Optical radiation from low-energy hydrogen atomic and molecular ion-surface collisions

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(Received 27 March 1978)

The energy and oxygen-pressure dependence of Balmer radiation photon yield due to ion-surface collisions on polycrystalline molybdenum using hydrogen atomic and molecular ions were measured in the energy range from 200 to 10 keV. These results, obtained under ultrahigh-vacuum conditions, provide new information on the ways in which the photon yield is produced by electronic interactions of the emerging particles with the surface. Radiation yield, normalized to current and backscatter yield, varied in a consistently exponential manner over the entire incident-ion energy range. The molecular state and the charge state of the incident particles were measured to have no discernable effect on the final excitation for clean surfaces. At partial pressures of oxygen below 10^{-11} Torr, surface concentrations of oxygen below 2% of a monolayer on molybdenum could be maintained during the experiments. Increased surface coverages (up to 0.5 to 1 monolayer) raised the photon yield for molybdenum by a factor of 7. These oxygen-dependent effects are tentatively interpreted as owing mainly to changes in the deexcitation probability in the vicinity of the surface.

I. INTRODUCTION

Optical radiation measurements from ion-surface interactions have received increasing attention.[1-5] In addition to their intrinsic fundamental interest, these studies provide information on charge exchange and other inelastic processes occurring between a fast-moving particle and a solid surface. However, so far these previous experiments have lacked the refinement of surface cleanliness and definition reached in other fields of surface studies, i.e., vacua in the low 10^{-10}-Torr range and additional surface analysis by standard means (Auger-electron spectroscopy and ion-scattering spectroscopy, for example). Important areas of concern include the role of the surface in the initial excitation of the emerging backscattered particle and the role of competing radiationless deexcitation processes.

In this paper we report results on radiation from excited backscattered hydrogen atoms obtained using hydrogen beams (H^-,H^+,H_2^+, and H_3^+) in the range from 200 eV to 10 keV on molybdenum targets cleaned under UHV conditions and monitored by low-energy-ion scattering. The data show significant deviations from earlier reports,[1,4,5] and may lead to a better understanding of the underlying physical phenomena.

II. EXPERIMENTAL TECHNIQUE

The apparatus for these experiments consists of an ion source, electrostatic focus lenses, a Wien velocity filter, and a target chamber. This system is capable of producing mass-separated atomic and molecular-ion beams in the range from 200 eV to 10 keV. The target chamber is an ultrahigh-vacuum chamber capable of sustaining an ambient pressure of 10^{-10} Torr. Sensitive single-photon counting techniques with a 0.3 m-f/5 monochromator were used to detect and process the photon signals measured at 90° to the beam direction. The molybdenum polycrystalline target samples were chemically cleaned in a standard manner and sputter cleaned within the target chamber with a 6-keV beam of argon for approximately $\frac{1}{2}$ h at an angle of incidence of 60° to the surface normal. By this means oxygen could be removed from the targets to less than 2% of a monolayer. The amount of oxygen and other contaminants was monitored using a low-energy ion-scattering-spectroscopy (ISS) system consisting of an electrostatic analyzer free to move through laboratory scattering angles ranging from 20° to 135°,[6] and associated electronics. The detection limit of the ISS system is estimated to be approximately 2% of a monolayer.[7]

III. RESULTS

The principle feature in each observed spectrum was Balmer-line radiation. The only other discernable feature was broadband continuum radiation previously reported.[8-11] An example of a spectral scan is shown in Fig. 1. The dependence of the backscattered photon yield on primary current was found to be linear over a range of beam current from 1 to 30 μA. All measurements were performed within the linear region and the photon yield normalized to the current (i.e., the number of incident molecules). Doppler-shift measurements were performed on the H_α (6562.8 Å) backscattered hydrogen line owing to H^+,H_2^+, and H_3^+ bombardment of Mo each at 6-keV-beam energy

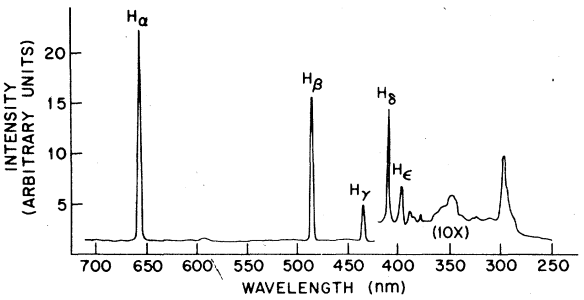

FIG. 1. Optical spectrum from a molybdenum surface under 6-keV H_2^+ bombardment at normal incidence. H_α to H_ϵ are the first seven emission lines from the Balmer series of hydrogen. The continuum below 370 nm is characteristic of Mo (see Ref. 8).

