Identification of the Mechanism for Kinetic Emission in keV Proton Cu(110) Collisions

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Absolute electron spectra arising from grazing collisions of keV protons with a single-crystal Cu(110) surface are reported. From the experimental data, and from a comparison with known ionization cross sections in gas phase collisions, it is concluded that the mechanism responsible for kinetic emission is the perturbation of localized electrons during several "distant collisions" of the neutralized H atom in its ground state. For the first time an approximate theoretical description for kinetic emission formulated for keV collision energies is found to be consistent with the experimental data.

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The emission of electrons in collisions of ions or atoms with surfaces plays a central role in the physics of particle-solid interactions and has therefore been studied extensively in the past. One may distinguish two fundamentally different types of processes that contribute to electron emission: potential emission, which may be viewed as a spontaneous electronic transition that even occurs at vanishing particle velocity, and kinetic emission, which is caused by particle velocity and therefore has a kinetic energy threshold. Our present contribution concerns kinetic emission. A number of reviews on this subject have been published recently. The experimental situation is surveyed in the articles of Hofer [1], Hasselkamp [2], and Varga and Winter [3], and an overview of recent theoretical work may be found in articles by Roesler and Brauer [4] and Sigmund [5]. In spite of the huge amount of published work on kinetic emission, there are still many open questions. This is especially true for particles velocities (v_p) that are smaller or are of the same order of magnitude as the velocities (v_{el}) of the bound electrons of the solid target. The fundamental problem in this velocity region is the following: While the main ionization mechanism operative at high particle velocities ($v_p \gg v_{el}$)—namely, the momentum transfer from the swift projectile to a free target electron in a direct binary encounter—does not lead to ionization anymore, still high ionization yields of the order of one electron per projectile are observed and lead to electron spectra extending up to 100 eV and more. No mechanisms that could explain these findings have been identified so far [5]. The reasons are that (i) the physics of ion-surface collisions is rather complex as compared to gas phase collisions, for which the ionization phenomena in this energy region are well understood [6] and (ii) the experiments carried out in the past have usually not been sufficiently selective, allowing, in principle, several possible mechanisms to participate. For instance, if a particle beam is directed onto a surface, many atomic collisions at different impact parameters, as well as mechanisms related to the collective nature of the electronic system of the target, may contribute to the electron yield. We report in this Letter experimental results that have been obtained under rather selective conditions that avoid most of the mentioned difficulties of interpretation. Guided by these results we were able to clearly identify the main mechanism of kinetic emission at low particle velocities.

The present experiment is carried out in an UHV apparatus at a base pressure of 2×10^{-10} torr. A beam of mass-selected H^+ ions in the keV range is directed at a grazing angle of incidence of 2° onto a sufficiently clean and stepless Cu(110) surface. The quality of the surface was checked by standard ion-scattering techniques. The azimuthal angle of incidence is chosen as 22° with respect to the closest packed surface row. Under these conditions the H^+-ion trajectories remain above the outermost layer of surface atoms throughout the collision, and no "hard" collisions with surface atoms can occur because the surface atoms lie in each other's "shadow cones." This is also verified by measuring the backscattered particles, which are observed to be specularly deflected. The electrons emitted due to these "distant collisions" are energy analyzed and detected in the direction of the surface normal. Three examples of absolute spectra, observed at proton energies of 2, 3, and 4 keV, are shown in Fig. 1. The spectra are corrected for an energy dependent transmission function of the electrostatic analyzer. The decrease of intensity of all spectra below ca. 5 eV is probably caused by stray fields. The absolute calibration was achieved by estimating the detection efficiency for the electrons from the geometry of the setup in addition to measuring the primary beam intensity by a Faraday cup and is expected to be accurate within a factor of 2. The total electron intensity of the 3 keV spectrum is 0.5–1 electron per projectile.

