

Ultraviolet-laser induced dissociation and desorption of water adsorbed on Pd(111)

Cite as: J. Chem. Phys. **92**, 1509 (1990); <https://doi.org/10.1063/1.458111>

Submitted: 30 October 1989 . Accepted: 09 November 1989 . Published Online: 31 August 1998

M. Wolf, S. Nettesheim, J. M. White, E. Hasselbrink, and G. Ertl



View Online



Export Citation

ARTICLES YOU MAY BE INTERESTED IN

[Dynamics of the ultraviolet photochemistry of water adsorbed on Pd\(111\)](#)

The Journal of Chemical Physics **94**, 4609 (1991); <https://doi.org/10.1063/1.460589>

[Degassing a vacuum system with in-situ UV radiation](#)

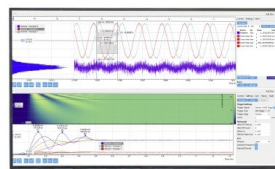
Journal of Vacuum Science & Technology A **30**, 060601 (2012); <https://doi.org/10.1116/1.4754292>

[A desorption mechanism of water following vacuum-ultraviolet irradiation on amorphous solid water at 90 K](#)

The Journal of Chemical Physics **132**, 164508 (2010); <https://doi.org/10.1063/1.3386577>

Challenge us.

What are your needs for
periodic signal detection?



Zurich
Instruments



The Letters to the Editor section is subdivided into four categories entitled Communications, Notes, Comments, and Errata. The textual material of each Letter is limited to 1200 words minus the following: (a) 200 words for a square figure one-column wide. Larger figures are scaled in proportion to their area; (b) 50 words for each displayed equation; (c) 7 words for each line of table including headings and horizontal rulings. Proof will be sent to authors. See the issue of 1 January 1990 for a fuller description of Letters to the Editor.

COMMUNICATIONS

Ultraviolet-laser induced dissociation and desorption of water adsorbed on Pd(111)

M. Wolf, S. Nettesheim, J. M. White,^{a)} E. Hasselbrink, and G. Ertl

Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-1000 Berlin 33, Faradayweg 4-6, West Germany

(Received 30 October 1989; accepted 9 November 1989)

An understanding of the basic photodriven processes at the metal-water interface is of fundamental importance in several areas, such as catalysis and photoelectrochemistry. We report on the observation of dissociation and desorption of molecular water adsorbed on a Pd(111) surface stimulated by UV-laser light. In the wavelength region used gas phase water and amorphous ice are practically transparent.¹

The UHV apparatus has been previously described.² A Pd(111) crystal kept at 90 K was dosed using a molecular beam of H₂O. The coverage was typically kept below saturation of the first monolayer. The sample was then irradiated with pulsed excimer light (6.4 eV and 5.0 eV) at normal incidence using fluences below 5 mJ/cm². A rotatable quadrupole mass spectrometer (QMS) allowed thermal desorption spectroscopy (TDS) and time-of-flight (TOF) spectroscopy of desorbing molecules.

Water adsorbs molecularly on Pd(111). Up to saturation of the first layer H₂O desorbs in a single TDS peak at 170 K [Fig. 1(a)]. Presumably a bilayer structure is formed,³ even at submonolayer coverages. At higher coverages multilayers of ice are built up, which desorb with zero-order kinetics above 150 K. UV irradiation of the bilayer leads to a shift of the H₂O desorption peak towards lower temperatures, approaching the desorption temperature of multilayer ice, and simultaneously to a new desorption feature which is observed at higher temperatures (185 K). Conversion into this new state is completed after irradiation with $\sim 3 \times 10^{18}$ photons/cm² [Fig. 1(b)]. Further irradiation leads to progressive depletion of the first water desorption state [Fig. 1(c)], due to laser induced desorption of H₂O, which can be observed using the QMS. No desorption of molecular fragments was observed.

