Observation of Direct Inelastic Scattering in the Presence of Trapping-Desorption Scattering: Xe on Pt(111)

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Velocity and angular distributions for Xe scattered from clean Pt(111) have been observed which permit the scattering process to be experimentally divided into a direct inelastic channel and a trapping-desorption channel. The trapping-desorption channel leads to Maxwellian velocity distributions at the surface temperature and a $\cos\theta$ angular dependence, while the direct inelastic channel exhibits a linear relationship between exit kinetic energy and both incident kinetic energy and surface temperature.

We report velocity distribution measurements for thermal-energy Xe-atom scattering from a clean Pt(111) surface showing two clearly resolved structures that can be separately studied and characterized. Measurements of angular and velocity distributions as a function of beam energy and surface temperature allowed the identification of the two structures as a direct inelastic scattering channel on the one hand and a trapping-desorption channel on the other. This identification was facilitated by a previous study on the Ar/W system[1] in which the direct inelastic channel was present almost exclusively and its characteristics could be determined.

While many experimental studies of velocity distributions of noble gases scattered from metal surfaces have been made, few[2,3] have been performed on demonstrably clean metal surfaces, and none have shown anything but a single velocity peak.

The present experiments were performed in a molecular-beam surface apparatus described previously,[4] with the addition of a sample tilt and azimuth adjustment stage to the crystal manipulator and a liquid-helium-cooled cold finger capable of cooling the sample to 30 K. The sample was a 0.8-mm-thick disk, 6 mm in diameter, prepared from a single-crystal Pt rod (Metals Reserve Company 99.99+% pure) oriented to within 1° of the (111) plane and mechanically polished by standard metallurgical techniques. After acid etching the sample was spot welded to two 0.7-mm-diam Pt wires which were the mechanical supports, electrical leads, and thermal conductors to the cold finger. Surface temperatures were monitored with a Pt/Pt-10%Rh thermocouple calibrated for use below room temperature spot welded to the back side of the sample. The estimated error in measuring and regulating the surface temperature was ± 3 K.

The surface was cleaned with standard techniques[5] for Pt and subsequent Auger-electron spectroscopy (AES) indicated surface contamination by Ca, Si, C, O, and S as < 1% each. He scattering, which has been shown to be sensitive to microscopic surface roughness and surface cleanliness,[6] gave a reflected He-beam peak intensity 16% of the incident beam with full width at half maximum (FWHM) 1.3° at a surface temperature of 400 K. The FWHM of the beam as measured by the detector was 1.1°. Such a high reflection coefficient at high angular resolution is indicative of a clean, well-ordered surface. The incident Xe, a well-collimated supersonic beam, was mechanically chopped into pulses of 28 μsec FWHM so that time-of-flight (TOF) measurements could be made on the scattered atoms. Background pressures in the scattering chamber were typically 2×10^{-10} Torr rising to 7×10^{-10} Torr when the Xe beam was on. The chopper-sample and sample-ionizer distances were 21.21 and 14.45 cm, respectively. The measurements involved flashing the sample to 730 K to remove adsorbed residual background gases, followed by 3.6 min of data accumulation. During this time surface contamination from background gases was estimated by He scattering and AES to increase from <1% to about 5%.

Figure 1 shows the detected TOF distributions for (curve *a*) the incident Xe and (curves *b*, *c*, and *d*) the scattered Xe exiting from the surface at 0° (normal), 45°, and 75° (specular), respectively. Data were also taken at − 30° which appear identical to the data at 0°. The experimen-

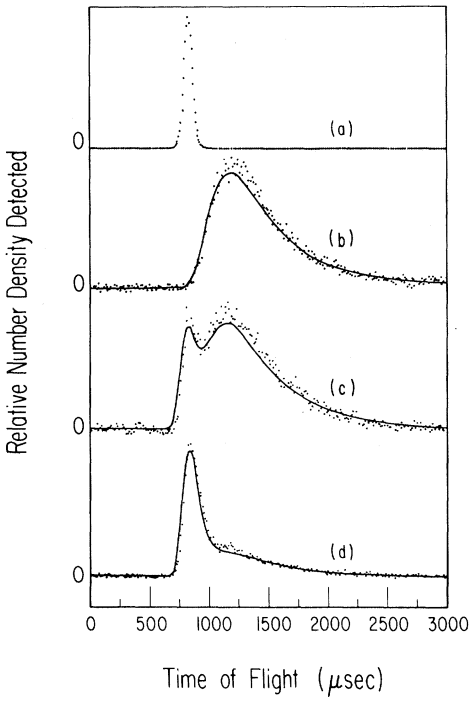

FIG. 1. Detected time-of-flight spectra for $T_s = 185$ K, angle of incidence 75° from normal. Curve a, incident Xe beam with $\langle E_{\rm kin}\rangle_i/k = 1615$ K; curve b, Xe scattered at 0° (normal); curve c, 45°; and curve d, 75° (specular). Solid lines are predicted TOF spectra from model.

tal conditions $T_s = 185$ K, incident angle = 75°, and $\langle E_{\rm kin}\rangle_i/k = 1615$ K were chosen to enhance the separation of the two channels in angle and velocity while keeping residence times negligibly short.

