the experimental side, state-resolved measurements of the internal energy content of the desorbing product molecules are needed to substantiate any further energy balance argumentation.

5. Frictional modelling

The fs-laser-induced desorption from a metal surface can be described by coupled heat baths for the electron, phonon and adsorbate degrees of freedom, each characterized by its own temperature [6, 34]. As outlined above, the evolving reaction dynamics are described in a frictional picture, where the energy is transferred from the laser-excited substrate to the reactants in the adsorbate layer by either adiabatic (i.e. phonon) or nonadiabatic (i.e. electron) coupling or potentially both. In the following, the presented fluence dependence and the two-pulse correlation data of the associative CO desorption will be simultaneously modelled with parameter sets consisting of the coupling coefficients to the electron and phonon heat baths $\eta_{\text{el}}$ and $\eta_{\text{ph}}$, respectively, and the activation energy $E_a$. The coupling strengths are treated as fit parameters, whereas the activation energy is kept fixed at certain values. The experimental data are expressed coverage-independently in terms of desorption probabilities $P_{\text{des}}$, which are obtained from the cross sections $\sigma_{\text{eff}}$ derived above. Thus, measured and modelled absolute yields can be directly compared.

A purely electron mediated reaction with coupling times shorter than the electron–phonon equilibration time of $\tau_{\text{el–ph}} = 1.6 \text{ ps}$ for Ru(001) [7] is excluded, since this typically leads to 2PC widths narrower than 5 ps [59, 64]. Thus, solely a purely phonon-mediated energy transfer ($\eta_{\text{el}} = 0$, i.e. $\tau_{\text{el}} = \infty$) and a reaction scenario involving both electron and phonon coupling will be considered. As the activation energy $E_a$ in Redhead’s analysis depends on the
Table 1. Frictional parameters of the different reaction scenarios to reproduce the experimental data of the fs-laser-induced CO recombination. The activation energy $E_a$ is kept fixed, whereas the coupling times $\eta_{el}^{-1}$ and $\eta_{ph}^{-1}$ are used as fit parameters. $Y_{exp}/Y_{mod}$ describes the desorption yield ratio between experiment and friction calculation. $\nu^{RW}_{mod}$ denotes the respective rate-weighted pre-exponentials obtained for Kramers’ low friction limit, see text.

| Reaction scenario mediated by | $E_a$ (eV) | $\eta_{el}^{-1}$ (ps) | $\eta_{ph}^{-1}$ (ps) | $Y_{exp}/Y_{mod}$ | $\nu^{RW}_{mod}$ ($s^{-1}$) |
|-----------------------------|------------|------------------------|------------------------|-------------------|--------------------------|
| A: electrons and phonons    | 1.5        | 0.5                    | 1.2                    | 2                 | $2.2 \times 10^{13}$ |
| B: phonons                 | 1.5        | $\infty$              | 1.2                    | 17                | $0.9 \times 10^{13}$ |
| C: phonons                 | 1.0        | 1.2                    | 1                      | 1                 | $0.6 \times 10^{13}$ |

The outcome of this modelling is shown in figure 8 for three different reaction scenarios together with the experimental data; the corresponding best fit parameter sets are summarized in table 1. Scenario A involving both electron and phonon contributions yields coupling times $\eta_{el}^{-1}$ and $\eta_{ph}^{-1}$ of 0.5 and 1.2 ps, respectively, whereas scenarios B and C both accounting for purely phonon-mediated energy transfer at different, but fixed activation energies lead to an optimum coupling time of $\eta_{ph}^{-1} = 1.2$ ps. Generally, the wavelength dependence (400 nm versus 800 nm) of the C + O desorption yield is well reproduced in all scenarios solely by taking into account the different penetration depths which enter the two-temperature model. This corroborates that the energy absorption closer to the Ru(001) surface for 400 nm causes the observed enhanced reaction yield. The actual fluence dependencies for both wavelengths are also quite reasonably described by all coupling scenarios, as seen in panel (a) of figure 8. Furthermore, the width of the modelled two-pulse correlation for either of the reaction scenarios is reproduced to a more or less satisfactory extent (17, 20 and 28 ps for A, B and C, respectively, as compared to ~ 20 ps FWHM of the experimental data). However, a purely phonon-mediated energy transfer at an activation energy of 1.5 eV significantly underestimates the CO desorption probability in the 2PC at large pulse–pulse delays $\Delta t \geq 50$ ps, a fact which clearly excludes this scenario from being relevant. Consequently, this means that despite the fact of a 20 ps broad two-pulse correlation, the experimental data are qualitatively well modelled considering either also nonadiabatic coupling at an activation energy of 1.5 eV or taking into account a lower barrier height of 1.0 eV and exclusively adiabatic adsorbate–substrate coupling. This is further supported if one calculates the absolute reaction rates (and the corresponding yield $Y_{mod}$) in Kramers’ low friction limit (see equation (6)) and compares these results with the experimentally derived values $Y_{exp}$. As listed in table 1, excellent agreement is found for scenarios A and C, whereas the modelled yield of scenario B (pure phonon mediation at $E_a = 1.5$ eV) is more than one order of magnitude too low.

