



Issue no. 17

GAS SURFACE NEWS

Editor - Sue Free. Cambridge University Chemistry Department, Lensfield Road,
Cambridge, CB2 1EW, UK. Tel/Fax +44 1223 336536. EMail - SJF1000@cus.cam.ac.uk
Web page containing Contact List <http://www.fhi-berlin.mpg.de/gsd/>.

Research Reports

Current activities in Photodynamics at the Department of Chemical Physics at the Fritz-Haber Institute in Berlin

Katharina Al-Shamery and Hans-Joachim Freund,
Fritz-Haber Institut der Max-Planck Gesellschaft, Faradyweg 4-6, D-14195, Berlin, Germany

Overview

The general goal of the research group is to obtain a microscopic view of elementary processes in heterogeneous catalysis including light induced processes. Reactions of adsorbates on complex surfaces such as oxides, nitrides and carbides and surfaces modified by metal cluster deposition are the subject of our investigations. The model systems are generally based on single crystals or epitaxially grown films respectively.

During 1996 our group moved from the Ruhr-Universität in Bochum to the Fritz-Haber Institut in Berlin. As a consequence we were able to extend our research activities so that certain experiments listed below are in the stage of development. Currently the group is divided into six different subgroups. The first subgroup investigates geometrical, vibrational and electronic properties of the model systems using methods such as infrared spectroscopy, HREELS (high resolution electron energy loss spectroscopy), UPS (UV photoelectron spectroscopy), XPS (X-ray photoelectron spectroscopy), NEXAFS (near edge absorption fine structure) and others. Microspectroscopic methods employing synchrotron radiation for spatially resolved investigations are currently under development at BESSY II in Berlin. In a second subgroup mainly structural information is collected using SPA-LEED (spot profile analysis low energy electron diffraction), video-LEED, AFM (atomic force microscopy), STM (scanning tunneling microscopy) and TEM (transmission electron microscopy). A further microscopical method, PEEM (photoelectron emission microscopy), is also being employed. FEM/FIM (field electron/ion microscopy) is used in a third group to study diffusion and aggregation of metals on thin dielectric surfaces. The magnetic properties of the model systems and dynamical information are obtained via ESR (electron spin resonance spectroscopy). A fifth group is actually being built up to investigate chemical reactions using crossed molecular beams on model catalysts. A sixth group is dealing with investigations on the dynamics of photoinduced processes using state selective laser spectroscopic methods. A second experimental activity of the laser group will be the application of non-linear optics to study in-situ chemical reactions at dielectric surfaces under ambient conditions in the near future.

We shall report about the activities of the photodynamics group. Information on other activities mentioned can be obtained from our WWW home page (<http://www.fhi-berlin.mpg.de/cp/cp.html>).

The group

The research subgroup related to investigations on the dynamics of photoreactions at surfaces currently consists of 2 research associates, K. Al-Shamery and W. Drachsel, 5 graduate students, 2 undergraduate students and 1 technician, W. Hänsel-Ziegler. Th. Klüner and an undergraduate student are responsible for calculations related to the experiments. Both work partly in our group and will start to work partly in the group of M. Scheffler at the Fritz-Haber-Institut. During our time in Bochum a similar agreement existed between our group and the theoretical group of V. Staemmler. There are a number of collaborations between our group and other research groups world wide. Related to our photodynamics work is the funded collaboration with the group of Murata and Fukutani and the group of Petek at Hitachi (both in Japan) and R. Kosloff (Israel). An informal exchange exists between our group and the group of H. Zacharias (Essen) and more recently with other groups within the Fritz-Haber Institute.

The methods

Our investigations concentrated on one of the most simple photoreactions, the laser induced rupture of the molecule surface bond after excitation with UV laser light followed by desorption, shortly called DIET (desorption induced by electronic transition). The goal of our investigations is to understand the dynamics of the underlying fundamental processes. The experimental approach to this problem is to study the final state distributions of the desorbing molecules of well characterised adsorbate systems using state selective spectroscopical methods. Information on the efficiency of the desorption process and on the energy partitioning into the different molecular degrees of freedom can be obtained.

