Final Technical Report

Project Title "Interaction of Highly Vibrationally Excited Molecules With Clean Metal Surfaces"

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Abstract

We present results from a grant funded under the Department of Energy Office of Basic Energy Sciences. A collaboration between Prof. Alec Wodtke of the Department of Chemistry at UCSB and Daniel J. Auerbach of IBM Almaden Research Labs has allowed new experiments on the dynamics of surface chemical reactivity to be successfully executed. High quality data has been generated which provides an excellent test of theoretical models of surface reactivity, a topic of importance to catalysis. We have obtained the first experimental measurements on the influence of reactant velocity on the steric effect in a chemical reaction: The dissociative adsorption of Hydrogen on Copper. We have also designed and built a molecular beam scattering apparatus for the study of highly vibrationally excited molecules and their interactions with clean and oxidized metal surfaces. With this apparatus we have observed the vibrational energy exchange of highly vibrationally excited NO with an oxidized Copper surface. Multi-quantum vibrational relaxation was found ($\Delta v = 1-5$). Such remarkably strong and efficient vibrational energy transfer represents a qualitatively new phenomenon and is representative of the exciting new behavior that we had hoped might be observable in this project. Evidence of Chemical reactivity of vibrationally excited NO on a clean Copper surface was also found.

Objectives and Background

One of the most exciting and important goals in the study of heterogeneous catalysis is the challenge of developing a detailed microscopic picture of surface chemical dynamics. This involves understanding the intra- and inter-molecular motions of species as they undergo chemical reactions at a surface and the related issues of energy disposal, flow and consumption associated with the microscopic interactions which make-up a surface chemical reaction. Our approach to this task has employed quantum-state-specific preparation and detection methods in conjunction with molecular beam and time-of-flight (TOF) techniques. Laser spectroscopy is used to prepare and/or detect specific quantum states of reacting molecules, characterizing their internal energy content and spatial alignment. Molecular beam methods and TOF techniques are used to control and/or determine the translational energy of the reacting molecules. These experiments are intended to disclose the effects of rotational, vibrational and translational energy as well as molecular alignment on fundamental surface chemical processes such as adsorption, energy exchange and covalent bond cleavage. By performing such detailed state-specific alignment and velocity resolved measurements, we are attempting to provide a basis for the development of theoretical models of surface reactivity.

Results of the project

The Steric Effect in Surface Chemical Reactions

As an example of such work, we have performed experiments to investigate the *steric* effect in the dissociative chemisorption reaction, (R1),

occurring on Cu(111). This reaction is a prototypical example of an activated dissociative chemisorption event, an elementary step in the catalytic activation of a chemical bond. Figure 1 shows a two-dimensional model potential energy surface for this reaction. The distance from the H_2 center-of-mass to the surface is shown along the y -axis

Figure 1: Model 2-D potential energy surface for an activated dissociative adsorption reaction.

and the H-H bond length is shown on the x -axis. The reactant H_2 in the upper left-hand corner of the figure, must pass over a ~ 0.6 eV activation barrier (1) to reach the adsorbed state in the lower right-hand corner. Clearly, a two dimensional picture is far too simple to fully describe a reaction like (R1). Indeed, vibration, rotation and translation of the H_2 molecule are all found to strongly influence the probability for adsorption (2). The effect of surface temperature has also been observed indicating a modest but non-negligible role of surface atom motion in the reaction.

Although this reaction has been studied with a large number of methods by many different groups^a, the lack of information on the *steric* effect in this reaction is a notable gap. The *steric* effect characterizes how the reactant alignment influences the reaction probability and can be a sensitive measure of the minimum energy pathway along the multidimensional potential energy surface. As will be shown below, we are able to observe the steric effect as a function of reactant rotational, vibrational and translational excitation. To our knowledge, this is the first time that such detailed measurements of the steric effect of any chemical reaction have been observed (4,5).

Figure 2 shows a schematic diagram of the instrument we have built for these experiments. Hydrogen or Deuterium permeates a Cu(111) single crystal held at 925K, producing a small fraction of a monolayer of atomically adsorbed Hydrogen (6-8). H_2 , HD or D_2 formed in the reverse of reaction (R1) is ejected from the surface into the gas phase. 1+1' Resonance-Enhanced Multiphoton Ionization (REMPI) is used to probe the alignment of single quantum states of the desorbing species. This is accomplished with a frequency-doubled, 10 Hz, Nd:YAG pumped dye laser, which after

Figure 2 Schematic representation of the desorption machine

^aIndeed, this reaction has been referred to as the $H+H_2$ of surface science (3)

doubling, produces ~25 mJ/pulse tunable around 318 nm.

