INTERACTIONS OF MOLECULES WITH SURFACES

MASTER

Progress Report

for Period 1 May 1980 - 31 March 1981

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E. F. Greene
Brown University
Providence, Rhode Island 02912

March 1981

Prepared for
The U.S. Department of Energy
under Contract ER-78-S-02-4974

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ABSTRACT

An improved apparatus has been designed and constructed to measure the angular distribution of rare gas atoms scattered elastically, or nearly elastically, from the surfaces of crystals.

The yields of ions produced when neutral beams of Li, Na, K and Tl hit surfaces of Si (111) or Pt are recorded as they vary with the temperatures of the surfaces. The ions are identified by mass spectroscopy and the surface cleanliness monitored by Auger measurements.

Reactions can be activated when fast beams of molecules hit a stationary surface. Above a threshold in kinetic energy beams of $W(CO)_6$ leave a non-volatile deposit of decomposition products on a glass surface. Raman spectra of these deposits show bands in the carbonyl and metal-carbon stretching regions. Similar experiments with beams of paraldehyde show it decomposes to acetaldehyde in one energetic collision.

INTERACTIONS OF MOLECULES WITH SURFACES

The work supported by the contract is in three separate projects each of which is concerned with a different aspect of the interaction of molecules with surfaces. In the last year they have progressed as follows:

1. The elastic scattering of atoms from crystalline surfaces. In this experiment a beam of rare gas atoms is to be scattered from the surface of a single crystal, and the angular distribution of atoms interpreted to reveal features of the atom-surface potential. The original plan was to adapt an apparatus that had been used for gas-gas scattering for the present gas-surface experiment. In spite of considerable effort this adaptation has not been successful. The base vacuum was not good enough, and more differential pumping was needed to improve the isolation of the various components. During the past year a decision was made to redesign the apparatus to provide the improvement that seemed needed. A diagram of the new apparatus is shown in Figure 1. A nozzle beam in Chamber 1 is to be driven at a high Mach number to yield a narrow velocity distribution ($\Delta v/v \approx 0.1$ or approximately Mach 10). Chamber 2, which houses a chopper for the beam, is separately pumped to isolate the source from the crystal target in Chamber 3 where the scattering is to take place. The crystal is mounted on a manipulator, and this chamber can be baked to provide an ultra-high vacuum. The scattered beam, leaving this chamber through a port to which Chamber 4 is attached, passes through a velocity selector in Chamber 4 before reaching the detector, a mass spectrometer, in Chamber 5. The angular distribution will be obtained by varying the angle the crystal makes with the incident beam, while the angle between the incident and reflected beams may be varied by connecting the selector and detector to any of the 6 exit ports available on Chamber 3. This apparatus promises to be greatly improved compared to the

original one. The number of beam atoms incident on an area of 0.5 cm^2 on the crystal is estimated to be 10^{16} s^{-1} . From earlier tests the background at the output of the mass spectrometer is expected to be small enough so a scattered signal only one in 10^6 of the incident beam should be measurable.

All the vacuum chambers have been built and assembled on the rack to be used for the experiment. The internal components are ready and most have been tested. After some more preliminary checks the first experiments can be attempted. The first system to be used will probably have Ar or Kr as the gas and graphite (0001) as the crystal.

When results are available they will be compared to various theoretical predictions. One of these is the result of a semiclassical calculation for elastic scattering carried out as described by Miller, Masel, and Merrill (J. Chem. Phys. 64, 45 (1976)) modifying the classical theory of Klein and Cole (Surf. Sci. 81, L 319 (1979)) for Steele's one dimensional model, a corrugated hard wall and an attractive Lennard-Jones well (W. A. Steele, Interaction of Gases with Solid Surfaces, Pergamon, Oxford 1974, pp 320-332). As a sample Figure 2 shows the angular distribution for atoms of energy 68 meV scattered from the surface. The parameters (amplitude of the corrugation $0.083 \text{ \AA}$, well depth 78.7 meV, and the zero-crossing point for the potential $3.27 \text{ \AA}$) are chosen to give a rough approximation to the Kr-graphite system. The rainbow peaks at scattering angles $\theta_I = -3$ and 33° are clearly visible as are several diffraction peaks at intermediate angles. If the scattering appears to be sufficiently classical, it will also be compared with the predictions of a simple model (E.F. Greene and E.A. Mason, Surface Science 75, 549 (1978)) that may permit fitting observed features of the scattering by variation of parameters of the model. Such comparisons are expected to yield a better understanding of

the nature of the crystalline surface and of how it is altered when foreign atoms are adsorbed on it. Because the scattering of low energy atoms probes only the outermost layer of the surface, results from this kind of experiment are expected to be useful supplements to other information about surfaces.

