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Formation and survival of H^- and C^- ions transiting ultrathin carbon foils at keV energies

Herbert O. Funsten
Mail Stop D466, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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The fraction of negatively charged projectiles existing in a bulk foil and their neutralization at a foil's exit surface are characterized using exit charge-state distribution data for 1–30-keV/amu H and C that transit 1.1-μg cm^{-2} carbon foils. The equilibrium fraction of negative ions in the bulk foil is derived and is observed to decrease exponentially with increasing projectile velocity.

Understanding the evolution of the charge-state distribution, and in particular the negative-ion fraction, of projectiles that interact inside or at the surface of a metal is of interest in low-energy ion scattering, stopping-power studies, negative-ion-beam formation, and fundamental particle-solid physics studies. For projectiles emerging from a solid with a velocity v less than several v_0 where v_0 equals the Bohr velocity, the charge-state distribution can be modified by interactions that occur at the exit surface so that the experimentally measured exit charge-state distribution is potentially quite different from its bulk equilibrium distribution. Numerous studies have examined the observed negative-charge-state fraction by considering the formation of the negative ion only at the surface.[1–4] In light of the possibility that negative ions can exist within a metal,[5,6] we first describe charge exchange in the bulk foil and at the exit surface with particular emphasis on the evolution of the negative charge state, and then we examine experimental results of H and C beams impinging at normal incidence on a 1.1-μg cm^{-2} carbon foil within this framework.

A projectile beam transiting a solid with $v<v_0$ rapidly reaches a charge-state equilibrium that is maintained until reaching the exit surface of the foil. In the bulk, we refer to the equilibrated fraction of a beam of projectile species X in charge state q as $f_B(X^q)$. Charge-exchange interactions have been theoretically modeled over a wide velocity range,[6–9] and results show that the charge-state distribution is driven to a more positive average charge state with increasing velocity.

Numerous calculations[5] indicate that H and other species at rest in a simple metal will preferentially form a stable electron affinity level that, when filled, we refer to as a negative ion. In general, these calculations suggest that the affinity level in a metal is below the conduction band by an energy equal to its affinity level at an infinite distance outside the metal. This results in a large population of negative ions in a metal at low projectile velocities that decreases with increasing velocity as the system is driven toward a higher positive charge state. Indeed, recent calculations on the stopping power of H in Al conclude that the dominant contribution to the stopping power at low velocities is due to H^-.[8,9] Therefore, we assume $f_B(H^-)\approx 1$ in the adiabatic limit $v\rightarrow 0$. A carbon projectile with $v=0$ becomes an interstitial in the foil, and interactions with the foil (e.g., covalent bonding) are highly localized. Therefore, the C interstitial may not be considered a negative ion. However, for $v>0$ we presume that the C projectile interacts with C foil atoms collectively as a metal, so that $f_B(C^-)\approx 1$ for $v \ll v_0$. We furthermore note that excited states of neutral projectiles in the bulk should not be observed due to screening by the valence electrons.[10]

As a projectile beam transits the exit surface of the foil, the bulk charge-state distribution can be altered by resonant and Auger processes, which are dependent on the solid's band structure and the projectile's energy levels. The carbon foils used here are likely amorphous and possibly hydrogenated, with electronic properties similar to graphite, a semimetal, so we represent the band structure as a metal. The carbon foil is assumed to have a valence-band width ε_F of 20 eV and a Fermi level E_F at -4.6 eV relative to the vacuum level E_V.[11]

We define the following projectile energy levels relative to E_V: the ground state $E_I(z)$, the first excited state $E_I^*(z)$, and the affinity level $E_A(z)$. Here, z is the distance from the solid surface and $z=0$ is defined as the point of maximum affinity level width, typically 1–3 Å outside of the image plane. At $z=\infty$ the projectile has discrete atomic levels; closer to the surface, the levels shift due to an image charge in the foil [$E_I(z)$ and $E_I^*(z)$ shift up toward E_V whereas $E_A(z)$ shifts down], and the levels undergo Heisenberg broadening due to an increased electron transition rate between the electron levels in the projectile and solid.[12]

