State-Resolved Dynamics of Chemical Reactions at Surfaces

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Contents

I. Introduction 91
II. Experimental Methods Available 92
A. Surface Preparation and Characterization Methods 92
B. Product- and Reactant-State Resolution Methods 92
III. Inelastic Scattering of Diatomics 94
IV. Atom Recombination Dynamics 95
V. State-Resolved Adsorption of Diatomics 97
VI. State-Resolved Studies of CO Oxidation 98
VII. Summary 99

I. Introduction

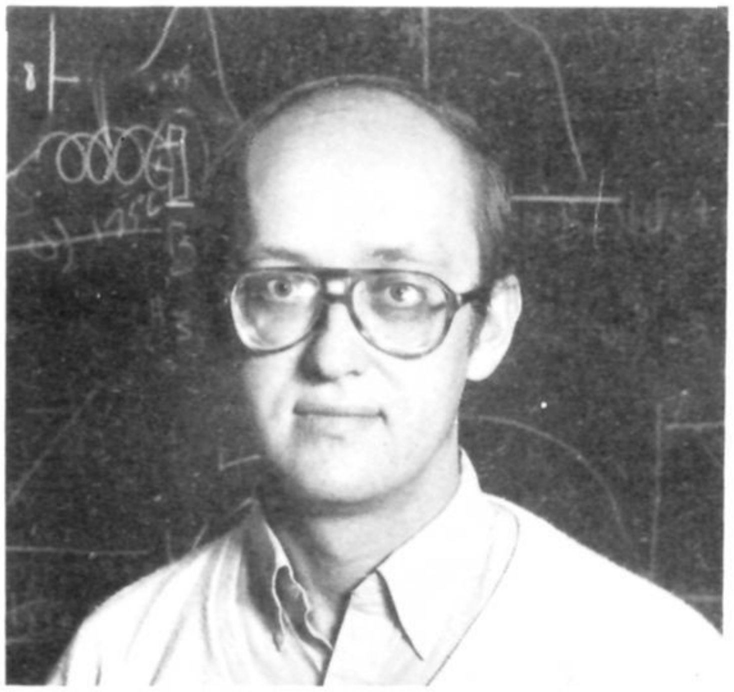
The study of the state-resolved dynamics of chemical reactions in the gas phase is an established area of chemical physics, which has provided much insight into the way in which molecules are formed and transformed. Reviews and monographs[1] on this topic are numerous and reflect the many advances which have been made in the detailed understanding of the dynamics of molecular reactions. The massive amount of experimental and theoretical work, which these reviews and monographs summarize, has led to a reasonably clear picture of how small-molecule reactions occur in the gas phase and has provided rules for the understanding and prediction of the dynamics of reactions which have not been directly investigated.

Our knowledge of the dynamics of molecular processes in condensed phases is much less detailed. In particular, our knowledge of the state-resolved dynamics of surface reactions, the subject of the present review, is much more limited than our knowledge of gas-phase molecular reaction dynamics. This situation arises from the facts that heterogeneous systems are both experimentally and theoretically more difficult to treat than single-phase systems and that the tools for the preparation and characterization of solid surfaces have only fairly recently become available.

This situation provides an opening, however, for the rapid development of this field of chemical physics, by the application of both the methods and the insights developed in gas-phase molecular dynamics studies, to the study of the state-resolved dynamics of surface reactions. It is our intention in this review to indicate where this is already taking place and to indicate what insights have been already gained. We intend also to indicate where, in our opinion, further advances will soon be made and to assess the prospects for further understanding of the molecular dynamics of surface reactions.

It is important at the outset to define the limits of the subject areas which we will address. The study of the dynamics of surface reactions includes a wide range of approaches. As our title implies, we intend to limit our discussion to studies of the state-resolved dynamics of surface reactions, especially experimental studies. Energy-state resolution is very useful, since it provides reasonably direct information about the potential energy surface governing the reaction dynamics. Of course, the wide range of surface spectroscopic tools available also provide reaction dynamic information, but the route to the interaction potential is perhaps less direct. In any case, the present review will be limited to surface reaction studies in which some attempt was made to control or determine the energy state of the reactants involved in the surface reactions or the products formed. Examples will be drawn from our own work and from other laboratories.

The emphasis will also be on actual reaction systems, where the reactant and product molecules are not identical. This eliminates from detailed consideration the many inelastic scattering studies which have been carried out recently and which have resulted in the development of many of the techniques which are directly applicable to reactive scattering studies. We will



Steven L. Bernasek was born in Holton, KS, in 1949. He received his Bachelor's degree from Kansas State University in 1971, and his Ph.D. from the University of California, Berkeley, in 1975. At Berkeley, he worked with Professor G. A. Somorjai, and after completion of his degree, stayed on as a postdoctoral associate for a few months at the Lawrence Berkeley Laboratory. He joined the faculty of Princeton University in the summer of 1975, where he is presently Professor of Chemistry. Professor Bernasek is a recipient of the Exxon Faculty Fellowship in Solid State Chemistry (1981) and of an Alexander von Humboldt Foundation Fellowship (1986). His research interests include the dynamics of heterogeneous reactions, spectroscopic studies of adsorbed molecules, solid-state chemistry, and heterogeneous catalysis.

