PHYSICAL REVIEW A VOLUME 17, NUMBER 1 JANUARY 1978

Excited H formation by 2–200-keV H_1^+, H_2^+, and H_3^+ ion impact on metal surfaces

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(Received 24 August 1977)

The coefficient for emission of the Balmer β line from backscattered H atoms has been measured for 2–200-keV hydrogen ion impact on polycrystalline targets of Mo, Cu, and stainless steel. The dependence on primary energy is successfully modeled using a modification of a formulation used previously at low (2–30-keV) impact energies.

When an energetic hydrogen-ion beam is incident on a metal surface, a small fraction of the projectiles will backscatter as excited hydrogen atoms. These atoms may lose their excited electron by radiationless mechanisms during interaction with the surface, or they may recede beyond the interaction region and subsequently emit photons by normal radiative decay. The integrated photon intensity in a spectral line is related to the backscattered flux of excited atoms whereas the line profile yields information on the distribution in speed and angle of the particles. The observed spectral lines are Doppler broadened because most particles escape from the surface with an energy greater than 1 keV (Ref. 1).

A model which can predict the backscattered flux of all particles (independent of charge or excited state) was developed by McCracken and Freeman[2] and utilized by Baird *et al.*[3,4] to predict backscattering of excited particles for impact energies to 30 keV. It was assumed that the projectile penetrating a target undergoes a single large-angle scattering event and returns to the surface, while in the target the particle loses its energy by electronic stopping. Because of variations in energy loss, penetration depth, and scattering angle, the backscattered flux will exhibit a velocity distribution. By summing the contribution to the backscattered flux over all possible velocities of the emergent particle, this model predicts the integrated intensity of emission in a particular transition. The following equation has been used[5] to predict γ_j, the number of backscattered atoms in the excited state j per incident ion:

$$\gamma_j(E_0, \phi) = \int_{v_l}^{v_u} f(v_\perp, E_0, \phi) F_j(v_\perp) \times \exp(-A/av_\perp)\, dv_\perp \,. \qquad (1)$$

Here E_0 is the incident particle energy and ϕ the angle of incidence. The factor $f(v_\perp, E_0, \phi)\, dv_\perp$ represents the flux of backscattered particles emerging with a velocity component perpendicular to the surface between $v_\perp$ and $v_\perp + dv_\perp$; this can be obtained from the predictions of McCracken and Freeman.[2] The factor F_j is the probability that the backscattered particle is in an excited state j; this may be written as a product between P_0, the fraction of recoils which are neutral, and P_j, the fraction of neutrals which are excited (i.e., $F_j = P_0 P_j$). The exponential factor in Eq. (1) is explained in our earlier work and accounts for the loss of excited atoms by radiationless decay mechanisms; it has been suggested[3,4] that the decay mechanism is by an Auger transition, and the constants A and a are related to the height and width of the potential barrier between the recoiling atom and the solid. In performing the integration of Eq. (1), we use[5] an upper limit of velocity (v_u) that corresponds to projectile scattering from a surface atom without penetration, and we adopt a lower velocity limit corresponding to an emergent energy of 20 eV; below this lower limit we presume that projectiles are trapped in the lattice and do not recoil.

Strictly speaking, Eq. (1) predicts the formation of an excited state j while the observations are of emission in the transition $j \rightarrow k$. We have however shown[5] that cascade population of $n=4$ states of hydrogen is negligible so that the measured emission coefficient γ_{jk} (Balmer β photons per incident ion) is proportional to the predicted excitation coefficient γ_j (reflected atoms in the $n=4$ state per incident ion). In our previous work[1,3-5] we have made relative measurements of γ_{jk} as a function of impact energy E_0 in the range 5–30 keV and fitted γ_j from Eq. 1 to the data, permitting us to derive a value for the ratio A/a; the assumption was made that F_j was a constant. For targets of Cu, Mo, and type 304 stainless steel, the value of A/a was determined[1] to be 1.7×10^8 cm/sec with an accuracy of ±25%.

