

Dynamical probes of chemical interactions at interfaces

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Dynamical Probes of Chemical Interactions at Interfaces

We report on the application of two experimental techniques developed in the field of atomic and molecular physics to investigate the dynamics of catalytic processes on a molecular scale in (model) catalysts. With these techniques, time-resolved pump-probe laser spectroscopy and molecular beam scattering, better insights into the fundamental processes relevant to catalysis can be obtained. With the first technique, time-resolved (picosecond) non-linear infrared spectroscopy, zeolite catalysts and zeolite-adsorbate interactions are investigated. Microscopic structural information on the bare catalyst, as well as insights into the dynamics of interaction processes between catalyst and reactant (*viz.* zeolite and adsorbate) on a molecular scale are obtained. With the second technique, a molecular beam experiment, we obtain dynamical information on the interaction between catalytic metal surfaces and molecules; transient surface species and steric effects are observed.

I. INTRODUCTION

The past decades have seen a tremendous increase in the development and application of catalysts in industrial processes, ranging from small-scale applications in, e.g., medicine production to large-scale hydrocarbon cracking.¹ Due to the complexity of the catalysts themselves and the catalyzed reaction, the exact mechanism behind the catalytic activity and the reaction pathways is not always clear. As a consequence, the development of new catalysts, their optimization and the location of their optimum working conditions have been achieved mostly through trial and error. Conversely, it is evident that knowledge of the microscopic characteristics of the catalyst along with the relevant mechanisms and

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dynamics at a molecular level, in principle, allows for the *a priori* knowledge of catalytic behaviour and, ideally, the design of specifically active catalysts. Generally, attempts to obtain this type of information on the dynamics of the catalyzed reaction on a molecular scale are made from *indirect* studies of overall chemical kinetics, often with the help of various classical (static) spectroscopic techniques. Direct access to the dynamics requires the use of more complicated experimental techniques: One has to employ the methods developed and currently used by the atomic and molecular physics community to study intermolecular interaction dynamics. Such techniques are not commonplace in the catalysis community. We will show how (ultra-fast) time-resolved infrared spectroscopy is excellently suited for the study of zeolite catalysts, and how molecular beam methods applied to single crystal (catalytic) metal surfaces under well-defined conditions in ultra-high vacuum can give information concerning the dynamics of catalytic reactions. The drawback of the use of this kind of methods in catalysis research is that the equipment used is usually applicable to only a limited number of systems. Furthermore, the experimental circumstances under which systems can be investigated are sometimes not very realistic; thermodynamic variables such as temperature and pressure have to be very well defined and generally have to be kept within a limited range to allow for a straightforward interpretation of experimental data. Inevitably, this leads to experimental circumstances different from those encountered in industrial catalysis. Despite these disadvantages, it is evident that by means of fundamental techniques derived from atomic and molecular physics, new insights into reaction mechanisms are obtained and novel concepts are introduced. More strongly, in case *all* the details of the reaction mechanism, kinetics and thermodynamics are revealed, this allows for the extrapolation of the findings to predict the catalytic behaviour under more extreme (realistic) conditions. Another justification of this type of experiment lies in the verification of a different approach to a fundamental understanding of catalysis: that of (e.g., *ab initio*) modeling of the catalyst. In this rapidly growing field, the results of the modeling inherently provide insights into microscopic mechanisms and, possibly, the relevant dynamics. However, where possible, the results of these molecular modeling techniques should be verified experimentally to establish the validity of the computational procedure.

In this Comment, we will give examples of dynamical studies of bare catalysts and catalyst-reactant interaction. We will limit ourselves to

examples from two experimental techniques employed in our group. We will briefly present the experimental methods and then directly give some results derived from these experiments to give the reader a feel for what kind of information can be obtained. We will not present the data from which this information has been obtained, because this is described in the publications cited.

II. EXPERIMENTAL

The study of the dynamics of chemical processes, in the gas phase, in condensed phases, and at interfaces, is actively pursued in the chemical physics community. The goal of this type of research is to develop a fundamental understanding of the microscopic interaction dynamics as well as the elementary steps involved in chemical reactions on a molecular level. To do so, one has to resolve the rates at which (chemical) bonds are dissociated, and new chemical bonds are created, along with energy dissipation rates and mechanisms. For example, one of the goals is to unravel the nature of the transition state.² The transition state is the saddle point in phase space, separating the reactants and the products.* Since the time scales associated with processes of relaxation, dissipation and the formation of new chemical bonds are usually very short (less than a few picoseconds), static spectroscopies are generally unable to detect the system in these excited states (e.g., the transition state). Using time-resolved laser spectroscopy it is possible to detect molecules in this state *directly*. A somewhat more indirect picture of such reactive, excited states can be obtained using molecular beam methods. In this section, we will illustrate how these two techniques can be applied to extract information on the dynamics of reactive systems, and to what *catalytic* systems we apply them.

