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The Reflection and Thermal Accommodation of Helium Beams on Platinum*

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Molecular beam techniques have been used to investigate gas–surface interactions which are preliminary processes in gaseous heterogeneous catalysis. These first investigations studied the nature of the reflection of helium beams from platinum surfaces and their concomitant thermal accommodation (α'). At least three different conditions for the platinum surface, as judged by the nature of the reflection of a beam of helium atoms, were observed. Surfaces achieved by an oxygen treatment of the incandescent platinum target gave intense specular reflection of helium atoms and $\alpha' < 0.1$, and were, therefore, believed to be clean.

One approach to the study of gaseous heterogeneous catalysis is the investigation of the precursory process: the interaction of gas molecules with solid surfaces. One of the most suitable methods for studying gas–surface interactions is with molecular beams, with which the consequences of the collisions of particles with surfaces may be carefully examined under controlled conditions. Significant investigations, not so much directed to the study of catalysis as to surface physics, have been carried out for the past 50 years using this technique (*1*), and great sophistication of the method has developed during the past 10 years under the stimulus of space research.

Several years ago we undertook to investigate surface catalysis using molecular beam methods. We proposed to study the H_2–D_2 exchange reaction on platinum, but the first experiments with either pure gas were so surprising (*2*) that catalytic experiments were postponed until the more elementary system could be investigated more thoroughly.

Although the catalytic study has not yet been realized, our recent results deal with two related physical phenomena which are precursors to the gaseous heterogeneous catalytic process. Using conventional molecular beam techniques with phase- sensitive detection, simultaneous determination of the efficiency of energy transfer between a surface and an impacting atom or molecule and of the character of the rebound of the impinging atom has been achieved.

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Experimental

The work to be reported here used essentially the same apparatus which has already been described, but with emphasis on the detection of changes in velocity of the molecules upon reflection from the platinum. A schematic diagram of the apparatus is shown in Fig. 1. Three individually pumped vacuum chambers, separated by beam collimating slits and pumped by mercury diffusion pumps with liquid nitrogen trapping contained in order: (1) The molecular beam effusion source, either (a) a tungsten furnace capable of being heated to $\sim$3000°K, with a slit 2.5 mm $\times$ $\sim$0.5 mm, or (b) a low-temperature source fabricated from a standard Graham coil-type glass condenser fitted with $\sim$0.5 mm wide beam-forming slits at one end and capable of cooling the gas flowing through the spiral

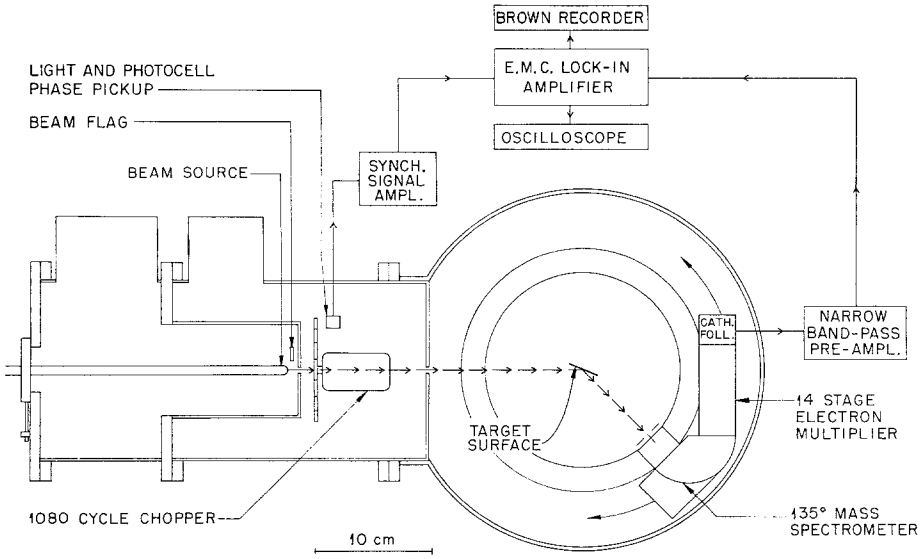

FIG. 1. Schematic diagram of the apparatus.

coil by maintaining liquid nitrogen in the outer jacket. The beam gas was admitted to either source from a compressed gas cylinder through a needle valve. (2) A mechanical chopper for modulating the molecular beam at 1080 cps. (3) The platinum target and mass-spectrometric beam detector.