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likewise not discuss the results of elastic scattering studies, even though again the atomic and molecular beam scattering methods characteristic of these studies are used to advantage in studies of state-resolved chemical reactions on surfaces. Both elastic and inelastic scattering studies provide detailed information about the molecule–surface interaction potential and from that viewpoint are important in understanding state-resolved surface chemical reactions. Recent reviews have discussed elastic and inelastic scattering from surfaces, and the interested reader is referred to these reviews.[2]

In the present review, then, we will concentrate on the discussion of three model reaction systems of increasing complexity. These model systems are chosen both because they are particularly instructive of the insights which may be gained from these studies and because they have been most extensively studied. These three model systems are (1) the dynamics of atom recombination, (2) the dissociative adsorption of diatomics, and (3) the oxidation of CO. In each case, the particular studies discussed relied on the determination of the energy state of the reactant or product in order to investigate the dynamics of the particular surface reaction. These model systems have been studied from other viewpoints as well, and where connections can be made with this work regarding the dynamics of the model reaction, we will do so.

In the following pages we first review the important methods which are available for the study of state resolved chemical dynamics at surfaces. This includes a brief discussion and guide to general literature on methods of surface characterization, which are a necessary prerequisite to studies of surface reaction dynamics. Then, specific techniques for characterization of the energy state of surface reactants or products will be discussed, with an emphasis on those methods which figure strongly in the model reaction systems discussed later. We then briefly mention some of the studies of the inelastic scattering of diatomics by surfaces, as these studies illustrate well the type of information which may be obtained from state-resolved studies. As indicated above, however, our emphasis is not on these investigations.

The first model system to be discussed is the recombination of atoms to form diatomics on solid surfaces. In particular, the N atom recombination, the H atom recombination, and the reaction of adsorbed C and O to form CO are discussed. We then discuss the initial state-resolved dissociative adsorption of diatomics on solid surfaces, again using H_2, N_2, and CO as our examples. The final, and most complex model system to be discussed is the heterogeneous oxidation of CO by O_2. The review ends with a summary of the major insights gained from studies of this type and indicates the future directions which work of this type will take, in our opinion. We hope to convince the reader that real progress has been made in our understanding of the dynamics of heterogeneous reactions, arising from the sorts of state-resolved studies discussed here. More importantly, we intend to suggest to the reader the many unanswered questions which remain. Perhaps this will serve to stimulate the application of new approaches and new techniques from the field of molecular dynamics which will further increase our understanding of this complex class of chemical reactions.

II. Experimental Methods Available

A. Surface Preparation and Characterization Methods

A large number of experimental techniques have been developed in the past 20 years for the preparation and characterization of solid surfaces. In general, characterization techniques provide information about the geometric structure, the composition, or the electronic structure of the solid surface. In some instances, an individual technique can provide information in all three areas. Most often, however, these techniques are used in combination in order to more fully characterize the solid surface and any adsorbed layer present on the surface. Most of these techniques have been developed for use in ultra high vacuum ($<10^{-9}$ torr), so that the surface under study may be prepared and characterized, and be expected to remain free of adsorbed gases for a reasonable period of time.

Methods of surface preparation must be in situ techniques, since again the adsorption of unwanted atmospheric gases must be avoided. These methods depend strongly on the particular material being studied and range from high-temperature annealing in vacuum to particular cycles of ion bombardment and chemical reaction cleaning. In the case of compound surfaces (oxides, etc.), the stoichiometric surface must be maintained. Thus sample cleavage in vacuum is often used to prepare the nascent surface. In some cases, epitaxial growth of the surface *in situ* is the method of choice for preparing a particular surface.

A proper discussion of the methods available for surface preparation and characterization would provide enough material for several review articles. In fact this is the case, as there are many review articles, research monographs, and textbooks available which discuss the techniques of surface science.[3] It is not possible to list all of the useful literature in this category, although enough references of general interest have been provided for the reader new to this field to find the pertinent information. In the following discussion, it is assumed that the reader has some knowledge of the common methods of surface science, particularly low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), photoelectron spectroscopy, and high-resolution electron energy loss spectroscopy (EELS). These methods, which provide, respectively, geometric structure, surface composition, electronic structure, and surface vibrational (and therefore structural) information, are perhaps the most widely used methods for surface characterization. These techniques, along with thermal desorption spectroscopy, for the characterization of the binding energy of adsorbed molecules, will be referred to in the examples which follow.

B. Product- and Reactant-State Resolution Methods

The list of methods available for preparing and determining the energy state of the reactants and products involved in surface reactions is not yet as long as the list of techniques for surface preparation and characterization. The list is steadily growing, however, as more of the methods developed for gas-phase reaction dynamics studies are successfully applied to the study of surface reactions. In order to discuss the results of the model systems which illustrate studies of state-resolved chemical dynamics at surfaces, several of these methods will be briefly described here. This is by no means a complete discussion of the techniques available. Rather, the purpose is to provide enough information about the technique so that the reader may readily understand and judge the results of the model systems to be discussed later.

In each case, these techniques have been first developed for use in studies of gas-phase molecular reaction dynamics. The methods have then been adapted and modified to probe the dynamics of surface reactions. These methods allow the experimenter to determine, and in some cases to control, the translational and internal energy state of the gas-phase reactant or product participating in a heterogeneous reaction.

Of these methods molecular beam scattering has the longest history of use in the study of heterogeneous reaction dynamics.[4] In this technique, a well-collimated beam of molecules is generated in a vacuum system, and allowed to impinge upon the characterized solid surface in an ultra-high-vacuum scattering chamber. The scattered molecules are then detected as a function of angle from the surface normal, usually by a small mass spectrometer detector. The translational energy of the incident beam can be controlled in a number of ways. For an effusive beam source, the translational temperature is determined by the source temperature. In this case, the range of incident translational energies is very broad, being determined by the Maxwellian distribution of velocities at the source temperature. A more monoenergetic beam may be obtained through the use of a slotted-disk velocity selector, but this results in significant loss in intensity.