The essence of the first technique, time-resolved pump-probe laser spectroscopy, is that the system is perturbed from equilibrium by a very short (20 picosecond) powerful laser (pump) pulse. A second, much weaker laser pulse probes the system as it evolves through this state, and eventually decays back to equilibrium. This scheme allows for the direct observation of the dynamic behaviour of the system. The use of *infrared* laser pulses allows one to excite specific (well-localized) vibrations in

*Many reactions actually involve more than one transition state.

the sample. In the experiments on zeolite catalysts, we use this quality to investigate the energy dynamics specifically at the catalytic site, by exciting the vibration located at this site.

Zeolites, also known as molecular sieves, are crystalline aluminosilicates with large internal surfaces due to the microscopic channel and pore structure. A schematic picture of Y-zeolite is shown in Fig. 1. Zeolites have cation exchange capacity, and when H⁺-exchanged they are solid acids. The acidity is due to the so-called Brønsted hydroxyl (O-H) groups, located between a silicon and an aluminum atom, sticking into the zeolite cavities. The absorption band of the O-H stretch vibration of the catalytically active hydroxyl (O-H) groups is well separated from other vibrations in the zeolite. Therefore, conventional, linear (Fourier transform) infrared spectroscopy is a widely applied tool in the investigation of acidic zeolites. These acidic zeolites find a large-scale use in the petrochemical industry³ as hydrocarbon conversion (e.g., cracking) catalysts.

For the experiments, ultrashort (20 ps), powerful (~100 μJ) infrared laser pulses are obtained by means of parametric infrared generation and amplification of infrared light pumped by 1064 nm pulses from a Nd:YAG laser in LiNbO₃ crystals. The generated pair of laser pulses (pump and probe) are independently tunable in wavelength from 2200 to 4500 cm⁻¹, so that the spectral effect of the pump pulse can be monitored. A schematic picture of the pump-probe set-up is shown in Fig. 2.

The powerful pump pulse is tuned to the O-H stretch vibration ($\tilde{\nu}_{OH} = 3600 \text{ cm}^{-1}$) of the zeolite catalytic acid group or a specific vibration of an

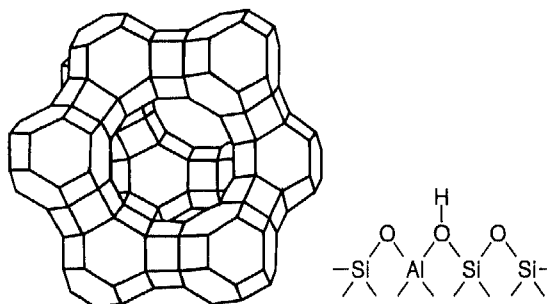


FIGURE 1 Left: Schematic picture of the structure of Y zeolite. The lines represent oxygen atoms connecting silicon or aluminum atoms (situated at the intersection of lines). Right: close-up of the bridging hydroxyl O-H group responsible for the catalytic acidic properties of zeolites.

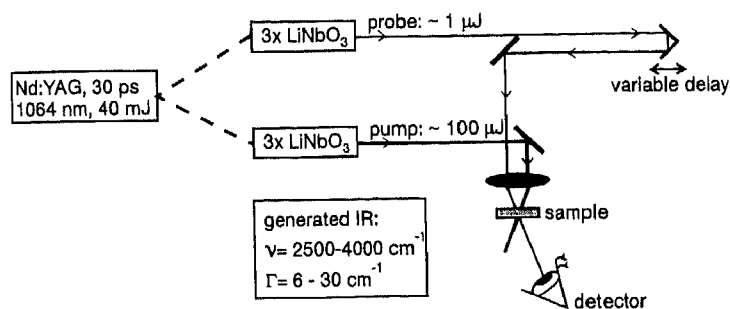


FIGURE 2 Outline of the experimental set-up for non-linear infrared spectroscopy. After the generation from 1064 nm pulses in LiNbO₃, the infrared pump (~100 μJ) and probe (~1 μJ) pulses are focused onto the zeolite sample. The infrared pulses are tunable over a wide frequency range (2500–4000 cm⁻¹) and have a spectral width Γ of 6–30 cm⁻¹. The probe pulse, which is independently tunable and can be variably time-delayed, is used to monitor the effect of the pump pulse.

adsorbate (e.g., the O–H stretch vibration of adsorbed methanol). The non-linear character of this spectroscopic technique lies in the fact that this pump pulse excites a significant fraction (~10%) of the O–H groups from their vibrational ground ($\nu = 0$) state to their first vibrationally excited ($\nu = 1$) state. For the duration of the excitation (the excited state population lifetime), these O–H groups can no longer absorb the infrared probe light at this transition frequency, since they are already excited. Hence the pump-induced changes in the infrared absorption spectrum can be investigated by monitoring the transmission of the much weaker probe pulse. The decay back to the equilibrium state can be followed in real time, since the probe pulse can be variably delayed with respect to the pump pulse (each mm additional pathlength corresponds to 3.3 ps time delay). With this technique the excited state vibrational lifetime can be obtained as well as information on absorption line broadening mechanisms, neither of which can be obtained with conventional, linear spectroscopy. With time-resolved non-linear infrared spectroscopy new insights into the behavior of acid sites in zeolites can be obtained, both structural and dynamical, on the catalytic site itself as well as on the interaction of this site with adsorbates.

