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Computer simulation studies of IR laser excitation of water on a metal surface

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We have performed classical Molecular Dynamics studies of laser induced heating and desorption of adsorbed water molecules on a model metal surface. The study focuses on the excitation of water modes. The laser field is simulated as an oscillatory time-dependent external electrical field that interacts with the molecular dipoles. Unrealistically high field strengths of the order of 10^{10} V/m were used in order to observe significant energy absorption and also molecular desorption on the time scale from 10 to 20 ps. Frequencies of 400, 1700, and 3750 cm^{-1} were chosen to excite the molecule in the librational, bending, and stretching modes, respectively. The rates for desorption of isolated molecules are substantially lower for excitation in the bending and stretching modes than for excitation in the librational modes. At higher adsorbate coverages, intermolecular energy transfer plays a major role in the behavior of molecules in the adsorbate layer.

1. Introduction

Laser-induced surface processes have been the subject of a variety of experimental and theoretical investigations. Experimentally, it has been shown that molecules can be desorbed either by heating of the metal surface following absorption of UV/VIS radiation [1], by resonant excitation of intramolecular vibrations in the IR spectral region [2], or by transient electron attachment [3]. Some of the proposed desorption mechanisms have been modeled by molecular dynamics (MD) [4,5] or by wave-packet dynamics [6]. Holme and Levine [5] showed that, in classical MD simulations, molecules with high frequency vibrational modes desorb vibrationally cold if the metal is heated, due to bottlenecks in the energy transfer from low to high frequency modes.

In the present study, we investigate the direct excitation of intramolecular degrees of freedom of adsorbed water molecules on a platinum surface by classical MD simulations. The choice of the model system was motivated by our interest in the effect of strong lateral adsorbate–adsorbate interactions on surface processes (see also ref. [7]) and by the fact that adsorbed water possesses modes

over a wide range of IR frequencies (from librational modes around $400\text{--}700\text{ cm}^{-1}$ that are nearly resonant with the metal–water stretching mode at 400 cm^{-1} to stretching modes above 3000 cm^{-1}). Thus, a variety of different energy transfer mechanisms is possible in this system.

We have simulated the laser excitation as the coupling of the molecular dipole with a monochromatic sinusoidally time-dependent electrical field. This model provides a convenient and efficient method of selectively exciting a specific degree of freedom. In cases where thermal equilibrium is achieved rapidly compared with energy absorption from the laser field (which is the case for the strongly interacting water adsorbate layer), this approach furnishes a practical way of heating a system at an approximately constant heating rate other than explicitly rescaling particle velocities from time to time.

2. Method

The physical system of interest is a platinum crystal consisting of 11 layers with 50 atoms in

each layer. On top of one of the (100) faces of the crystal, 1 or 40 water molecules are adsorbed (equivalent to coverages $\theta = 0.02$ and 0.8, respectively). Classical MD simulations are used to describe the time evolution of the system. Periodic boundary conditions in the two dimensions parallel to the surface plane are used in order to simulate an extended crystal slab and an extended adlayer (for $\lambda = 0.8$).

The following Hamiltonian describes the interactions between the various atoms and molecules and the coupling to the radiation field:

$$H = E_{\text{Kin}} + H_{\text{WW}} + H_{\text{WM}} + H_{\text{M}} + H_{\text{Intra}} + H_{\text{Laser}}, \quad (1)$$

where E_{Kin} is the kinetic energy, H_{WW} represents the (pairwise additive) intermolecular water–water interactions [8], H_{WM} the (pairwise additive) water–metal interaction potential (model II in ref. [7]), H_{M} the (pairwise additive) nearest neighbor force field for metal–metal interactions [9], H_{Intra} the three-body intramolecular water force field [8], and H_{Laser} the interaction of the molecule(s) with the laser field.

In the dipole approximation, the laser field can be described as an oscillatory time dependent electrical field E interacting with the molecular dipole μ (in the case of excitation of molecular modes like librations or vibrations) or the metal–water dipole (in the case of direct excitation of the metal–water bond, which will be discussed in a future communication):

$$H_{\text{Laser}} = -\mu(t) \cdot E, \quad (2)$$

where

$$\mu(t) = \sum_1^3 q_i r_i(t) \quad (3)$$

is the (time dependent) dipole moment and

$$E(t) = E_0 \cos(2\pi c \tilde{\nu}_0 t). \quad (4)$$

q_i are the atomic point charges in the BJH water model (-0.6596 for oxygen, $+0.3298$ for hydrogen atoms), $r_i(t)$ the instantaneous atomic coordinates, c the velocity of light, E_0 the electrical field strength, and $\tilde{\nu}_0$ the frequency of the electrical

field in cm^{-1} . The same excitation method has been used by Lim and Tully [10] to directly excite the Xe metal bond in a study of laser-induced desorption of Xe from Pt(111). Note that in the present work, the intramolecular water modes are excited rather than the adsorption bond directly.