The objective of the present work was to extend the previous studies (limited to a maximum impact energy of 30 keV) up to impact energies of 200 keV. It was to be anticipated that at high energies the factor F_j would be energy dependent and the assumption of a constant F_j made in earlier work

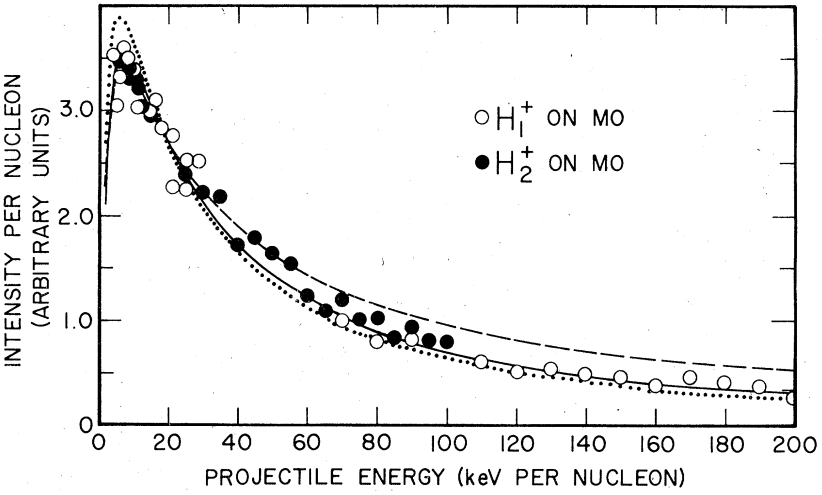

FIG. 1. Projectile-energy dependence of Balmer β line emission coefficient γ_{jk} for hydrogen backscattered from a Mo target. Data points, experimental measurements; lines, predicted values from the model normalized to experiment at 30 keV. Dashed line, for F_j constant and $A/a = 1.7\times10^8$ cm/sec; dotted line, for an energy dependent F_j and $A/a = 1.7\times10^8$ cm/sec; solid line, for an energy dependent F_j and $A/a = 1.9\times10^8$ cm/sec.

would be invalid. Thus, this present extended study will permit a determination of how the formation of backscattered excited atoms varies with impact energy, and might provide a test of recent theoretical predictions.

The only substantive change in experimental details from our previous work[3] has been the use of a different ion accelerator to increase the projectile energy from the previous upper limit of 30 keV to the present limit of 200 keV. Briefly, the accelerated ions strike the target at an incident angle of 60° (angle between the ion beam and target normal). An optical monochromator views the target at 90° with respect to the ion beam. Wide entrance and exit slits were employed on the monochromator to maximize signal-to-noise ratio; this resulted in a rather poor resolution (48 Å). We scanned through the Doppler-broadened Balmer β line and integrated the area under the peak. All values of γ_{jk} reproduced here are relative values; absolute measurements of γ_{jk} have been presented in earlier work.[4,5] The integrated line intensity as a function of incident projectile energy is shown in Figs. 1–3 for targets of Mo, Cu, and type 304 stainless steel, respectively. Data at energies less than 30 keV were reported earlier,[1] but are also reproduced here. We used not only H_1^+, but also H_2^+ and H_3^+ projectiles, because it was previously[6] shown that at low ambient oxygen pressures ($\sim 10^{-11}$ torr) in the target, all γ_{jk} for H_2^+ and H_3^+ with energy E are the same as γ_{jk} for H_1^+ with energy $\frac{1}{2}E$ and $\frac{1}{3}E$, respectively.

The intention was to model the data using Eq. (1) to predict γ_j and to compare it with experiment assuming that this also represented the relative behavior of the measured emission coefficient γ_{jk}. The velocity distribution of backscattered par-

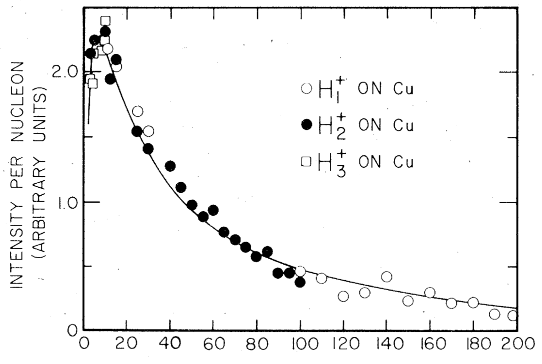

FIG. 2. Projectile-energy dependence of Balmer β line emission from backscattered H* atoms for a Cu target. The solid line indicates theoretical values with A/a 1.9×10^8 cm/sec and F_j is dependent on emergent particle energy.