We focus on charge transfer at the exit surface involving a negative ion emerging from the bulk. Since the wave functions of metal and atomic states decrease exponentially at sufficiently large z, the level width of $E_A(z)$ that describes their coupling can be represented using $\Delta(z)=\Delta_0\exp(-\alpha z)$, where Δ_0 equals the half width at half maximum of $E_A(0)$ and α^{-1} represents a characteristic interaction path length over which charge transfer occurs. Since the carbon foils are a relatively high work-function material, $E_A(z)$ resides above E_F for a majority of the interaction time at the exit surface. Therefore, the fraction of negative ions surviving the resonant neutralization interaction at the surface is[12]

$$f(X^-)=f_B(X^-)\exp\left(-\frac{2\Delta_0}{\alpha v}\right). \tag{1}$$

The ratio Δ_0/α provides a measure of the probability of neutralization of negative ions at the exit surface. In Eq. (1), neither Δ_0/α nor $f_B(X^-)$ are known.

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We first derive Δ_0/α by examining the measured charge-state distribution ratios $f(X^{q+1})/f(X^q)$, in particular $f(X^0)/f(X^-)$, which we now quantify. The observed neutral fraction $f(X^0)$ consists of the sum of (a) the fraction of bulk negative ions that are neutralized at the exit surface, $f_B(X^-)-f(X^-)$, (b) the bulk neutral fraction $f_B(X^0)$, and (c) the net fractional gain or loss $\delta(v)$ of the bulk neutral fraction $f_B(X^0)$ resulting from neutralization of positive ions and positive ionization of neutrals at the exit surface. The ratio $f(X^0)/f(X^-)$ is therefore

$$\frac{f(X^0)}{f(X^-)}=\frac{f_B(X^-)\left[1-\exp\left(-\frac{2\Delta_0}{\alpha v}\right)\right]+f_B(X^0)[1+\delta(v)]}{f_B(X^-)\exp\left(-\frac{2\Delta_0}{\alpha v}\right)}, \tag{2}$$

where

$$\delta(v)=\frac{\varepsilon_N(v)f_B(X^+)}{f_B(X^0)}-\varepsilon_I(v). \tag{3}$$

Here, $\varepsilon_N(v)$ represents the neutralization probability of positive ions emerging from the bulk at the exit surface, and $\varepsilon_I(v)$ equals the ionization probability of bulk neutrals at the exit surface.

Several arguments indicate that $\delta(v)\ll 1$ and can be ignored in Eq. (2). First, at low velocities, the small observed fraction of singly ionized projectiles [$f(\mathrm{H}^+)=5.6\%$ at $0.19v_0$ and $f(\mathrm{C}^+)=7.1\%$ at $0.12v_0$] indicates that ε_I is likewise small. Furthermore, with increasing v, ε_I decreases exponentially as expected for resonant ionization.[12] Therefore, we conclude that $\varepsilon_I(v)\ll 1$ in Eq. (3).

We now show that $\varepsilon_N(v)f_B(X^+)\ll f_B(X^0)$ in Eq. (3). In the adiabatic limit $v\ll v_0$, $\varepsilon_N(v)$ approaches unity, but the bulk charge-state distribution is driven toward $q=-1$ so that $f_B(X^+)\ll f_B(X^0)$. This is shown in calculations of H in Al for which $f_B(\mathrm{H}^+)\approx 0$ below $0.2v_0$.[9] With increasing velocity, $f_B(\mathrm{H}^+)$ slowly increases as the bulk charge-state distribution is driven toward a more positive value,[9] but, like $\varepsilon_I(v)$, $\varepsilon_N(v)$ decreases exponentially. Since (a) the calculated H 1s level width [$\sim 10^{-4}$ eV at 7 a.u. (Ref. 13)] is much less than the H affinity level width [~ 0.5 eV at 7 a.u. (Ref. 14)] and (b) the results of this study show that for $v=v_0$ approximately half of the negative ions emerging from the bulk are neutralized at the exit surface, then we obtain $\varepsilon_N(v_0)\ll 0.5$. Therefore, $\varepsilon_N(v)f_B(X^+)\ll f_B(X^0)$ over the velocity range of this study.