The detector was a magnetic 135° sector mass spectrometer with a radius of curvature of 2.5 cm and was mounted on a goniometer whose center was the midpoint of the platinum target. The mass spectrometer could be rotated from —40° to +135° with respect to the original beam direction without interfering with the beam and could be positioned to ±0.1°. A modulated ion beam was produced from the modulated molecular beam by electron impact and analyzed in a permanent magnetic field of ~3000 gauss using an accelerating voltage of ~550 V for focusing mass 4 at the collector plate of a 14-stage electron multiplier. The multiplier output was coupled to the external circuit through a cathode follower and thence through a narrow bandpass, variable Q preamplifier to a commercial lock-in amplifier for amplification and detection. An oscilloscope connected across the phase detector bridge in the amplifier circuit produced a pattern by which differences between the signal and reference phases could easily be distinguished even in the presence of appreciable noise.

The platinum foil target was a 5–10 mm wide by ~4 cm long ribbon, 1, 2, or 4 mils thick, which was mounted under slight spring tension in order to prevent buckling and misalignment at high temperature, which was achieved by direct I^2R heating.* Temperatures above 800°C were measured by optical pyrometry and below 800°C by Pt–Pt, 10% Rh thermocouples discharge-welded above and below the target area. The target assembly could be moved vertically in or out of the beam and rotated. The absolute angular orientation of the foil relative to the beam was determined by rotating the foil until a sharp light beam, emitted by the incandescent tungsten beam source, was reflected precisely through the slit system of the mass spectrometer oriented at right angles to the original beam direction and observed through a window in the vacuum chamber. This method established the 45° incidence angle to ±1°.

With the platinum foil raised out of the

* It was apparently this combination of stress and high temperature that transformed the originally polycrystalline platinum foil to atomically smooth, large, nearly parallel single crystals as described in ref. (2).

beam path, the intensity and phase (the reference phase, ϕ_1 at the known mean velocity v_1) of the primary beam were measured at the start and were also verified during an experiment. Then with the target in place at the desired incidence angle the angular distribution and phase (ϕ_2 for the unknown mean velocity v_2) of the molecular beam reflected from the target were determined by moving the mass spectrometer about the scattering center. Chiefly because of the modulation frequency (1080 cps, at which $1° \phi$ represents 2.6 μsec) relatively small changes in the beam temperature, which changed the mean velocity and the time of flight of the beam particles, caused significant shifts in phase.* The relation between phase shift in degrees, $\Delta\phi = \phi_1 - \phi_2$, and the mean velocities is

$$1/v_2 = 1/v_1 - \Delta\phi/(360fd) \qquad (1)$$

where f is the modulation frequency of the beam and d is the flight path length of the modulated beam particles at the mean velocity v_2. If the distribution of velocities in the beam obeys the Maxwell distribution law, the most probable velocity is related to the temperature of the molecules by $v = (2kT/m)^{1/2} = 0.645 \times 10^4\ T^{1/2}$ for mass 4 helium atoms. Thus, Eq. (1) becomes in terms of gas temperatures

$$1/T_2^{1/2} = 1/T_1^{1/2} - 17.9\Delta\phi/(fd) \qquad (2)$$

In the direct beam where $d = 30$ cm (distance between chopper and detector), phase shifts of 3–4° (due, for example, to beam temperature changes from 300° to 320°K) were easily detected. With the target in place, d becomes 8 cm (distance between target and detector) and with the lowered signal-to-noise ratio, the sensitivity of phase detection was determined experimentally to be about 8° (i.e., a change in temperature from 300°K in the incident beam to 590°K in the reflected beam).

Results and Discussion

Our earlier work (*2*) had shown that at platinum temperatures above about 300°C the pattern of reflection of helium (and deuterium) was pseudospecular (i.e., a directed reflection in which the maximum appears not at the specular angle but closer to the normal), while below about 150°C it was almost random (cosine distribution). The high-temperature behavior was tentatively attributed to a clean surface, the low-temperature behavior to a surface contaminated by adsorption from the ambient gas (about 3×10^{-7} Torr with air and water vapor as the predominant species even with additional liquid-nitrogen trapping surfaces in the experimental chamber). By investigating the effect of the experimental variables of temperature of the platinum surface and incident beam, of incident angle, and of the presence or absence of surface impurities, appreciable interaction between the gas molecules and the surface was evident. However, the singular influence of oxygen on the reflective behavior provoked further investigation with emphasis on the detection of changes in velocity of the molecules upon reflection from the surface.

It was expedient to relate the changes in phase, characterizing changes in velocity, between the uninterrupted main beam and the peak of the reflected distribution to an "accommodation coefficient," α', defined as

$$\alpha' = \frac{T_2 - T_g}{T_s - T_g} \qquad (3)$$

where T_2 is the "temperature" of the reflected beam [obtained from Eq. (2) in which T_1 is set equal to T_g] and where T_s and T_g are the temperatures of the platinum surface and the beam source (i.e., the beam gas), respectively. This is a somewhat unconventional expression of "accommodation coefficient" although our definition is not very different from that used previously in studying hyperthermal free molecule drag coefficients in which the squares of the velocities of rebounding and incident gas particles were related to an "α" (*4*). In our usage α' is an index of energy transfer in which measured differences in mean flight times (hence, mean velocity differences) are related to temperature differences by assuming the Maxwell distribution law.

