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Final Technical Report
for
Department of Energy
Award No. DE-FG-02-89-ER 13933

Quantum State Resolved Desorption of CO from
Solid Surfaces

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I. Introduction

The goal of my the work supported by the Department of Energy by this grant was to determine detailed reaction mechanisms for reactions which end in the desorption of CO from solid surfaces. In particular, I wanted to implement laser techniques that have been successfully used in the gas phase to understand reaction mechanisms in remarkable detail. Although reactions on surfaces are much more complicated, in general, than those in the gas phase, it should be possible to make significant progress toward understanding reactions in terms of trajectories on potential energy surfaces rather than to simply catalog the condition under which reactions proceed as is often now the case.

Since laser based studies of dynamics on surfaces is a fairly recent activity, much remains to be done in terms of developing the techniques to be used. For this reason we chose rather simple model reactions for our studies. Even though the reactions chosen were rather simple, the results that we obtained are still rather surprising. This illustrates, I believe, the need for further such studies such as those performed here.

The work consists of two major efforts. First, we studied the recombinative desorption of hydrogen atoms from a Si(100) surface.¹ Much to our surprise, and that of the community in general, the desorption kinetics turned out to scale with the first power of the hydrogen atom coverage on the surface. This was a surprise since it was expected that a mechanism which required two atoms to find each other by diffusion would apply, and such a mechanism implies that the kinetic should scale with the second power of the H atom coverage. The interpretation of these results is rather controversial, and will be discussed in some detail below. The second series of studies focus on the mixing of isotopic composition between CO molecules on a Ni(111) surface.^{2,3} Again, the results were quite surprising. The isotopic mixing reaction was found to proceed at modest surface temperatures, but not to go to completion even at high surface temperatures.

These unexpected results illustrate that even for the simplest examples of gas surface reactions the mechanism can be quite different from *a priori* expectations. In part, this is because much of our knowledge of reactions on surfaces is qualitative, or only indirectly related to the part potential energy surface that determines the outcome of the reaction. For instance, organic

chemists have a remarkable database of bond energies available to them to provide a basis for thinking through the possible outcomes of the reactions that they run. For reactions on surfaces, there are very few such bond energies available even for the simplest species. For the case of hydrogen on Si, for example, estimates for the bond energy vary over a range of 40%. For the case of CO reacting on a potassium promoted nickel surface, we are still trying to figure out in a very general way what might be the structure of the reaction intermediate.

It is clear that the results of laser based experiments, such as those performed in this study, are complementary to those of more traditional techniques. With further development, it should be possible to address the problem of the potential energy surface in a more direct manner. In the sections below, the results obtained with support from this grant will be outlined in some detail. At the end, a list of publications is given for more information.

II. Desorption of Hydrogen from Si(100)

Our first effort under DOE support was to modify an existing ultrahigh vacuum chamber for laser induced thermal desorption (LITD) studies. The resulting apparatus is illustrated in Fig. 1. Although the primary goal of the project is to study reactions involving the CO molecule, the desorption of hydrogen from Si(100) was chosen for our first experiments because we expected the results to be particularly strait forward to interpret and thus provide a "warm up" project for the more demanding CO work. Instead, the results were quite surprising, and the study lasted much longer than had been planned.

UHV System for Laser Desorption Experiment

FIG. 1. Schematic diagram of the apparatus used in the LITD experiments.

The method for performing the LITD studies is as follows. After the surface is prepared and cleaned, hydrogen atoms are dosed onto the surface by filling the chamber with 10^{-6} Torr of H_2 and heating a filament located near the surface to 2100 K. H_2 is converted on H atoms upon collision with the filament, and these H atoms will stick on the Si(100) surface. The desired sample dose is calibrated using temperature programmed desorption curves. To obtain the recombinative desorption rate for a given surface temperature, the surface is first heated to the desired temperature to initiate the recombinative desorption reaction. Next the 308 nm radiation from a pulsed excimer laser is attenuated and lightly focused onto a 2.6 mm^2 spot on the surface. This pulse of radiation heats up that part of the surface within the spot to temperatures high enough to desorb the hydrogen from that spot, but without desorbing hydrogen from other parts of the surface. The desorbed hydrogen is monitored with a quadrupole mass spectrometer. By rastering the laser spot across the surface, it is possible to obtain the remaining hydrogen coverage as a function of time. An important aspect of this experiment is that the laser serves only as an analytical tool, it does not initiate the part of the recombinative desorption that we are studying. Thus the data obtained represent isothermal desorption kinetics.