Such an experimental value for $E_a$ is in reasonable agreement with recent DFT calculations by the Nørskov group yielding 1.8 eV [65].

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Figure 8. Frictional modelling of the fs-laser-induced associative CO desorption. Experimental data and friction calculations are shown for (a) the fluence dependence for 400 and 800 nm excitation and (b) the two-pulse correlation measurement at 800 nm. Panels (c) and (d) show the 2PC on a logarithmic timescale for clarity. Calculations are performed for three frictional coupling scenarios with parameter sets A, B and C and the results are plotted with solid, dashed and dotted lines, respectively. The fit parameters involve phonon and electron contributions (A: $\eta^{-1}_{\text{el}} = 0.5 \text{ ps}$, $\eta^{-1}_{\text{ph}} = 1.2 \text{ ps}$ and $E_a = 1.5 \text{ eV}$) and purely phonon mediation at the same activation energy (B: $\eta_{\text{el}} = 0$, $\eta^{-1}_{\text{ph}} = 1.2 \text{ ps}$ and $E_a = 1.5 \text{ eV}$) and at a considerably lowered $E_a$ (C: $\eta_{\text{el}} = 0$, $\eta^{-1}_{\text{ph}} = 1.2 \text{ ps}$ and $E_a = 1.0 \text{ eV}$).

In the further course of the quantitative analysis based on Kramers’ low friction limit, the pre-exponential in the Arrhenius-like expression for the reaction rate can be determined via

$$\nu = (\eta_{\text{el}} + \eta_{\text{ph}}) \cdot E_a / (k_B T_{\text{ads}}),$$

(8)

whereby the transient adsorbate temperature $T_{\text{ads}}$ is represented best by the rate-weighted adsorbate temperature $T_{\text{ads}}^{\text{RW}}$ as introduced above. With this $T_{\text{ads}}^{\text{RW}}$, the coupling parameters $\eta_{\text{el}},$
Figure 9. Temperature transients of the coupled heat baths and the resulting desorption rate calculated for scenario A (electron and phonon contributions) and C (pure phonon mediation) with coupling parameters and activation energies given (see table 1). The laser excitation corresponds to experimental conditions of the 2PC experiment at zero delay ($\langle F \rangle = 170 \text{ J m}^{-2}$).

$\eta_{ph}$ and the activation energy $E_a$, a rate-weighted pre-exponential $v_{RW}^{\text{mod}}$ can now be calculated. For all three coupling scenarios, one obtains similar values for $v_{RW}^{\text{mod}}$ on the order of $10^{13} \text{ s}^{-1}$ (see table 1) due to similar frictional coupling strengths needed to reproduce the width of the measured 2PC. However, if one considers that in thermally induced desorption, an activation energy of $E_a = 1.0 \text{ eV}$ corresponds to $v_{TDS} \sim 10^9 \text{ s}^{-1}$, the values of $v_{RW}^{\text{mod}}$ derived for the fs-laser-induced process are four orders of magnitude larger. This means that for $E_a = 1.0 \text{ eV}$ the pre-exponential cannot be expressed in the low friction limit (equation (8)).

When describing processes like the desorption of adsorbates from a substrate in the frictional approach, the energy in a 1D model flows directly into the coordinate relevant to the reaction, whereas in multidimensional dynamics the energy is not exclusively transferred into the reaction coordinate but also into coordinates not necessarily leading to the reaction of interest. As a consequence, a $v$ derived under thermal excitation conditions, which includes the multidimensionality of the desorption process, can be considered as an upper bound, since processes far off from equilibrium conditions (e.g. fs-laser induced desorption) can result in a significant decrease of the pre-exponential [62, 66]. Based on this $v_{fs\text{-laser}} \leq v_{TDS}$ at $E_a = 1.0 \text{ eV}$, also the modelled rate and yield of the fs-laser-induced reaction should be four orders of magnitude smaller, which is in contrast to the experimental results reported here. However, a desorption scenario with a barrier height of $E_a = 1.5 \text{ eV}$, where $v_{TDS} \approx v_{RW}^{\text{mod}}$, consistently describes the fs-laser and the thermally induced C + O recombination within the low friction limit. This means that despite the seemingly qualitative agreement in the fluence dependence and two-pulse correlation, no quantitative agreement is found for a purely phonon-driven energy transfer. Instead, adiabatic and nonadiabatic substrate–adsorbate coupling have to be considered in the fs-laser-induced desorption process of C + O from Ru(001).