A more satisfactory means of controlling the incident beam translational energy is through the use of a supersonic nozzle beam source.[5] A high-pressure gas is expanded through a small opening into vacuum. The free-jet expansion is skimmed by a conical skimmer which extracts the central core of the expanding jet. This is then collimated and introduced into the scattering chamber. The advantages of this beam source over the effusive source are quite significant. In the expansion, net translational motion along the beam path is gained by the molecules, resulting in a higher peak velocity at a fixed source temperature than would be expected for random effusion. In addition, the high collision rate in the expansion results in a translational and internal energy cooling, which gives a very narrow velocity distribution, and quite low vibrational and rotational energies for the molecules in the beam. The high-pressure expansion also results in a significant (2–4 orders of magnitude) increase in beam intensity, over the effusive source.

For these reasons, almost all molecular beam surface scattering studies today utilize nozzle beam sources. Translational and internal energies of the beam molecules are readily controlled by the expansion conditions (expansion pressure, source temperature, nozzle size, nozzle to skimmer distance). A wide range of translational velocities can be obtained by seeding the molecule of interest in a lighter or heavier gas. For example, a mixture of 20% N_2 in He has the expansion properties of a gas with the average atomic mass of the mixture, $0.2(28) + 0.8(4) = 8.8$ amu. Since the velocity of the molecule depends on its mass, the effective speed of the N_2 molecule is significantly increased by seeding in helium. Expansion conditions can also be used to control internal energies, although the mechanisms of molecular cooling in the expansion are not completely understood for every case. Direct measurement of the incident beam rotational or vibrational energy is often used to characterize the degree of cooling in the incident beam.

Obviously, the angle of incidence of a well-collimated beam of molecules, with respect to crystallographic directions in the target surface, can also be controlled. This provides a means of controlling perpendicular vs. parallel velocity for a fixed incident beam energy. It also provides control over possible structural variations in the reaction interaction potential, for example differences in reactivity for molecules incident parallel or perpendicular to step directions on the target surface.[6]

The molecular beam experimental configuration also provides the possibility of state preparation of the incident molecules. In addition to the control over translational and internal energy provided by the control of source expansion conditions, the molecular beam configuration allows the direct excitation of particular internal states by laser irradiation. The collision-free conditions of the collimated beam prevent rapid relaxation of the prepared state, and state-selected processes can in principle be directly investigated. The molecular beam configuration also makes measurement of translational and internal energy after the surface collision possible. The translational energy can be determined directly by time-of-flight methods, i.e., modulating the scattered beam and measuring the time for a burst of molecules to travel to a detector displaced some distance from the surface. Recently, psuedo random chopping coupled with cross correlation methods have been used to extract velocity distribution information, with a considerable increase in the quality of the measurements due to the increased duty cycle of this approach.[7] Internal energy can in principle be measured in the scattered or incident beam by one of the state-specific detection methods which will be discussed in the following paragraphs.

There are a number of methods which have been developed to probe the internal state of gas-phase molecular species. These methods rely on molecular spectroscopy, and vary in choice depending on the particular molecule to be investigated. Three methods will be discussed here, as they have been used in the examples described later. Certainly other methods are being developed. The three methods are laser-induced fluorescence/multiphoton ionization (LIF/MPI),[8] electron-beam-induced fluorescence (EBIF),[9] and infrared chemiluminescence.[10]

Laser-induced fluorescence uses a tunable laser source to excite an electronic transition in a molecular species, which then fluoresces. By scanning the excitation wavelength, the total emitted fluorescence as a function of excitation wavelength reflects the vibrational and rotational structure of the molecular ground state. The fluorescence intensity of each rovibrational line is indicative of the population of that level in the ground electronic manifold. In this way, a sensitive measure of the internal energy of a molecule may be made. This technique has been used widely for the study of NO, as the fluorescence intensity for the $A_2\Sigma^+ \leftarrow X_2\Pi_{1/2,3/2}$ transition is quite high.[11]

A related technique, multiphoton ionization, can also be used to obtain internal energy information. In this case, an intense laser beam is used to ionize the gas-phase molecule, by resonant multiphoton absorption. Again, if the wavelength of the exciting radiation is tuned, the production of ions at a particular exciting wavelength is a measure of the ground-electronic-state population of a particular rovibrational level. Since essentially all the ions formed can be detected easily, not just the photons which can be focussed on a photomultiplier as in LIF, MPI is often a more sensitive technique than LIF for the measure of molecular internal energies.[12] It has the disadvantage that the multiphoton ionization spectroscopy must be well understood before internal-energy information can be extracted. Unfortunately, neither LIF nor MPI are universally applicable to every molecule of interest in state-resolved surface dynamics. The list of possible molecules is growing however, as new laser sources become available, and as the pertinent high-resolution spectroscopy is completed.

Most molecules accessible by LIF or MPI techniques rely on the presence of a dipole in the molecule since dipolar transitions dominate. This essentially eliminates from study by these methods all the homonuclear diatomics. Electron-beam-induced fluorescence (EBIF) provides a way around this difficulty, especially for molecular nitrogen, and to some extent for H_2 and O_2. In EBIF, a high-energy electron beam is used to excite and ionize a gas-phase molecule. The electronically excited molecule then fluoresces, and the wavelength-resolved fluorescence contains information about the rotational and a vibrational energy state of the ground-state molecule. Again, the spectroscopy of the molecule under study must be well-known in order to extract internal state information.[13] The ionization cross section for electrons must also be high, so that significant fluorescence intensity is available. Both of these requirements are well met for N_2, and less so for H_2 and O_2. For this reason, EBIF has as yet only been applied to state-resolved surface dynamics studies involving N_2.