Apart from the laser field, the Hamiltonian is the same as the one used in previous studies. The particle–particle interactions describe the major features of water–water interactions like hydrogen bonding and like hydrogen bond induced gas–liquid frequency shifts of the intramolecular vibrations, of the water–platinum interactions like adsorption site and geometry (on-top site adsorption with an oxygen–metal bond of a frequency of approximately 400 cm^{-1} and a binding energy of about -64 kJ/mol), and of the bulk phonon spectrum of platinum [7,9,11].

In the present study the laser field is perpendicular to the metal surface in agreement with the boundary conditions for Maxwell's equations on conducting surfaces. The field strengths were chosen to be of the order of about 10^9 to 10^{10} V/m so that the laser-induced forces acting on the atoms are of comparable size to the intermolecular forces. This procedure leads to a response of the system on the time scale of picoseconds. No local field corrections were made so that the field strength is not necessarily the one that would be deduced from laser fluence (see e.g. discussion in ref. [12]).

In order to observe the intermolecular energy transfer from excited to non-excited molecules in the adlayer calculations, only 4 out of the 40 adsorbed water molecules were coupled to the radiation field. The choice of four is a compromise between the ideal choice of one absorbing molecule and the requirement of averaging over different local environments.

3. Desorption of a single adsorbed molecule

We have performed simulations in which a single molecule is subject to laser fields at frequencies of 400, 1700, and 3750 cm^{-1} , corresponding to driving the excitation of the water librational, bending, and stretching regions, re-

spectively. Some characteristic results are compiled in table 1. Each entry in table 1 has been computed as the average over 20 trajectories, lasting 15 ps each. The length of the integration time step was determined by the requirement that the trajectory can be integrated backward in time over several picoseconds. Fig. 1 shows the observed desorption rates k_d as a function of energy absorption rate k_E for excitation at 400 cm^{-1} (\diamond), 1700 cm^{-1} (+), and 3750 cm^{-1} (\square). Desorption occurs at all frequencies. The desorption rates at fixed rate of energy absorption, however, are significantly larger for excitation in the librational region than for excitation in the bending and stretching regions.

The high desorption rates at 400 cm^{-1} are not surprising because of the near-resonance between librational modes between 400 and 700 cm^{-1} and the metal-oxygen stretching mode at about 400 cm^{-1} . The rates at 1700 and 3750 cm^{-1} are sig-

Table 1

Electrical fieldstrength E , excitation frequency $\tilde{\nu}_0$, desorption rate k_d , energy absorption rate k_E , and integration step Δt for simulations of an isolated adsorbate on the (100) face of a platinum crystal; the desorption rate is calculated as the average of the inverse of the time delay between switching on the interaction of the molecule with the field and the time of desorption; the energy absorption rate is calculated as the average of the ratio of the total energy increase of the system and the time during which the water molecule interacts with the field; errors are about $\pm 0.05\text{ ps}^{-1}$ for k_d and about $\pm 0.05\text{ eV ps}^{-1}$ for k_E

| E_0 (10^{10} V m^{-1}) | $\tilde{\nu}_0$ (cm^{-1}) | k_d (ps^{-1}) | k_E (eV ps^{-1}) | Δt (fs) |
|--|---|-------------------------------|----------------------------------|--------------------|
| 1.000 | 400 | 0.62 | 0.93 | 0.2 |
| 0.707 | 400 | 0.46 | 0.60 | 0.2 |
| 1.000 | 1700 | 0.23 | 1.47 | 0.05 |
| 0.866 | 1700 | 0.18 | 1.16 | 0.05 |
| 1.000 | 3750 | < 0.06 ^{a)} | 0.16 | 0.1 |
| 2.000 | 3750 | 0.13 | 0.73 | 0.05 |

^{a)} Upper bound, as only 2 out of 20 trajectories desorbed within 15 ps.