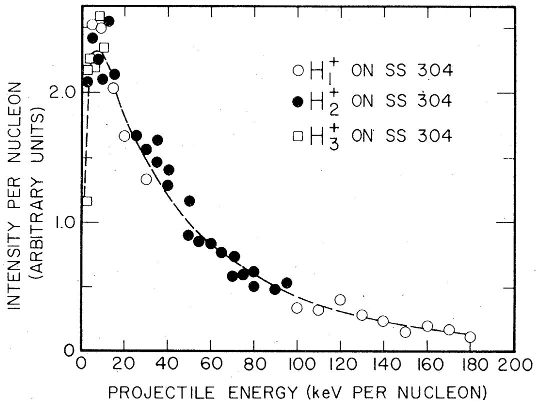

FIG. 3. Projectile-energy dependence of Balmer β line emission from backscattered H* atoms for a stainless steel target (SS304). The dashed line indicates the trend of the data.

ticles, $f(v_\perp, E_0, \phi)\,dv_\perp$ was to be obtained from the formulation of McCracken and Freeman.[2] This formulation is strictly valid only for those incident velocities less than the velocity of an electron in the first Bohr orbit where the LSS theory of electronic stopping is valid[7]; this limits applicability to protons of less than 25-keV incident energy. However, McCracken and Freeman[2] showed that the formulation agreed very well with direct experimental measurements of backscattering with 120-keV incident protons. Therefore we have continued to use that prediction here.

In the analysis of earlier experiments at lower impact energies (<30 keV) we have assumed that the probability of a recoil being an excited neutral, F_j, was independent of recoil velocity. This is not likely to be correct at the higher energies of the present experiment, and we have examined various energy-dependent forms. The factor F_j can be written as the product $P_0 P_j$, where P_0 is the probability of the recoil being a neutral and P_j is the probability of the neutral recoil being excited. There are two recent theoretical predictions of P_0. One is by Cross[8] and considers the projectile to be undergoing successive processes of charge-transfer neutralization and stripping in the solid. The other is by Kitagawa and Ohtsuki[9]; it considers the projectile to remain stripped in the solid and allows neutral formation by an electron-ion recombination mechanism as the projectile escapes from the surface. Unfortunately, the success of Cross's theory is confined to carbon targets and to particles with exit energies $\gtrsim 100$ keV. The predictions of Kitagawa and Ohtsuki[9] are for Au and differ from the experimental data by up to 70% within the energy range 30–200 keV, although at energies below 30 keV the predictions agree with experiment. Since neither prediction adequately covers the range of our experiment, we decided instead to use the experimental measurements of P_0 for H^+ on Mo and Cu by Behrisch *et al.*[10] and to extend their range by using the low-energy approximation of Kitagawa and Ohtsuki[9] at energies $\lesssim 20$ keV and the high-energy approximation of Cross[8] at energies $\gtrsim 150$ keV. It would appear that the value of P_0 is not a sensitive function of material. The experimental data of Behrisch *et al.*[10] for Mo and Cu are within 20% of experimental data for C, Au, Cr, Ni, and Al by Chateau-Thierry and Gladieux[11]; the theoretical values by Cross[8] for C are similar to the theoretical values of Kitagawa and Ohtsuki[9] for Au. Consequently we feel that our use of experimental data with extrapolations from theory is quite reliable. For completeness we reproduce in Fig. 4 the actual values of P_0 that we employed. Both the theory of Cross[8] and that of Kitagawa and Ohtsuki[9] suggest that the probability of a neutral being in an excited state, P_j, is inversely proportional to the cube of the principal quantum number, so we assume that relationship here. Thus the energy dependence of $F_j(=P_0 P_j)$ is given in relative terms simply by the variation of P_0.

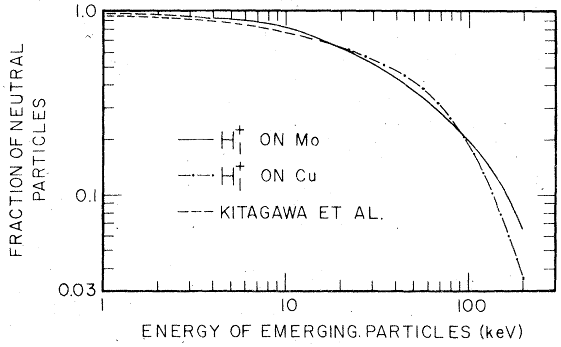

FIG. 4. The values of neutralization probability P_0 assumed in the model. These are determined from the experimental data of Behrisch *et al.*[10] extrapolated to low energies by the theory of Kitagawa and Ohtsuki[9] and to high energies by the theory of Cross.[8]

In Fig. 1 we show a variety of computed excitation coefficients γ_j [from Eq. (1)] normalized to the experimental emission coefficients γ_{jk}; both computed and experimental data are relative values. One computed curve employs a constant F_j and a value for A/a of 1.7×10^8 cm/sec; these are the conditions used in our earlier analyses[1] for data at energies below 30 keV. As expected there is a discrepancy between computation and experiment at high energies. A second computation employs the same survival parameter A/a, but an energy dependent F_j obtained in the manner described above. In this case the predictions of the model agree well with experiment. For completeness a computation is also shown with the F_j derived as described above and the survival parameter A/a adjusted to give the best fit to experiment. In this case, the value of A/a derived by fitting to the data comes out as 1.9×10^8 cm/sec; within the accuracy we assign[1] to A/a (±25%) this is not significantly different from the previously derived[1] value (1.7×10^8 cm/sec). We have also utilized Kitagawa and Ohtsuki's prediction of P_0 and find the predicted γ_j to be less than 10% different from the predictions using P_0 from Fig. 4; this prediction is not shown to avoid confusion with the other lines on Fig. 1.