The final technique for state-resolved measurements which will be mentioned is the use of infrared luminescence from the products of surface reactions to monitor the product molecule's internal energy. In this case, product molecules which are infrared active emit radiation which is characteristic of the internal-state distribution of the molecule. This chemiluminescent emission is resolved by filtering methods or interferometric techniques and detected with a sensitive IR detector. The resolved emission can then be used to assign a temperature or population distribution to the infrared active modes of the molecule. This method has been used both in a molecular beam configuration,[14] and in a simple flow apparatus,[15] for the study of CO oxidation on platinum. These studies will be discussed in detail below.

Other methods for the preparation and characterization of the energy state of the gas-phase reactant or product in heterogeneous reactions are available, and more are being developed. The very healthy interchange of techniques and concepts between gas-phase molecular dynamics and state-resolved surface dynamics is stimulating the rapid increase in understanding of the dynamics of heterogeneous processes. In the sections which follow, we will present some examples which illustrate where this interchange has been most useful in increasing our understanding of molecular reaction dynamics at surfaces.

III. Inelastic Scattering of Diatomics

Before discussing examples of state-resolved chemical reactions at surfaces, where the identity of the product molecule differs from that of the reactant molecule, we will briefly describe some recent studies of state-resolved inelastic scattering from well-characterized surfaces. These studies provide an introduction to the level of detail which is available in the study of surface reaction dynamics. They also serve to illustrate well the techniques which have been used in the reaction dynamics studies described below. Inelastic scattering studies have been recently reviewed,[2] and the reader is referred to these reviews for further information.

Perhaps the most carefully studied inelastic molecular scattering system is the scattering of NO molecules from various well-characterized substrates. Both LIF and MPI have been used to determine the internal energy state of the scattered molecule as a function of incident translational energy and angle, surface temperature, and surface composition. The scattering of NO from Ag(111), for example, indicates the existence of a direct inelastic scattering channel when the incident energy is high, and a trapping–desorption channel for lower incident velocities and grazing incidence angles.[16]

Under conditions which emphasize the direct inelastic scattering channel on Ag(111), the measured rotational state distribution of scattered NO depends only weakly on the surface temperature. There is, however, a strong dependence of the scattered rotational energy on the incident molecular velocity, suggesting that direct translational to rotational energy exchange occurs upon impact of NO with the Ag(111) surface. In addition, the measured rotational state distribution is decidedly non-Boltzmann, especially for high rotational quantum numbers. The variation of the scattered rotational-state distribution with incident energy has been interpreted as being due to a rotational rainbow effect, similar to that postulated to occur in gas-phase molecular scattering studies.[17]

When NO is scattered from a substrate with a deeper attractive well than the NO/Ag system, Pt(111) for example, the scattered rotational-state distribution reflects this increased interaction.[18] In this case a much stronger dependence of the scattered rotational energy on surface temperature is observed. Also, the scattered rotational-state distribution is observed to be very nearly Boltzmann in form. Vibrational energy measurements have been made for the NO/Pt(111) system as well, and indicate that for molecules trapped and desorbed, significant vibrational excitation can occur.

State-resolved scattering or desorption of NO from several other substrates has also been investigated. For example, from copper, graphite, and ruthenium, the rotational state distribution is Boltzmann-like, though not at the same temperature as the substrate. In the case of NO scattering from Cu,[19] the scattered NO rotational temperature is greater than the surface temperature, whereas for NO desorbing from Ru(001) a rotational temperature much less than the surface temperature is measured.[20] In each of these cases the range of conditions studied, such as incident angle and energy and surface temperature, is limited. Much more work is needed for a complete understanding of the inelastic scattering of NO and other diatomics from well-characterized substrates.

The state-resolved scattering of N_2 from various substrates has also been studied, though not as extensively as has NO. The earliest inelastic scattering studies of N_2 from solid surfaces used appearance potential mass spectrometry to infer vibrational excitation in N_2 molecules scattered from uncharacterized platinum and stainless steel surfaces.[21] More recent work from our group has investigated the inelastic scattering of N_2 and N_2 clusters from well-characterized iron single-crystal surfaces. Both angular distributions and rotational energies of the scattered molecules and clusters were measured using electron-beam-induced fluorescence.

For the Fe(111) surface, N_2 monomer scattering is difficult to characterize due to the significant out-of-plane scattering caused by the highly corrugated open surface structure.[22,23] Under beam expansion conditions where N_2 clusters are formed, broad specular scattering distributions were observed for incident translational energies below about 90 meV.[23] At incident translational energies above this value, the angular distributions begin to look bimodal, with significant scattered intensity at the surface normal, as well as an intense scattered lobe at high scattering angles (near the surface tangent). This observation has been tenatively explained as being due to the fragmentation dynamics of the clusters at high velocities. The details of the angular distributions also depend upon the type of clusters formed in the expansion, and to some extent on transfer of energy from the surface to the recoiling cluster.

The measured rotational energy of the scattered N_2 cluster fragments depends strongly on the incident cluster velocity. For every incident velocity, the measured rotational temperature of the scattered clusters is much greater than the incident rotational temperature, suggesting significant translational to rotational energy transfer upon scattering and cluster fragmentation. The scattered clusters have rotational temperatures lower than the surface temperature, and there is only a very weak dependence of the scattered rotational energy on surface temperature. All of these observations suggest an inelastic scattering process, accompanied by fragmentation of the incident clusters.

The dependence of the scattered N_2 rotational energy on final scattering angle indicates that the most highly rotationally excited fragments are scattered back towards the surface normal. This is consistent with ideas concerning the dynamics of the cluster fragmentation, which were suggested by the angular distribution data. A better understanding of these observations must rely on further experimental results concerning the velocity and composition of the scattered N_2 clusters at various scattering angles, as well as detailed comparisons with classical trajectory calculations. These calculations are presently underway in our laboratory.