The second experimental technique consists of molecular beam scattering. In these experiments, a pulsed beam of O₂ or NO molecules with very-well-defined properties (*viz.* spatial and energy distributions) is allowed to interact with a single-crystal metal surface [Ag(111) or

Pt(111)] in ultra high vacuum. The time of a single collision between a thermal molecule and a surface is on the order of a few picoseconds. By carefully modeling the measured scattering patterns using molecular dynamics simulations, one can get insight into the dynamics of the reactive event and the nature of its transition state. For example, the possibility to detect the scattered molecules and their time-resolved energy distribution allows for the observation of, amongst others, transient surface species and the reconstruction of the potential energy surface of the interaction, which determines the dynamics.

Both techniques presented here, which are capable of providing access to the interaction dynamics between catalyst and reactants, have as underlying principle that the system is brought to a high-energy region of the potential energy surface which cannot be entered thermally. Clearly, the system will subsequently return to equilibrium. The rate and—perhaps even more important—the pathway of this relaxation process contain the information that will help unravel the mechanisms at work. In the case of laser excitation the first laser pulse brings the system out of equilibrium. In the case of molecular beams it is the controlled translational or internal energy of the molecules incident on the surface that allows the sampling of the potential energy surface.

III. DISCUSSION

A. Time-Resolved Infrared Spectroscopy in Zeolites

In the very symmetric zeolite Y, depicted in Fig. 1, there are only four crystallographically different possible positions for the hydroxyl groups, one of which is not occupied.⁴ In the time-resolved infrared experiments, the pump pulse can be tuned to the absorption band associated with hydroxyl groups located on *one* of these crystallographic sites. We find that only at the frequency of the excitation does the absorption band decrease due to the excitation⁵⁻⁷ (the bandwidth of the infrared pulses is smaller than that of the absorption band). This results in what is usually referred to as a “spectral hole”: After excitation, the original absorption band decreases only at the excitation frequency, and remains undiminished at other frequencies. The concept of hole-burning is schematically depicted in Fig. 3. If a spectral hole can be burnt, as is the case for the zeolite, this means that, within the overall absorption band, a *sub-ensemble* of O–H groups can be selectively excited: O–H groups on *one*

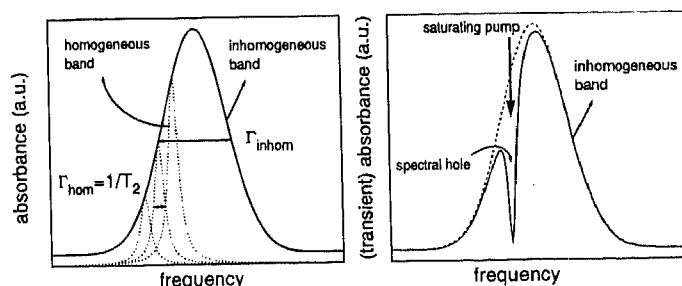


FIGURE 3 Left panel: Inhomogeneous and homogeneous broadening of an absorption band. An inhomogeneously broadened absorption band (solid line) is composed of several homogeneous absorption bands (dotted lines). Right panel: The technique of spectral hole-burning reveals inhomogeneous broadening and allows for the determination of the homogeneous linewidth. An intense, narrow-banded light source selectively excites a subset of resonant homogeneous lines. The width of the hole is determined by the homogeneous linewidth and the laser bandwidth.

crystallographic site exhibit different vibrational frequencies. This spectral hole is very short-lived; its lifetime is determined by the lifetime of the excitation, which is typically 50 ps. The fact that a spectral hole can be burnt in the zeolite O–H absorption band means that with this experiment, we can differentiate between hydroxyl groups located on *one* crystallographic site. This amounts to the first *direct* proof for an inhomogeneous distribution of catalytic sites in acid zeolites.^{5–7} The width of the spectral hole which is burnt is determined by the spectral width of the laser pulses, and the width of the absorption line of the *sub-ensemble* of O–H groups which is selectively excited (the *homogeneous* linewidth).

