INTERACTION OF MOLECULES WITH SURFACES

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Research Scope and Objectives

The aim of our research is to study the interaction of beams of molecules with surfaces in three kinds of experiments. These are measurements of: 1) the angular and velocity distributions of elastic scattering of rare gas atoms from crystals, 2) the efficiency with which atoms are ionized in collisions with surfaces and the rates at which they desorb, and 3) the effectiveness of kinetic energy in activating reactions when fast molecules hit stationary surfaces.

Description of Research Effort

When a beam of monoenergetic atoms at thermal energies strikes a crystal, the angular and velocity distributions of the scattered atoms are sensitive to the structure of the outermost layers of the surface. An apparatus built to study this scattering shows clear diffraction peaks for He beams scattered from the (100) face of LiF. It has also been used for the scattering of nozzle beams of He and Ar from the basal plane of graphite. It will be used next to obtain the velocity and angular distributions of beams of several rare gases reflected from LiF for comparison with the predictions of simple models. Plans are completed and the equipment obtained to produce still more nearly monoenergetic beams by using two rotating disks to select narrow portions of the velocity distribution of a beam emerging from a pulsed nozzle. The timing for the nozzle, disks, and detector will be controlled by a small computer. This modification should produce velocity distributions with half widths as narrow as 1% of the central velocity for all the rare gases and permit experiments with resolution not previously achieved except for He.

Surface ionization, the transfer of an electron between an incoming molecule and a surface, provides a convenient way of detecting the rate of desorption of alkali atoms from surfaces. The technique has been used in an extended study of desorption from the (111) and (100) surfaces of Si crystals in the temperature range 800-1000K. Interpretation of the results yields energies and entropies of the adsorbed atoms and rates of diffusion into the bulk of the crystals. Because the surfaces can be produced in metastable forms supercooled below transitions at 1120 ± 40K (111) and 980 ± 20K (100) and the rates of desorption vary with the state of the surface, measurement of these rates also permits study of the rates of the transitions. Similar work on desorption from SiC(111) and graphite(1000) are in progress. On both crystals alkali atoms are adsorbed, even at low coverages, in at least two kinds of sites differing in energy. At temperatures above 1200K there is rapid diffusion of part of the incoming atoms into the

crystals.

In most studies of chemical kinetics the reacting molecules are activated thermally or by the adsorption of photons. An alternative is to accelerate molecules to high speeds and then bring them suddenly to rest by impact with a stationary surface. Work of this kind with $W(CO)_6$ and $Mo(CO)_6$ shows decomposition to form a non-volatile deposit on the surface occurs when the kinetic energy rises above thresholds at about 500 and 200 kJ mol^{-1} respectively. In a similar experiment with fast molecules of tetramethyldioxetane the threshold is near 50 kJ mol^{-1}. The reaction is followed by counting the photons produced from the electronically exited acetone that is formed as a result of the impact. The yield of light varies with the nature and temperature of the surface being largest for fluorinated polyethylpropylene among the surfaces used so far. Some light is detectable also from fast impacts on stainless steel, glass, polyethylterephthalate, polyvinylidene chloride and polyethylene.

Future Research

The apparatus for the study of the scattering from crystals will be used to study other surfaces such as WS_2 and MoS_2. These are useful catalysts for dehydrosulfurization. Information about the arrangement of adsorbed atoms on their surfaces would be helpful. Another attractive possibility is to follow the motion of molecules on surfaces by recording changes in the intensity of specular scattering that appear when adsorbed molecules diffuse together to form aggregates.

The surface ionization experiments will be extended in several directions: 1) an attempt to measure surface diffusion over distances of the order of 1 mm by depositing atoms from a beam and observing ions desorbing after they have diffused to new positions; 2) the recording of neutrals as well as ions leaving the surface by ionizing the neutrals on another surface having a high ionization efficiency; and 3) studying the rate of electron transfer between the atoms of the beam and the surface by recording changes in the ionization efficiency with the speed of the incoming atoms.

Experiments on the activation of molecules by impact will be directed toward understanding the role of the surface in the activation of tetramethyldioxetane and in testing for the presence of acetone ions that may be produced by transfer of the excited electron from the acetone to the surface. More general detection of the activation would be possible with an improved apparatus having differential pumping to isolate the surface from most of the carrier gas used to accelerate the molecules and with a detector capable of recording the angular distribution of the products.