A single photon at ~106 nm, generated by third harmonic generation (THG) in Xe, excites the $B^1\Sigma_u^+ - X^1\Sigma_g^+$ system.

A second photon at 318 nm is used to ionize the $B^1\Sigma_u^+$ state and the ions are collected and detected on a two-

stage microchannel plate assembly. Ions are counted with a multichannel scalar operated with 30 ns per channel

dwell time. By adjusting the laser power so that the

ionization step is saturated, the signal is related to the M_J -state dependent Hoenl-London factors of the $B^1\Sigma_u^+ - X^1\Sigma_g^+$ transition and thereby the alignment of the desorbing sample. This REMPI detection scheme is less sensitive than the more commonly used 2+1 scheme through the E,F state (8). Unfortunately, the strong two-photon Q-branch of that more sensitive scheme cannot be used to detect molecular alignment. Consequently, we are forced to use the VUV 1+ 1' scheme.

$$\mathcal{P} = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$$

EQ. (1) Definition of the polarization signal. "I" indicates the number of ion counts obtained at each laser polarization

Figure 3 Geometry of the polarization experiment. Note that the transition dipole moment lies along the molecular bond.

The polarization of the light is varied using a photo elastic modulator (also shown in fig. 2) and signal is accumulated for 50 laser shots for two polarizations, parallel and perpendicular to the surface normal. This process is repeated until signal from ~100,000 laser shots has been accumulated at each polarization. Typical signals are between 0.1 and 2 ions per laser shot. The raw data is represented by the polarization, $\mathcal{P}$, which is defined according to equation (1). In this equation, parallel and perpendicular refer to the surface normal. Therefore a negative polarization indicates a preference for desorbing molecules whose transition dipole moments lie parallel to the metal surface. For the parallel $B^1\Sigma_u^+ - X^1\Sigma_g^+$ bands, this would

indicate a preference for the H_2 molecular bond to be parallel to the surface, so-called *helicopter* motion. Likewise, a positive polarization indicates molecules, desorbing with their bonds perpendicular to the surface, so-called *cartwheel* motion. This can be seen better in fig. 3.

Figure 4 Polarization for various quantum states of D_2 desorbing from Cu(111). Note that the y-axis is negative, indicating *helicopter* motion

An example of the observed polarization data is shown in fig. 4, where the opposite of the polarization, $-P$, is plotted vs. j for both $v=0$ and 1 of D_2 desorption products. These experiments expose the alignment of molecules populating individual rotation-vibration states of D_2 produced by the reverse of reaction (R1). One can see that there is an obvious negative polarization, whose magnitude increases markedly for increasing rotational excitation and is roughly independent of vibrational excitation of the products. Using the principle of detailed balance, which has been shown to hold for this reaction by many different experiments (3), observation of alignment in the desorbed D_2 is a direct indication of steric preferences in the dissociative chemisorption, reaction (R1).

Because we are using a state-specific laser-based probe, we obtain information about the steric effect for each rotation-vibration state of D_2 . The results clearly indicate a preferred *helicopter* motion in the desorbing molecules, consistent with *ab initio* calculations that the minimum energy path in the potential energy surface has the Hydrogen molecular bond parallel to the metal surface (10, 11).

In order to gain maximum information, one would also like to measure the recoil velocity for each quantum state. Consider again fig. 4. Here, one sees that the alignment increases with increasing rotational angular momentum of the D_2 . Detailed balance suggests that molecules in $J = 11$ react more favorably when aligned as

Figure 5 Set-up for field free ion TOF measurements of the polarization

helicopters prior to collision with the surface than do pre-aligned molecules in $J = 3$. This may be a sign of the way in which centrifugal rotational energy contributes to motion along the reaction coordinate; however, it is also known that different rotational states are born with different translational energies (12). Therefore, one cannot say with certainty whether the increasing alignment is related to the change in rotational angular momentum or to the concomitant change in translational energy, or to both. Moreover, the observation of little alignment for low j is not unambiguous, since it represents the average over all translational energies. If the alignment were to depend strongly on translational energy the picture might be more complex than that represented in fig. 4. To answer this question one needs a more complete kind of data.