Further details about this experiment are given in ref. 1. Here I will summarize the most interesting results. The first major surprise of the experiment is illustrated in Fig. 2. When the inverse of the remaining hydrogen coverage is plotted against the time that the surface is at the reaction temperature, the plot is a curved line. This indicates that the reaction is not characterized by a second order rate law with respect to the hydrogen coverage. Such a rate law is expected when the H atoms have to diffuse before they recombine, and this is what was observed for hydrogen recombination on the Si(111) surface. Instead, we find that when the data for recombination on the Si(100) surface is plotted on a semi-log plot, the a straight line is observed. This indicates that the rate law scales with the first order of the hydrogen coverage. This result was found to be independent of both the surface temperature and the initial hydrogen coverage below one monolayer. This result was quite controversial when we first reported it. It has since been confirmed by other laboratories,^{4,5} although Heinz et al. see deviations from first order for low coverage.⁵

FIG. 2. Comparison of first- and second-order kinetics of D_2 desorption from Si(100) using the LTD method at $T_d = 735$ K.

The second major surprise of the project is illustrated in Fig. 3. An Arrhenius plot of the data yields an activation energy of 45 kcal/mole. This is lower than the expected reaction enthalpy, which we estimate to be 76 kcal/mole. It is certainly very unusual for an activation energy to be less than the reaction enthalpy. This result has also created some controversy. Subsequent values for the activation energy are somewhat higher than ours, but are still lower than the expected enthalpy.

FIG. 3. Arrhenius plots for the desorption of H_2 and D_2 from Si(100).

These results have led us to propose that there is a dynamical bottleneck in the recombinative desorption mechanism that impedes activated hydrogen species from re-equilibrating with the surface. There is independent evidence that such a process may occur. When a surface is prepared so that one half of the available sites are filled with deuterium atoms; the temperature is held below that at which thermal desorption takes place; and the surface is then exposed to H atoms, it is observed that the H atoms strip of D atoms from the surface. This stripping reaction constitutes a modified Eley-Rideal type mechanism that implies that the H atoms never accommodate to the surface temperature. If they did, they would become permanently bonded to it.

Associated with the experimental study of hydrogen on Si, we have recently performed a theoretical study.⁶ The motivation for this is the conundrum in the experimental data that the observed activation energy is less than the reaction enthalpy. One possible way out of this conundrum is that the reaction enthalpy is less than our estimate. This is very little reliable data for bond energies between adsorbed species and surfaces. For the theoretical study we simulated the Si(100) surface with a Si₉H₁₂ cluster. There is a pair of Si atoms in this cluster that are very similar to those of the surface. We calculated the energy for addition of two hydrogen atoms to the cluster using high level ab initio quantum theory. The calculated reaction enthalpy is 55 kcal/mole. This is a frustrating result because it does not provide a clear resolution of the controversy. The value is low enough that it keeps the possibility open that the actual value might be consistent with the experimental data and a simple mechanism. However, it is high enough that we believe that the more complicated mechanism is correct.

III. Desorption of CO from Ni(111)

Activation of the C-O bond in chemisorbed carbon monoxide is one of the most widely studied problems in surface science, yet the primary steps of CO activation are still not well understood at a fundamental level. Several recent reviews highlight the vast body of data on the efficiency of various metallic combinations as catalytic systems.⁷ A particularly interesting model system for the heterogeneous catalytic activation of CO is a single crystal Ni(111) surface promoted by potassium. Although the CO/K/Ni system has received much attention over the past decade, the mechanism for CO bond activation on this important model surface has yet to be determined.