at three different target orientations: (i) target normal oriented along the incident-beam direction, (ii) target normal oriented at 60° from the incident-beam direction facing the spectrometer (H_α shifted toward the blue), and (iii) target normal oriented at 60° from the incident-beam direction facing away from the spectrometer (H_α shifted toward the red). Doppler line shifts may be simply calculated from the equation

$$\Delta\lambda = -(v/c)\lambda\cos\theta\,, \tag{1}$$

where v is the primary ion velocity $= (2E/M)^{1/2}$, E is the primary ion energy, M is the primary ion mass, λ is the unshifted wavelength which is 6562.8 Å, and θ is the angle between the direction of the scattered particle and the spectrometer. A summary of the data is given in Table I. Here an effective angle of scattering is calculated from the data as

$$\theta_{\text{eff}} = \cos^{-1}\left(-\frac{\Delta\lambda}{\lambda}\frac{c}{v}\right). \tag{2}$$

The effective scattering angles listed in Table I show that the distribution of excited hydrogen atoms peaks not in a specular direction but at exit angles which are more nearly grazing with respect to the surface. The large Doppler shifts are strong evidence that the particles that contribute most to photon emission are those that are reflected from the surface with velocities near the primary incident ion velocity. Note that the blue-shifted data in Table I indicates that as the energy per nucleon decreases, the scattering angle approaches the specular reflection angle ($\theta_{\text{specular}} = 30°$).

TABLE I. Doppler-shifted spectral line measurements. [a]

		Red shift		Blue shift	
	$\Delta\lambda$ (calc) [b] (Å)	$\Delta\lambda$ (meas) (Å)	θ_{eff} (deg)	$\Delta\lambda$ (meas) (Å)	θ_{eff} (deg)
H^+	20.3	13.8	53.9	15.0	50.2
H_2^+	14.3	9.7	54.1	11.6	45.5
H_3^+	11.7	7.8	54.8	10.0	42.3

[a] All measurements were performed at 6-keV-beam energy on molybdenum.

[b] Calculation assumes perfect specular reflection ($\theta_{\text{specular}} = 30°$).

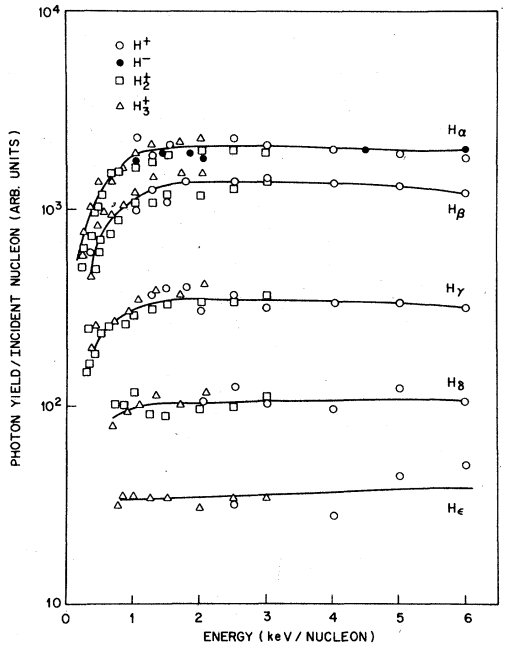

FIG. 2. Energy dependence of the yield per incident nucleon of Balmer-series photons for bombardment of molybdenum with H^- (black circles), H^+ (open circles), H_2^+ (squares), and H_3^+ (triangles) at normal incidence.

The dependence of the photon yield on primary ion energy is illustrated in Fig. 2. The results are independent of the primary particle (atom or molecule) and of initial-charge state, and dependent only on velocity per incident nucleon. Although quite different from earlier reports,[4] all the Balmer-series spectral lines have a similar distribution of photon yield as a function of primary energy.

The dependence of H_α photon yield on partial pressure of oxygen is illustrated in Fig. 3 for H^+, H_2^+, and H_3^+ bombardment of an initially clean molybdenum surface. The amount of oxygen contamination at low partial pressure (10^{-11} Torr) was monitored to be less than 2% of a monolayer using the ISS system. At higher oxygen pressures (10^{-7} Torr) surface coverage was measured (by observing the decrease in the molybdenum surface backscatter peak) to approach a monolayer (see

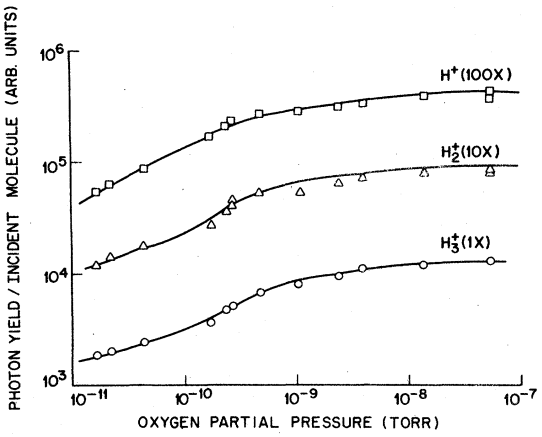

FIG. 3. Dependence of the molybdenum bombardment induced H_α yield normalized to beam current on oxygen partial pressure (particle energy: 2-keV/incident nucleon, normal incidence).

