

Low-Energy He⁺ Scattering from Deuterium Adsorbed on Pd(110)

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We show that low-energy, helium ion scattering in the forward direction provides a surface-specific means for directly observing adsorbed deuterium. Energy spectra of 1-keV ⁴He⁺ scattered at angles less than 30° from a surface with adsorbed D contain the two maxima predicted for classical single scattering. Angular studies indicate that D atoms adsorbed on the Pd(110) surface at room temperature reside in the troughs between atom rows.

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The interaction of hydrogen with solid surfaces is of wide scientific and technological interest, and many techniques have been used to study hydrogen on surfaces. For example, the surface structure of the Pd-H system provides insight into the mechanism of hydrogen uptake and has been studied extensively with low-energy electron diffraction (LEED),¹⁻³ helium diffraction (HeD),^{4,5} and impact-collision ion-scattering spectroscopy (ICISS).^{6,7} These techniques provide detailed information about the arrangement of substrate atoms, but the location of adsorbed hydrogen can only be determined indirectly. Two techniques, low-energy ion scattering (LEIS)⁸ and low-energy recoil scattering (LERS),⁹ offer the possibility of directly observing and locating surface hydrogen isotopes. Of these, LEIS using He⁺ provides the greater surface specificity due to the high neutralization rate of He⁺, but scattering from hydrogen isotopes is restricted to the far-forward direction. Previous LEIS studies, which typically have been arranged to detect ions scattered through large angles, have not explored this region.

In this Letter, we report results from experiments designed to detect hydrogen isotopes on solid surfaces by energy analyzing forward-scattered ⁴He⁺. The ability to detect surface ²H(D) by LEIS is demonstrated for D adsorbed on a Pd(110) metal surface. Two kinematically allowed scattering energies of He⁺ from D are clearly observed over a range of forward-scattering angles. The higher-energy peak is the more intense and provides a convenient means for directly studying surface D. As an example, we have used angle-resolved LEIS measurements to locate the binding site of D adsorbed at ≈ 300 K on a Pd(110) surface.

The classical velocity-angle relation for a projectile elastically scattered in a binary collision with an initially stationary target is given by¹⁰

$$2 \cos \theta = (1 + \mu)v + (1 - \mu)/v, \quad (1)$$

where θ is the laboratory scattering angle, μ is the target

to projectile mass ratio, and v is the relative velocity of the scattered particle [$v = (E/E_0)^{1/2}$ where E/E_0 is the relative energy of the scattered particle]. Equation (1) is a circle in polar coordinates (v, θ) with its center at $(x, 0^\circ)$ and radius μx where $x = 1/(1 + \mu)$. When $\mu < 1$ it is apparent that there is a cutoff angle for scattering, $\theta_{\max} = \sin^{-1} \mu$, and that two scattered ion velocities exist at each $\theta < \theta_{\max}$. One must observe at an angle less than θ_{\max} in order to detect scattering from a target atom less massive than the projectile. For ⁴He scattering from D, $\mu = 0.5$, and $\theta_{\max} = 30^\circ$.

Angle-resolved, low-energy ion scattering measurements were made using a gas-discharge ion source and a scattering chamber (base pressure ≈ 4×10^{-8} Pa) equipped with a 50-mm-diam hemispherical electrostatic energy analyzer. The source column produces mass-analyzed, neutral-free He⁺ or Ar⁺ beams in the energy range 0.1–3 keV [ΔE (FWHM) < 3 eV at 1 keV]. The angular position of the analyzer can be adjusted to within 1° throughout the range of scattering angles from 0° to 90°. The detector is a channel electron multiplier operated in a pulse counting mode.

An oriented Pd(110) single crystal was cleaned by numerous cycles of 1-keV Ar⁺ bombardment at 800 K followed by brief annealing to 1000 K. Carbon, oxygen, and sulfur surface impurities were monitored by LEIS (< 1% monolayer detection limit¹¹) and were removed from the surface by this process. A gas-dosing tube positioned about 2 cm from the sample was used to expose the clean, annealed sample to D₂(g).