We have succeeded in obtaining a small amount of data on the *velocity* dependence of the steric effect for individual rotation-vibration states of D_2 (5). This was achieved using a slightly modified experimental arrangement shown in fig. 5. Here, great pains have been taken to ensure a nearly field-free region in the vicinity of the laser ionization region. A grounded grid, treated with colloidal graphite (Aquadag) to remove contact potential differences and patch effects, and heated to remove surface impurities surrounds the ionization region. This allows velocity dispersion of molecular hydrogen ions produced in the 1+1' REMPI of single quantum states of the desorbing products. TOF spectra of the ions are recorded for the two polarization states of the ionizing light ($\parallel$ and $\perp$ to the surface normal). The photo elastic modulator is automatically varied between the two polarizations during the signal averaging period (which lasts about 8 hours). This prevents signal intensity drift from contaminating the data and guarantees that the two TOF spectra are automatically normalized to one another.

The results of these quite difficult experiments are shown in figure 6. In the upper panel, two TOF

Figure 6 Upper Panel: Time-of-Flight spectrum of D_2 desorbed in $J=11$, $v=0$ with polarization parallel, $\square$, and perpendicular, $\circ$, to the surface normal polarization. Lower Panel: $-P$ as a function of arrival time.

spectra are shown for $D_2(v=0, j=11)$ recoiling from Cu(111). The circles show the TOF spectrum for molecules detected when the laser is polarized perpendicular to the surface normal. The squares show the TOF spectrum for the polarization parallel to the surface normal. The lower panel shows the opposite of the arrival-time dependent polarization, $\mathcal{P}$, as defined above in Equation (1). One can clearly see a smoothly increasing magnitude of polarization with increasing arrival time. That is, molecules emerging from the surface with low velocity are more strongly polarized than those emerging with high velocities. Indeed, one sees that for the fastest moving molecules, there is hardly any alignment at all. At first glance, this result may appear puzzling. Many if not all alignment experiments, for example in gas phase photodissociation, show an increasing polarization with increasing product recoil velocity, a simple prediction of any pseudo-triatomic impulsive dissociation model (13). According to this picture, molecules appearing with larger velocities typically suffer a larger and consequently more anisotropic impulsive force upon dissociation than do those appearing with low velocity. In this experiment, we observe that increasing the velocity eliminates the polarization. This can be understood on a qualitative and indeed a quantitative level by consideration of the principle of detailed balance. The observation of unpolarized "fast $D_2(v=0, j=11)$ " in the desorption experiments, indicates that for the reverse adsorption reaction, $D_2(v=0, j=11)$ approaching with high velocity must not be aligned in any particular way in order to react. On the other hand, if $D_2(v=0, j=11)$ approaches with low velocity it must approach with a *helicoptering* like motion, presumably so that rotational energy can couple strongly to the reaction coordinate. This type of measurement of the velocity dependence of the steric effect in a surface reaction is the first of its kind in the field of physical chemistry and represents one of the best experimental opportunities to obtain a full and quantitative picture of all of the factors which affect transmission over the activation barrier of a simple surface reaction. Furthermore $H_2/Cu(111)$ is among the best theoretically characterized surface reactions.

Surface Scattering of Highly Vibrationally excited NO

In addition to the experiments on the Copper Hydrogen reaction we have designed and constructed a new machine for the investigation of highly vibrationally excited molecules on clean metal surfaces. A schematic diagram of the gas-surface scattering UHV apparatus is shown in Figure

Figure 7 Schematic Diagram of the new surface scattering machine: Booster pumps (BP) evacuate the molecular beam source, within which a pulsed valve (PV) and a chopper wheel assembly (CWA) are housed. View Ports (VP) allow for access of the PUMP and DUMP laser beams. The Sample Manipulator (SM) controls the position and orientation of the Sample Assembly (SMA) within the UHV chamber, which is evacuated by a Diffusion pump (DP) and a Titanium Sublimation Pump (TSP). Three Quadrupole Mass Spectrometers (QMS) are available for: 1) beam diagnostics, 2) Temperature programmed desorption and 3) (not shown) surface scattering product detection. Argon Sputtering (Ar), Auger analysis (AUGER) and X-ray Photoelectron Spectroscopy (XPS) are used for surface preparation and analysis.