CO is relatively unreactive on a clean Ni(111) surface. It bonds to the surface molecularly as terminal and bridge CO species, depending on the coverage, and desorbs when the surface is heated to 430 K.⁸ CO stretching frequencies provide a measure of the CO-surface interaction. At full coverage, terminally-bonded CO exhibits a CO frequency of 2058 cm⁻¹, and bridge bonded CO exhibits a frequency of 1914 cm⁻¹.⁸ These frequencies may be compared to 2143 cm⁻¹ for the free gas phase molecule.⁹ The bonding of CO on Ni changes dramatically as potassium is added to the surface. The CO vibrational frequency is strongly dependent on the magnitude of both the CO and K coverage. At 0.3 K/Ni coverage the CO frequency drops to near 1400 cm⁻¹, and the CO desorption temperature increases to 640 K.¹⁰ Evidence from metastable quenching spectroscopy suggests that the CO adsorbed at the site with a 1400 cm⁻¹ frequency is nearly parallel with the surface, but the detailed structure is not known. Several different K-CO complexes have been proposed to account for this behavior, but no conclusive evidence has been presented to support any one model.

Another dramatic signature of the strong CO/K/Ni interactions in this system is that when the potassium promoted surface is dosed with a mixture of CO isotopes and then heated, the CO desorbed from the surface exhibits a limited amount of isotopic scrambling. (This reaction does not occur on the potassium free Ni surface.) Previous to our work, the extent of isotopic mixing for this system had only been observed in thermal desorption experiments, so that little was known about the reaction mechanism.^{7,10,11} The possibilities ranged from a dissociative chemisorption of the CO to some type of complex missing process during desorption. For reasons that still are not clear, there was no evidence for mixed isotopic species being formed on the surface.¹⁰

We applied the LITD technique to determine the rate law for the isotope mixing reaction:

The first step of this study is illustrated in Fig. 4. To obtain the data for Fig. 4, the potassium promoted Ni surface was dosed with an equimolar mixture of the reactant isotopic species at 100 K and heated (at 0.25 K/sec) to 700 K. During the heating ramp, the LITD laser was fired periodically (each shot was directed to a

new spot on the surface) to measure the coverage of reactant and product isotopic species. To avoid damaging the surface, the laser power was kept low enough so that even the reactant isotopic species were not desorbed efficiently until the surface temperature reached 300 K. When the surface temperature reached 400 K, all of the CO within the laser spot is desorbed by each shot. The important result represented in this plot is that the reactant species, e.g. $^{12}\text{C}^{18}\text{O}$, can be desorbed at temperatures as low as 350 K, but product species do not appear until over 450 K. At 600 K both reactants and products disappear because all of the CO has desorbed from the surface.

FIG. 4. LITD signals for one of the reactant isotopic species, $^{12}\text{C}^{18}\text{O}$, and one of the product species, $^{13}\text{C}^{18}\text{O}$, as the K promoted Ni(111) surface is heated from 100 K to 700 K.

Figure 4 proves two important points. First, since reactants give a strong signal for a surface temperature of 350 K, but products do not, we can be sure that the laser pulse does not induce the isotope mixing effect. Second, since the product signal starts out much weaker than the reactant signal, but becomes comparable as the temperature is further raised, we can be sure that the isotope mixing reaction proceeds smoothly at temperatures intermediate between 350 K and 600K, and is not associated with the desorption step.

Rate data for the mixing reaction were next obtained by the following procedure. After the K and the mixture of CO isotopic species were dosed onto the surface, the surface temperature was rapidly ramped up to the desired reaction temperature for a specified amount of time, then cooled to 350 K. Next, 18 laser pulses were fired (each at a new spot on the surface) and the intensity of one of the CO isotopic species was monitored for each laser pulse. Figure 5 shows a plot of the isotope mixing ratio (product signal over total signal) as a function of the time that the surface was held at 475 K. Similar data were obtained for reaction temperatures between 400 K and 525 K.