There are several reasons to study laser induced desorption. The energy redistribution processes after laser excitation are very fast. On metals the electronic excitation of the adsorbate may only last a few femtoseconds. However, the energy partitioning is very sensitive to the potential energy surfaces involved and the lifetimes of the excited states. Thus by monitoring the final state distributions one is able to get an insight into the relevant processes when experiments are connected with theoretical calculations. The highest sensitivity is obtained when looking at desorbing molecules. We use REMPI (resonance enhanced multi photon ionization) and are able to detect easily 10^5 molecules per cm^3 per molecular state. This is many orders of magnitude better than the detection limit of measurements of the energy partitioning at the surface.

Our experiments are complemented by *ab initio* calculations using CASSCF-CI (complete active space self-consistent field and configuration interaction) methods in order to obtain the electronically excited state potential energy surfaces. The dynamics of the desorption process is simulated employing wavepacket calculations with up to three degrees of freedom.

The model systems

In our photodesorption work we have studied the laser induced desorption from epitaxially grown films of transition metal oxide surfaces such as NiO with the two crystallographic orientations (100) and (111) and $\text{Cr}_2\text{O}_3(0001)$ [1]. As adsorbates we used NO, CO and K. Those systems have been well characterised with a variety of different electron spectroscopic methods [2-4]. Oxidic surfaces are particular interesting in photocatalysis. Oxides show large desorption efficiencies and are very suitable for state selective experiments. The rather local character of the metal d-bands and the simple fcc structure in case of NiO allows to use small clusters to calculate the excited electronic states in *ab initio* calculations. With coadsorption of potassium we manipulated the electronic structure of $\text{Cr}_2\text{O}_3(0001)$.

The laser induced desorption of simple molecules

We found that the desorption from our systems is due to an excitation process within the substrate when exciting the systems above the band gaps of the substrates. This is apparent from the energy dependence of the desorption cross sections. We detected a high vibrational excitation which is indicative for a charge transfer from substrate to adsorbate followed by a stretching of the NO or CO bond. Verification of our experimental results were obtained from *ab initio* calculations on the system NO/NiO(100) [5+6]. A complete charge transfer from

the O2p-orbitals of the substrate to the NO 2π -orbitals leads to potential energy surfaces different in shape to the molecular ground state. Strong electrostatic interactions due to this ion pair formation have as a consequence a deepening of the potential energy surface by a factor of about ten with respect to the ground state and a shortening of the molecule-surface distance. This is depicted in Fig.1. Such a finding is likely to be quite general for systems in which the electrostatic interaction between a molecule and a substrate is dominant. Final state measurements revealed that there is a strong rotational to translational coupling of NO to the substrates NiO(100) and $\text{Cr}_2\text{O}_3(0001)$. This is indicative for a geometry change within the excited state. Our *ab initio* calculations confirmed that the strong Pauli repulsion between the O2p-orbitals of the substrate and the 2π -orbital of the excited NO- pushes the molecule from a bent into an upright position when being accelerated towards the surface.

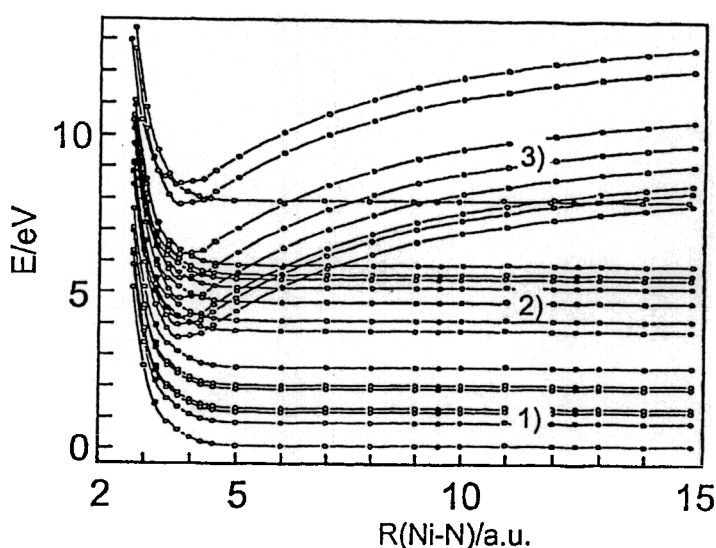


Figure 1: *Ab initio* potentials of electronically excited states of NO/NiO(100) (from [6]) Plot of the manifold potential curves of the different types of excited states of a cluster modelling (NO/NiO(100): NO-NiO₅⁸⁻ embedded in an unmodified Madelung field, calculations obtained with CASSCF-CI *ab initio* calculations

- 1) ground state and d-d excitations
- 2) O2p-Ni3d charge transfer states
- 3) cluster NO-charge transfer states (potential energy surface dominated by a strong Coulomb attraction, electronic states relevant for the photodesorption process).