7. Argon sputtering is used to clean the surface. Auger analysis is employed to characterize the surface. This apparatus (5) has been used in a series of experiments on REMPI detections of highly vibrationally excited NO and vibrational excitation dependence of the NO/Cu and NO/Cu₂O interaction. Vibrationally excited NO molecules were prepared just before the UHV chamber and between two view ports.

First, we have examined the chemical reaction of ground state NO, NO₂ and N₂O molecules on the Cu(111) surface using Auger spectroscopy. We recorded the Auger spectra under different exposure times to $\sim 10^{14}$ molecules per cc beams at 10Hz and 80 μ s duration. While oxygen signal was found to increase exponentially with the exposure time to the NO beam, no nitrogen signal was

identified at any time. Under our experimental conditions, an oxidation rate constant of 0.021 min^{-1} was determined for NO molecules to oxidize the Cu(111) to a 0.10 oxygen monolayer coverage surface, a long lasting metastable Cu_2O surface. While no oxygen signal was identified in the $\text{N}_2\text{O}/\text{Cu}(111)$ interaction, NO_2 was found to oxidize the Cu(111) surface 100 times faster than NO under similar conditions.

NO ($v=0$) gas- Cu_2O Surface interaction: We have developed a method to prepare a Cu_2O surface with a constant oxygen monolayer coverage of 0.10 using NO_2 and thermal annealing technique. This has allowed us to carry out energy transfer experiments on a well characterized oxidized Copper surface. A rotationally cold NO beam ($T_{\text{ROT}} \leq 5 \text{ K}$) was directly used in this rotational energy transfer experiment. Specific rovibrational states of the scattered NO molecules were detected by (1+1) REMPI via the (0,0), (1,1) and (0,1) bands of the $\text{A } ^2\Sigma^+ \leftarrow \text{X } ^2\Pi$ system. The rotational state distribution in the $v''=0$ level and ratio of the two spin-orbit ($^2\Pi_{1/2}$, $^2\Pi_{3/2}$) states were found to depend strongly on the surface temperature and weakly on the incident collision energy. This is consistent with recent results on NO/Cu(110) gas-surface interaction (14).

No experimental evidence for the collision induced vibrational excitation of NO ($v''=0 \rightarrow v''=1$) in the scattering from Cu_2O surface was found. This is in contrast with early results on the NO/Cu(110) (11) and NO/Ag(111) systems (15-17), where vibrational excitation probabilities were measured to be $\sim 0.6\%$ and 4% , respectively, under similar experimental conditions to ours. The survival probability of the ground state NO molecules upon collision to the Cu_2O surface was determined to be close to unity.

Interaction between NO ($v''=2$) and Cu_2O surface: In another series of experiments on relatively low levels of vibrational excitation in NO, we prepared NO in the $v''=2$, $J''=1.5$, $\Omega=1/2$ via infrared overtone pumping (18). We estimated that $\sim 0.1\%$ of NO in the beam was pumped to the desired state. The vibrational population ratio for $v''=2$ and $v''=1$ levels was measured to be 16. Presuming, the population of NO in the $v''=0$ level, is not more than that of $v''=1$, the branching ratio for the $\Delta v=0$, -1 and -2 vibrational energy transfer channels is $16:1:\leq 1$ and the survival probability for

NO($v''=2$) upon interaction with Cu₂O surface is ≥ 0.89 . We also failed to detect any NO population in $v''=3$ level from this energy transfer process with much greater detector sensitivity and higher MCP voltage. An upper limit for the population in the $v''=3$ level was determined to be 0.1%. A similar trend in the scattered rotational state distribution in NO($v''=1$ and 2) and ratio of two spin-orbit ($^2\Pi_{1/2}$, $^2\Pi_{3/2}$) states were observed to depend strongly on the surface temperature and weakly on the incident collision energy.

Highly vibrationally excited NO molecules on Cu₂O surface: Similar experiments were carried out on highly vibrationally excited NO molecules ($v''=12, 13, 15, 19, 20$ and 21) prepared by the stimulated emission pumping (SEP) techniques as shown in Figure 8. Product rotational state distributions of $v''=10, 12, 13$ and 19 were measured via one color two-photon (1+1) REMPI of (2,10), (3,12), (4,13) and (4,19) bands of the NO A $^2\Sigma^+ - X^2\Pi$ system, respectively. We estimate that $\sim 10^{11}$ highly vibrationally excited NO molecules per pulse were introduced to the Cu₂O surface.