* Less direct methods for determining velocities of beam particles have been used (*3*).

The previously reported difference in reflection patterns between platinum above 600° and below 450°K (for example, Curves I and II respectively, Fig. 2A) was again observed, but the pseudospecular reflection was found to be accompanied by a phase shift corresponding to an "accommodation coefficient" of 0.3 to 0.6 for helium (or D_2) at 100° or 200°K on platinum at 1200°K. So large an energy exchange should not occur between helium and a surface platinum atom if the pseudospecular reflection pattern means direct rebound without adsorption. This is so because the maximum fraction of energy which can be transferred is given by $4\ M_1M_2/(M_1+M_2)^2$

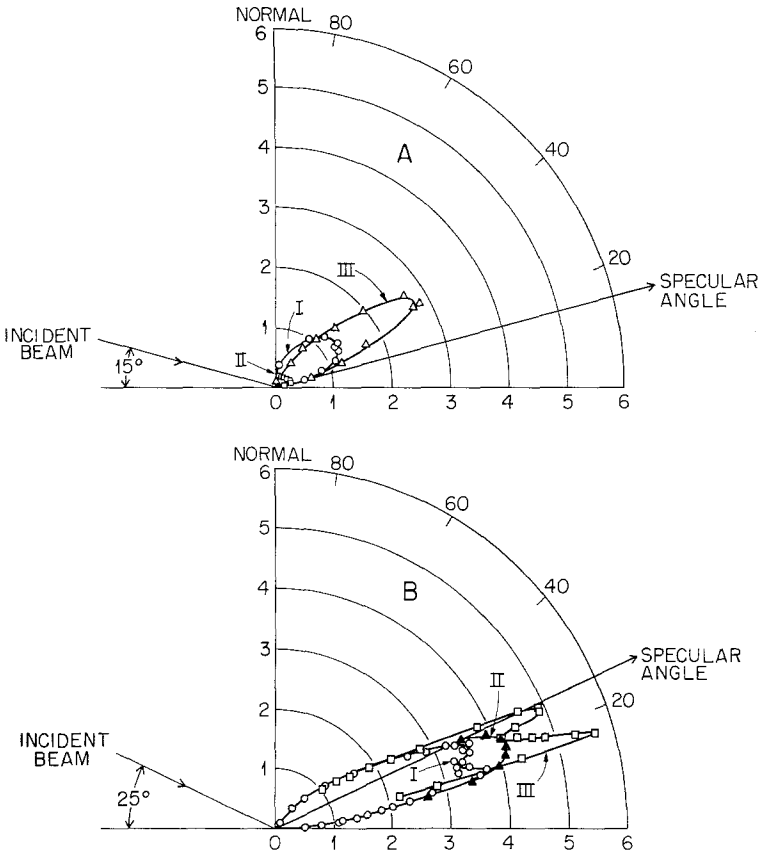

FIG. 2. Angular distribution of the modulated helium intensity reflected from platinum. In those cases where oxygen was admitted to the system, the mass spectrometer efficiency decreased somewhat because of poisoning of the mass spectrometer filaments. Since this was observable as a decrease in the DC background signal, the modulated signals were normalized to the same DC level. The intensity units in plots A and B are comparable.

	Curve	T_{He}(°K)	T_{Pt}(°K)	Conditions
A	I	300°	1300°	Vacuum, 5.5×10^{-7} Torr
	II	300°	300°	Vacuum, 5.5×10^{-7} Torr
	III	300°	1300°	Added 5.4×10^{-6} Torr O_2
B	I	300°	1300°	O_2 pretreat, O_2 added to 1.1×10^{-6} Torr
	II	1370°	1300°	O_2 pretreat, O_2 added to 1.1×10^{-6} Torr
	III	300°	900°	O_2 pretreat, O_2 added to 1.3×10^{-6} Torr

(*5*), the value of which is 0.08 for helium ($M_1 = 4$) and platinum ($M_2 = 195$). This naive classical approximation can hardly be expected to yield more than the relative *maximum* energy transfer but does serve to stress the importance of the ratio of the mass of the gas atom to the mass of the lattice atom ($M_1/M_2 = 0.02$). To account for a measured (total) $\alpha' = 0.3$ to 0.6 some 4 to 11 multiple collisions each of $\alpha' = 0.08$ would have to take place. But through so many collisions the reflected particles would be randomly directed, so that one can conclude by virtue of the pseudospecular reflection and the relatively large α' that under these experimental conditions the surface must be covered with foreign atoms of low mass ($M_2 < \sim 30$) from which the beam molecules rebound directly without appreciable adsorption.