Moreover, we observe that within one absorption band, the lifetime of the excitation can vary over a factor of 4, from 20 to 80 ps, whereas the energy of the vibration changes by only ~1%.^{8,9} This leads us to conclude that, for the zeolite in vacuum, the hydroxyl groups are hydrogen-bonded to the zeolite lattice⁹: There exists a weak hydrogen-bond between the hydrogen atom of the hydroxyl group and oxygen atoms incorporated in the zeolite framework (e.g., on the other side of the cavity). Hydroxyl groups that are more strongly hydrogen-bonded will exhibit a lower vibrational frequency and a faster decay. The observed catalytic site inhomogeneity is therefore attributed to local variations in hydrogen-bond strengths, presumably caused by an inhomogeneous microscopic distribution of aluminum and silicon atoms throughout the zeolite lattice.

It is remarkable that, upon adsorption of simple molecules (such as nitrogen, methane, oxygen, etc.), it is no longer possible to burn a spectral hole⁶: Apparently, upon adsorption, the range of transition frequencies for the different OH groups increases considerably (by over a factor of 20). The homogeneous absorption lines exhibit strong overlap. In other words, the observed inhomogeneity decreases strongly. This observation, and the behaviour of the transition frequency distribution for different adsorbates, leads to the schematic hydrogen-bond potentials drawn in Fig. 4.

Shown in this figure is the variation of the energy of the system with the hydrogen-bond coordinate. For the OH groups in vacuum (hydrogen-bonded to the zeolite lattice) this coordinate is the $O_H \cdots O_{latt}$ distance; for the OH groups with, e.g., adsorbed nitrogen, it is the $O_H \cdots N_2$ distance. In the presence of nitrogen, the potential is strongly anharmonic. In our experiments, we excite the O-H stretch vibration to its first excited state (arrows pointing up in Fig. 4 designate such a transition; the presence of the H-bond lowers the frequency from ~3750 to

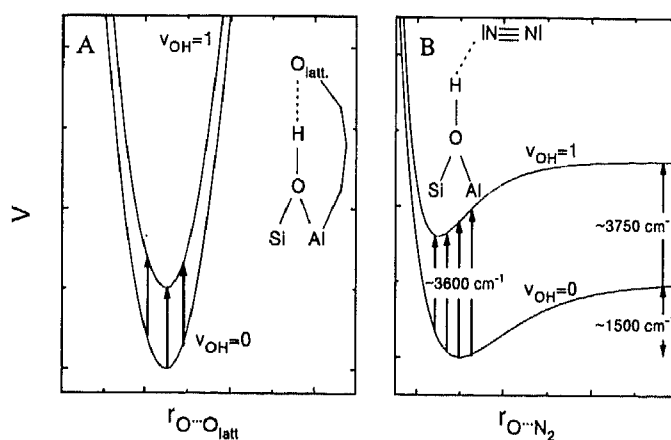


FIGURE 4 Schematic hydrogen bond potentials $V(r_{O \cdots x})$ for two zeolite hydroxyl groups: (A) for a hydroxyl group in vacuum, hydrogen bonded to fixed lattice oxygen atoms, very harmonic; (B) for a hydrogen bond to an adsorbate, strongly anharmonic. For both panels, the lower curves denote the O-H stretch vibration in the ground state, upper curves first excited state. Arrows pointing upwards indicate transition energies; for the hydroxyl with adsorbate (B), the absorption frequency is lowered from ~3750 to ~3600 cm^{-1} due to the H-bond, and the exact transition frequency is sensitive to the exact adsorbate position, in contrast to situation (A).

$\sim 3600 \text{ cm}^{-1}$). For the weakly bound adsorbates, it is well known that the excited ($\nu_{\text{OH-stretch}} = 1$) state potential is different from the ground ($\nu_{\text{OH-stretch}} = 0$) state potential¹⁰; the hydrogen bond is stronger for the $\nu = 1$ excited state than for the $\nu = 0$ ground state, and hence the potential energy minimum is situated at smaller $\text{O} \cdots \text{N}_2$ distance for $\nu = 1$.¹⁰ This means that for the O–H groups with adsorbates a variation of the $\text{O} \cdots \text{N}_2$ distance will result in a change (modulation) of the $\nu = 0 \rightarrow \nu = 1$ O–H stretch transition frequency. In other words, the exact transition frequency for the O–H group depends on the $\text{O} \cdots \text{N}_2$ distance. This explains the relatively large homogeneous linewidth, and the accompanying impossibility to burn a spectral hole. Moreover, if this interpretation is correct, this leads to the well-known phenomenon in magnetic resonance spectroscopy called “motional narrowing”: faster movement of the adsorbate in its potential well to and from the zeolite hydroxyl group will lead to a *narrowing* of the (homogeneous) absorption band of the O–H stretch vibration.⁶ Indeed, we observe that the presence of a lighter adsorbate results in a narrower spectral hole (*viz.* a narrower absorption line), due to faster adsorbate motion.⁶