For the interpretation of the spectra it is important to point out the following: (i) During the rather slow approach to the surface there is sufficient time for the ion to be converted to a neutral atom in its ground state by Auger-type neutralization processes at distances of ~5 a.u. from the surface [7]; kinetic emission is not

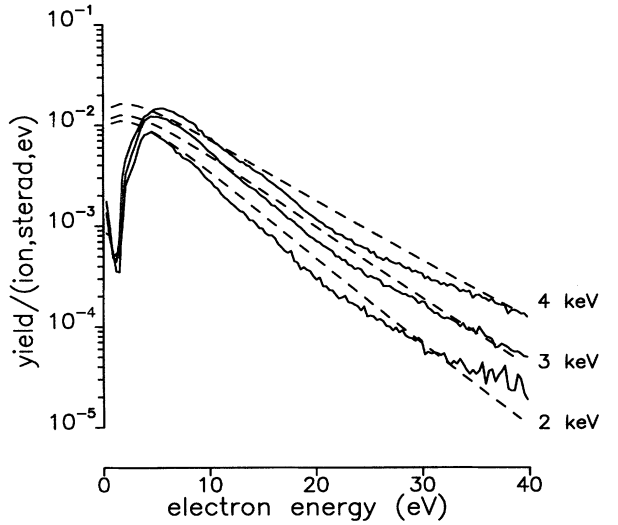

FIG. 1. Kinetic emission spectra for protons colliding at a grazing incidence angle of 2° with a Cu(110) surface at 2, 3, and 4 keV. Solid lines: experiment; dashed lines: calculations.

expected to be effective at these large distances. (ii) The recombination energy of H^+ is so low that the electrons excited in the Auger-type neutralization processes either do not have sufficient energy to escape from the surface, or they appear at energies close to zero. These electrons are therefore not visible in our spectra.

The spectra of Fig. 1 are therefore pure kinetic emission spectra resulting from "distant collisions" of ground-state H atoms. The relevant range of impact parameters and the number of collisions within this range can be estimated from classical trajectory calculations. In our calculations we used a potential obtained by summing 150 projectile-target atom pair potentials. The pair potentials used were screened Coulomb potentials modified to account for extra screening by the free metal electrons. For our conditions (3 keV, 2° grazing angle, 22° azimuth angle) we find that the distances of closest approach to the surface layer vary between 0.55 and 1 a.u., depending on the impact point. If one averages the different trajectories one arrives at an average number of collisions with impact parameters within a certain range. For the range between the smallest impact parameter 0.55 a.u. and about 1.5 a.u., where kinetic emission is expected to be effective, this number is found to be approximately 10.

To explain the measured yield of the order of one electron per ion in terms of "distant collisions" we therefore have to look for a mechanism which leads to collisional ionization with a probability of approximately 0.1 per collision for impact parameters in the range indicated above. From the study of gas phase collisions it is well known that ionization, in collisions between atoms at velocities comparable to the ones in our experiment, occurs due to the perturbation of a localized atomic electron by a swiftly passing charge with cross sections that are quite generally of the order of 1 a.u. [8]. Applying such cross sections to our experimental situation, i.e., to the ionization of Cu by the H atom and of the H atom by Cu, leads to the right order of magnitude for the electron emission. Our qualitative argumentation therefore leads to the conclusion that kinetic emission in the case of our collision system is due to a number of "distant" binary collisions between H atoms and first layer Cu atoms. This conclusion is supported by the fact that electron spectra observed for ion-atom collisions in the gas phase [9] show a similar exponential decrease with electron energy as the ones shown in Fig. 1.

We now show that the predictions of a theoretical description of kinetic emission based on the mechanism identified above are consistent with our experimental data. For this goal we make a few simplifying assumptions.

(i) We describe a single collision, and we do this semiclassically. This means a collision with a given impact parameter is described in terms of an electronic system which is influenced by a time dependent perturbation.

(ii) We assume the system to behave adiabatically in zeroth order. This means we assume that the transition probabilities between the adiabatic electronic states are small compared to 1. This assumption also implies the validity of the "two state approximation" in which only direct transitions from an initial adiabatic state $|i\rangle_a$ to a final state $|f\rangle_a$ are considered.

