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Vibrationally enhanced associative photodesorption of molecular hydrogen from Ru(0001)

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Dedicated to Professor Jörn Manz on occasion of his 60th birthday.

Abstract

The effect of vibrational excitation, for example by infrared (IR) laser pulses, on the photodesorption of H_2 and D_2 from a Ru(0001) surface has been investigated theoretically. Based on information from first principle electronic structure theory, a minimal two-mode and two-state model is developed for Desorption Induced by Electronic Transitions (DIET) in the single-excitation limit. In the model, the finite excited state lifetime of a few femtoseconds (fs) is accounted for by a lifetime averaging scheme. Using the vibrational ground state as initial state for averaging, the energy partitioning into different degrees of freedom and isotope effects are investigated. We then consider vibrationally excited states and vibrational wavepackets as initial states, which are found to have a large influence on the outcome of the reaction. To show that IR excitation of the adsorbates is feasible, we use optimal control theory to design pulses in the sub-picosecond range. For these, vibrational relaxation in the ground state due to coupling of adsorbate vibrations to electron–hole pairs of the metal is accounted for. Our major result is that isotope- and bond-selective control of photoreactions should be possible to some extent, even in strongly dissipative media.
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1. Introduction

The associative desorption of hydrogen or deuterium molecules from a Ru(0001) surface at (1 × 1) H(D) coverage (saturation), is another interesting recent example of femtosecond-laser induced photoreactions at surfaces [1–3]. With 120–130 fs laser pulses at 800 nm center wavelength (1.55 eV), the following observations were made. First, a huge isotope effect was found, with H_2 desorbing with about 10-fold probability compared to D_2. Second, the molecules come off the surface both vibrationally and translationally "hot". Translation appears to be much more excited than vibration, indicating a non-thermal, unequal energy partitioning into various modes. Third, the desorption yield increases non-linearly with laser fluence, F, according to $Y \propto F^n$ with $n \approx 3$. Finally, from two-pulse correlation (2PC) measurements an ultrafast response time (~1 ps) of the system has been confirmed.

Some of these findings are evidence for an electronic, hot-electron mediated rather than thermal mechanism. Accordingly, the laser pulse heats the substrate electrons to high electron temperatures, $T_{el}(t)$, which then couple to the adsorbate–surface bond to selectively break it without distributing the energy over many other modes. This

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picture was recently corroborated by Luntz et al. [4]. They used the well-known two-temperature model [5] to obtain $T_{\text{el}}(t)$, in conjuction with molecular dynamics (MD) with electronic friction, the latter calculated with periodic density functional theory (DFT). The theory was applied with great success to $H_2/D_2/\text{Ru}(0001)$ [4]. In their model, two degrees of freedom r and Z were used (plus one "phonon mode"), with r being the H–H distance and Z the distance of H_2 from the Ru surface. Desorption occurs in the ground state, through random forces which are related to the electronic friction coefficient, $\eta_{ij}(r,Z)$ (with $i, j = r$ or Z), and the electron temperature, $T_{\text{el}}(t)$.

As an alternative to this and similar friction models, "non-adiabatic" models have been suggested in which photodesorption is described as being due to explicit, repeated participation of (an) electronic excited state(s), and "vibrational ladder climbing" in the ground state. The excited states are non-stationary, with lifetimes that are typically very short at metal surfaces, $\tau_{\text{el}} \sim$ fs. This scenario was coined desorption induced by multiple electronic transitions (DIMET) [6]. The dynamics can be treated by classical surface hopping [6], by stochastic or jumping wavepackets [7], or by open-system density matrix theory [8]. These non-adiabatic models require obviously more than one potential energy surface, and are equally applicable to multiple-excitation (DIMET, with femtosecond lasers) and single-excitation limits (DIET, typically with nanosecond lasers), i.e. also to situations where the concept of thermalized electrons is clearly inapplicable.