In contrast, for the $\text{OH} \cdots \text{O}_{\text{lat}}$ the potential energy curves are dictated by *lattice* parameters; the $\text{O}_H \cdots \text{O}_{\text{lat}}$ distance is not determined by the electrostatic interaction between the hydrogen and the O_{lat} , but by the geometry of the zeolite lattice. To move the O_{lat} away from the O–H group requires a local deformation of the zeolite lattice, energetically very unfavorable. Hence the potential is very narrow and harmonic, and very similar for the ground and excited state of the O–H vibration. The fact that the ground and excited state potentials are the same implies that, in contrast to the O–H groups with adsorbates, the transition frequency of the O–H stretching mode does not depend on the $\text{O} \cdots \text{O}_{\text{lat}}$ distance: the presence of this type of hydrogen bond does not affect the absorption line of a sub-ensemble of O–H groups with the same center frequency. Indeed, the absorption lines of a sub-ensemble of O–H groups with the same center frequency (homogeneous absorption line) are much narrower for the $\text{OH} \cdots \text{O}_{\text{lat}}$ groups than for the O–H groups with adsorbates. This information cannot be obtained with linear spectroscopy, because the width of the *overall* absorption line is determined by static inhomogeneities, which can be overcome only with non-linear spectroscopic techniques.

A second experiment was performed on the O–H stretch vibration of methanol (CH_3OH) molecules adsorbed to the sodium form of Y zeolite.

The interest in this system stems from the fact that zeolites are frequently used as catalysts in methanol-to-gasoline conversion. The methanol adsorbs to the sodium atoms in the zeolite as clusters.¹¹ An example of a cluster of methanol molecules, and the different vibrational frequencies of the methanol O–H groups, is depicted in Fig. 5. For liquid methanol dissolved in a non-polar solvent such as carbontetrachloride (CCl₄), self-association of the methanol molecules is also observed. Indeed, the resulting absorption spectra are very similar for the two systems.¹¹ In contrast, the vibrational *dynamics* of the methanol clusters in the two systems exhibit large differences. Exciting the O–H groups of internal methanol molecules, hydrogen bonds between methanol molecules are broken, resulting in the photo-dissociation of the cluster into two fragments. This occurs for both the cluster in the zeolite as well as in solution. However, the process of breaking the intermolecular hydrogen bond takes three times longer (10 ± 3 ps) in the zeolite than in the liquid (≤ 3 ps). An even more remarkable observation is that whereas in the liquid the hydrogen bond is rapidly restored after breaking, in the zeolite this re-association does not occur: The methanol re-association in solution takes 25 ps, in the zeolite it takes longer than nanoseconds, i.e., with time scales differing by orders of magnitude. The time scale for re-association in the zeolite is apparently determined by molecular diffusion, which is slow on the time scales of our experiments. For methanol in solution, due to the apolar nature of the solvent, the interaction of the methanol with the solvent is very weak. Apparently, the dissociated fragments are kept in each others vicinity by the solvent sufficiently long for re-association to occur. In the zeolite, in contrast, the photo-fragments are free to move away from each other. What is more, these fragments

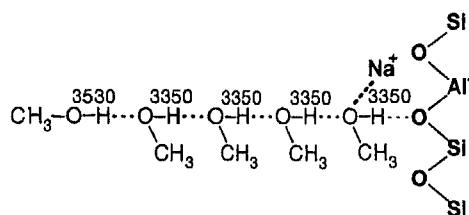


FIGURE 5 Microscopic configuration of a methanol cluster adsorbed to a sodium site in cation form of zeolite Y (NaY), and the O–H stretch vibration frequencies. Bold letters indicate zeolite atoms. In this schematic picture, multiple adsorption to one Na⁺ site or the formation of cyclic (sub)structures are not considered.

are stabilized by interactions with the strongly polarizable oxygen atoms incorporated in the zeolite lattice.

Thus, insights into the behavior of the catalytically active Brønsted sites, the interaction of these sites with adsorbates, and the behavior of the adsorbates themselves on ultra-short time scales are obtained.

B. Molecular Beam Methods

The rate-limiting step in many heterogeneous catalytic systems involves the collision of a molecule with a surface (catalyst), leading to dissociative adsorption, and subsequently to reaction. In order to understand the processes involved and obtain accurate parameters for them, we would like to study the collision in a very-well-defined manner. The adsorption rate of a molecule on a surface depends on many variables, including its kinetic and internal energy, its angle of incidence, the surface temperature and the degree of adsorbate coverage. Under thermal reaction conditions these parameters are ill defined and generally dependent upon the global parameters, reaction temperature and pressure.