The state-resolved inelastic scattering of CO from LiF has also been studied.[24] In this case, vacuum ultraviolet laser-induced fluorescence (VUV LIF) was used to measure the scattered rotational energy. Incomplete rotational accommodation was observed, and the degree of accommodation decreased with increasing surface temperature. No dependence on incident velocity was seen, suggesting that trapping–desorption dominates in this scattering system. Although the results for this scattering system are somewhat limited, it is mentioned here briefly to point out the use of VUV LIF for state-resolved detection of CO, a very important molecule in the study of surface reaction dynamics. Application of this method to reactive scattering systems which produce CO product molecules is bound to provide some interesting dynamical information.

As a final example of state-resolved inelastic scattering of diatomics from surfaces, mention must be made of the rotationally inelastic scattering of H_2 from surfaces.[25] In this case, direct determination of the product rotational energy is not attempted, but rotational excitation is inferred from changes in the scattered angular or velocity distribution. This approach is due to the fact that measurable differences in these distributions do occur for light molecules, as opposed to the case for heavier molecules such as N_2, NO, and CO, and because, until very recently, no state specific methods were available for directly measuring the internal energy state of scattered H_2 molecules.[26] In the case of light-molecule (H_2, HD, D_2) scattering from surfaces, rotational transitions on scattering are indicated by new diffraction peaks, or new velocity peaks in the scattered TOF distribution which are due to T–R processes on collision, or which result from phonon creation or annihilation on collision. This area of inelastic scattering from surfaces has provided some of the most extensive information concerning molecule surface interaction potentials. The results of these light-molecule inelastic scattering studies have also been recently reviewed, and the reader is referred to these reviews for more information.[27]

IV. Atom Recombination Dynamics

As our first example of true state-resolved dynamics on surfaces, we will discuss the dynamics of three atom recombination reactions; N atom recombination, H atom recombination, and the reaction of C and O to form CO molecules. Each of these systems has been studied by state-specific methods on well-characterized solid surfaces.

The earliest direct measurement of the internal energy of the product of a heterogeneous reaction was the determination of the rotational and vibrational energy of N_2 molecules formed by N atom recombination on polycrystalline iron, using electron-beam-induced fluorescence (EBIF).[28] This study used a permeation recombination geometry which supplied reactant N atoms to the iron surface by permeation through the back side of the iron membrane at reasonably high temperatures. This method provides a continuous supply of N atoms to the surface, and the desorbing N_2 flux is then probed directly by the exciting electron

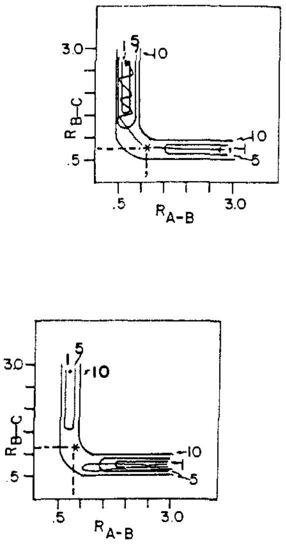

Figure 1. Potential energy surfaces for the atom–diatom exchange reaction applied to N atom recombination on iron. R_{A-B} is the N–N separation and R_{B-C} is the Fe–N_2 separation. The position of the crest in the reaction trajectory (*) is changed by the presence of sulfur on the surface (ref 30).

beam.[29] These studies indicated that the vibrational temperature of the desorbing N_2 was significantly greater than the surface temperature for iron surfaces contaminated with sulfur. This excess vibrational energy decreased as the sulfur coverage decreased, so that N_2 desorbing from the clean surface was essentially at the same vibrational temperature as the surface. Under all conditions of surface temperature and surface composition, the measured rotational temperature was found to the quite low, approximately 400 K.

These results were interpreted with reference to gas-phase interaction potential surfaces for atom–diatom collisions.[30] In particular, the excess vibrational energy for N_2 desorbing from the sulfur covered surface was attributed to a barrier in the potential energy surface early in the reaction trajectory when sulfur is present, as indicated in Figure 1. This early barrier results in vibrational excitation of the product N_2, as is the case for a barrier in the entrance channel for the atom–diatom potential energy surface. The low rotational temperatures were ascribed to a postulated colinear collision mechanism (N atoms colliding with small impact parameter) for the N_2 formation on the iron surface, where steric restrictions limit the rotational motion of the desorbing molecule. Attempts to test this model using single-crystal iron membrane surfaces were not successful due to the difficulty and expense of reproducibly preparing iron single-crystal permeators.

The recombination of H atoms on copper surfaces has also been probed by direct measurement of the product H_2 internal energy.[31] This system is of particular interest due to the central importance of H_2 in surface chemistry and because extensive studies of the angular and velocity distributions of H_2 desorbing from Cu after H atom recombination have been made.[32] In these studies again a permeation–recombination geometry was used for the investigation. H atoms were supplied by permeation through the back side of a Cu(110) or Cu(111) single-crystal disk and the desorbing product probed by MPI of the H_2 molecule. Vibrational population in the $v = 1$ level, 50–100 times above that expected for equilibration with the copper surface, was observed. Rotational temperatures on the other hand, were slightly below the surface temperature, and the distribution was observed to be non-Boltzmann. Similar results were obtained for the rotational-state distribution of H_2 desorbing from Pd[33] following permeation/recombination. In this case LIF was used to determine the internal energy directly.