The most striking feature of these distributions is the double-peak structure observed at 45° and 75° from the normal. Because of the large angular separation of the two channels as indicated by the lack of a short-time channel in Fig. 1, curve b, for Xe exciting at − 30° and 0° from the normal, it was possible to characterize the long-time channel independently as arising from atoms that trap, become equilibrated with the surface, and then desorb. Four observations support this interpretation. First, the characteristics of this channel were found to be independent of incoming beam energies in the range $\langle E_{\rm kin}\rangle_i/k = 800$ to 1615 K. Second, the data at both 0° and − 30° were fitted by a Boltzmann distribution with the temperature T_f as an adjusted parameter. The resulting fits reproduced the data within statistical error and $T_f = T_s \pm 3$ K. Third, nonnegligible residence times for the trapped fraction were observed when surface temperatures were run below 170 K. Fourth, the data analysis for separating a Boltzmann channel from a scattering channel with an arbitrary supersonic distribution with flexible breadth and mean flow velocity[1] and described more fully below was used to determine the Boltzmann scattering channel intensity versus scattering angle. The angular intensity distribution of the Boltzmann scattering channel was difficult to measure accurately because of difficulties in determining angular viewing factors and difficulties in the channel separation procedure. The angular distribution is not determinably different from a cosine distribution.

We now characterize the short-time (direct inelastic) channel. Although the scattering data for Xe on Pt(111) do not determine whether elastic scattering is present or not, the scattering of Ar on W showed conclusively that little elastic scattering occurs. We therefore interpret the data of Xe on Pt as possessing no elastic channel because the conditions for elastic scattering are even less favorable; there is a more equal atomic-mass match between gas and solid and a deeper well. For the angles of observation where it was obviously present, we determined its characteristics by the method used for Ar on W.[1] Briefly, the TOF data were least-squares fitted by a model for the scattered velocity distribution of the following form:

$$I(v) = FI_T(v) + (1-F)I_I(v), \tag{1}$$

where F is the fraction of exiting atoms coming from the trapping-desorption channel, and $I_T(v)$ and $I_I(v)$ are the flux-weighted velocity distributions for the trapping-desorption and direct inelastic channels, respectively. $I_I(v)$ was assumed to be of the form

$$I_I(v) = Nv^3 \exp[-(v-v_0)^2/\alpha^2]. \tag{2}$$

The quality of the fits can be judged by examination of Fig. 1.

The energy in the direct inelastic exhibits a large variation with the incident beam energy and a somewhat smaller variation with the surface temperature energy. For Ar/W (Ref. 1) these variations are represented over a wide range of beam energies and surface temperatures by a relationship of the form

$$\langle E_{\rm kin}\rangle_e = B_2\langle E_{\rm kin}\rangle_i + B_3(2kT_s), \tag{3}$$

where $\langle E_{\rm kin}\rangle_e$, $\langle E_{\rm kin}\rangle_i$, and $2kT_s$ represent the average exit kinetic energy, average incident kinetic energy, and the average kinetic energy for particles exiting in thermal equilibrium with

the surface at temperature T_s, respectively. B_2 and B_3 are found to be independent of both incident beam and surface temperatures. They depend somewhat on angle of observation with $B_2 = 0.8$, $B_3 = 0.4$, and $B_2 = 0.9$, $B_3 = 0.1$ for observation at 75° (specular) and 45° from normal, respectively. For comparison the values obtained for Ar incident on polycrystalline W at 45° were $B_2 = 0.8$ and $B_3 = 0.2$ (independent of angle of observation). For Ar/W another linear proportionality relationship between the characteristic temperature $m\alpha^2/2k$, which is a measure of the width of the velocity distribution, and T_s was found:

$$m\alpha^2 = B_1(2kT_s), \tag{4}$$

where m is the atomic mass. For the Xe/Pt(111) system the coefficient of proportionality is $B_1 = 0.3$ while, for comparison, $B_1 = 0.2$ was found previously for Ar/W. The behavior of the direct inelastic channel with changes in beam energy and surface temperature was determined with $\langle E_{\rm kin}\rangle_i$ ranging from 800 to 1615 K and T_s from 100 to 210 K.

The angular distribution for the direct inelastic channel is peaked near specular with FWHM $\approx 40°$ and is quite asymmetric with a long, slowly decreasing tail toward the surface normal. We estimate that approximately 10% of the total exiting Xe flux is in the direct inelastic channel for the conditions given in Fig. 1.

Previous angular distribution studies of noble-gas scattering on clean metal surfaces categorized the scattering as being due to diffuse and lobular channels. For example, for the Xe/Pt(111) system Stoll, Smith, and Merrill[7] assumed that there was a trapping-desorption channel that had a $\cos\theta$ distribution. For an incident effusive beam with 973 K source temperature and 373 K surface temperature 50% of the scattered flux was calculated to be diffuse, assuming a $\cos\theta$ angular distribution, and hence arising from the trapping of the Xe gas. The present work shows that there can be a Maxwellian component thermalized at T_s that is consistent with the assumption that a trapping channel has a $\cos\theta$ (diffuse) angular distribution. Previously the nature of the velocity distribution in the lobular channel was not clear. The present work shows that it has a particular variation with incoming beam energy, surface temperature, and angle of observation, among other factors.

The scattering of the heavier noble gases can be understood as the sum of a trapping-desorption channel and a distinctive direct inelastic channel. Depending on the relative importance of these two channels, the scattering is "trapping dominated" or "inelastic."[8]

The most natural physical interpretation of the distinction between the two channels is given in terms of interaction times of the gas with the surface. The existence of two distinct peaks in the velocity distribution suggests that the interaction times divide into two distinct groups and that the direct inelastic peak arises from shorter interaction times. This is in agreement with the results of Hurkmans *et al.*[9] who observed two separate residence-time peaks for hyperthermal K scattered from W. They observed a short-time peak corresponding to reflected particles and a long-time peak corresponding to trapped-desorbed particles. If, on the contrary, there were significant contributions from particles with interaction times intermediate between those required for trapping with complete equilibration and those characteristic of direct inelastic scattering, we would expect the direct inelastic channel to show a smear of final kinetic energies merged with the trapping-desorption channel. At higher surface temperatures and/or weaker binding energies the trapping-desorption channel will tend to merge into the direct inelastic channel as residence times become too short for complete equilibration.

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