We observed mainly desorption of neutrals. This means that the charge carrier is transferred back to the substrate before desorption. The excited state lasts a few tens of femtoseconds as was obtained from early two dimensional trajectory calculations [7] and later wavepacket calculations [5]. The strong difference in potential energy surfaces and the lifetimes explain why the desorption efficiency from oxidic surfaces are

two to four orders of magnitude larger than from metals. Enough kinetic energy can be accumulated in the intermediate excited state to overcome the potential energy barrier of the ground state by a large number of excited molecules.

Furthermore we observed different vibrational populations of the two spin states of NO for a desorption from NiO(111) but not for desorption from NiO(100) [8]. Here the different magnetic properties of the two surfaces come into play. We attribute our observation to a spin state dependent coupling of the desorbing molecule to the surface if the spin lattice orientation shows a preferential orientation. This is the case for NiO(111) (parallel orientation of the spins within neighbouring nickel atoms) and not in NiO(100) (alternating orientation).

In the near future we shall extend our nanosecond experiments to femtosecond experiments. We shall then work in a time regime close to the processes themselves.

Stereodynamics

The properties of the desorbing molecules can be classified into either scalar quantities such as the energy in a particular molecular degree of freedom or vector quantities such as the direction of a particular motion. The part of photochemistry dealing with the particular spatial and steric details of the desorption process is called stereodynamics.

Our work includes the detection of angular distributions of the desorbing particles using methods like two dimensional imaging or Doppler profile analysis of single rovibrational states. From the angular distributions information on the influence of lateral movements on the surface onto the desorption process are obtained. In the systems investigated so far, i.e. NO/NiO(111), NO/Cr₂O₃(0001) and CO/Cr₂O₃(0001), we found that the desorption is strongly peaked normal to the surface with the peaking increasing with desorption velocity. Distributions up to \cos^{15} have been found [9]. Our interpretation is that the kinetic energy is mainly gained along the surface normal. The lateral motions of the adsorbate only give a constant contribution and can thus be treated as being decoupled. Similar results have been found on metals and are reviewed in [10].

The initial and intermediate bonding geometry of the adsorbed molecules may lead to a pronounced alignment of the rotational axis of the desorbing molecules within the laboratory frame. We measured the rotational alignment of CO desorbing from Cr₂O₃(0001) as a function of translational, rotational and vibrational excitation [11]. CO is bound flat to the surface and thus can perform either a helicopter

(angular momentum J parallel to the surface normal z) or a cartwheel motion (angular momentum J perpendicular to the surface normal z). Such an alignment means that the transition dipole moment of the molecule has a preferred direction within the laboratory frame. As a consequence higher or lower intensities of the REMPI transitions will be measured depending on the orientation of linearly polarised laser light with respect to the transition dipole moment of the molecule. From the intensity changes related to a rotation of the laser polarisation of the detection laser one can obtain a series of multipole moments for which the quadrupole moment ($A_0^{(2)} = 2\langle P_2(Jz) \rangle$) is the dominating parameter. $A_0^{(2)}$ ranges from -1 (pure cartwheel) to 2 (pure helicopter motion). Fig.2 shows the quadrupole moment ($A_0^{(2)} = 2\langle P_2(Jz) \rangle$) plotted as a function of rotational quantum number for different vibrational and translational states. It can be seen that