A strong enhancement of vibrational relaxation due to vibrational excitation of the

prepared NO was observed for the first time in gas-surface collision. For example, when NO was prepared in the $v''=12$ to 15 region, vibrational relaxation branching ratio from the NO(v'')-Cu₂O surface interaction was determined to be 3:1.25:1:1:1 for $\Delta v=0, -1, -2, -3$ and -5 channels, respectively. Similar results (5:1.5:1 for $\Delta v=0, -1$ and -2) were also obtained when NO was prepared in the $v''=19$ - 21 region. Again, no signals from the collision induced vibrational excitation channel ($\Delta v=1$) were found. We concluded that the survival probability of the prepared vibrational state upon single collisions with the Cu₂O surface drastically decreases with vibrational excitation.

Figure 8 Schematic diagram of stimulated emission pumping, a method for optical preparation of highly vibrationally excited molecules.

The vibrationally inelastically scattered product rotational temperatures and spin-orbit state ratio's were found to be much higher than in experiments carried out on NO in $v \leq 2$. These quantities both exhibit a strong dependence on the surface temperature and the beam kinetic energy, in contrast with results from experiments on molecules on low v'' -states. The product velocity distribution was also determined from the TOF measurements. A very narrow angular distribution was found from the spatial measurements and Doppler profile measurements. Detailed data analysis is ongoing.

NO chemical reactivity on Cu(111) surface enhanced by vibrational excitation: We have attempted to measure the collision dynamics of highly vibrationally excited NO on a clean Cu(111) surface, but this effort was complicated by the fact that it is difficult to prevent oxidation of the Copper surface, when it is exposed to a molecular beam of NO. As mentioned above we observe a finite oxidation rate for Copper by Nitric Oxide. We have therefore, observed vibrational energy transfer as a function of time as the Copper surface is oxidized by the NO molecular beam. While setting the probe laser frequency to probe rotationally and vibrationally inelastically scattered NO, we observe that the relaxation signals grow with the same rate as surface oxidation.

In this discussion, signal intensities at time zero (I_0) and infinity (I_∞) correspond to the NO prepared state scattering from a clean Cu(111) and Cu₂O (0.10 oxygen monolayer coverage) surface, respectively. For the kinetics of the ground state $v''=0$ NO on Cu(111)/Cu₂O surface, I_0/I_∞ was measured to be 0.90 with a rate (associated with growth of the inelastic scattering signal) of $\sim 1 \times 10^{-4} \text{ min}^{-1}$. This shows that the correlation between rotational redistribution probability of $v''=0$ molecules and oxidation to the surface is weak. We concluded that most of the NO molecules survive a single collision with a clean Cu(111).

In contrast, I_0/I_∞ was found to be ~ 0.18 with a rate constant of 0.020 min^{-1} for NO $v''=2$ and 13 levels, respectively. As mentioned above, a rate constant of 0.021 min^{-1} for the ground state NO to oxidize the Cu(111) to a 0.10 oxygen monolayer coverage surface was determined independently with Auger analysis under our experimental conditions. This indicates that the survival probability of the laser prepared vibrational level of NO increases linearly with the coverage of oxygen on the copper surface.

The vibrational population ratio for $v''=2$ and $v''=1$ at time zero was measured to be also 16 when NO in $v''=2$ was introduced to the Cu(111) surface. The prepared state, rotational and vibrational relaxation channels showed the same kinetic behavior for the interaction of NO $v''=2$ and 13 levels and Cu(111)/Cu₂O surface. This means that Cu(111) surface doesn't enhance the rovibrational relaxation channels.

In other words, the experimental results suggest that it is the NO(v) survival probability which increases as the surface is oxidized. This suggest that 85~90% of the vibrationally excited NO molecules dissociatively adsorb due to a single collision on a clean Cu(111) surface. Rovibrational relaxation becomes the dominant channel only after Cu(111) is oxidized to Cu₂O.

Two mechanisms (19-21) have been suggested to account for the oxidation of metallic surfaces and the formation of N₂O at low temperature. The first involves a dissociative adsorption followed by the interaction with ground state NO:

The second mechanism is non-dissociative pathway with a NO dimer formation:

We believe that the first mechanism is more consistent with our experimental findings of vibrational enhancement of NO reactivity. At room temperature, N₂O will desorb and leave the surface in a short period amount of time, explaining the lack of nitrogen Auger signal. Experimental identification of the reaction products is presently being pursued.