The TDS-feature at 185 K has also been observed when H₂O was dosed on a surface precovered with 0.05 ML of atomic oxygen [Fig. 1(d)]. The same TDS is obtained after irradiation of the H₂O bilayer with 3×10^{18} photons/cm² ($h\nu = 6.4$ eV) and subsequent redosing of the amount of desorbed water. It is well known from EELS studies of water coadsorbed with oxygen on Pt(111) and Pd(100) that water reacts with atomic oxygen above 150 K forming hydroxyl

groups, which recombine at higher temperatures leading again to desorption of water.⁴ For this reason we attribute the TDS peak at 185 K to recombination of dissociated H₂O formed photochemically by UV light. This interpretation is further supported by the observation of thermal desorption from atomic oxygen and hydrogen in TDS after irradiation. Whether atomic oxygen or hydroxyl is the photolysis product can not be decided, but the latter seems most likely from energy considerations.

From a series of TDS measurements we determined the cross sections for the conversion and desorption process. The number of converted H₂O molecules N saturates exponentially with the number of photons n_{ph} irradiating the surface as $N = N_{max} [1 - \exp(-\sigma_{con} n_{ph})]$. Evaluating the area of the conversion peak in TDS (185 K) as function of photon fluence we obtain a cross section σ_{con} of 7×10^{-19}

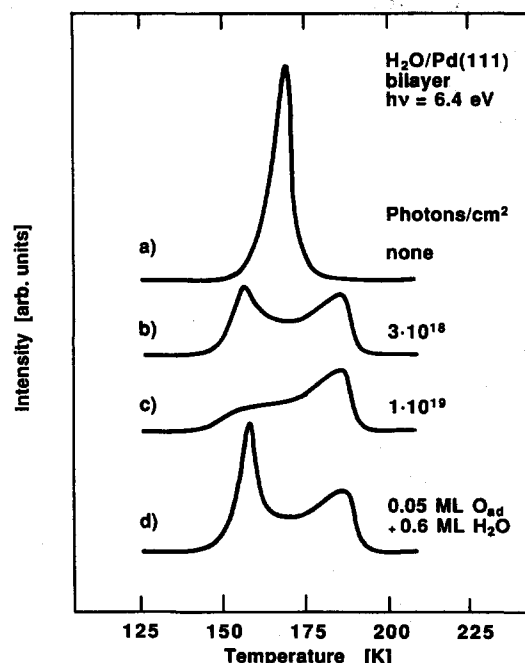


FIG. 1. Thermal desorption spectra of the water bilayer (a), after irradiation (b, c) and for coadsorption with atomic oxygen (d).

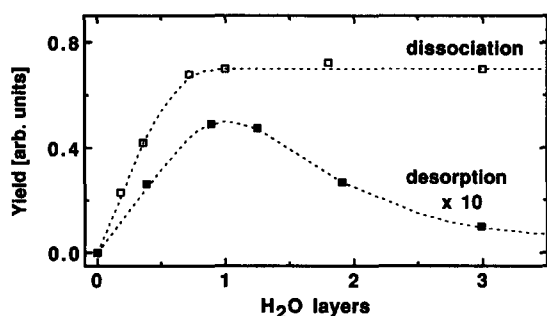


FIG. 2. Desorption (■) and dissociation (□) yield vs H₂O coverage. The desorption yield has been multiplied by a factor of 10.

cm², for $h\nu = 6.4$ eV. For 5.0 eV photon energy the cross section drops by more than one order of magnitude to $\sigma_{\text{con}} = 4 \times 10^{-20}$ cm². From the exponential decrease of the total H₂O-TDS area (after saturation of the conversion peak) we obtain a desorption cross section σ_{des} of 5×10^{-20} cm² and 1×10^{-21} cm² for 6.4 eV and 5.0 eV excitation, respectively. Observation of the desorbing flux with the QMS indicates that the buildup of the conversion feature is not a prerequisite, but rather a parallel reaction.