With these approximations the expression for the transition probability p_{if} for a complete collision extending from $(t = -\infty)$ to $(t = +\infty)$ follows directly from the adiabatic approximation [10] (atomic units are used throughout the paper):

$$p_{if} = \left| \int_{-\infty}^{\infty} {}_a\langle f|dH/dt|i\rangle_a/[\omega_{fi}(t)] \times \exp\left\{ i \int^{t} \omega_{fi}(\tau) d\tau \right\} dt \right|^2 ,$$

$$\omega_{fi}(t) = E_f(t) - E_i(t) . \qquad (1)$$

$E_i(t)$ and $E_f(t)$ are the time dependent energies of initial and final electronic states. In the approximation of independent electrons assumed here, relation (1) holds for one-electron transitions. In our case we consider the ionization transition of the one electron of H and of the ten $3d$ electrons of Cu. The transition energy $\omega_{fi}(t)$ in relation (1) is given by

$$\omega_{fi}(t) = \mathrm{IP}(t) + \varepsilon , \qquad (2)$$

as the sum of the time dependent ionization energy of the respective electron in its initial state, $\mathrm{IP}(t)$, and the kinetic energy of the electron in its final state, ε. A drawing showing the relation between the time dependent quantities used is given in Fig. 2.

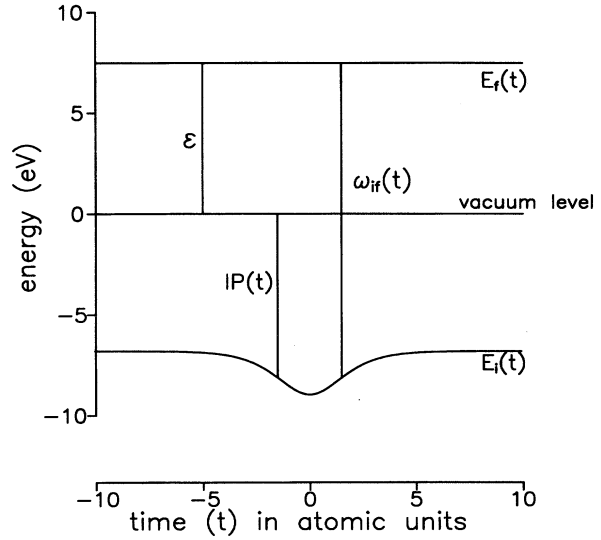

FIG. 2. Diagram showing the relation between the time dependent quantities used in the theoretical description of kinetic emission. The situation depicted corresponds to a collision at 3 keV with impact parameter $b = 0.7$ a.u. and to the ionization of one of the $3d$ electrons of Cu by the swiftly passing neutral H atom.

In order to arrive at an expression that can be evaluated numerically, we approximate the matrix element in relation (1) as

$$ {}_a\langle f|dH/dt|i\rangle_a \approx d({}_d\langle f|V(t)|i\rangle_d)/dt = dV_{fi}(t)/dt\,, \quad (3) $$

in which $V_{fi}(t)$ is calculated using the diabatic wave functions $|i\rangle_d$ and $|f\rangle_d$, which are eigenfunctions of H_0 in $H = H_0 + V(t)$.

The emission probability for an electron of energy ε thus becomes

$$ p_{if}(\varepsilon) = \left| \int_{-\infty}^{\infty} [dV_{fi}(t)/dt]/[\omega_{fi}(t)] \times \exp\left\{ i \int^{t} \omega_{fi}(\tau) d\tau \right\} dt \right|^2 . \quad (4) $$

It is interesting to note that expression (4), whose region of validity is the region of slow time variations and small perturbations, is closely related to the expression for the transition probability in the Born approximation, which is valid for fast time variations and small perturbations [9]. Therefore, in the case of transitions for which the time variation of the transition frequency is small compared to its asymptotic value, expression (4) will be a good approximation also for fast time variations.