In Fig. 2 we show a single prediction for the Cu target utilizing the neutral formation probability P_0 from Fig. 4 and a survival coefficient A/a of 1.9×10^8 cm/sec; again the prediction agrees with measurement within experimental accuracy. We show no predicted γ_j for the case of stainless steel in Fig. 3 since there is not experimental data for P_0 on which to base the model; the line on that figure is drawn freely to indicate only the general trend of the experimental data.

Some measurements of Doppler-broadened line shape were performed and compared with the predicted shape from the model in the manner of our earlier work.[1] These results are not presented in detail since they were taken with a poor spectral resolution (to enhance signal strength) and therefore are dominated by the instrumental linewidth. As an example, the width of the line at half maximum intensity for 180-keV H^+ on Mo was measured to be 75 Å using the instrumental resolution of 48 Å. The predicted width using the model with P_0 from Fig. 4 and $A/a = 1.9\times 10^8$ cm/sec with allowance for instrumental linewidth is 77.1 Å; this is in satisfactory agreement within the experimental accuracy. By contrast the predicted width assuming probability of excited-state formation is not dependent on energy (i.e., $F_j = \text{const}$) is 87.7 Å. Similar figures are found for the Cu target. Thus the line shape is consistent with the adopted model.

The present work has extended the previous measurements[1,3-5] to higher impact energies and demonstrated that the model adopted for predicting the emission coefficient remains valid provided account is taken of the energy dependence of the probability of recoils being excited F_j. It is clear from Fig. 1 that the emission coefficient is not a sensitive function of F_j; assumption of a constant F_j at all energies overestimates the emission coefficient by only a factor of 2 at 200 keV. The emission coefficient for a high-impact-energy proton is dominated by the low-energy recoils which constitutes the greatest part of the recoil energy spectrum.

The predictions of the model are not significantly altered as one changes the adopted value of P_0 from the experimental data of Fig. 4 to the predictions of Kitagawa and Ohtsuki[8] and finally to those of Cross.[9] Although the two theoretical predictions[8,9] are based on entirely different concepts, their predictions are sufficiently close that they agree equally well with our experiment. Thus the present experiment does not provide a test as to which prediction is most accurate.

Our earlier success in modeling[1,3-5] emission coefficients at low energies with a constant F_j is explained by the insensitivity of the model results to the form of F_j adopted.

ACKNOWLEDGMENT

This work was supported in part by the Magnetic Fusion Energy program of ERDA.

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[1] E. O. Rausch and E. W. Thomas, Phys. Rev. A 14, 1912 (1976).

[2] G. M. McCracken and N. J. Freeman, J. Phys. B 2, 661 (1969).

[3] W. E. Baird, M. Zivitz, J. Larsen, and E. W. Thomas, Phys. Rev. A 10, 2063 (1974).

[4] W. E. Baird, M. Zivitz, and E. W. Thomas, Phys. Rev. A 12, 876 (1975).

[5] W. E. Baird, M. Zivitz, and E. W. Thomas, Nucl. Instrum. Methods 132, 445 (1976).

[6] E. O. Rausch, M. W. Murray, H. Inouye, and E. W. Thomas, J. Appl. Phys. 48, 4347 (1977).

[7] J. Lindhard and M. Scharff, Phys. Rev. 124, 128 (1961).

[8] M. C. Cross, Phys. Rev. B 15, 602 (1977).

[9] M. Kitagawa and Y. H. Ohtsuki, Phys. Rev. B 13, 4682 (1976).

[10] R. Behrisch, W. Eckstein, P. Meischner, B. M. U. Scherzer, and H. Verbeek, in *Atomic Collisions in Solids*, edited by S. Datz, B. R. Appleton, and C. Moak (Plenum, New York, 1975), Vol. I, p. 315.

[11] A. Chateau-Thierry and A. Gladieux, in *Atomic Collisions in Solids*, edited by S. Datz, B. R. Appleton, and C. Moak (Plenum, New York, 1975), Vol. I, p. 307.