In the following, we shall use a "non-adiabatic" model, to study DIET of molecular hydrogen from Ru(0001). Our primary goal is not to reproduce the (DIMET) experiments and previous theory [4], but rather to (laser) control a photoreaction in strongly dissipative environments. Since the electronic excitation step is substrate-mediated and indirect, coherent control of this step is evidently not straightforward. Here we suggest a "hybrid scheme" scheme instead, in which the adsorbate is vibrationally excited by an IR pulse, prior to electronic excitation. The IR excitation is direct and controllable, and prepares the system for the subsequent photoreaction. Similar IR + UV/vis strategies to control the photodesorption or other reactions of molecules at surfaces have been suggested elsewhere [8–16].

Our strategy is similar to "vibrationally mediated chemistry" in gas phase dynamics [17–20], where mode- and isotope-selective IR excitation using shaped laser pulses has been realized for systems with only a few modes [18]. It appears much more difficult to achieve the same goal for complex systems, including condensed phases and adsorbates. Only recently the goal was achieved to selectively excite and break an adsorbate–surface bond by IR photons without thermalization, for the example of associative desorption of H_2 from H/Si(111), in the ground electronic state [21,22]. In this system the adsorbate–substrate coupling is due to phonons and weak, leading to comparatively long (vibrational) lifetimes, τ_{vib}, in the ns range. (Direct desorption by blackbody radiation, of very weakly bound,

physisorbed H_2 [23] and He has also been achieved [24].) It is the purpose of this paper: (i) to find out whether IR control in a strongly coupled, chemisorbed system with much shorter vibrational lifetimes is possible ($\tau_{\text{vib}} \leqslant 1$ ps), and (ii) if so, can affect the subsequent photoreaction via an electronic excited state with an electronic lifetime τ_{el} as short as a few fs. Vibrational (pre)excitation of the adsorbate in the ground electronic state may not only be due to IR excitation, but also, more unselective, due to temperature, or via multiple-excitation–deexcitation cycles as in DIMET. Therefore, to study of vibrationally excited states serves also to estimate temperature effects and peculiarities of DIMET, relative to DIET.

This paper is organized as follows. In Section 2, the open-system density matrix model to treat DIET of hydrogen from Ru(0001) will be outlined. We use a two-state model in which the ground state potential energy surface is obtained from periodic DFT calculations, and a "representative" excited state surface is constructed based on additional information from a cluster model. In Section 3, the dependence of the desorption probability and the energy partitioning of the desorbing molecules as a function of the initial vibrational state will be investigated. Section 4 discusses possibilities to excite, ideally selectively, vibrational modes of adsorbed hydrogen with shaped laser pulses. The IR excitation on the one hand, and vibration–electron coupling on the other, are treated by using optimal control theory in an open-system density matrix frame, similar to Ref. [25]. The vibration–electron coupling will be estimated from cluster calculations and perturbation theory [26,27]. The cluster calculations also deliver transition dipole matrix elements for the IR excitation. Finally, Section 5 summarizes this paper.

2. Model and method

2.1. Two-state, two-mode model to treat DIET

In the following, we use a two-state open-system density matrix model to treat associative desorption of H_2 and D_2 from fully covered Ru(0001):H-(1 × 1) and Ru(0001):D-(1 × 1) surfaces.

In this model, we treat DIET by assuming that a single, "representative" excited state, $|e\rangle$, promotes the desorption. The excited state lifetime is τ_{el}. Using a "jumping wave packet" model first introduced by Gadzuk [7,28], DIET is treated in two steps. In step one, the initial wave function ϕ_0, a vibrational eigenstate of the electronic ground states, for example, is projected on the excited state $|e\rangle$, propagated there for a residence time τ_{R}, transferred back to the ground state $|g\rangle$, and propagated to a final time, t:

$$|\psi(t;\tau_{\text{R}})\rangle = \exp\left\{-\frac{i\hat{H}_{\text{g}}(t-\tau_{\text{R}})}{\hbar}\right\}|g\rangle\langle e|\exp\left\{-\frac{i\hat{H}_{\text{e}}\tau_{\text{R}}}{\hbar}\right\}|\phi_0\rangle.$$

(1)