COO-4974-12

# INTERACTIONS OF MOLECULES WITH SURFACES

Progress Report

for Period 1 February 1989 - 1 January 1990

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January 1990

Prepared for
The U. S. Department of Energy
Grant DE-FG02-85ER13441

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This is a report of the progress made on four projects supported by DOE Grant DE-FG02-85ER13441 in the period 1 February 1989 to 31 December 1989.

1. A long term study of the rate of transfer of electrons between gas atoms and the surfaces of crystals, using the technique of surface ionization, reached a point where it could be submitted for publication. Measurement of the energy dependence of the yields of $Na^+$, $K^+$, and $Cs^+$ ions formed when beams of the corresponding alkali atoms M hit a Si(111) surface and of $Na^+$ for Na striking a Pt surface at a temperature T are those expected for equilibrium for thermal kinetic energies of the incident atoms. Above a threshold energy of 0.5-1.0 eV the yields rise abruptly to maxima greater than 0.1 and then remain approximately constant as the energy increases to 100 eV. In this range they are nearly independent of T from 300 to 1100 K. The results are represented well by a classical model having: 1) a rate of electron transfer that varies exponentially with the distance z of M from the surface; 2) potentials that slow the incoming atom down as it nears the surface; and 3) energy transfer by elastic two-body collisions with the surface represented as hard cubes each having the mass of an integral number n of surface atoms. At z = 5 A the rate for Na and K near a Si surface is $10^{12.5\pm0.2}\ s^{-1}$ with n equal to 3 and 5 respectively while for Cs it is three times less with n equal to 20. For Na on Pt it is $10^{12.9\pm0.1}s^{-1}$ with n equal to 1.

2. Energy transfer to surfaces has been studied by measuring the temperature rises of thermocouple surfaces exposed to molecular beams. For example, a platinum surface initially at room temperature intercepts intense molecular beams of He, Ar, $H_2$, $N_2$, and $SF_6$ emerging from a nozzle also at room temperature. If the mass of the Pt is small, after a few minutes it reaches a steady temperature uniform throughout the sample. Because the rate of heat loss to the surroundings is low, a thermocouple records temperature rises that for pure gases are as much as 30 K and that for mixtures of He with Ar can exceed 100 K. Interpretation of the results shows that these rises can be understood quantitatively and thus provide information about energy transfer occurring when gaseous molecules collide with surfaces. In particular the method gives (1) a way of measuring the temperature $T_S$ a surface attains at steady state due to interaction with gas molecules in the absence of heat conduction or radiation, (2) a simple determination of the average kinetic energy $E_i = 2k_BT_S$ of an incoming atomic beam without the need for measurement of the velocity distribution or the flux in the beam, and (3) a quantity $\gamma$ that, like an energy accomodation coefficient, is a measure of the effect of the temperature of the surface on the scattering.

3. He diffraction has been used to follow structural phase transitions on the (111) and (100) surfaces of Si and Ge. The seventh-order peaks of the Si(111)-7x7 reconstructed surface observed at room temperature first decrease with increasing temperature and then disappear near 1140 K where there are also a sharp decrease in the specular intensity and an increase in the diffuse scattering. This confirms earlier evidence that the 7x7 to "1x1" phase transition at

1138 ± 7 K On Si(111) is an order-disorder one. The specular scattering of He from the Si(100)-2x1 reconstructed surface stable at room temperature shows a change in the Debye-Waller slope at 930 ± 20 K which is evidence for the existence of a surface phase transition previously deduced in this laboratory from kinetic measurements of the desorption of alkali atoms.

4. Work is in progress to measure the effect of adsorbed atoms on the forces parallel to the surface of a crystal as they are revealed by changes in the curvature of the surface. The first experiments are being done with alkali atoms adsorbed on a Si(111) surface. As others have shown, the opposite process of producing changes in the surface by bending the crystal can be observed. There is the expectation that control of the surface forces will provide another degree of freedom in experiments on the interaction of molecules with surfaces.

Publications and a manuscript in preparation based on this work are:

1. Observations of phase transitions on the (111) and (100) surface of Si near 1000 K with He atom diffraction. J. S. Ha and E. F. Greene, J. Chem. Phys. **91**, 571 (1989).

2. Temperature rises produced by a molecular beam striking a Pt surface. E. F. Greene, T. Tao, and N. Thantu, J. Phys. Chem. **93**, 6778 (1989).

3. He diffraction study of the structural phase transition on the Ge(111) surface at 550 K. J. S. Ha and E. F. Greene, J. Chem. Phys. **91**, 000 (1989) (in press).

4. The ionization of thermal and hyperthermal beams of Na, K, and Cs on Si(111) surfaces. J. Chem. Phys. (in press).

5. Temperature rises produced by a molecular beam striking a Pt surface. II. T. Tao and E. F. Greene (in preparation).