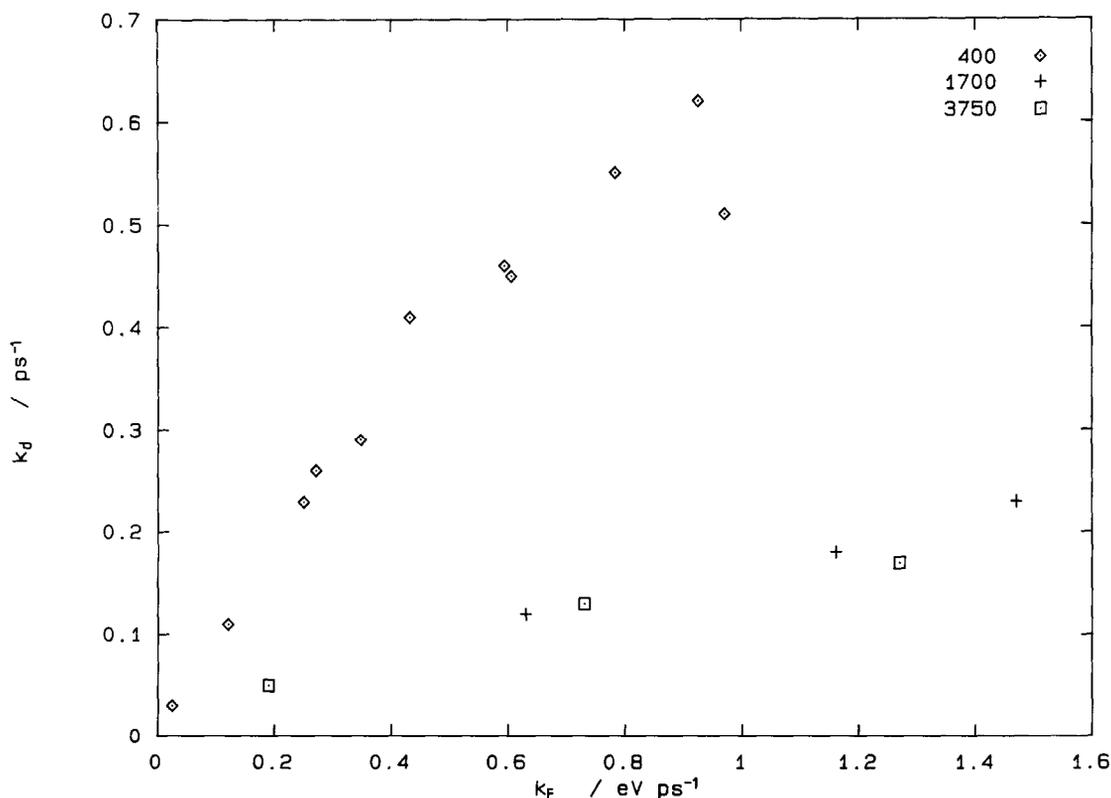
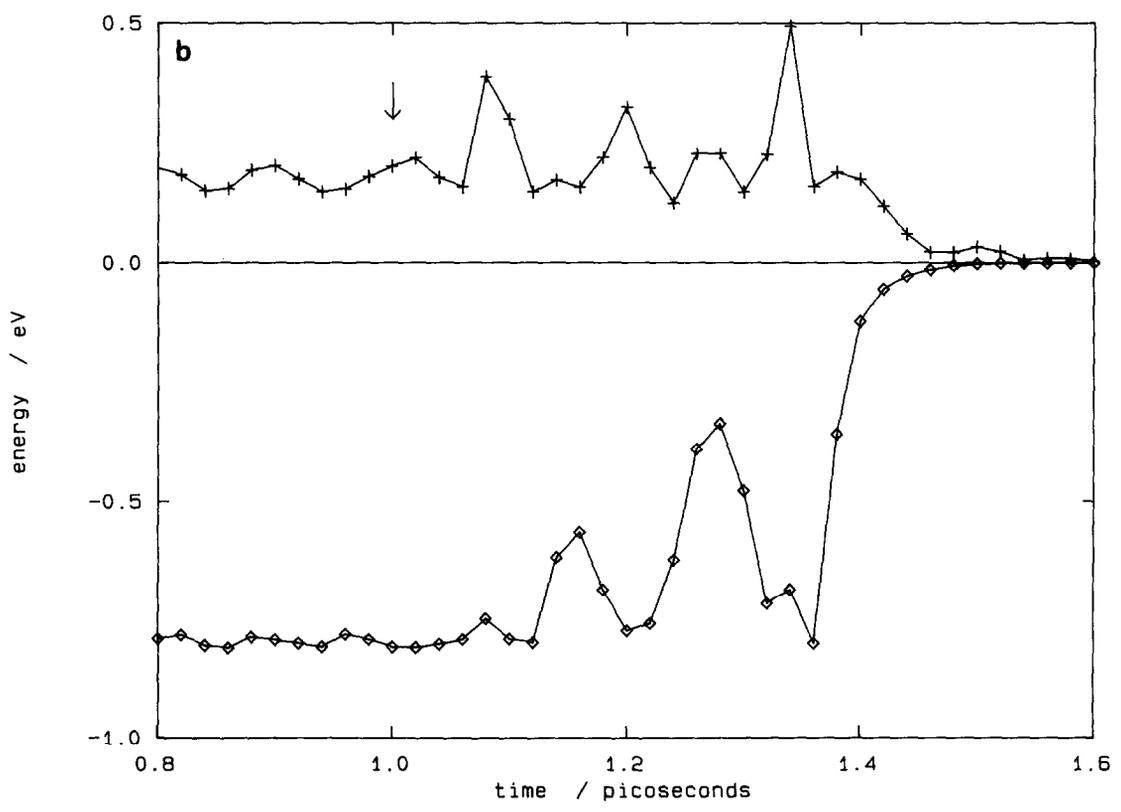
