MOLECULAR EFFECTS IN ION–ELECTRON EMISSION FROM CLEAN METAL SURFACES

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We have measured electron emission yields from clean Al, Cu and Ag under 2–50 keV H^+, D^+, H_2^+ and D_2^+ impact. It is found that molecular ion yields are lower than twice the yield of atomic ions. No isotope effects are observed for equal-velocity ions.

When ions strike the surface of a solid, electrons can be liberated. This phenomenon, known as ion–electron emission (IEE), can be characterized by a coefficient γ defined as the number of electrons ejected per incident ion.

IEE from clean metal surfaces can proceed by two different mechanisms [1]. For projectile velocities v larger than a certain threshold v_{th}, usually of the order of 10^7 cm/s, kinetic electron emission (KEE) occurs, in which the energy to excite target electrons is provided by the kinetic energy of the projectile. At velocities lower than v_{th}, potential electron emission (PEE) may occur, in which the energy required to excite electrons into vacuum is provided by the energy I released in the neutralization of the ion by a target electron. PEE can occur if I is larger than twice the work function of the metal. If we consider these two processes as acting independently, we can write $\gamma = \gamma_p + \gamma_k$, where γ_p and γ_k are the potential and kinetic emission coefficients, respectively. For $v > v_{th}$, we cannot measure γ_p directly, but its value, which is known to be fairly constant for $v < v_{th}$, is expected to drop at higher velocities [2].

The majority of measurements of IEE yields reported in the literature were performed with atomic ions. In the few experiments made using diatomic molecular ions, it was generally found that the yields for these ions were slightly smaller than the sum of the yields for each component of the molecule at the same velocity v; that is: $\frac{1}{2}\gamma(X_2^+, v) < \gamma(X^+, v)$.

An explanation for this molecular effect, first noticed by Hill et al. [3] was offered by Dorozhkin et al. [4]. These authors assumed $\frac{1}{2}\gamma_k(X_2^+) = \gamma_k(X^+)$ and proposed therefore that the effect was due to the fact [4] that PEE yields for molecular ions are generally much smaller than for atomic ions. From this they conclude that measurements of the differential yields $\Delta\gamma$, defined through $\Delta\gamma = \gamma(X^+) - \frac{1}{2}\gamma(X_2^+)$, could be used to derive values of $\gamma_p(X^+)$ above v_{th}, since according to their hypothesis, $\Delta\gamma \approx \gamma_p(X^+)$. Dorozhkin et al. presented results for nitrogen, oxygen and hydrogen ions incident on the (110) face of Cu single crystals. $\Delta\gamma$ was shown to decrease with energy to $\Delta\gamma = 0$ at ~2.8 keV/amu for N ions and at ~4.5 keV/amu for O ions, whereas for hydrogen ions, they found $\Delta\gamma = 0$ over the whole energy range studied, 0.2 to 15 keV. These results are in contradiction with earlier measurements on polycrystalline Cu [5] but it may be possible that channelling played a role in Dorozhkin's experiments.

In order to investigate molecular effects more extensively, we have measured electron yields from clean Al, Cu and Ag surfaces under H^+, D^+, H_2^+ and D_2^+ bombardment in the energy range 2–50 keV. The experimental

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apparatus is described in detail elsewhere [6]. In brief, measurements were performed at pressures in the 10^{-10} Torr range on targets produced by in-situ evaporation of high-purity (>99.99%) materials on a polished stainless steel substrate. In the experiments, the ion beams were incident normal to the target surface. Experimental errors are ± 4% in the yields and $\pm 0.03\gamma$ in the difference $\Delta\gamma$, where cancellation of a number of uncertainties has been taken into account. Special care was taken in the measurements of the beam energy, since to examine molecular effects, the yields for H^+ at an energy E must be compared to those for H_2^+ at energy $2E$. The same sort of comparison is needed to examine isotope effects between H^+ and D^+ ions at the same velocity. In our experiments, E is known to within ±(0.1% + 30 eV); furthermore we found no evidence for isotope effects which are known to be negligible in our energy range [1].