Figure 1 shows energy spectra of 1-keV ⁴He⁺ forward scattered from the Pd(110) surface with and without adsorbed D. The beam is incident at an angle, α , of 77.5° from the surface normal and θ is 25° from the incident beam direction. Two peaks are clearly visible when the sample is exposed to 1×10^{-4} Pa D₂ at ≈ 300 K. The observed peak energies are near the values given by Eq. (1) for He scattering from D, indicated at positions D1 and D2. The existence of two scattering peaks expected

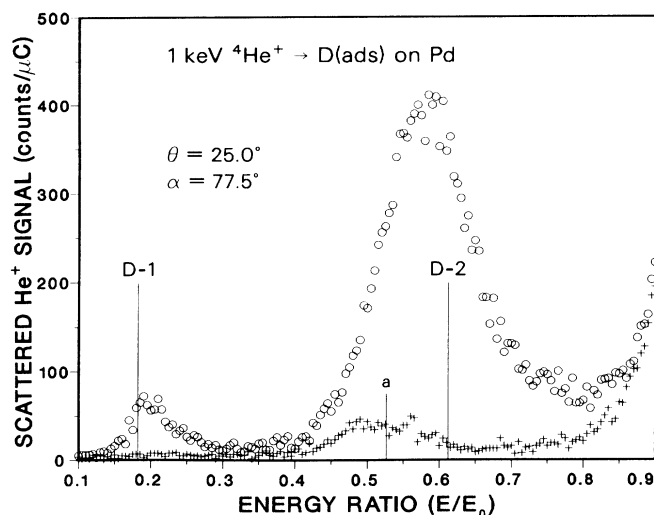


FIG. 1. Energy spectra of ${}^4\text{He}^+$ scattered from Pd with (open circles) and without (plus marks) adsorbed D at 300 K. The incident He^+ energy, E_0 , is 1 keV, the incident polar angle, α , is 77.5° from the sample normal, the scattering angle, θ , is 25° , and the azimuthal angle, ϕ , is 90° . Positions D1 and D2 are the energies calculated from Eq. (1) for ${}^4\text{He}^+$ scattering from D. The weak peak labeled *a* is due to recoil H or O.

at a given angle $\theta < \theta_{\max}$ when $\mu < 1$ has been reported for scattering measurements in the gas phase,¹² for Ne^+ scattering from C impurities on gold,¹³ and for Kr^+ scattering from a solid Cu target.¹⁴ The work reported here appears to be the first observation of the phenomenon involving an adsorbate on a solid.

The velocity-angle dependence of the scattered He^+ intensity is shown in Fig. 2. The experimentally measured He^+ intensity contours follow closely the scattering circle given by Eq. (1) with $\mu = 0.5$. It is clear that the observed signals are from scattered ${}^4\text{He}^+$ rather than recoil D^+ , which has a much different angular dependence. The scattered ion intensity increases strongly in going to smaller center-of-mass scattering angles, consistent with the angular dependence of the scattering cross section.¹⁵

We find that adsorbed deuterium can readily be observed from scattering ${}^4\text{He}^+$ energy measurements at scattering angles less than 30° . Near 30° the peak is broad, since small variations in the scattering angle cause large changes in the scattered particle energy. Going to lower scattering angles sharpens the scattering peaks and the intensity of the higher-energy peak increases, but interference from scattering by the substrate or from recoil emission can occur. For ${}^4\text{He}$ projectiles, the scattered-ion energy is the same as the energy of recoil D at $\theta_{\text{eq}} = 17.9^\circ \{ \cos^2 \theta_{\text{eq}} = (1 - \mu^2) / [4(\sqrt{\mu} - \mu)] \}$. Consequently, the optimum scattering angle for D detection appears to be between 20° – 25° .