Since $\varepsilon_I(v)\ll 1$ and $\varepsilon_N(v)f_B(X^+)\ll f_B(X^0)$, we conclude that $\delta(v)\ll 1$. Equation (2) simplifies to

$$\frac{f(X^0)}{f(X^-)}=\left(\frac{f_B(X^0)}{f_B(X^-)}+1\right)\exp\left(\frac{2\Delta_0}{\alpha v}\right)-1. \tag{4}$$

For the limiting case of $v\to\infty$ in which the projectile's transit time across the exit surface is much less than the characteristic charge-transfer period for surface processes, the observed ratio $f(X^0)/f(X^-)$ equals the bulk ratio. For the adiabatic case $v\to 0$, $f_B(X^0)/f_B(X^-)\to 0$ so that $f(X^0)/f(X^-)\approx\exp(2\Delta_0/\alpha v)$.

The experimental approach used to measure and analyze the exit charge-state distributions and the procedure for thickness measurements of these foils has been described elsewhere.[15] The ratio $f(X^{q+1})/f(X^q)$ that is derived from the measured exit charge-state distributions is shown for H and C projectiles in Figs. 1(a) and 1(b), respectively, including C data for $v>0.7v_0$ from Lennard, Phillips, and Walker[16] and Christensen, Veje, and Hveplund.[17] For all ratios $f(X^{q+1})/f(X^q)$ of both H and C, a similar power dependence on the exit velocity is clearly observed for velocities at which surface effects should be either small or slowly varying, i.e., $v>0.8v_0$. We note that a power dependence of $f_B(X^{q+1})/f_B(X^q)$ for H and He transiting Al where $q\geq 0$ has been predicted from dynamic screening calculations.[6,7] Extrapolation of this power dependence to lower velocities provides the basis for an estimation of the functional form of $f_B(X^{q+1})/f_B(X^q)$. The ratio $f_B(X^0)/f_B(X^-)$ should decrease smoothly with decreasing velocity toward a value of zero at $v=0$, so we choose a power representation of the form $f_B(X^0)/f_B(X^-)=Av^C$. Using this, Eq. (4) was fit to the data in Fig. 1 using A, C, and Δ_0/α as the fit parameters. For the bulk charge-state ratios, we obtain $f_B(\mathrm{H}^0)/f_B(\mathrm{H}^-)=28.4v^{2.89}$ and $f_B(\mathrm{C}^0)/f_B(\mathrm{C}^-)=16.3v^{1.64}$ that are shown as the dashed lines in Figs. 1(a) and 1(b), respectively.

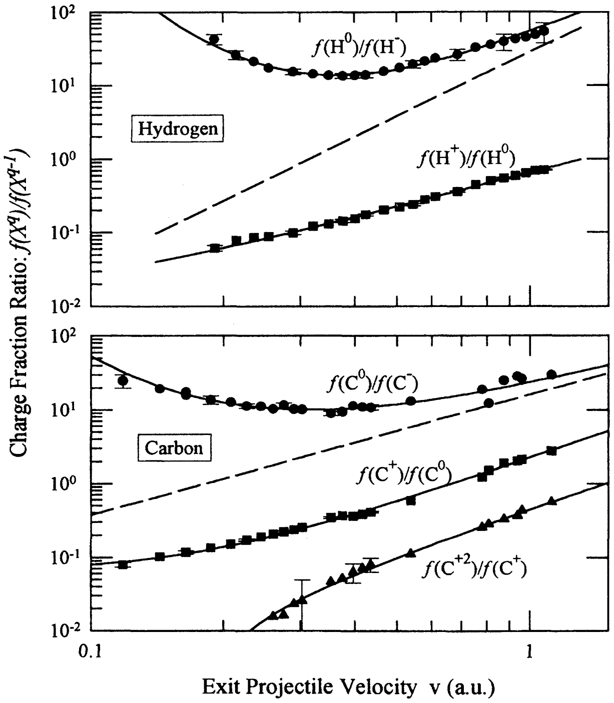

FIG. 1. The ratios of the observed charge-state distributions are plotted as a function of projectile velocity for (a) H and (b) C projectiles. The solid lines are fits to the data, and the dashed lines represent the ratio $f_B(X^0)/f_B(X^-)$ extrapolated to lower velocities. Error bars are based on counting statistics uncertainties.