Fig. 1 shows our results of γ for atomic ions and the differences $\Delta\gamma$. An upper limit to $\Delta\gamma$ for the targets investigated, in the limit of low velocities, was estimated as $\Delta\gamma_u = 0.04$ electrons/ion $> \gamma_p(H^+) - \frac{1}{2}\gamma_p(H_2^+)$, from measurements by Carlston et al. [7] of γ for low-energy Kr ions. $\gamma(Kr^+)$ is an upper bound to $\gamma(H^+)$ since (i) $\gamma(Kr^+)$ from ref. [7] may contain a kinetic contribution; (ii) the ionization potential of Kr is slightly larger than that of H, and so $\gamma_p(Kr^+) > \gamma_p(H^+)$ [8] and (iii) the incident beam in the experiments of Carlston et al. may have contained long-lived excited ions and neutrals.

It is apparent from our results that $\Delta\gamma$ is larger than $\Delta\gamma_u$ and that it increases with ion velocity, contrary to the results and predictions of Dorozhkin et al. Therefore, and since γ_p should be a decreasing function of projectile velocity in our range, we must conclude that a molecular effect exists in kinetic ion–electron emission.

Molecular or non-linear effects in electronic excitations have previously been observed in ionization in gas-phase collisions [9] and in the energy loss of fast ions in solids [10]. On general grounds we can expect non-linear effects to occur when the excitation produced by one of the constituent particles of the molecule depends to an appreciable extent on the perturbation which is being produced in the target by the other particles. This will happen when the effective range of action of the field of each particle, a, is of the order of or larger than the interparticle separation r. For

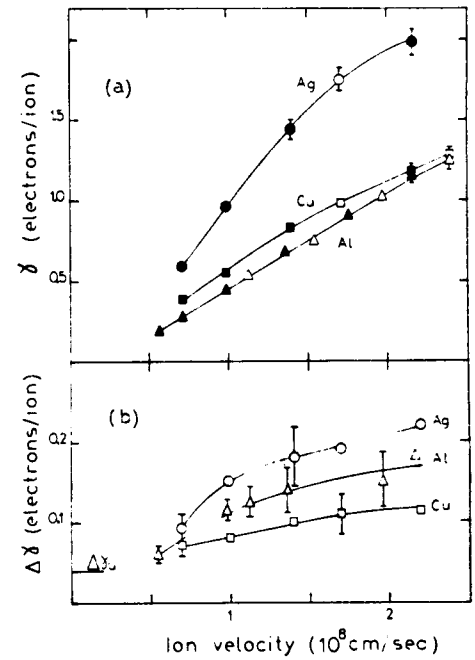

Fig. 1. (a) Ion–electron yields γ for protons (open symbols) and deuterons (filled symbols) on polycrystalline aluminium, copper and silver. Error bars (± 4%) are shown when they are larger than the size of the symbols. (b) $\Delta\gamma$, the difference between the yields for H^+ (D^+) and one-half the yields for H_2^+ (D_2^+); $\Delta\gamma_u$ represents an upper bound to $\Delta\gamma$ in the limit of low velocities (see text). Only some representative error bars are shown for clarity. Lines are meant to guide the eye and have no other meaning.

excitation of the valence electrons of the solid at high velocities ($v > v_F$), $a = v/\omega_p$, where v_F and ω_p are the Fermi velocity and the plasma frequency of the valence electrons [11]. At low velocities, the important parameter to compare to r is the de Broglie wavelength λ_F associated with the electrons at the Fermi surface; Arista [11] has recently shown that interference effects in single-particle excitations by correlated charges at low velocities occurs when $r < \lambda_F = 2\pi/v_F$.

The mean internuclear distance r of H_2^+ will not vary much as a result of multiple scattering when the ions penetrate the solid over distances of the order of the mean electron escape depth (~20 Å [1]) and so r will be only slightly larger than that for a free H_2^+ molecule, $r \approx 1$ Å. This value is smaller than λ_F for the targets investigated (3.7–5.3 Å) and of the order of the spatial extent of the easily excitable d-shells of Cu and Ag [12]. Therefore, non-linear effects should occur in the exci-

tation of valence and d-shell electrons above the vacuum level as observed.

Molecular effects in IEE with low-velocity heavy ions should be smaller since in this case multiple scattering will be more important in causing the initial internuclear separation to increase upon penetration in the target. Furthermore, an effect additional to the one discussed above will occur at high velocities. Electron loss from the projectile [13] will give an additional contribution to γ_K, this effect will act in an opposite way as observed in this work, since it will contribute to $\gamma_K(H_2^+)$ but not to $\gamma_K(H^+)$.

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