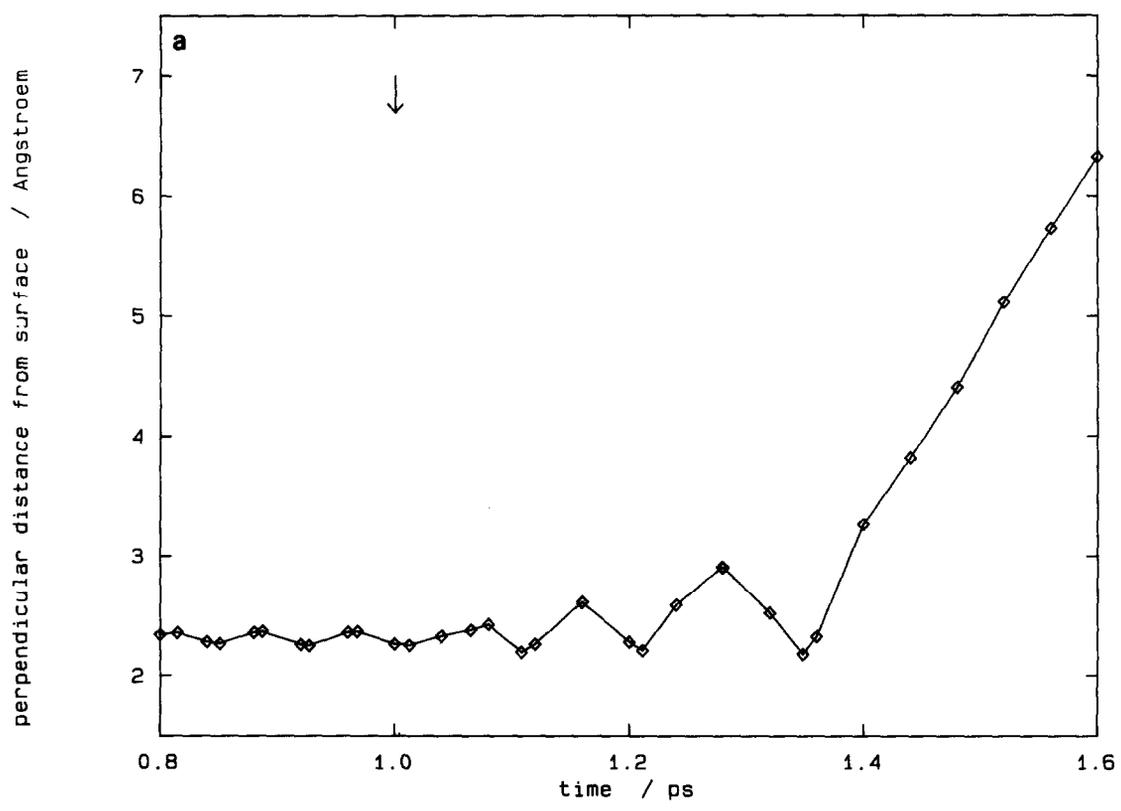