The results for the recombination reaction on copper were interpreted with reference to a possible $H^{\delta-}$ species recombination pathway. The newly formed molecule is postulated to move along the H_2^-/Cu interaction potential prior to desorption. The point along this potential surface where the extra electron returns to the unoccupied levels of Cu, determines the degree of vibrational excitation of the desorbing neutral molecule.[34] The excess vibrational energy also suggested that there should be an enhanced sticking coefficient for H_2 molecules in the $v = 1$ vibrational state incident on Cu surfaces. This conclusion is based on the principle of microscopic reversibility and has not yet been directly tested, although techniques for producing a sufficient flux of H_2 molecules in the $v = 1$ state have been developed.[35] The results of these measurements are in qualitative, though not quantitative agreement with the trends predicted by detailed balance arguments, and with those predicted by classical trajectory calculations for the H_2/Cu system. At this time, no correlation of internal energy with specific desorbing angles or velocities has been made, since there is not enough signal for angle-resolved state-specific measurements.

As a final example of direct detection of the internal energy of the product of a heterogeneous atom recombination reaction we will consider the recombination of C and O on a platinum surface to form CO.[36] In this case, the internal energy was determined by infrared chemiluminescence of the desorbing molecule. The emitted fluorescence was resolved by Fourier-transform interferometry and a vibrational-state distribution assigned to the desorbing CO. For surface temperatures ranging from 1000–1400 K, relaxed rotational distributions were observed, but vibrational excitation in the product CO as high as the seventh level was seen. The vibrational distribution was nearly Boltzmann with some excess population in the $v = 1$ state. Similar results were obtained when molecular O_2 was incident on the C covered surface, suggesting that the CO is formed by reaction between C and O atoms. Based on a simple energy partitioning argument, it was concluded that the reaction occurs via an activated complex involving 2 or 3 Pt atoms, a strongly bound C atom, and a mobile, chemisorbed O atom. The nascent CO molecule then loses some of its reaction energy to the surface and desorbs still in a highly vibrationally excited state.

From the preceding examples of atom recombination, we can see the level of detail that is available from studies of the state-resolved dynamics of surface reactions. For simple reactions such as atom recombination, direct measurement of the internal energy of the product molecules provides information which can be used to develop models for the transition state and reaction trajectory of the heterogeneous process. These models must then be further tested by more detailed state-specific measurements and by comparison with trajectory calculations. The interaction potential sur-

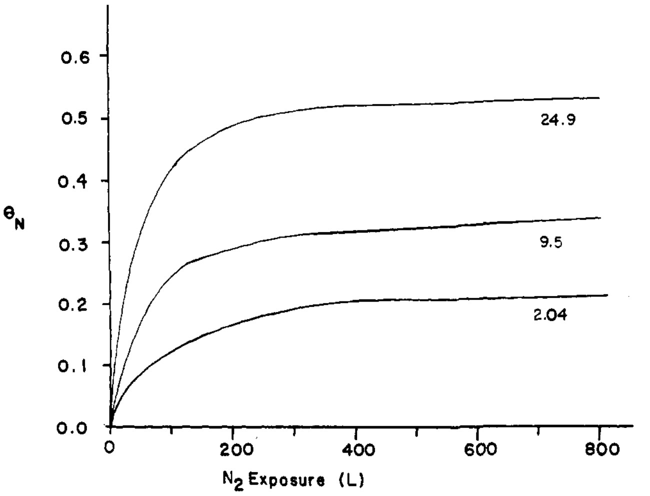

Figure 2. N atom coverage versus N_2 exposure for various N_2 beam energies. Beam energies are in kcal/mol (after ref 38).

face is the goal of this model building effort.

V. State-Resolved Adsorption of Diatomics

An alternate approach to the direct measurement of the energy state of the product of a heterogeneous reaction, which also provides detailed information about the dynamics of small molecule reactions on surfaces, is the state-resolved study of adsorption of diatomic molecules. In this case, the energy state of the incident molecule is controlled, and the dependence of adsorption probability on such conditions as the velocity of the incident molecule is determined. We will discuss three examples: (1) the dissociative adsorption of H_2 on copper, (2) the dissociative adsorption of N_2 on tungsten, and (3) the associative adsorption of CO on nickel. In each case, the translational energy of the incident molecule is varied and adsorption probability measured by various methods.

In the case of the dissociative adsorption of H_2 on copper, the reaction of the dissociated H_2 molecule with preadsorbed D atoms to form HD was used to monitor the degree of dissociative adsorption. This product HD flux was monitored as a function of the incident H_2 translational energy and angle. Three single-crystal planes were studied, (100), (110), and a high-index (310) surface.[37] For each surface, the production of HD was found to depend upon the perpendicular component of the incident hydrogen translational energy. This dependence was explained based upon a one-dimensional barrier to dissociatve adsorption, which varied in height, depending on the crystal plane, from 3 to 6 kcal/mol. The one-dimensional barrier model was then used to calculate the expected angular distribution of H_2 desorbing from these three faces following permeation–recombination. The calculated angular distributions agreed quite well with the measured distributions indicating that microscopic reversibility was indeed valid for this adsorption–desorption system, in the framework of a one-dimensional barrier to dissociative adsorption.

This one-dimensional-barrier model is apparently not applicable to the activated dissociative adsorption of N_2 on W(110).[38] For this system, the initial sticking coefficient was found to increase by a factor of 80 when the translational energy of incident N_2 was increased from 2 to 30 kcal/mol. The translational energy was varied by seeding N_2 in He and by heating the nozzle source. The coverage of nitrogen on the W(110) surface, following exposure to the variable-energy N_2 beam, was determined by thermal desorption spectroscopy and by Auger electron spectroscopy. Initial sticking probability could then be determined from coverage vs. exposure plots, such as the ones shown in Figure 2 for various N_2 beam energies.