With the ability to detect surface deuterium by ion scattering, it is possible to obtain structural information

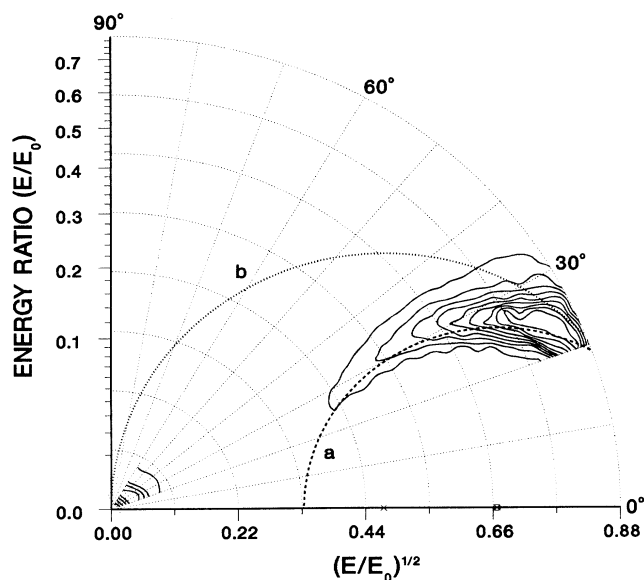


FIG. 2. Contour plot of the experimentally measured velocity-angle dependence of ${}^4\text{He}^+$ scattered from D adsorbed on Pd for 20° – 60° scattering angles. $E_0 = 1$ keV, $\alpha = 77.5^\circ$, $\phi = 90^\circ$, and $T = 300$ K. The contour interval is 50 counts/ μC . Contour lines greater than 500 counts/ μC are not shown. The scattering circle for ${}^4\text{He}^+ \rightarrow \text{D}$ from Eq. (1) is shown as the dashed curve *a* and the dotted curve *b* is the recoil circle for D. The signals seen at $E/E_0 < 0.01$ are from secondary ions.

about the position of adsorbed deuterium on a solid substrate. One such experiment is shown in Fig. 3, in which the scattering signal is plotted as a function of crystal azimuth for D adsorbed on Pd(110) at ≈ 300 K. The 1-

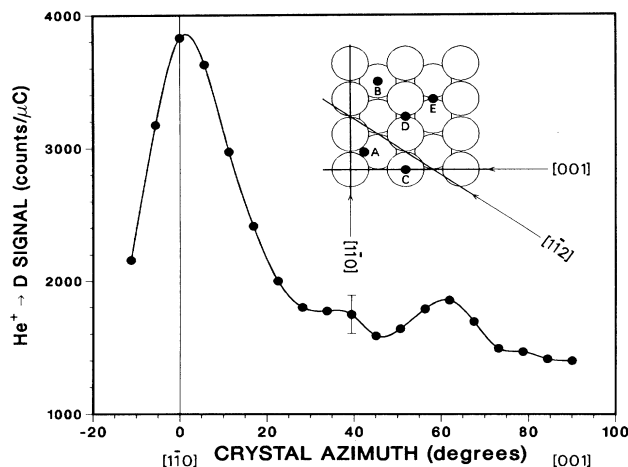


FIG. 3. Intensity variation with Pd(110) azimuthal orientation of ${}^4\text{He}^+$ scattering from D. $E_0 = 1$ keV, $\alpha = 80^\circ$, and $\theta = 20^\circ$. The incident beam is aligned with the Pd rows when $\phi = 0^\circ$. Inset: Model of Pd(110) surface showing five high-symmetry adsorption sites. *A*: quasithreefold, *B*: hollow, *C*: top, *D*: short bridge, *E*: long bridge.

keV $^4\text{He}^+$ beam is incident at $\alpha=80^\circ$ and scattering is measured at $\theta=20^\circ$. Thermal desorption data indicate that at this temperature only the most tightly bound states (denoted β_2) are appreciably occupied.¹⁶ When the scattering plane is aligned parallel to the $[1\bar{1}0]$ direction ($\phi=0^\circ$), a strong signal is observed. As the crystal azimuth is rotated the signal diminishes, goes through a second, smaller maximum near $\phi=60^\circ$, and becomes weakest at $\phi=90^\circ$. The main result is that strong scattering from deuterium is observed when the incident He^+ beam is aligned with the Pd atom rows, but is attenuated by nearly a factor of 3 when the beam is aligned perpendicular to the atom rows.