FIG. 5 The fractional production of product isotopic species as a function of the time that the surface was at $T_s = 475$ K was measured as described in the text. Note that if the reaction went to a statistical limit, the ratio would be 0.5 at long times.

From the data such as shown in Fig. 5 it is apparent that the isotope mixing reaction proceeds smoothly over a period of several minutes. It is also apparent, however, that even for long reaction times the product yield does not achieve the statistical ratio, 0.5. The line through the data points is calculated using a standard second order rate law for the forward and back reactions, incorporating the initial coverages and forcing the final product ratio as a boundary condition. Data taken at several temperatures yield an activation energy for the rate constant of 72 kJ/mole.

The fact that the final product ration does not achieve a statistical distribution of CO isotopic species indicates that the CO is not mobile on the surface. The final product ratio, which would be close to 0.25 if the initial sample were pure, indicates that the active site has two CO molecules in it. Calibration of the overall coverage shows that the maximum mixing ratio is achieved when the K:CO ratio is 1:1.

On the basis of the data summarized above, we have proposed a new intermediate for this reaction, which is shown in Fig. 6. The proposed intermediate obeys the standard electron counting rules, and is consistent with a very low activation energy for isotope mixing, since the overall bond order does not change substantially from reactants to products.

FIG. 6. Proposed $K_2C_2O_2$ intermediate to explain our isotopic mixing results.

We made three attempts to find independent evidence for the existence of the complex shown in Fig. 6. First, we tried to observe direct desorption of the complex. Second, we tried to find infrared spectra that would be characteristic of the complex. Finally we tried to measure the rotational state distribution for CO desorbed under different conditions of coverage. The first two of these attempts gave interesting, but inconclusive results. These will be discussed in subsequent paragraphs. The last attempt was not fully implemented by the time the project was terminated.

If there were a stable complex on the surface, than one might have thought that fast laser desorption would allow desorption of the entire complex, rather than just the individual species that are seen in thermal desorption. We were encouraged to attempt to see desorption of the complex by the fact that for thermal desorption experiments the CO and the K atoms come off at the same temperature. However, when the laser desorption intensities were low enough that only neutral species were desorbed from the surface, only K and CO were observed in the mass spectrometer: no higher mass species that indicate a complex were observed. When the laser intensity was increased to a level where ionic species were observed to leave the surface, both K^+ and CO^+ ions were observed. There may have been a very small shoulder in the data that could correspond to KCO^+ . Any such signal was very small, however, and we did not consider it to be conclusive.

One of the enigmas associated with this problem is that it has not been possible to observe any evidence for the occurrence of the isotope mixing reaction in spectroscopic studies. For instance, Ng et al. made an early attempt to observe the formation of $^{12}C^{16}O$ when the surface was dosed with $^{12}C^{18}O$ and $^{13}C^{16}O$ using IRAS. Since they could not find evidence for the product isotope, they concluded that products were only formed upon desorption. Since we now know that products are formed before desorption, and since Professor Yates has a higher resolution IRAS available than was used for the previous studies.

Assuming that the vibrational splitting scales with the reduced mass the same way it does for gas phase species, the $\Delta\nu/\nu$ for $^{12}C^{16}O$ and $^{13}C^{18}O$ should be 2.5 %. On the surface, at coverages at which the reaction occurs, $\nu \approx 1550\text{ cm}^{-1}$, so a splitting, or perhaps a total width for the transition of 40 cm^{-1} might be expected when a mixture of reactant and product isotopic species exist on the

surface. Of course, things are never so simple for species on a surface as they are for gas phase molecules. In particular, there are large cooperative effects between adjacent oscillators. Figure 8 shows an IRAS spectrum for the mixture of isotopic species at the coverage at which reaction the mixing reaction is efficient. Although the total width of the transition is about 40 cm^{-1} there is no evidence for individual species in the spectrum.