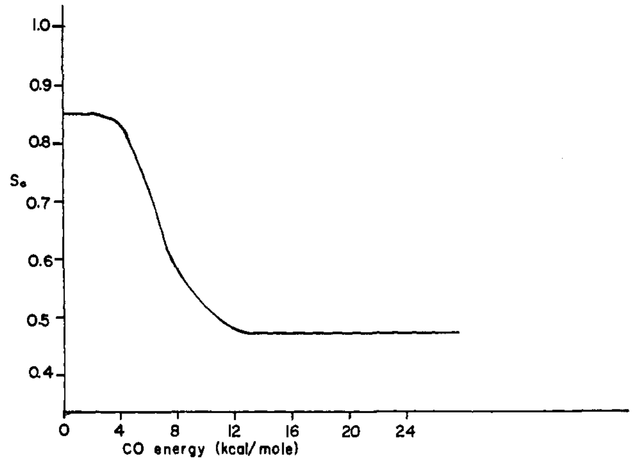

Figure 3. Initial sticking coefficient versus CO incident energy (after ref 39).

In the context of a one-dimensional-barrier model, the point of inflection in a plot of initial sticking coefficient vs. beam energy gives the normal component of the beam energy corresponding to the height of a one-dimensional barrier. This was determined in this case to be 9.7 kcal/mol. The wide transition region which was observed (4 kcal/mole) argues against a simple one-dimensional barrier. Moreover, the insensitivity to incidence angle observed for the behavior of S_0 vs. N_2 beam energy is inconsistent with a simple one-dimensional activation barrier.

In addition to the increase in initial sticking coefficient observed as N_2 translational energy is increased, two addiitonal dissociative adsorption states are observed following adsorption at higher translational energies. Taken together, these observations suggest that dissociative adsorption of N_2 on W(110) is a translationally activated process. As translational energy is increased, the molecule is driven deeper into the repulsive barrier and is able to sample new regions of the molecule–surface interaction potential. In these regions, W–N bond formation is facilitated by the presence of new stable adstates now directly accessible to the incident N_2 molecule.

The variation of incident molecule translational energy has been used to characterize adsorption via a precursor state as well, in contrast to the direct, translationally activated process observed for N_2/W(110). In this case, the associative adsorption of CO on a Ni(111) surface was studied.[39] Again, incident CO translational energy was varied by seeding and heating the nozzle source. CO coverage was determined as a function of beam exposure at different translational energies by thermal desorption spectroscopy. The results of these measurements are summarized in the plot of S_0 vs. CO incident energy shown in Figure 3. In contrast to the N_2/W(110) results, the measured initial sticking coefficient decreases with incident translational energy.

Below about 4 kcal/mol, the initial sticking coefficient is 0.85. Above about 7 kcal/mol, the sticking coefficient drops to less than 0.5 and stays constant up to energies greater than 25 kcal/mol. The apparent saturation CO coverage also varies with incident energy, being about twice as high for low incident CO energy. Spatially resolved Auger studies indicate that low incident energy molecules are more mobile on the Ni(111) surface than those directly adsorbed at higher energies. EELS studies of the saturation layers show that the final adstate is identical for low and high incident energies. These observations suggest that CO is adsorbed through a mobile precursor state at low incident energies, and that at higher incident energies it is adsorbed directly. This difference in adsorption mechanism as a function of incident energy is again a result of the different regions of the molecule–surface interaction potential sampled.

Studies of the state resolved adsorption of diatomic molecules discussed in this section have provided examples of the wide range of dynamics observed for small molecule reactions on surfaces. In these three examples we have presented evidence for a simple one-dimensional-barrier model for adsorption, evidence for a direct translationally activated adsorption process, and for adsorption via a precursor state which allows access to a low-energy adsorption pathway. In the following section, studies using state-resolved detection of the product of surface reactions will be discussed. These studies provide dynamic information about a much more complex system, the oxidation of CO on a solid surface.

VI. State-Resolved Studies of CO Oxidation

The oxidation of CO on platinum surfaces is an especially useful example of the use of state-resolved methods to study the dynamics of surface chemical reactions. Both the translational energy and the internal energy of the product CO_2 molecules have been measured in molecular beam experiments and in more simple flow experiments.

Angular distribution measurements and translational energy measurements using time-of-flight techniques have been carried out in molecular beam studies of this reaction.[40,41,42] The reaction occurs via a Langmuir–Hinshelwood mechanism between adsorbed CO and adsorbed oxygen atoms. The overall reaction is slightly exothermic and has an activation energy of about 24 kcal/mol. The activation energy is found to depend on oxygen coverage, ranging from 24 kcal/mol on the clean surface to about 12 kcal/mol at higher oxygen coverage. The angular distribution of product CO_2 molecules has also been measured. These angular distribution measurements have been variously fit by $\cos^d \theta$ distribution forms,[43,44] and by a two-channel model in the most recent work.[42] The two-channel model developed initially by Comsa and David,[45] divides the observed angular distributions into two parts, as shown by eq 1:

$$I_{CO_2}(\gamma_r) = a \cos \gamma_r + (1 - a) \cos^d \gamma_r \qquad (1)$$

The fraction a is associated with product molecules desorbing in thermal equilibrium with the surface, and the fraction $(1 - a)$ is associated with molecules desorbing with excess energy. In all cases, the exponent d for the angular distribution of the excess energy fraction could be kept constant at 7. The value of the parameter a, however, was found to vary considerably with surface temperature, and with oxygen and CO coverage.[42]

Time-of-flight measurements of the translational energy of CO_2 molecules desorbing in this excess energy fraction confirm the prediction of the two-channel model.[40] Excess translational energy is indeed observed in CO_2 molecules desorbing normal to the surface with the molecules exhibiting velocities corresponding to temperatures as much as 2500 K above the surface temperature.

