INTERACTIONS OF MOLECULES WITH SURFACES

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ABSTRACT

An apparatus is being set up to measure the elastic scattering of a velocity selected beam of Kr atoms from the surface of a graphite crystal. The angular distribution and energy dependence of the scattering will be compared with the predictions of a simple model to learn about the nature of the surface.

The yields of positive ions produced when beams of neutral alkali atoms hit hot surfaces of silicon or alumina have been measured for various temperatures of the surfaces. A quasi-equilibrium model for the ionization fits the results for Si well but is inadequate in the case of Al_2O_3 . In the latter case the ion yield is increased somewhat in the presence of visible radiation, and some of the dynamics of the ionization process may be measurable.

Decomposition and polymerization reactions are found to occur when molecules of high kinetic energies are suddenly stopped by hitting a surface. The yields of products depend on the internal as well as the kinetic energy. Beams of CCl_4 , C_2Cl_6 and trioxane have been studied.

Interactions of Molecules with Surfaces

The progress made on the work supported by the Contract since its start on 1 August 1978 can be summarized under the three headings given in the original proposal.

1. The elastic scattering of atoms from crystalline surfaces.

The object of the experiment being set up is to measure the angular distribution of a velocity selected beam of atoms scattered, with little or no change in speed, from the surface of a crystal. This distribution is expected to contain useful information about the structure of the surface which will complement that obtained in other experiments such as low energy electron diffraction (LEED). When results are obtained, they will be compared first with the predictions of a simple classical model (E.F. Greene and E.A. Mason, Surf. Sci. 75, 549 (1978)). The system chosen for the first test is a beam of Kr atoms scattered from a graphite surface.

Fig. 1 shows a schematic diagram of the apparatus. The Kr beam emerges from a parallel array of fine capillaries, passes through a velocity selector, and is incident on the crystal at an angle θ_i ; then atoms scattered at an angle θ_r pass through a velocity analyzer and are detected in a mass spectrometer mounted in a separately pumped chamber. The Kr source, the velocity selector and analyzer, the crystal and its mount and the mass spectrometer are ready. In preliminary tests the Kr beam has been detected and appears to have the signal-to-noise ratio expected and described in the original proposal (January 1978). The crystal has been mounted and heated, but scattering experiments have not yet begun. If more differential pumping is needed, it will be added.

The system was chosen because Kr atoms are heavy enough so the classical model should be adequate (quantum effects should not be resolved) and because of the expectation that the graphite crystal may be cleaned and kept clean by holding it at temperatures in the range 1000 - 2500K. Monitoring of the cleanliness and

Fig. 1. Schematic drawing of apparatus for measurement of elastic scattering from the surface of a crystal.

structure of the surface will be possible when an Auger-LEED system is available.

2. The ionization of neutral molecules at surfaces.

Work has begun with studies of the ionization of atoms, particularly alkali atoms, at the surfaces of Si and Al_2O_3 . A schematic drawing of the apparatus is shown in Fig. 2. A beam of atoms (Li, Na, K, In or Tl) produced in a separate chamber enters from the right and is intercepted by either a Re or a Si surface. The Re when oxidized by heating in 10^{-5} torr of O_2 has a work function of $\sim 5.7\text{eV}$ (A. Persky, J. Chem. Phys. 50, 3835 (1969)). At 1400K this surface ionizes even Li atoms with an efficiency, $\beta_{\text{Re-O}}$, near unity. The current of positive ions from it serves to monitor the flux of the atomic beam. After this flux is measured, the Re is rotated out of, and the Si into, the beam. In this position ions formed at the Si surface can be guided into a quadrupole mass spectrometer. Alternatively, the ions formed can be collected, without mass discrimination, on an electrode positioned near the Si. Some results from the latter arrangement are shown in Fig. 3 which gives the temperature dependence of the efficiency of ionization $\beta_{\text{Si}}(T)$ of various atoms on the Si surface. This data confirms and extends the earlier work of E.Ya. Zandberg and V.I. Paleev (Sov. Phys. - Tech. Phys. 10, 1602 (1966)) in showing that the Saha-Langmuir "equilibrium" model for surface ionization (N.I. Ionov, Progress Surface Sci., 1, 237 (1972)) predicts the ionization efficiency satisfactorily.