Starting with different H₂O coverages the saturation value of the conversion TDS peak increases first, but then remains constant for initial H₂O coverages above 60% of the saturation of the bilayer (Fig. 2). Even for multilayer coverages above 5 ML, dissociation in the first layer still proceeds. Focusing on the yield of desorbing H₂O molecules we observe a clear maximum at saturation of the first layer and a rapid decrease with the formation of multilayers. Adsorp-

tion of a second layer of H₂O already leads to a decrease of the desorption yield by a factor of two, indicating that desorption occurs only from the first layer and higher coverages trap desorption.

At both wavelengths the TOF spectra of desorbing water can be well represented by a Maxwell-Boltzmann distribution with a mean translational energy $\langle E_{\text{trans}}/2k \rangle$ of ~ 600 K. The angular distribution is strongly peaked towards the surface normal and can best be described by a \cos^4 dependence.

The observed TOF spectra together with the dependence on photon energy clearly establish the photochemical origin of the processes observed. These occur exclusively at the metal/water interface, thereby illustrating that the adsorbate-substrate interaction might open channels in surface photochemistry which are not present in the gas phase. Work is currently under way to characterize in more detail the adsorbate layer after irradiation in order to establish the photolysis products, and to study the isotope effect and polarization dependence which will give further insights into the dynamics.

^{a)} Humboldt Senior Scientist; permanent address: Department of Chemistry, University of Texas, Austin, Texas 78712.

¹M. Watanabe, H. Kitamura, and Y. Nakai, in *Vacuum Ultraviolet Radiation Physics*, edited by E.-E. Koch, R. Hänsel, and C. Kunz (Pergamon, New York, 1974), p. 70.

²E. Hasselbrink, S. Jakubith, S. Nettesheim, M. Wolf, A. Cassuto, and G. Ertl, *J. Chem. Phys.* (in press).

³P. A. Thiel and T. E. Madey, *Surf. Sci. Rep.* **7**, 211 (1987).

⁴G. B. Fisher and B. A. Sexton, *Phys. Rev. Lett.* **44**, 683 (1980); E. M. Stuve, S. W. Jorgensen, and R. J. Madix, *Surf. Sci.* **146**, 179 (1984); C. Nyberg and C. G. Tengstål, *J. Chem. Phys.* **80**, 3463 (1984).

A new technique to calculate steepest descent paths in flexible polyatomic systems

Alexander Ulitsky and Ron Elber^{a)}

Department of Chemistry, The University of Illinois at Chicago, Box 4348, Chicago, Illinois 60680

(Received 24 October 1989; accepted 15 November 1989)

Many algorithms are available for search of saddle points and transition states on molecular energy surfaces.¹ Nevertheless the calculation of steepest descent paths (SDP) in flexible polyatomic systems (FPS) still presents a significant challenge. The difficulties in calculating SDP for FPS are the following: (a) A large number of minima and steepest descent paths complicates the search for SDP between two minima specified prior to the calculations. (b) In large systems manipulations of second derivatives and related matrices^{1(c),1(d)} commonly employed in small systems become too expensive.

Several studies addressed in the past the above issues.^{1(e)-1(g),2} Available computational techniques which do not use second derivatives or prior knowledge on the position of the transition state provide only *approximate* SDPs

and the range of validity of these approximations is not always clear.

Here we present a new algorithm which uses first derivatives only and is capable of calculating the SDP starting with the coordinates of the minima to an arbitrary accuracy specified by the setup conditions. In this Communication we report the results of two test cases: (1) Muller potential,^{1(b)} (2) conformational changes in a dipeptide.

The algorithm is based on discretizing the SDP by a grid of M points $\{\mathbf{r}^k\}_{k=1,M}$. Each of the points is a replica of the complete system. Let \mathbf{s}^k be a unit vector along the slope of the path at \mathbf{r}^k . For \mathbf{r}^k to be on the steepest descent path, it is required that $\nabla V_{\text{proj}} = \nabla V - (\nabla V \cdot \mathbf{s}^k) \mathbf{s}^k = 0$, where V is the potential energy. Hence the potential is minimized in all directions except in the direction of the path. If $\{\mathbf{r}_k\}_{k=1,M}$