The derived values of Δ_0/α were 0.32 for H^- and 0.18 for C^-. We note that the value of Δ_0/α was found to be relatively insensitive to the power dependence used: for example, for v^2 to v^5 dependencies of $f(X^0)/f(X^+)$ we obtained Δ_0/α values for H ranging from 0.26 to 0.37. This compares with theoretical values for H^- reflected from W and cesiated W of 0.06,[4] 0.44,[18] and 0.28,[19] and with an

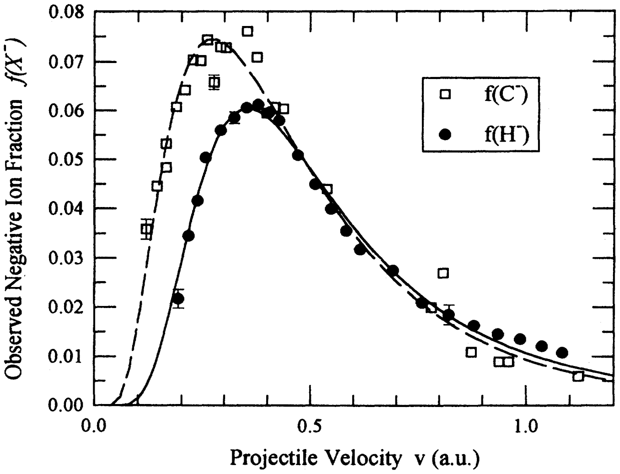

FIG. 2. The observed fractions of H$^-$ and C$^-$ exiting a carbon foil are plotted as a function of projectile velocity. The lines, which agree well with the data, represent Eq. (5) using Eq. (4) for $f_B(X^0)/f_B(X^-)$ and empirical power-law fits for the other charge fraction ratios.

experimental value of 0.14 for H$^-$ exiting a carbon foil based on a different analytical approach.[20] In particular, the value of $\Delta_0/\alpha=0.32$ for H$^-$ derived here is significantly less than the value of $\Delta_0/\alpha=0.82$ for H exiting Al calculated by Nordlander using accurate models of the surface potential and near-surface level shifts.[14] However, calculated values of Δ_0 define $z=0$ as the image plane instead of the definition used here, i.e., the point at which $\Delta(z)$ is a maximum. Since $\Delta(z)$ decreases within 1–4 a.u. of the image plane due to a decrease of the density of states near E_F,[14,21] the calculated values of Δ_0 (and, therefore, Δ_0/α) are overestimates. Consequently, if we use 2 a.u. from the image plane as the cutoff for the calculated transition rate in Nordlander,[14] then we obtain $\Delta_0/\alpha=0.36$, which more closely agrees with our results.

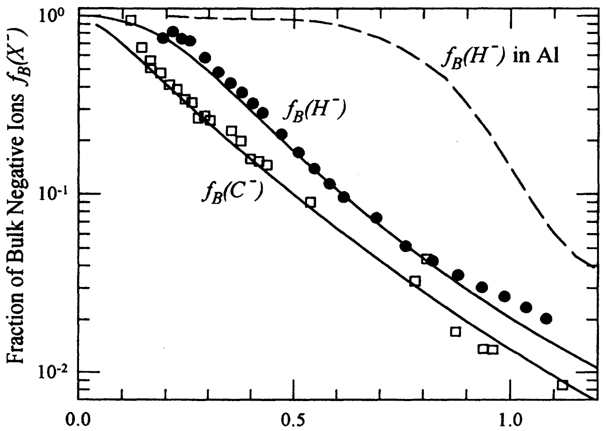

FIG. 3. The derived equilibrium fractions of negative ions in the bulk as a function of projectile velocity for H and C. The dashed line corresponds to the calculated $f_B(\mathrm{H}^-)$ in Al (Ref. 9).