Fig. 4 shows results of related experiments. A beam of Li atoms was incident upon a Si crystal which had previously been exposed to a K beam. The mass spectrometer was used and first tuned to respond to Li ions. Note that $I_{\text{Li}}(T)$ drops abruptly for $T \gtrsim 1480\text{K}$. When the Li beam was kept on, but the mass spectrometer was turned to detect K atoms, the signal varied with temperature as shown. Note that it rises at just the temperature at which that for Li dropped. Although the work is not complete, there is a tentative interpretation. The K dissolves in the bulk of the

Fig. 2. Schematic drawing of apparatus for study of ionization at surfaces. The Si and Re surfaces are heated by electrical conduction. Rotation of Re support by θ places Re surface in the beam.

Fig. 3. Temperature dependence of the ionization efficiency β_{Si} of three alkali metal atoms on a Si surface.

Fig. 4. Temperature dependence of ion current from a Si crystal in a beam of Li atoms and previously exposed to a beam of K atoms.

Si, but evaporation from the surface is so rapid that the surface remains free of K and produces Li^+ from the Li beam. For temperatures above 1480K the K emerges from the bulk more rapidly than it evaporates, and the surface becomes partly covered with K. The presence of the K atoms suppresses the ionization of the Li, so the yield of Li^+ drops. This kind of experiment may permit study of the rates of diffusion of alkali metals in bulk Si as well as electron transfer reactions at the surface.

Ionization of beams of Li and Na have also been studied on the surface of an Al_2O_3 tube heated by current passed through a wire inside the tube. In these cases $\log I_{\text{Al}_2\text{O}_3}(T)$ is not linear in $1/T$ as the Saha-Langmuir model predicts, (see Fig. 5). Furthermore the yield of ions is increased when the surface is illuminated by visible light. These results both suggest that there is not even a quasi equilibrium on the Al_2O_3 surface and that the experiments may be sensitive to some of the kinetic processes of adsorption and electron transfer which occur at the surface. Much remains to be done, but this preliminary work raises the expectation that intriguing information may be available.

The interpretation of results of this kind of experiments will be much more straightforward and convincing when more definite information about surface cleanliness and structure is available. Equipment has been ordered for making LEED and Auger analyses, and it should meet this need very well.

3. Reactions stimulated by the conversion of kinetic to internal energy when fast molecules hit a surface.

In these experiments the molecules being studied are added to an excess of carrier gas and then formed into a molecular beam by expansion from a heated nozzle. The molecules are incident normally on the surface of a glass target (a microscope slide) where they either react or reflect without reaction before being condensed on a liquid-nitrogen cooled shield or being pumped away. A velocity selector measures the speed of the molecules in the jet from the nozzle,

Fig. 5. Temperature dependence of ion current from Al_2O_3 in a beam of Na atoms.

so there are three parameters that characterize the experiment, E_k the kinetic energy of the molecules, T_N the temperature of the nozzle, and T_S the temperature of the surface. Most of the experiments up to the present have been done with CCl_4 and C_2Cl_6 seeded into H_2 , He, Ar or Kr as carrier gases. One of the substances produced from both molecules is a non-volatile deposit which seems to be a polymer of C and Cl. Fig. 6 shows the variation in its yield with E_k for 3 different values of T_N and $T_S = 300$ K. The reproducibility is not good, but there seems to be a threshold in E_k for formation of the deposit at $T_N = 573$ K. Collisions of CCl_4 with the target produce small amounts of C_2Cl_4 and C_2Cl_6 while C_2Cl_6 collisions produce C_2Cl_4 and CCl_4 .

Preliminary runs also suggest that the decomposition of trioxane to formaldehyde, a unimolecular reaction in the gas phase, can be produced by energetic collisions of trioxane with the target. Studies of this kind may be expected to show the relative importance of internal energy (determined by the value of T_N), kinetic energy (produced by the expansion), and the temperature of the target to the reactions of molecules undergoing violent collisions.

The paragraphs above give the status of work on the three projects which made up the original proposal. Since the beginning of the Contract the principal investigator has spent approximately half of his time on the work of the project during the academic year and full time during the summer. This distribution of his effort is expected to continue for the duration of the Contract.

The work supported by the Contract has not yet reached the stage at which it is ready for publication. However, two reprints of articles describing previous work supported by DOE have become available and are included with this progress report. The first describes the model to be used in first attempts to analyze the

Fig. 6. Variation of yield of non-volatile deposit produced by impact of C_2Cl_6 molecules on glass target with speed for three nozzle temperatures T_N .

elastic scattering from surfaces and pertains directly to the work of the present contract.

1. E.F. Greene and E.A. Mason, Surface Science, 75, 549 (1978). Cut-offs and shadows in classical scattering of atoms from surfaces.
2. R.P. McGinnis and E.F. Greene, J. Chem. Phys. 69, 4073 (1978).
The inelastic scattering of alkali halides by rare gases.