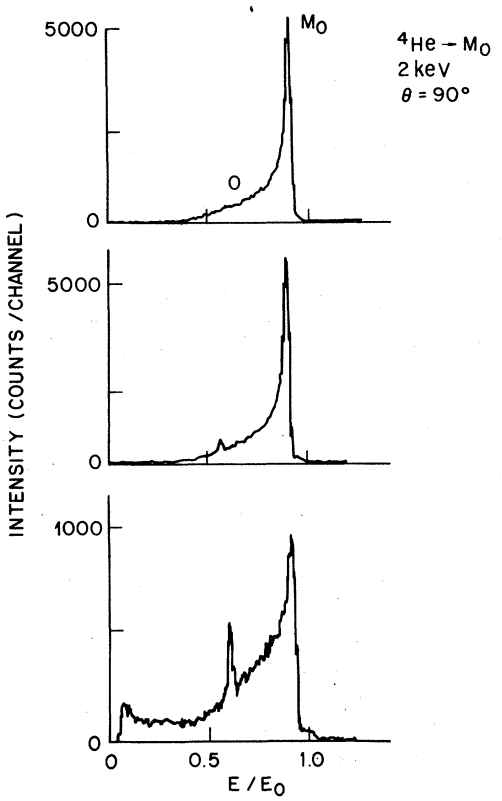

FIG. 4. Low-energy ion-scattering spectroscopy (ISS) measurements of surface composition of molybdenum at a partial pressure of oxygen below 10^{-11} Torr, after Ar^+ bombardment (top); after 1 h at 10^{-11} Torr with H^+ beam on (middle), and at 2×10^{-7}-Torr oxygen partial pressure (bottom). The spectra are a measure of backscattered He^+ with a primary energy of 2 keV observed at a laboratory scattering angle of 90°. The ISS system is capable of detecting oxygen to 2% of a monolayer (see Ref. 7).

Fig. 4). From Fig. 3, we observe that the H^+, H_2^+, and H_3^+ photon yield results normalized to beam current plotted as a function of oxygen pressure exhibit equivalent behavior. Indeed, we observe an increase by a factor of approximately 7 in photon yield in each case with increased partial pressure of oxygen over the pressure range measured. Rausch *et al.*,[5] also studying hydrogen on molybdenum over nominally the same pressure range of oxygen, reported an increase in yield by only a factor of approximately 1.5. The larger effect observed in this work is presumably a result of the fact that we have eliminated oxygen from the surface much more thoroughly in our clean experiments than was accomplished in previous studies. It is clear that a low partial pressure of oxygen is a necessary, but of course not a sufficient, condition to obtain an oxygen-free target surface.

IV. DISCUSSION

It will be useful for this discussion to write the following approximate relation for the photon yield:

$$Y \propto P_{ie} P_{id} RN , \tag{3}$$

where P_{ie} is the excitation probability, P_{id} is the subsequent radiationless deexcitation (or ionization) probability, R is the particle reflection coefficient, and N is the incident nucleon flux. Thus, at least tentatively, we will picture the phenomenon as a two-step process, excitation via violet collision at or near the surface followed by deexcitation as the atom recedes. Experimental evidence for and against this picture will be outlined below.

First, linearity of the photon yield with respect to N, the incident nucleon flux, was demonstrated in our experiments to a high degree of accuracy over a current range from about 0.1 to 30 μA. Thus, we are looking at the results of individual particle-surface encounters and not any cooperative or overlapping cascade effects. In fact, our observation that photon yield per nucleon is the same for incident H^+, H_2^+, and H_3^+ demonstrates that each nucleon in the molecular species behaves essentially independently of its partners.

The particle reflection coefficient R in Eq. (3) can be computed quite accurately from assumed interaction potentials. Using reflection coefficients computed by Oen and Robinson[12] we have divided the measured photon yields by RN. As shown in Fig. 5, the resulting reduced yield depends very nearly exponentially over a wide range of the reciprocal of perpendicular particle velocity; i.e., the product $P_{ie}P_{id}$ of Eq. (3) depends exponentially on $v_\perp^{-1}$. The data represented in Fig. 5 (and Fig. 2) were taken with the beam at normal incidence to the target with the resulting photons originating