The combination of supersonic molecular beams with single crystal surfaces in an ultra-high vacuum provides an excellent way of individually defining and examining the role of the relevant parameters. In particular, molecular beams provide access to high energy (high reactor temperature) processes which are otherwise very difficult to investigate. The price that must be paid for this control is the abstraction of the experiments from the conditions of "real" synthesis. A schematic picture of a molecular beam experimental set-up is shown in Fig. 6.

A large body of literature exists on the subject of molecular beam scattering, and we refer the reader to a number of review articles. General theoretical and experimental aspects of supersonic molecular beam generation are well described by Scoles¹² and their application to the study of gas-surface interactions has been addressed by Barker and Auerbach.^{13,14} A recent review of research in the field illustrates the type of studies currently possible.¹⁵

The time resolution of molecular time-of-flight measurements (μs) means that the interaction dynamics cannot be observed directly. Instead, steady state quantities such as the reaction probabilities or cross sections, internal state distribution, momentum transfer and surface residence times ($>\mu\text{s}$) are measured. In order to obtain information on the reaction dynamics, models of the interaction (potential energy surfaces) must be constructed. These can then be used in simulations, and their

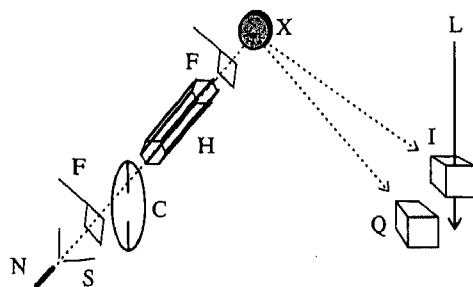


FIGURE 6 Schematic diagram of a typical molecular beam experiment. A (pulsed) molecular beam is generated by the expansion of gas through an $\sim 80 \mu\text{m}$ nozzle (N) and passes through a number of skimmers (S) and a mechanical chopper (C) into an ultra-high vacuum chamber which contains a polished single crystal sample (X). The inclusion of a hexapole lens (H) allows single state selection, and beam flags (F) control the total gas dose on the surface. A quadrupole mass spectrometer (Q) and laser (L) ionization detectors (I) are mounted on a rotatable stage, allowing angular as well as time-resolved detection of the scattered molecules.

validity tested by comparison of the results with the experimental observations. This method provides detailed information on the reaction mechanism, activation barriers, pre-factors, steric effects and so forth, which are the raw materials required for accurate computer modeling of industrial catalysis.

We will look at two case studies as examples: the interaction of NO with Ag and Pt, and the adsorption of oxygen on Ag.

The interaction of NO with a number of metal surfaces has been examined because of its obvious relevance to NO reduction catalysts, but also because it offers the opportunity to study steric effects in surface reactions. This interaction has been studied for many years, initially with non-oriented beams, and the literature has been reviewed.¹⁶ It is intuitive that collisions with the nitrogen or oxygen end of the molecule should lead to different reaction probabilities. By using oriented molecular beams these steric effects can be accurately measured. The ability to perform the angularly resolved spectroscopy of a scattered oriented molecular beam is unique to our experimental system. The sticking probability for molecules oriented with the oxygen atom towards the surface was found by Brandt and co-workers¹⁷ to be lower than when the nitrogen atom is oriented towards the surface. This is consistent with bonding models which predict NO to bind to the surface through the nitrogen atom. Figure 7 shows a theoretical potential energy surface for the

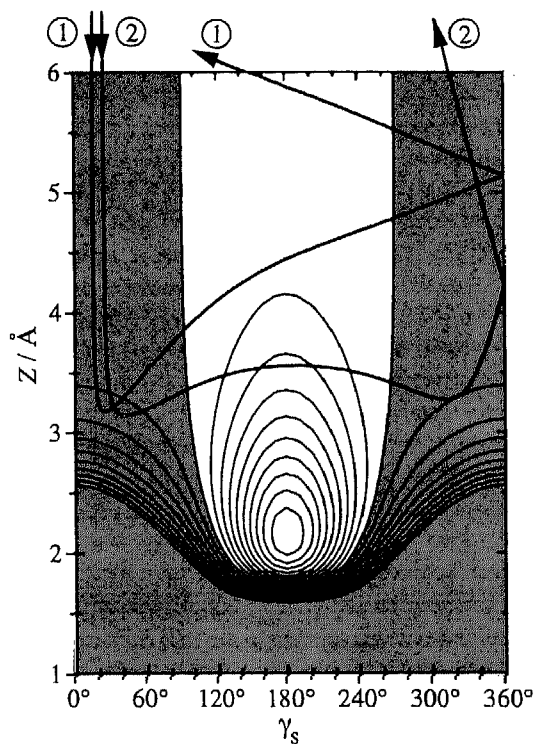


FIGURE 7 Theoretical potential energy surface for NO atop a platinum atom in the Pt(111) surface. Z is the distance between the NO center of mass and the Pt(111) surface plane and γ_s is the orientation of the molecule with respect to the surface normal ($\gamma_s = 180^\circ$ corresponds to the nitrogen atom down to the surface). Two trajectories are shown for an NO molecule of 0.3 eV, with initial orientations of $\gamma_s = 16^\circ$ and 25° (Ref. 18). The contour spacing is 0.1 eV. The repulsive part of the potential is shaded. The trajectories are folded back to the $0 < \gamma_s < 360$ interval.