Additionally, Nordlander[14] calculated values of α, which is a function of the electron affinity, for H$^-$ and several other species. Interpolating these values of α for C results in $\alpha(\mathrm{H}^-)/\alpha(\mathrm{C}^-)=0.73$. Using this and the values of Δ_0/α for H$^-$ and C$^-$ derived in this study, we obtain $\Delta_0(\mathrm{H}^-)/\Delta_0(\mathrm{C}^-)=1.27$, which indicates enhanced neutralization of H$^-$ relative to C$^-$. A larger value of Δ_0 correlates with a larger value of E_A-E_F (3.85 eV for H and 3.3 eV for C), which is consistent with observations in which a larger fraction of H$^-$ is observed when the quantity E_A-E_F is decreased by modifying the exit-surface composition.[12,22]

Rearrangement of the identity $\Sigma_q f(X^q)=1$ yields an expression describing the observed negative-ion fraction $f(X^-)$:

$$f(X^-)=\left\{\frac{f(X^0)}{f(X^-)}\left[\frac{f(X^+)}{f(X^0)}\left(\frac{f(X^{+2})}{f(X^+)}+1\right)+1\right]+1\right\}^{-1}, \qquad (5)$$

where $f(X^{+2})=0$ for H. After substituting Eq. (4) for $f(X^0)/f(X^-)$ and then using empirical representations $f(\mathrm{H}^+)/f(\mathrm{H}^0)=0.64(v^{1.6}+0.019)$, $f(\mathrm{C}^+)/f(\mathrm{C}^0)=2.21(v^{2.1}+0.028)$, and $f(\mathrm{C}^{+2})/f(\mathrm{C}^+)=0.46(v^{2.0}-0.029)$ (solid lines in Fig. 1), we obtain the solid lines shown in Fig. 2 for $f(\mathrm{H}^-)$ and $f(\mathrm{C}^-)$. These results show that Eq. (5), derived using Eq. (4) with a power representation of $f_B(X^0)/f_B(X^-)$, accurately represents the observed negative-ion data.

Since $f(\mathrm{H}^-)$ and $f(\mathrm{C}^-)$ are known and Δ_0/α values were derived for H$^-$ and C$^-$, inversion of Eq. (1) into $f_B(X^-)=f(X^-)\exp(2\Delta_0/\alpha v)$ yields the fraction of H$^-$ and C$^-$ in the bulk. The result is shown in Fig. 3, where the points represent $f_B(X^-)$ derived using $f(X^-)$ data (points in Fig. 2) and the lines represent $f_B(X^-)$ derived using $f(X^-)$ in Eq. (5) (solid lines in Fig. 2). Both $f_B(\mathrm{H}^-)$ and $f_B(\mathrm{C}^-)$ approach a value of unity when $v\to 0$ and decrease exponentially with increasing projectile velocity. We note that for $v\approx 0.5v_0$, $f_B(\mathrm{H}^-)$ for a carbon foil is nearly an order of magnitude less than $f_B(\mathrm{H}^-)$ calculated for H transiting Al (dashed line in Fig. 3).[9]

The maximum of the observed negative-ion yield of H$^-$ and C$^-$ occurs at approximately $0.4v_0$, which is similar to the results of high-angle scattering studies in which projectiles penetrate into the bulk.[1–4] Indeed, negative-ion yields for large work-function solids have been found to be considerably higher for large-angle scattering and foil transmission than for grazing angles of incidence in which the projectile interacts with the surface only,[2,3,23] indicating that bulk processes are responsible for the high negative-ion yield. In contrast to numerous high-angle scattering studies[1–4] of H projectiles that attributed negative-ion formation to processes at the exit surface only, we assumed here that negative ions exist in the bulk foil, and we derived the bulk equilibrium fraction of negative ions, which was found to have an exponential dependence on the projectile velocity.

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