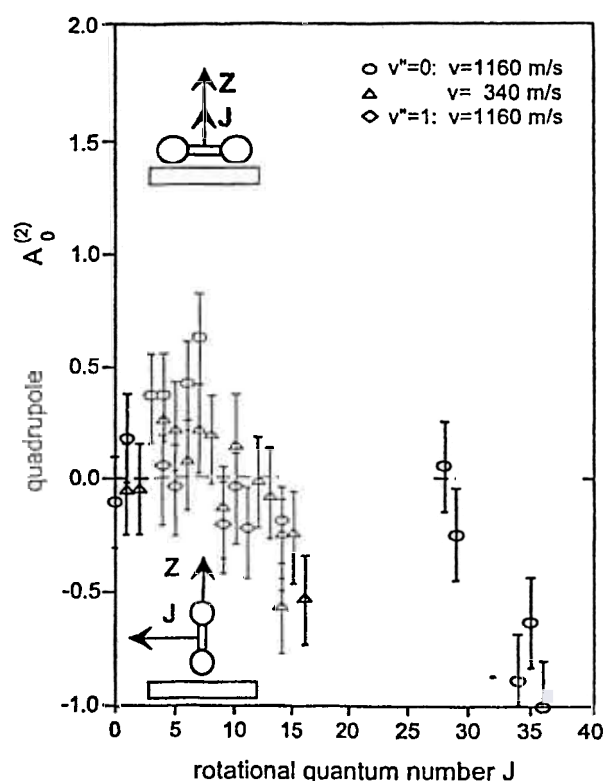


Figure 2: Rotational alignment of desorbing molecules: CO/Cr₂O₃(0001) (from [15]) Rotational alignment is quantified by a series of multipole moments for which the quadrupole moment is the dominating parameter ($A_0^{(2)} = 2\langle P_2(Jz) \rangle$ with $A_0^{(2)}$ ranging from -1 (pure cartwheel) to 2 (pure helicopter motion)). The obtained quadrupole moments are plotted as a function of the rotational excitation of CO with desorption velocities of 1160 m/s (filled dots) and 340 m/s (filled triangles) for the vibrational ground state and for $v=1160$ m/s for the first vibrationally excited state (open rhombs). The data can be interpreted as being due to a geometry change from a flat to a bent configuration in the intermediate excited state.

the desorption of CO from Cr₂O₃(0001) changes from a dominating helicopter motion for low rotational

excitation to a nearly pure cartwheel motion for high rotational excitation. We interpret this surprisingly strong change as being due to a change of the bonding geometry from flat to bent in the intermediate, excited state.

Modification of electronic states

The goal of fundamental investigations like our photodesorption work is to learn how one can systematically tailor an adsorbate/substrate system to obtain a wished photoreaction. Our next interest was how one can use surface dopants to modify the electronic surface states for promoting a desired reactivity. Well known promoters on metals in heterogenous catalysis are alkali metals. While the knowledge about the influence of alkali metals on metals is quite detailed [12], little is known about the behaviour on insulator single crystal surfaces, particular about their photoactivity.

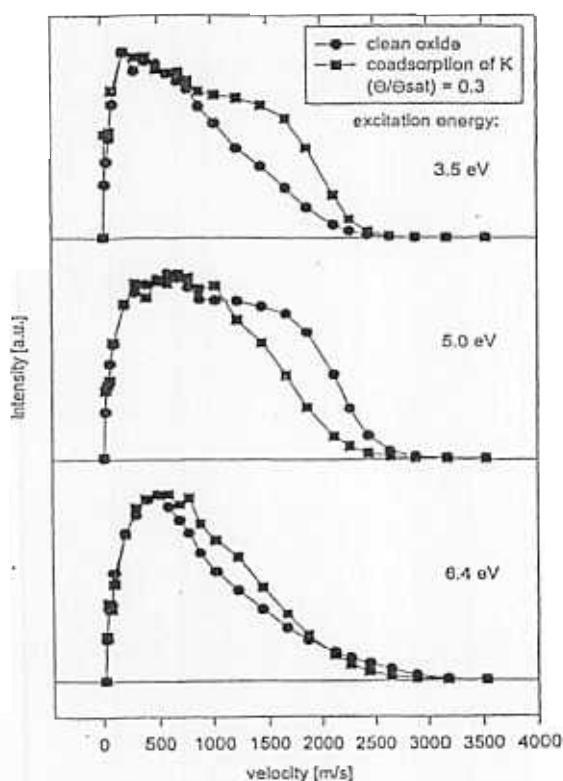


Figure 3: velocity distributions of desorbing NO molecules: the coadsorbate system NO/K/Cr₂O₃(0001) (6.4 eV: $J''=17.5, v''=0, {}^2\Pi_{1/2}$; 3.5 eV/5.0 eV: $J''=16.5, v''=0, {}^2\Pi_{3/2}$) dots: clean Cr₂O₃(0001) surface squares: coadsorption of K for a coverage of ($\Theta/\Theta_{\text{sat}}=0.3$) The intensity change of the fast desorption channel is attributed to a change of a surface charge transfer state when coadsorbing potassium. This has been observed for both spin states of the NO.