The calculated transient adsorbate temperatures $T_{ads}(t)$ and the reaction rates $R(t)$ corresponding to a combined electron/phonon-mediated and a solely phonon-driven reaction mechanism are shown in figure 9. Depending on the coupling scenario, $T_{ads}(t)$ follows mainly either the electron temperature $T_{el}$ or the phonon temperature $T_{ph}$. Consequently, rate and desorption yield of the former case exhibit a rather narrow temporal distribution; no significant
reaction rate is observed for times larger than 2 ps. In contrast, in a purely phonon-mediated process, the slow temperature rise and cooling of the phonon system cause desorption fairly smeared out in time. Furthermore, such an ultrafast response due to nonadiabatic coupling should in principle cause a clear isotope effect, however, in conflict with the yield ratio of unity found in the experiment. This apparent discrepancy is resolved, if one considers that the reaction barrier of the C + O association is located in the vibrational channel, i.e. mainly along the intramolecular distance $d$. Thus, the reduced mass $\mu$ of the nascent CO molecule has to be taken into account, which can be varied only by 5% within the available mass range of the reactants. With the optimum fit parameters for the combined electron/phonon-driven reaction scenario in conjunction with the mass-dependent electronic coupling coefficients $\eta_{el} \propto 1/m$ of the frictional description, isotope yield ratios for both oxygen and carbon substitution of $\sim 1.08$ are calculated, which is indeed consistent with the experimental values (1.05 ± 0.06 and 0.97 ± 0.06, respectively).

Additional information is obtained when one compares the strength of the nonadiabatic coupling derived for the C + O association with other related reaction systems excited with fs-laser pulses. For instance, the coupling coefficient $\eta_{el} = \tau_{el}^{-1} = 1/500 \text{ fs}^{-1}$ in the present case is of the same order as that found for the hot electron-mediated associative hydrogen desorption also from Ru(001) [35, 59]. This means that the reactants for the CO association, which are almost one order of magnitude heavier than H reactants, need to be accelerated on the same timescale which in turn requires mass-independent friction coefficients $\gamma_{el} = m \eta_{el}$ also one magnitude larger than in the hydrogen case. Note that this rather strong frictional coupling of both reactants C and O can be rationalized if one bears in mind that the formation of $\pi$-bonds on metal surfaces requires strong mixing between molecular states and metal bands [19]. Furthermore, based on DFT, Luntz and Persson [19] calculated the mass-independent electronic friction coefficients $\gamma_{el}$ for the N + N/Ru(001) system, which is expected to be comparable to the present isoelectronic C + O due to the similarities of the underlying PESs [14, 15]. For the N$_2$ association on Ru(001), an averaged $\langle \eta_{el} \rangle$ of the two frictional tensor components along the intramolecular distance $d$ and the distance $z$ between surface and centre-of-mass was determined to be $\langle \eta_{el} \rangle \approx 1/2 \cdot (\langle \gamma_{dd} \rangle/\mu + \langle \gamma_{zz} \rangle/m) = 1/560 \text{ fs}^{-1}$, where $\mu$ and $m$ denote the relative mass and absolute mass of the molecule, respectively. Such a result is in very good agreement with the $\eta_{el}$ value found in the present experiments on C + O recombination.

Finally, we consider the activation energy $E_a$, which enters the frictional model as the well depth of a truncated harmonic oscillator. It turned out that the values for $E_a$ extracted from modelling the experimental data frequently exceed the measured activation energies for desorption, e.g. in H$_2$ association on Ru(001) [59]. Recent calculations based on multidimensional friction in combination with molecular dynamic trajectories showed that in the case of inherently multidimensional reactions like association, phase space constraints are responsible for this difference in barrier heights [22]. However, unlike in H$_2$ formation, the nascent C–O complex in the C + O association has to overcome a pronounced barrier in the vibrational channel [10], which might be regarded as a 1D problem. It is only beyond the transition state where at least the second coordinate (the distance between the CO and Ru surfaces) becomes relevant. Yet, future multidimensional frictional calculations have to clarify the details of the energetics in associative CO desorption from Ru(001).

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6. Summary and conclusions

The fs-laser-induced associative desorption of C + O from Ru(001) has been experimentally studied and theoretically modelled within the frictional concept of energy transfer. With absolute rate calculations based on Kramers’ low friction limit, the experimental data are qualitatively and quantitatively successfully reproduced when both adiabatic and nonadiabatic (i.e. phonon- and electron-mediated) coupling between the laser-excited metal substrate and the reactants in the adsorbate layer are considered. While the electron contribution to the energy transfer causes the desorption process to occur within only a few picoseconds (≤ 2 ps), the coupling with the phonon system is the origin of a rather broad two-pulse correlation of tens of picoseconds (∼20 ps). The finding that a 1D model astonishingly well describes a multidimensional reaction like C + O associative desorption, is assigned to the reduced dimensionality of the activation step (the traverse of the pronounced barrier in the vibrational channel) which eventually leads to desorption.

Future state-resolved measurements in order to address the energy partitioning between different degrees of freedom and multidimensional frictional calculations will help to complete the picture of the fs-laser-induced desorption dynamics of C_{ads} + O_{ads} → CO_{gas} from Ru(001). Finally, resolving this reaction directly in the time domain via a pump-vibrational spectroscopy probe still remains an experimental challenge [67].

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