NO–Pt(111) interaction as a function of the orientation of the molecule to the metal.¹⁸ The potential includes a deep adsorption well for the molecule bound to the surface via the nitrogen atom ($\gamma_s = 180^\circ$) and a purely repulsive interaction for molecules with the oxygen atom closest to the surface ($\gamma_s = 0^\circ = 360^\circ$). This model has been tested in molecular dynamics trajectory calculations, and the results are in good agreement with the experimental observations. Two trajectories are shown in Fig. 7. Trajectory 1 approaches the surface with the molecule aligned close to the “oxygen atom down” orientation. When it collides with the

anisotropic potential energy surface it begins to rotate, passes through the "nitrogen atom down" configuration and continues to rotate rapidly as it leaves the surface. The "reflection" from the wall at $\gamma_s = 360^\circ$ is due to the symmetry used in the model. Trajectory 2 follows a similar path, but is initially rotated even more rapidly. This causes the molecule to reflect from the repulsive potential a second time, reducing the rotational energy of the molecule as it leaves the surface. The result is a pronounced maximum in the rotational excitation following oxygen end collisions with the surface. This is clearly observed in the experiments.¹⁹ Nitrogen end collisions, which enter the deep chemisorption well, are trapped and rapidly accommodate to the surface temperature. The phenomenon of "steering" the molecules into the deep chemisorption well, i.e., the reorientation of molecules initially aligned with the oxygen atom closest to the surface, results in an even higher (>90%) sticking probability.

The adsorption of oxygen on silver surfaces is of interest because silver is rather unique in its catalytic reactivity with oxygen. Silver is exclusively used for the epoxidation of ethene, i.e., $C_2H_4 + O \rightarrow C_2H_4O$, a cyclic molecule, which is an important intermediate in the chemical industry. Chemisorption of oxygen is the rate-limiting step in this reaction. However, the nature of the oxygen state involved is unclear, despite extensive investigations. Chemisorbed atomic oxygen is apparently too strongly bound to the surface to be reactive, and the possible involvement of a transient state, unobserved in spectroscopic studies of the stable species, has been surmised.²⁰

The interaction of oxygen with silver surfaces has been studied by many groups over the last two decades, and a review of the subject exists.²¹ At least three states of oxygen are known to be stable on a silver surface (Fig. 8a). These are a weakly bound physisorbed state (O_2), a chemisorbed molecular state (O_2^-) and the atomic state ($O + O$). Only one other group has measured the dissociative adsorption probability using a hyper-thermal molecular beam. On the Ag(110) surface excellent agreement exists between the results of Vattuone *et al.*²² and ourselves. On the Ag(111) surface^{21,23} a difference in the magnitude of the measured sticking probability on different crystals suggests a possible role for surface steps in the low energy dissociation channel.

In our experiments, as the kinetic energy of the incident oxygen molecules is increased, three different scattering channels are observed, which correspond to three different interactions with the silver surface.