Two groups have measured the internal energy of the CO_2 product of this surface reaction, using widely different experimental approaches. Mantell et al.[14] have used Fourier transform interferometric methods to resolve the emission from product CO_2 formed when a free jet of O_2 and CO is incident on a hot polycrystalline Pt ribbon. Our group has used filtering techniques to resolve the fluorescence of product CO_2 formed in the CO oxidation reaction on a polycrystalline platinum gauze in a pulsed-flow reactor.[15,46] The results of these investigations are in general agreement. The product CO_2 molecule is found to be highly vibrationally excited. Most of the excitation appears to be confined to the asymmetric stretching motion of the molecule and to bend–stretch combination bands.[14,15,46] The degree of vibrational excitation is found to depend strongly on the coverage of oxygen on the surface,[46] with the most highly excited molecules produced at low-oxygen coverages.

These several studies taken together suggest an interesting, and reasonably detailed, picture of the dynamics of the CO oxidation reaction on platinum. The measured decrease in the Langmuir–Hinshelwood activation energy for the reaction as oxygen coverage increases, along with the observed changes in CO_2 angular distribution and internal energy with oxygen coverage, suggest that a constant fraction of the reaction energy appears as excitation energy in the product molecules which are not accommodated prior to desorption. A certain fraction of the product molecules appear to accommodate with the surface and desorb with energies and angular distributions characteristic of the surface temperature. The nonstatistical distribution of internal energy in the nascent desorbing molecule, with most of the excitation appearing in the asymmetric stretch and bend–stretch modes of the molecule, is consistent with a bent molecule transition state for the newly formed CO_2.

The detailed dependency of the internal energy and product molecule angular distribution on oxygen coverage, CO coverage, and the presence of defects on the surface can not be adequately explained by resorting to simple one-dimensional reaction trajectory diagrams, as shown in Figure 4. The detailed shape of the interaction potential in the region of the transition state must depend strongly on these parameters. Higher resolution measurements of the internal energy, coupled with angular and velocity distribution measurements, should eventually provide the details from which the interaction potential and the true multidimensional reaction coordinate can be constructed.

The oxidation of CO on the platinum surface provides an excellent example of the degree of information and

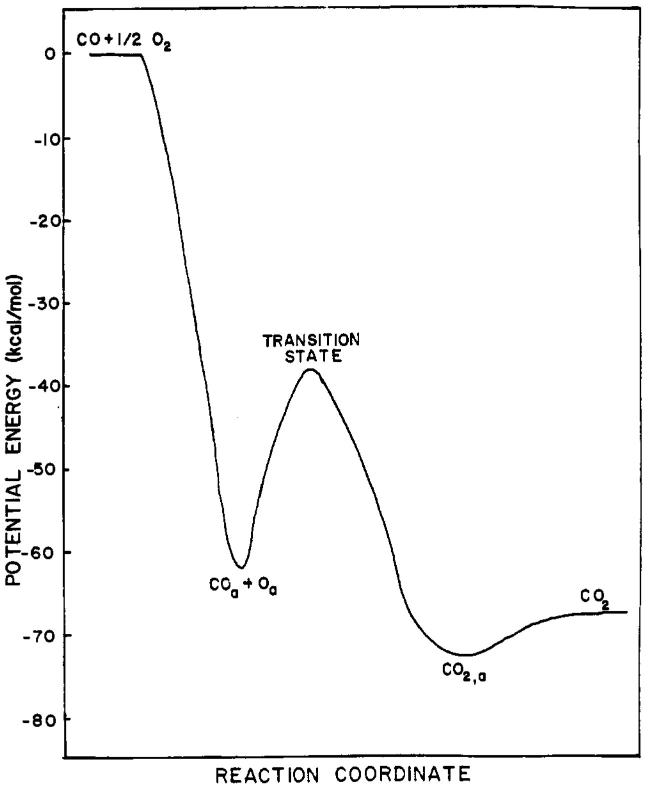

Figure 4. Reaction coordinate diagram for CO oxidation on platinum in the limit of low oxygen coverage (after ref 41).

understanding concerning surface chemical reaction dynamics which is presently available from state-resolved studies of reactions at surfaces. As can be seen, the degree of understanding is not as great as is the case for simple gas-phase molecular reactions. No interaction potential for a surface chemical reaction can, as of yet, be adequately constructed for this system. Indications of the qualitative nature of the potential surface are becoming available for CO oxidation on platinum.

VII. Summary

In this review we have used three model heterogeneous systems to illustrate the type of information on the dynamics of surface reactions which is becoming available by the application of methods and insights from the field of gas-phase molecular dynamics to the study of surface reactions. The ability to measure and control the energy state of the products and reactants involved in surface processes provides direct information about the molecule–surface interaction potential. Although much progress has been made, a detailed understanding of the dynamics of even the simplest surface reactions is still incomplete. Further understanding will be obtained in the future as a result of studies which determine simultaneously *all* of the energetic degrees of freedom of the reactants and products involved in the reaction. Complete specification of translational and internal energy for products and reactants, as well as careful characterization of the solid surface, all in the same experimental apparatus, will soon allow true state-resolved dynamics of chemical reactions at surfaces to be investigated. We can expect such studies to result in the level of understanding of heterogeneous reaction dynamics which has already been obtained in the field of gas-phase reaction dynamics. In addition, it is likely that as new techniques are developed for determining and controlling molecular energy states, they will be applied to the study of surface reaction dynamics. We hope that one result of this review will be to simulate further the fruitful interactions between gas-phase dynamicists and surface scientists which have resulted in the development of these methods and in the progress in understanding surface reaction dynamics which has already resulted.

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