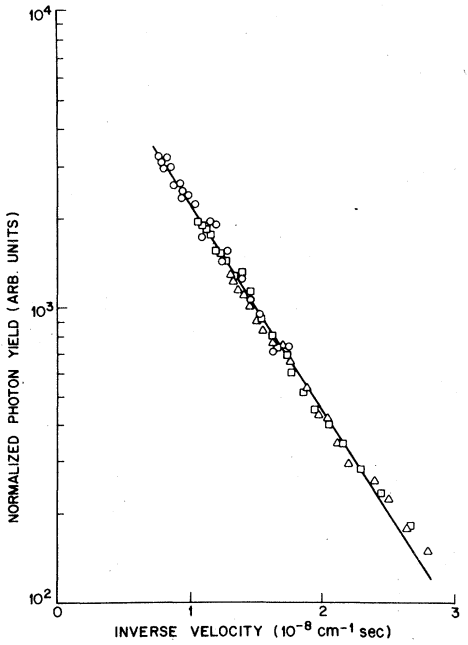

FIG. 5. Dependence of the H_α photon yield per reflected particle as a function of the reciprocal incident proton velocity for H^+ (circles), H_2^+ (squares), and H_3^+ (triangles) at normal incidence on clean Mo.

significantly in front of the target surface (approximately 2 mm). This experimental arrangement, along with the fact that the spectrometer wavelengths were selected in the middle of the Doppler curve, ensured that the emitted particles were backscattered largely perpendicular to the surface.

With this knowledge let us assume for now that the excitation probability varies slowly with incident velocity so that the exponential dependence on $v_\perp^{-1}$ is owing essentially to deexcitation. This is consistent with the Auger and resonance deexcitation mechanisms proposed by Hagstrum,[13] for which the deexcitation transition rate is approximated by

$$P(r) = A \exp(-ar), \tag{4}$$

where A is the radiationless transition rate at the surface and r is the distance from the surface. Using the rate equation we can then derive the probability P_{id} that the backscattered excited hydrogen atom can escape without undergoing radiationless deexcitation. This is given by

$$P_{id} = \exp(-A/av_\perp), \tag{5}$$

where $v_\perp$ is the velocity component normal to the surface. For H^+ on clean Mo the best fit to our experimental yields gives $A/a = 1.6 \times 10^8$ cm/sec. For Mo with about 0.5 monolayer of O adsorbed as measured by our ISS system A/a is reduced to about 1.0×10^8 cm/sec. These results are in excellent agreement with previous findings at higher energies (20 keV) of $A/a = 1.6 \times 10^8$ cm/sec for H on Mo at 10^{-9} Torr and $A/a = 1.2 \times 10^8$ cm^{-1} at 2×10^{-7} Torr.[5]

The exponential dependence of photon yield on velocity is strong evidence that deexcitation processes dominate our observations. The enhancement owing to oxygen is also consistent with this mechanism. Molybdenum has a high density of unfilled d states lying just above the Fermi level that are resonant with excited atomic levels and can be expected to promote efficient deexcitation and/or ionization; i.e., removal of excited states. The presence of an oxygen layer would be expected to cause these Mo d levels to contract and reduce their overlap with atomic levels, thereby reducing the rate of deexcitation. Thus we observe a smaller A/a value for oxygen-covered Mo than for clean Mo.

The primary excitation mechanism is less clear than deexcitation. We believe that excitation occurs primarily at or near the surface in a violent collision with one or more surface atoms, following which the excited particles leave the surface with high velocity. The great majority of backscattered neutral or charged hydrogen has in fact a broad energy distribution, which depends on the primary energy in a rather complex manner.[14-17] Here the nature of the backscattering process discriminates against slower particles which emerge from the bulk of the solid being excited in two ways. The first is that the slower particles will at most experience a less violent collision with a surface atom, resulting in generally lower excitation probability; and the second is that they are more effectively deexcited owing to their lower speed. The Doppler-shift measurements, which are consistent with the view that excited particles are moving with almost as high velocity as the incident beam, support the assumption that those atoms that are ultimately formed in excited states have not penetrated significantly into the solid.

It is interesting to note that the dependence of excited-state population on principal quantum number n is observed to fit very closely an n^{-6} behavior. The significance of this observation is not clear at this time.

Neither the excitation nor deexcitation processes are satisfactorily understood at this time. It has not even been established that these two processes can be treated as independent. We note in this regard that for H^+ on clean Mo, we observe that excited states of H with principal quantum number ranging from $n = 3$ to $n = 7$ all produce roughly the same value of A/a. If this parameter is truly a

measure of the deexcitation probability alone, then we would expect it to depend sensitively on the overlap of the electronic wave functions of the atom with those of the solid. This overlap should vary significantly for states of different principal quantum numbers. The experiments reported here provide some information, but more work is required. For example, experiments with a wide variety of target materials should verify whether the deexcitation process is sensitive to the density of unfilled levels above the Fermi level, as was suggested above. In addition, experiments, now in progress,[18] which monitor the polarization of radiation from excited atomic states should help identify and clarify the nature of these excitation and deexcitation mechanisms.

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