Fig. 1. Desorption rates k_d (in units of ps^{-1}) as a function of energy absorption rate k_E (in units of eV/ps) for excitation of librational modes (\diamond), of the bending mode (+), and of the stretching modes (\square).



nificantly lower. Notice that different field strengths E_0 are necessary to achieve approximately the same average energy absorption rate (see table 1). The differences in absorption cross section are, in part, due to differences in the simulation averages of the appropriate molecular dipole derivatives. Because the anisotropy of the water-metal interaction potential leads to preferred orientations of the water molecules with respect to the oscillating electrical field, the relative cross sections are not the same as would be obtained for a calculation corresponding to the gas phase. The discrepancy of the radiation field frequencies and the mode frequencies (i.e. the degree to which the driving field is in resonance with the molecular motion) also plays a role in determining the absorption cross section.

As will be shown in a future communication [13], energy transfer between librational and vibrational modes is slow on the time scale of several picoseconds. On the contrary, energy transfer within the 3 librational or within the 3 vibrational modes is very fast, which explains the similarity of the desorption characteristics for bending and stretching excitation. The differences in desorption rates after librational and vibrational excitation, respectively, can be rationalized on the basis of a picture where energy transfer is predominantly due to collisions of single atoms with the surface: The initial step of the energy transfer from an excited librational mode into water-metal modes appears to be an increase in the hydrogen-metal interaction energy. In the potential model used here, the hydrogen-metal interactions are repulsive thus favoring an oxygen-down configuration on the adsorption site. The hydrogen-metal interaction energy is then utilized for stretching the metal-oxygen bond which leads ultimately to desorption. The representative trajectory in fig. 2 illustrates this mechanism. After switching on the field, the hydrogen-

metal interaction energy increases; after this initial increase the oxygen-metal interaction energy increases and subsequently the values of the hydrogen-metal and oxygen-metal interaction energies oscillate several times before desorption occurs with substantial rotational excitation. Because the amplitudes of the hydrogen motions at constant excitation energy decrease with increasing frequency, a higher excitation energy is necessary for a similar mechanism to be responsible for desorption after vibrational excitation. This is in accord with the observed lower desorption rates at constant energy absorption rate for the vibrational excitation. In addition, as only a minor fraction of the absorbed energy is transferred into librational modes, collisions of hydrogen atoms with the surface do not dominate the energy transfer. It is possible for either the oxygen or a hydrogen atom to undergo the first collision with the wall, which makes the desorption mechanism less well-characterized than for the librational excitation (more details will be given in ref. [13]). It should be noted here that intermediate deexcitation of the acquired water-metal interaction energy can occur and that desorption takes place in these cases after a substantially longer time, only after the trajectory undergoes a second or even third cycle of excitation.

4. IR excitation of water molecules in an adsorbate layer

In an adlayer of water molecules adsorbed on the platinum surface, different energy relaxation mechanisms play a role. These are predominantly intermolecular in nature. The energy absorbed in one molecule flows readily through hydrogen bonds (or, more generally, water-water interactions) onto neighbor molecules. Fig. 3 illustrates this phenomenon by plotting a quantity that can

Fig. 2. (a) Oxygen atom trajectory from a simulation in which the librational modes of a water molecule adsorbed on a platinum surface are excited with a field strength of 10^{10} V/m at a frequency of 400 cm^{-1} . (b) Time dependence of the oxygen-metal (\diamond) and hydrogen-metal interaction energy (+) for the trajectory in (a). The lines are drawn to guide the eye and do not reflect a linear variation of the potential energies in the time interval between the symbols. The arrows indicate the begin of excitation. Notice that the hydrogen-metal interaction energy (repulsive) increases first, indicating a collision between hydrogen and surface.