2. The ionization of neutral atoms at surfaces. Several series of experiments have been carried out with beams of Li, Na, K, and Tl atoms incident on Pt and Si surfaces. The objective is to measure the yield of ions leaving the surface as the temperature of the surface and the number of incident atoms vary. Over a temperature range 800 to 1750 K for Pt and 840 to 1540 K for Si and beam intensities up to 10^9 atoms $\text{cm}^{-2} \text{s}^{-1}$ the results generally correspond to those predicted by the Saha-Langmuir equation which assumes that the ratio of ions to atoms leaving the surface will be the random statistical, or equilibrium, one prescribed by the parameters of the system (work function of the metal ϕ , the ionization potential of the atom, and the statistical weights of the ion and atom). Unfortunately in the present experiments there has frequently been contamination of the surfaces, particularly from carbon. This can be removed by heating, sometimes in a low pressure of oxygen. The cleanliness of the surface is tested by taking Auger spectra and by comparing the yields of ions to those predicted theoretically.

For Si(111) the work function ϕ_e obtained from the thermionic emission agrees with that ϕ_+ from the yield of positive ions and with the temperature dependence of this yield. In the case of platinum ϕ_e has always been low, probably because some additional impurity, not detected by the Auger scans, produces a low ϕ_e over a small fraction of the surface.

The difficulties with this experiment seem likely to be resolved soon. Then the results will be ready for description in a paper to be submitted for publication. An intriguing but as yet unexplained observation is that the

Si(111) surface, after use in several experiments and a few exposures to O_2 while it was heated to about 1400 K, showed remarkable structural changes. Electron micrographs revealed tiny craters and eruptions (diameter $\sim 5 \mu m$) as if some large amount of energy had been liberated below the surface.

The immediate objective of these experiments with ionization at surfaces is to find the ranges of temperature and concentration for which the equilibrium model is valid for several combinations of beams and surfaces. Then study of the probability of electron transfer from the atom to the surface under conditions for which the equilibrium model is not realistic should lead to information about the kinetics of the transfer, a subject of interest in many studies of catalysts.

3. Reactions stimulated by the conversion of kinetic to internal energy when fast molecules hit a stationary surface. A paper describing the first results of this work has been published, and reprints are enclosed. This appears to be the first example of this kind of experiment in which a threshold in kinetic energy has been observed for a molecule, in this case $W(CO)_6$, striking a surface. Work with $W(CO)_6$ has continued in an attempt to learn about the non-volatile deposit left on a glass surface as a result of the molecular impacts. Laser Raman spectra of the deposit show several bands in the carbonyl stretching region as well as others at lower frequencies where W-C stretching frequencies can be expected. Interpretation of the spectra is unlikely to be easy, for the material is probably not a single compound. However, any further information about the deposit will be welcome for there is considerable current interest in the deposition of tungsten-containing films.

Experiments with beams of other molecules also incident on glass surfaces, show that the impacts stimulate the decomposition of paraldehyde into three molecules of acetaldehyde. This reaction can be produced in the surprisingly high yield of 1% by single impacts when the molecules are accelerated to

kinetic energies of ca. 200 kJ mol^{-1} by seeding them into a beam of H_2 that emerges from a nozzle at room temperature. The yield is smaller but still appreciable at energies as low as 20 kJ mol^{-1} . This reaction is particularly interesting because it is known (C.C. Coffin, Can. J. Res. 7, 75 (1932)) to be a homogeneous, first order, endoergic ($\Delta E = 81 \text{ kJ mol}^{-1}$) reaction with an activation energy of 184 kJ mol^{-1} . More experiments are needed to map out further the dependence of the decomposition on the kinetic energy, the temperature of the nozzle, and the temperature of the surface the paraldehyde hits.

Because the transfer from kinetic to internal energy must occur very rapidly (in times of the order of $3 \times 10^{-13} \text{ s}$) when the molecule hits the surface, results of these experiments may help to show how large amounts of energy are redistributed in molecules and transferred to surfaces.

In addition to the three kinds of experiments described above there has been earlier work supported by DOE (Contract EY-76-S-02-3129 now expired) in this laboratory. Reprints of the last paper describing this work have now become available and are enclosed. The work involves the use of beams of electrons to control the motion of neutral molecules. The effect is a new one and may yield useful applications when it is understood more clearly.

The reprints enclosed with this report are:

1. E. F. Greene, W. M. Holber, and H. D. Lambropoulos, J. Chem. Phys. 73, 1212 (1980). Control of the Motion of Neutral Molecules by a Beam of Electrons.
2. M. S. Connolly, E. F. Greene, C. Gupta, P. Marzuk, T. H. Morton, C. Parks and G. Staker, J. Phys. Chem. 85, 235 (1981). Activation of Chemical Reaction by Impact of Molecules on a Surface.

Since the beginning of this Contract the principal investigator has spent approximately half of his time on the work supported by the Contract during the academic year and nearly full time during the summer. During the past year he has started a three-year term as Chairman of the Chemistry Department. These additional duties mean that he can expect to spend only about 40% of his time during the academic year and 60% during the summer for the remainder of his tenure as chairman.

Figure 1. Diagram of apparatus for measurement of elastic scattering from the surface of a crystal.

Figure 2. Calculated angular distribution of elastic scattering of Kr atoms from a corrugated hard wall.
Energy 68 meV, amplitude of corrugations 0.083 Å, depth of attractive well at surface 78.7 Å