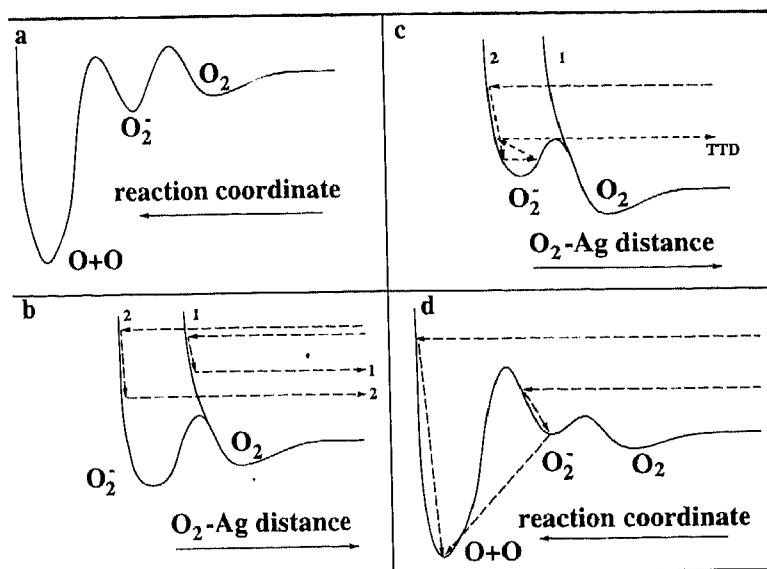


FIGURE 8 (a) One dimensional potential energy plot of the physisorption (O_2), molecular chemisorption (O_2^-) and atomic chemisorption ($O + O$) states of oxygen on silver as a function of a minimum energy reaction coordinate to dissociative adsorption. (b) As (a) with direct inelastic scattering trajectories from the physisorption and molecular chemisorption potentials shown. The atomic chemisorption potential is not included. (c) As (b) for the case where limited relaxation of the silver surface results in a weaker, metastable molecular chemisorption well. A trajectory corresponding to transient trapping-desorption from this well is shown. (d) Direct and indirect (via the molecular chemisorption well) pathways to oxygen dissociation on the silver surface (Ref. 26).

At the lowest energies (<0.25 eV), molecules are trapped and then desorb from the physisorption well. At kinetic energies above 1.0 eV most molecules simply rebound in an inelastic collision with the repulsive part of the potential energy surface (Fig. 8b). This reflection occurs from both the physisorption and chemisorption potentials but is dominated by the chemisorption potential at higher incidence energies. However, at kinetic energies between 0.25 and 1.0 eV, up to 30% of the molecules experience a different reaction channel.²⁴ These molecules lose all memory of their incident momentum, suggesting that they spend some time on the surface. The maximum probability for this channel follows the molecular sticking probability, indicating a close relationship to molecular adsorption. However, while chemisorbed molecules

are stable at a surface temperature of 150 K, these molecules spend less than 10^{-6} s on the surface. Apparently, the molecules are transiently trapped on the surface but fail to become strongly bound and rapidly desorb again. The "transient trapping-desorption" (TTD) of oxygen on silver has not been observed by any other technique. The *ab initio* interaction potential for oxygen adsorbed on a silver surface has recently been calculated²⁵ and indicates the need for a considerable relaxation of the metal surface in order to stabilize the molecule. This is difficult on the close-packed Ag(111) surface, and therefore most of the molecules do not experience the deep molecular chemisorption well of Fig. 8b, but the much weaker, metastable well shown in Fig. 8c.²⁶ This model²⁶ also explains the highly structure dependent sticking probability of oxygen on different silver surfaces.

Summarizing, with the molecular beam method we observe more species at the surface than can be isolated at room temperature. The mechanism of TTD requires high energies and low surface temperature and is therefore possibly very relevant for catalysis.

The probability for both molecular and dissociative sticking probabilities has been accurately measured and is divided into two kinetic energy regimes (Fig. 8d).²¹ Between a kinetic energy threshold of 0.25 eV and 1.0 eV a thermally inhibited dissociation mechanism overlaps the molecular sticking probability. In this region the mechanism of oxygen adsorption can be explained by an indirect dissociation model. Oxygen is first adsorbed as the intact molecule, which can subsequently dissociate at a favorable site or geometry on the surface. The inhibiting effect of the surface temperature arises through a reduction in the lifetime of the molecule during which it must locate such a favorable position.

Above 1.0 eV the probability for dissociative sticking is larger than that for molecular adsorption. In addition, dissociation is favored by increasing the surface temperature. This cannot proceed via the molecular state, but is a direct dissociation mechanism, occurring upon impact with the surface.

The kinetic energy dependence of these different mechanisms has allowed accurate values for the activation barriers to be determined. By modeling the indirect dissociation mechanism, the relative activation barriers and pre-factors for molecular dissociation and desorption have been obtained. Absolute probabilities for adsorption have been measured as a function of the kinetic energy, incidence angles, surface temperature and surface oxygen coverage.²¹ The result is a comprehensive set of

reaction mechanisms and parameters which can be used to model the catalytic behavior of the oxygen-silver system. Kinetic models based on microscopic data provided by surface science experiments have been successfully used to bridge the pressure gap to industrial catalytic systems such as the synthesis of ammonia.²⁷ In such a method the population of the various surface species, and hence the relative importance of the transient oxygen state, can be calculated as a function of the reaction conditions.

IV. CONCLUSIONS

We have illustrated the application of two techniques developed in the fields of atomic and molecular physics to study the dynamics of chemical reactions at (model) catalysts. We show that these techniques can provide novel information on the microscopic dynamics and interaction potentials, unobtainable with conventional, static tools. The first, picosecond non-linear infrared spectroscopy, is applied to zeolites. This technique provides information on the interaction *dynamics* between the zeolite catalyst and adsorbates, along with structural information on the catalytic sites.

The second technique is the molecular beam experiment applied to single crystal surfaces. Two examples illustrate the ability of molecular beam experiments, and the models constructed from them, to introduce new concepts to our understanding of surface reactivity and to supply accurate parameters for the processes involved.

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