The variation in the D scattering signal intensity with crystal alignment provides direct information about the D location on the Pd(110) surface. The signal variation results from shadowing or blocking of the D by Pd substrate atoms and cannot be attributed only to changes in He^+ neutralization along different azimuthal trajectories. Taglauer and co-workers¹⁷ have shown that He^+ scattered from a Ni(110) surface does not significantly change intensity with azimuth. We also observe only a small increase in scattered He^+ intensity from Pd(110) substrate atoms (in contrast to the large decrease seen in the scattering intensity from D), in going from $\phi=0$ to 90° . This azimuthal insensitivity in the scattering signal from the substrate results from the high probability for He^+ neutralization, which permits only ions undergoing single binary collisions in the first Pd layer to survive. Thus, second-layer Pd atoms are not seen and there is no increase in signal for alignment along $[1\bar{1}0]$. The slightly larger signal intensity along the $[001]$ direction can be attributed to the more open Pd spacing along this direction, which reduces neutralization. Adsorbed D, especially if in a trough site location, cannot cause appreciable shadowing of Pd or affect He^+ neutralization rates as strongly as other adsorbates.¹⁸

Five possible high-symmetry adsorption sites for D on the (110) surface are depicted in the inset of Fig. 3. The chemisorbed D responsible for the azimuthal dependence observed in the signal intensity clearly does not reside on top of the Pd atom rows (top-site or short-bridge positions). Instead, it must reside in the troughs between the atom rows, since only this location is consistent with the signal maximum at $\phi=0^\circ$. Deuterium is visible when the scattering plane is aligned parallel to the troughs, but at other angles the Pd atoms shadow the D.

The secondary maximum at $\phi=60^\circ$ gives additional information that helps locate the trough sites for adsorbed D. There is another surface channel, along the $[1\bar{1}2]$ direction, which is 55° from the $[1\bar{1}0]$ direction. The signal maximum near this angle indicates that D adsorption sites lie along this channel. Of the three possible high-symmetry binding sites in the trough, denoted quasithreefold, long-bridge, and hollow sites, only the quasithreefold and long-bridge sites lie near the $[1\bar{1}2]$

surface channel.

The trough sites indicated by the present work are the most tightly bound chemisorption sites predicted by embedded-atom¹⁹ and effective-medium calculations.²⁰ An embedded-atom calculation shows the long-bridge position to be nearly as stable as the quasithreefold position (0.08-eV difference), so it is reasonable that both sites are populated at 300 K. Further, Muscat has shown that the H-H pair interaction across top row Pd atoms is strongly attractive.²⁰ The axis of this interaction is along the line connecting the quasithreefold and long-bridge sites. At 300 K, some delocalization along this axis probably occurs.

We note that the quasithreefold site is the D chemisorption site identified by LEED studies at 130 K.² In the LEED work, a 2×1 periodicity due to an ordered array of H without substrate reconstruction was found at doses up to 0.3 L. At higher coverages, the surface reconstructs to a 1×2 paired row structure. Under our conditions of dosing at 300 K, no well-ordered superperiodicity exists and a LEED determination of the H location becomes problematic. A strength of forward LEIS, then, is that site determination can be made even in the absence of long-range order.

We have shown that forward LEIS can be used to detect surface D and that it provides a direct probe for locating the positions of adsorbed D on surfaces. We expect that this method, with its surface specificity and ability to resolve isotopes, will complement previously existing methods for observing the behavior of hydrogen on solid surfaces.

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