In order to evaluate expression (4) we need realistic functions of time for $V_{fi}(t)$ and $\omega_{fi}(t)$. To relate the particle distance R from the target atom to the time, we use the straight line trajectory approximation, leading to the relation $R(t) = [b^2 + v_p^2 t^2]^{1/2}$ with b the impact parameter and v_p the projectile velocity. For the case of our "distant collisions" leading to deflection angles below 1° per collision this is of course a good approximation.

We will now qualitatively sketch the procedure applied to obtain the functions $V_{fi}(R)$ and $\omega_{fi}(R)$. We estimate $\omega_{fi}(R)$ as the difference between interaction potentials for the respective initial and final states using screened Coulomb potentials. These potentials are modeled by the Coulomb interactions between effective charges consisting of bare charges multiplied by hydrogenic screening functions (Slater's rules [11]). Thereby we assume in the initial state the Cu atom to be singly ionized and the H atom to be in its neutral ground state. We consider the two transitions $Cu^+ \rightarrow Cu^{2+} + e^-$ and $H \rightarrow H^+ + e^-$. In order to account for the extra screening due to the free metal electrons, the effective charges of projectile and target atoms are reduced by an exponential screening factor [12].

We base our estimate of the functional form of $V_{fi}(R)$ on the relation

$$ V_{fi}(R) = {}_d\langle f|Z_{\rm eff}(|\vec{R} - \vec{r}|)/|\vec{R} - \vec{r}|\,|i\rangle_d\,, \quad (5) $$

where $Z_{\rm eff}(\vec{R} - \vec{r})$ is the effective charge of the perturber particle and $\vec{r}$ is the position vector of the electron to be ionized. Since for the relevant trajectories the perturber particle passes through the respective electron orbital, the leading term in an expansion of the matrix element will be the monopole term. As an estimate for the matrix element we therefore use the expression

$$ V_{fi}(R) = CZ_{\rm eff}(R)/R\,, \quad (6) $$

with C a constant to be determined. $Z_{\rm eff}(R)$ of the perturber particle is estimated using hydrogenic screening functions as described above. Using Eq. (6), the total ionization cross section for a gas phase collision can now be obtained in the straight line approximation by a numerical integration of expression (4) with respect to time, followed by integrations over impact parameters and electron energies:

$$ \sigma_{\rm tot} = \int_0^{\infty} d\varepsilon \int_0^{\infty} 2\pi b\; p_{if}(\varepsilon, b)\, db\,. \quad (7) $$

To determine the constant C in Eq. (6), we have applied this procedure to the collision system He^+/H at 10 keV collision energy, where $\sigma_{\rm tot} = 1.0$ a.u. [8]. We integrate in Eq. (7) from 0.5 a.u. and not from 0 a.u. because for small impact parameters the straight line trajectory approximation is not valid. The contribution to the cross section from the inner region we estimate as the geometrical value multiplied by an estimated average ionization probability of 50%. The total cross section of 1.0 a.u. is obtained for $C = 2^{-1/2}$. We now make the assumption that the same value of C can be used for the Cu^+/H collision system. In evaluating the expression for the ionization probability [Eq. (4)], the functions $IP(R)$ in Eq. (2) and $Z_{\rm eff}(R)$ in Eq. (6) appropriate for the respective transitions are used. For the ionization of H by

Cu^+ this is obviously a good assumption. For the case of the ionization of Cu^+ by H, where we consider the ionization of the ten $3d$ electrons, an overestimation of the ionization probability may arise because, due to the different orientation of the localized $3d$ electrons in the surface layer, not all 10 orbitals will be penetrated by the H atom, so that the estimate [Eq. (6)] probably should be applied to a reduced number of "active" $3d$ electrons. However, for the present purpose of an estimate the straightforward application of the approximations is used in order to avoid any arbitrariness.