We studied the coadsorbate system NO/K/Cr₂O₃(0001). Cr₂O₃(0001) has pronounced, optically active charge transfer surface states peaking around 4.5 eV. These surface states strongly

shift when alkali atoms are adsorbed as is known from EEL spectroscopy [13]. Fig.3 clearly shows that these surface states influence the photodesorption behaviour of NO. The picture shows the velocity distribution of NO in a single rovibrational state as a function of desorption energy for both cases, the pure Cr₂O₃(0001) substrate and a substrate covered with a low coverage of potassium. The desorption energy of 6.4 eV lies above the bulk O2p-Cr-3d charge transfer states starting at 6.2 eV. It is thought that those transitions are dominating and any surface state effects are strongly masked by the desorption feature resulting from charge carriers diffusing from the bulk to the surface. The two other desorption energies are situated at the low and high energy flank respectively from the mentioned surface states of the pure substrate. Apparently the high velocity component of the bimodal distribution is strongly influenced by the surface states. Shifting of the surface states by coadsorption of potassium leads to a change in intensity of the fast desorption channel. There are only very few examples in the literature in which a clear influence of surface states onto photoreaction processes have been demonstrated [14]. However, these are of particular interest as they are directly related to the surface molecule bond and thus are interesting concerning molecule specific photochemistry at surfaces.

Future activities concerning electronic structure modifications via metal deposition are planned.

References

- [1] K. Al-Shamery, Appl. Phys. A63, 509 (1996)
- [2] H. Kühlenbeck, G. Odöfer, R. Jaeger, G. Illing, M. Menges, Th. Mull, H.-J. Freund, M. Pöhlchen, V. Staemmler, S. Witzel, C. Scharfschwerdt, K. Wennemann, T. Liedtke, M. Neumann, Phys. Rev. B43, 1969 (1991)
- [3] H. Kühlenbeck, C. Xu, B. Dillmann, M. Haßel, B. Adam, D. Ehrlich, S. Wohlrab, H.-J. Freund, U. A. Ditzinger, H. Neddermeyer, M. Neuber, M. Neumann, Ber. Bunsenges. Phys. Chem. 96, 15 (1992)
- [4] D. Cappus, C. Xu, D. Ehrlich, B. Dillmann, C. A. Ventrice Jr., K. Al-Shamery, H. Kühlenbeck, H.-J. Freund, Chem. Phys. 117, 533 (1993)
- [5] Th. Klüner, H.-J. Freund, J. Freitag, V. Staemmler, J. Chem. Phys. 104, 10030 (1996)
- [6] Th. Klüner, H.-J. Freund, J. Freitag, V. Staemmler, Conference Proceedings CAT 1996, to be published in J. Mol. Catalysis, in press
- [7] B. Baumeister, H.-J. Freund, J. Phys. Chem. 98, 11962 (1994)
- [8] M. Menges, B. Baumeister, K. Al-Shamery, H.-J. Freund, C. Fischer, P. Andresen, J. Chem. Phys. 101, 3318 (1994)
- [9] M. Menges, B. Baumeister, K. Al-Shamery, H.-J. Freund, C. Fischer, P. Andresen, Surf. Sci. 316, 103 (1994)
- [10] F. M. Zimmermann, W. Ho, Surf. Sci. Rep. 22, 129 (1995)
- [11] I. Beauport, K. Al-Shamery, H.-J. Freund, Chem. Phys. Lett. 256, 641 (1996)
- [12] E. Bertel, M. Donath (Eds.), Electronic Surface and Interface States on Metallic Systems, World Scientific, London 1995
- [13] D. Ehrlich, Ph. D. thesis, Bochum 1995
- [14] L. J. Richter, S. A. Buntin, D. S. King, R. R. Cavanagh, Phys. Rev. Lett. 65, 1957 (1990)