Oxygen with a background pressure of 2 to 5×10^{-7} Torr, is a potential contaminant, but the earlier work (*2*) suggested that its role, if any, in the reflection was not simple. Furthermore, the fractional surface coverage on 1200°K platinum at this background pressure would be very small, since the measured heat of adsorption of O_2 on Pt is 65 kcal/mole (*6*). Carbon is another likely surface contaminant, since it was not only detectable (in combination) in the background gas ($<10^{-8}$ Torr) but had been used in the form of organic solvents to degrease the platinum foil from which the targets had been prepared. Fabian and Robertson (*7*) have reported the formation of carbon films on incandescent platinum by hydrocarbon vapors present at $\sim 10^{-9}$ Torr and such films have even been found on heated surfaces in ultra-high-vacuum systems (*8*). In any case, on the assumption that the contaminant might be removable as a volatile oxide, the platinum was cycled for several minutes between 900° and 1600°K in a relatively high pressure of oxygen ($\sim 10^{-3}$ Torr) and maintained in oxygen ($\sim 10^{-6}$ Torr) at high temperature (>900°K) before and during measurement.

With platinum cleaned in this way and held at 1300°K, a room-temperature helium beam incident at 20° to the surface was reflected specularly and no change in particle velocity was observed ($\alpha' < 0.1$). For incidence angles (with respect to the surface) from 22° to 37° the distribution of reflected molecules, while essentially specular in width and position, showed a fine structure. Figure 2B shows the distribution in this case; for comparison, Fig. 2A shows the pseudospecular reflection (curve I) observed with platinum at 1300°K but without the oxygen pretreatment. The presence of about 10 times the background oxygen pressure during an experiment (but without the oxygen pretreatment) increased the intensity of the pseudospecular reflection without appreciably altering the nonspecular position (too close to the normal) of the maximum (curve III, Fig. 2A). The diffuse reflection from platinum at room temperature is shown in curve II. In both pseudospecular and enhanced-intensity pseudospecular reflection, the "accommodation coefficient" measured through the phase shift was about 0.6.

These results suggest that at least three different surface conditions can exist on platinum, although the exact nature of these conditions remains undetermined. The surface producing specular reflection is probably relatively uncontaminated; evidence for this is the specular reflection and the poor accommodation of the beam to the surface temperature,† both of which preclude large concentrations of low-mass impurities on the surface.* Small surface concentrations would, of course, be undetected, and a coverage by oxygen of about 3% at 1300°K can be calculated from the oxygen pressure (2×10^{-6} Torr) and a heat of adsorption of 65 kcal/mole.

The cleaning of the surface by high-temperature oxygen treatment is similar to that used by Touw and Trischka (*11*) for

* The experimentally determined $\alpha' < 0.1$ agrees with the lowest reported values for helium on "clean" platinum determined by more conventional methods (*9*).

† Recently, there has been observed an intense, specular reflection of helium from a gold surface which was believed virtually free of adsorbed gases by reason of its continuous production *in situ* by rapid evaporative deposition (*10*).

producing their high-work-function condition and by Fabian and Robertson (*7*) and by Fogel *et al.* (*12*) for restoring catalytic activity to a platinum ribbon. In our case, heating without the addition of oxygen was not sufficient, and if the treated surface was allowed to stand without added oxygen it reverted slowly to the pseudospecular condition. Intentional contamination at high temperature with CO, CH_4, or C_2H_2 gave a surface with pseudospecular behavior. The effect produced by C_2H_2 was the most persistent of the three in the presence of oxygen.

The fine structure observed in the distribution from the specularly reflecting surface is unexplained. Our preliminary experiments suggest that micro features of the surface are not the source of the phenomenon since the fine structure could be made to appear or disappear by changing the nature and the temperature of the gas of the incident beam. Many of the characteristics of the phenomenon suggest diffraction by the surface atoms. It was observed with helium at 100°K where the associated deBroglie wavelength is 1.5 Å and less sharply at 300°K ($\lambda = 0.9$ Å), but the components merged into a single, symmetric distribution at higher beam temperatures ($\lambda < 0.3$ Å). It was observed only within a range of angles of incidence, and became sharper as either the beam or surface temperature was lowered. It was not observed at all with D_2. Examination of the surface by X-ray diffraction revealed large single crystals, almost parallel to each other, and oriented with the (111) plane in the surface. About the (111) axis the orientation was less perfect although most of the crystals were almost parallel. The orientation of a (110) direction in the surface was inclined at 13° to the plane in which the detector rotates. To conclude that molecular diffraction was observed would, however, not be justified at present, because of experimental uncertainties such as the orientation of the crystals about the (111) axis. Experiments with single crystals of completely known orientation will be undertaken to decide this point.

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