Absolute electron spectra calculated using Eqs. (4) and (6), with $C = 2^{-1/2}$, are compared in Fig. 1 with the absolutely normalized observed spectra. In the calculated spectra the energy dependent escape probability caused by the potential barrier at the surface is taken into account, the predominant effect of which is the decrease in intensity at low energies but which does not affect the slopes very much. The calculated spectra shown are an average over spectra with impact parameters ranging from 0.55 to 1.5 a.u. and normalized to three collisions per trajectory. In averaging we assumed a linear increase of the number of collisions with impact parameter, which is in accordance with our classical trajectory calculations. No parameter is adapted to reproduce the slope of the spectra or their dependence on collision energy. Judged from our Monte Carlo type trajectory calculations, the number of three collisions per trajectory is too low by approximately a factor of 3. This may well be due to the above mentioned overestimation of the contribution of the $3d$ electrons from Cu. Because of the satisfactory agreement of our theoretical calculations with the experimental results, we may state that the mechanism on which the theoretical treatment is based is the dominant mechanism at the conditions of the experiment.

We summarize the result of the present work as follows. We presented electron spectra that are due to purely distant collisions. From their absolute intensity the mechanism operative at these distant collisions was identified, namely, the time dependent perturbation of localized atomic electrons due to the fast distant passage of an incompletely screened charge. An approximate theoretical description of kinetic emission caused by this mechanism has been presented and has been proved to be able to reproduce the measured absolute electron yields as well as the electron spectra and their dependence on collision energy.

Finally we would like to point out briefly some important consequences of the present results.

(i) Since many "distant collisions" always occur in particle surface collisions, also at higher angles of incidence and for surfaces of polycrystalline or amorphous material, we have identified the main mechanism for kinetic emission in the low energy range. (ii) The considerable amount of published data on so-called "shell effects" in kinetic emission [1], on observed anisotropic angular distributions, and on the observed thresholds of 0.1 keV/nucleon for relatively light projectiles [3] can probably be explained on the basis of the proposed mechanism and are currently under study. (iii) The proposed mechanism contributes considerably to the stopping power for atomic projectiles passing through solid material at rather low velocities.

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[1] W. O. Hofer, Scanning Microscopy Suppl. **4**, 265 (1990).
[2] D. Hasselkamp, in *Particle Induced Electron Emission II,* edited by G. Hoehler, Springer Tracts in Modern Physics Vol. 123 (Springer, Berlin, 1992), p. 1.
[3] P. Varga and H. Winter, in *Particle Induced Electron Emission II,* edited by G. Hoehler, Springer Tracts in Modern Physics Vol. 123 (Springer, Berlin, 1992), p. 149.
[4] M. Roesler and W. Brauer, in *Particle Induced Electron Emission I,* edited by G. Hoehler, Springer Tracts in Modern Physics Vol. 122 (Springer, Berlin, 1991), p. 1.
[5] P. Sigmund, in *Ionization of Solids By Heavy Particles,* edited by Raul A. Baragiola (Plenum Press, New York, London, 1993), p. 59.
[6] For example, *The Theory of Atomic Collisions,* edited by N. F. Mott and H. S. W. Massey (Clarendon Press, Oxford, 1965).
[7] A. Niehaus, in *Ionization of Solids By Heavy Particles,* edited by Raul A. Baragiola (Plenum Press, New York, London, 1991), p. 79.
[8] *Electronic and Ionic Impact Phenomena,* edited by H. S. W. Massey and H. W. Gilbody (Clarendon Press, Oxford, 1974), p. 2441.
[9] For example, M. E. Rudd and J. H. Macek, in *Case Studies in Atomic Collision Physics III* (North-Holland, Amsterdam, 1974), p. 49.
[10] *Quantum Mechanics, Volume II,* edited by Albert Messiah (North-Holland, Amsterdam, 1964), pp. 753, 755; *Introduction to Quantum Mechanics,* edited by B. H. Bransden and C. J. Joachain (Longman Scientific & Technical, England, 1990), p. 430.
[11] J. C. Slater, Phys. Rev. **36**, 57 (1930).
[12] T. L. Ferrel and R. H. Ritchie, Phys. Rev. B **16**, 115 (1977).