FIG. 7. An laser desorption TOF mass spectrum obtained as described in the text. Note that CO^+ ions are observed for laser powers low enough that no Ni^+ is ablated from the surface.

Figure 9 shows a series of IRAS spectra recorded of the potassium promoted Ni(111) surface with a series of CO coverages. The spectra follow an intriguing pattern. Below $\theta=0.13$ there is essentially no IRAS signal. This is consistent with the MQS conclusion that at low coverages the CO is parallel to the surface. For $0.16 < \theta < 0.19$, there is a single strong transition at 1420 cm^{-1} and for $0.21 < \theta$ there is a single transition at 1560 cm^{-1} . The transitions between these coverages appears to be quite abrupt, as if quite different chemical species exist in each coverage range. For no coverage range is there the type of complex spectrum that would be associated with a polyatomic complex. We therefore conclude that the individual CO molecules exist on the surface at all coverages. The complex that we proposed to describe the statistics of the reaction kinetics may be an activated complex for the reaction, but it is not a stable species that exist at significant concentration.

FIG. 8. These IRAS spectra were recorded by dosing the surface with potassium and a mixture of $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$. Spectrum (a) was recorded after annealing to 220 K, spectrum (b) after annealing to 500 K. It was expected that spectrum (b) would show extra width due to formation of $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{18}\text{O}$. However no such change is observed.

FIG. 9. This series of IRAS spectra was recorded for the potassium promoted Ni surface with varying coverage of CO, as noted on the right side of the figure. The spectra are discussed in the text of this report.

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V. List of Publications

1. The Rate Law and Activation Energy of Isotope Mixing Between Chemisorbed CO Molecules on a K Promoted Ni(111) Surface, K. Sinniah, W. D. Sands, J. T. Yates, Jr. and K. C. Janda, *J. Amer. Chem. Soc.* **113**, 3684 (1991).
2. Calculation of the Si-H Bond Energies for the Monohydride Phase of Si(100), K. D. Jordan and K. C. Janda, *J. Chem. Phys.* **95**, 8652 (1991).
3. Isotope Mixing between Chemisorbed CO Molecules on a K Promoted Ni(111) Surface: An LITD Study K. Sinniah, W. D. Sands J. Hrbek, J. T. Yates, Jr., and K. C. Janda, *Surf. Sci.* **243**, L67 (1991).
4. The Rate Law and Activation Energy of Isotope Mixing Between Chemisorbed CO Molecules on a K Promoted Ni(111) Surface, K. Sinniah, W. D. Sands, J. T. Yates, Jr. and K. C. Janda, *J. Amer. Chem. Soc.* **113**, 3684 (1991).
5. Laser Induced Thermal Desorption of Molecules from Surfaces: A study of Propylene and hydrogen on Si(100), and CO Isotope Mixing on a Potassium Promoted Ni(111) Surface. Kumar Siniah, Ph. D. Thesis, University of Pittsburgh, 1991.
6. Investigation of a Proposed $K_2(CO)_2$ Complex on Ni(111) Using Infrared Reflection Absorption Spectroscopy, Lisa B. Lewis, MS Thesis, University of Pittsburgh, 1992.
7. Coadsorbed Molecules on Alkali Metal Promoted Surfaces: Investigation of the Extant of CO Isotope Mixing on K/CO/Ni(111) Using IRAS and TPD, Elizabeth A. Brown, MS Thesis, University of Pittsburgh, 1992.

VI. Students Supported or Partially Supported by this Grant:

Michael Sherman, Post Doctoral Fellow, Currently employed by Battelle Northwest Laboratory

Kumar Sinniah, Ph. D. 1991, Currently a postdoctoral fellow at the University of Maryland

Lisa B. Lewis, MS 1992, Currently a Ph. D. student at the University of California, Irvine.

Elizabeth A. Brown, MS, 1992, Currently seeking employment

James Mayhugh, currently writing his Ph. D. Thesis

William Sands, currently writing his Ph. D. Thesis

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