References:

1. H. A. Michelsen, C. T. Rettner, D. J. Auerbach, *Phys. Rev. Lett.* **69**, 2678 (1992)
2. H. A. Michelsen, C. T. Rettner, D. J. Auerbach, R. N. Zare, *J. Chem. Phys.* **98**, 8294 (1993)
3. H. A. Michelsen, C. T. Rettner, D. J. Auerbach, in *Surface Reactions* R. J. Madix, Eds. (Springer-Verlag, Berlin, 1993).
4. S. J. Gulding, H. Hou, H. A. Michelsen, C. T. Rettner, D. J. Auerbach, A. M. Wodtke, *J. Chem. Phys.* **105** 9702 (1996)
5. H. Hou, S.J. Gulding, C.T. Rettner, A.M. Wodtke and D.J. Auerbach, *Science* **277**, 80 (1997)
6. G. D. Kubiak, G. O. Sitz, R. N. Zare, *J. Chem. Phys.* **81**, 6397 (1985)
7. G. D. Kubiak, G. O. Sitz, R. N. Zare, *J. Chem. Phys.* **83**, 2538 (1985)
8. G. D. Kubiak, G. O. Sitz, R. N. Zare, *J. Vac. Sci. Technol. A, Vac. Surf. Films* **3**, 1649 (1985)
9. E. E. Marinero, C. T. Rettner, R. N. Zare, *Phys. Rev. Lett.* **48**, 1323 (1982)
10. G. Wiesenekker, G. J. Kroes, E. J. Baerends, *J. Chem. Phys.* **104**, 7344 (1996)
11. B. Hammer, M. Scheffler, K. W. Jacobsen, J. K. Norskov, *Phys. Rev. Lett.* **73**, 1400 (1994)
12. C. T. Rettner, H. A. Michelsen, D. J. Auerbach, *J. Vac. Sci. Technol. A, Vac. Surf. Films* **11**, 1901 (1993)
13. C. G. Morgan, M. Drabbels, A. M. Wodtke, *J. Chem. Phys.* **104**, 7460 (1996)
14. E.K. Watts, J.L. Siders and G.O. Sitz, *Surf. Sci.* **374**, 191(1997)
15. C.T. Rettner, F. Fabre, J. Kimman and D.J. Auerbach, *Phys. Rev. Lett.* **55**, 1904 (1985)
16. J. Kimman, C.T. Rettner, D.J. Auerbach, J.A. Barker and J.C. Tully, *Phys. Rev. Lett.* **57**, 2053 (1986)
17. C.T. Rettner, J. Kimman, F. Fabre, D.J. Auerbach and H. Morawitz, *Surf. Sci.* **192** 107 (1987)
18. M.D. Olman, M.D. McNelis and C.D. Hause, *J. Mole. Spectro.* **14**, 62 (1964)
19. J.F. Wendelken, *Appl. Surf. Sci.* **11-12**, 172 (1982)

20. A.R. Balkenende, R. Hoogendam, t. de Beer, O.L. Gijzeman and J.W. Geus, *Appl. Surf. Sci.* **55**, 1 (1992)
21. H.J. Jansch, C. Huang, A. Ludviksson, G. Rocker, J.D. Redding, H. Metiu and R.M. Martin, *Suf. Sci.* **214**, 377 (1989)

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Publications:

Alignment of $D_2(v,J)$ desorbed from Cu(111): Low sensitivity of activated dissociative chemisorption to approach geometry, S.J. Gulding, A.M. Wodtke, H. Hou, C.T. Rettner, H.A. Michelsen, D.J. Auerbach, *J. Chem. Phys.* **105**, 9702 (1996)

Chemical reaction dynamics using the Advanced Light Source, Yang, X., Blank, D.A., Lin, J., Heimann, P.A., Wodtke, A.M., Lee, Y.T., Suits, A.G. in *Synchrotron Radiation techniques in Industrial Chemical and Material Science*, Edited by D'Amico et al. , (Plenum Press, New York, 1996)

The Stereodynamics of a Gas-Surface Reaction, H. Hou, S.J. Gulding, C.T. Rettner, D.J. Auerbach, A.M. Wodtke, *Science*, **277** , 80 (1997)

A number of papers are being prepared which will report our recent work on the surface scattering and reactivity of highly vibrationally excited NO.