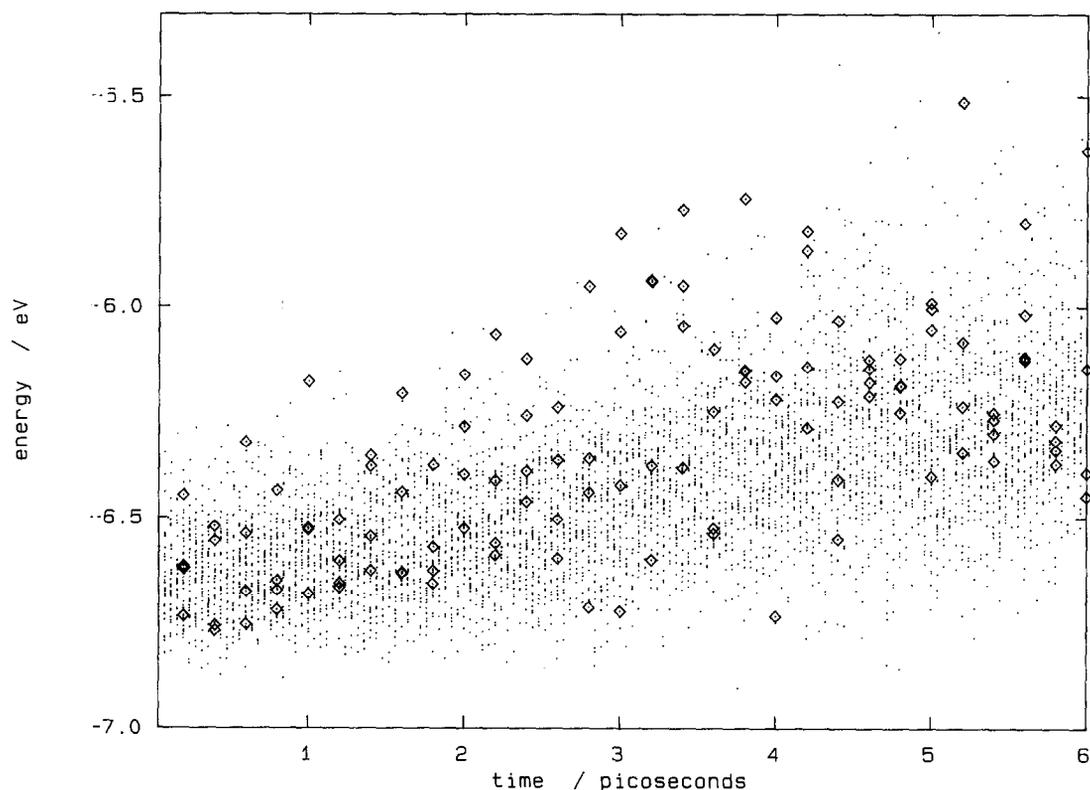


Fig. 3. Time evolution of the energy content of all 40 water molecules in an adlayer in a simulation where only four water molecules are excited by a laser field with field strength 10^{10} V/m and frequency 1700 cm^{-1} . The energy of a molecule is defined here as the sum of its intramolecular potential energy, of half its interaction energy with the other water molecules, the water-metal interaction energy, and of its kinetic energy: $E_{\text{water}} = V_{\text{intra}} + \frac{1}{2}V_{\text{WW}} + V_{\text{WM}} + E_{\text{kin}}$. The sum of the potential energy terms for the isolated fragments OH (at equilibrium) and H is zero. The dots represent molecules that did not couple directly to the external field whereas diamonds represents the 4 molecules directly excited.

be associated with an approximate single-molecule energy for each of the 40 molecules. It is evident that the energy contents of all the molecules increases in the 6 ps time interval. Although the directly excited molecules (diamonds) are predominant in the high energy tail of the distribution, their average energy content is less than 0.5 eV higher than that of the molecules not directly excited. Each excited molecule absorbs about 6.2 eV of energy. A major fraction of this energy is transferred onto neighbor molecules. Hence, no desorption occurs within 6 ps at an energy absorption rate of 1.03 eV/ps . Isolated molecules, excited at the same frequency, desorb with a rate of 0.18 ps^{-1} at this rate of energy absorption (see table 1). Similar results were found for excitation

at 3750 cm^{-1} where also no desorption in the adlayer was observed in a 6 ps time interval. Contrary to the case of an isolated adsorbed molecule, libration and vibration are in approximate equilibrium with each other, apparently a consequence of the rapid intermolecular energy transfer (more details will be given in ref. [13]).

5. Summary

The calculations show that, at least at the high field strengths used, laser induced resonant desorption of water molecules at low coverages is possible for excitation in the hindered rotational and the vibrational modes. The desorption rate at

constant rate of energy absorption is significantly higher for rotational excitation, due to larger amplitude motions, especially of the hydrogen atoms, which gives rise to more rapid energy transfer into the metal-water bond. Energy absorption by molecules in an adsorbate overlayer leads to rapid intermolecular energy exchange and, subsequently, to intramolecular thermalization.

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