Electron Emission Induced by Cluster Bombardment of Metallic Surfaces

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An experiment is described in which electrons are ejected from a metallic surface upon bombardment by molecular clusters formed in a supersonic jet expansion.

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Extensive molecular clusters can be prepared in a seeded molecular beam by means of a supersonic nozzle equipped with a conical headpiece.[1] Such clusters range in size from two to thirteen or more molecules with masses easily exceeding 1000 amu. The velocity of He atoms after room-temperature expansion in a supersonic nozzle is about 1600 m s^{-1}, imparting ~ 10 eV kinetic energy to a cluster of ~ 600 amu. If such an energy is transferred to a surface a local area is highly excited and if the excitation is present in the electronic system, electron emission may result.

This Letter describes an experiment in which such an effect was observed and in which the energy distribution of the emitted electrons was measured. A qualitative explanation of the effect and an interpretation of the electron energy distribution is given.

The molecular-beam equipment has been described elsewhere.[1] It basically consists of a large chamber with a pulsed supersonic nozzle (1 mm) with conical headpiece and two consecutive skimmers in front of two consecutive chambers, all differentially pumped. The pressures under beam-on condition were respectively 10^{-3}, 10^{-6}, and 10^{-8} Torr. An ultrahigh-vacuum chamber with x-ray photoemission spectrometer, electron and argon-ion guns, a high-resolution electron energy analyzer, and an ultrahigh-vacuum manipulator was attached to the third chamber. Polycrystalline metal targets could be attached to the manipulator. The energy of the emitted electrons could be analyzed with a spectrometer which had an energy width of about 0.3 eV. The electrons in a given energy range were measured by a Channeltron detector and counted, and the resulting signal, as well as the analyzer voltage, was registered by an Apple II+ computer.

In all cases electron emission due to clusters (as measured by mass spectrometry) was observed. If there were no molecules in the beam the signal was absent, as it was when Ar was used as a carrying gas. In the latter case it takes a cluster mass of more than 6000 amu to obtain a kinetic energy of 10 eV.

Measurements were carried out on argon-ion–cleaned polycrystalline surfaces of Cu, Ni, and Al and on a 700-Ω-cm single-crystal Si surface. All materials showed within experimental error the same electron energy distribution; the relative yields were in the order Ni > Cu,Al > Si. Absolute yield determinations are impossible as long as the neutral-cluster mass distribution is not known; the clusters fragment upon ionization.[1] Moreover, the yield depends on stagnation pressure (which probably also affects the neutral-cluster distribution) and it depends on the nature of the surface. For instance, in general "dirtier" surfaces yielded more electron emission; extensive cleaning by argon-ion bombardment reduced the emission by about 20%. The emission also depends strongly on the nature of the molecules making up the cluster. Benzene, for instance, yields a much lower though finite emission than carbon tetrachloride CCl_4 or acetonitrile (CH_3CN).

Some charged particles are emitted at energies below the work function of the metal. We then obtain a very steep rise and a falloff with energy characterized by $Y = Y_0 \exp[-(E-\phi)/kT_S]$ $(E \geq \phi)$, where Y is the electron yield, Y_0 the yield at $E=\phi$, E the energy of the electrons, ϕ the work function, and T_S the surface "temperature" as found from the experiment. The line drawn in Fig. 1 shows the convolution of this function with the width function of the energy analyzer for CCl_4 clusters on copper. A very good fit,

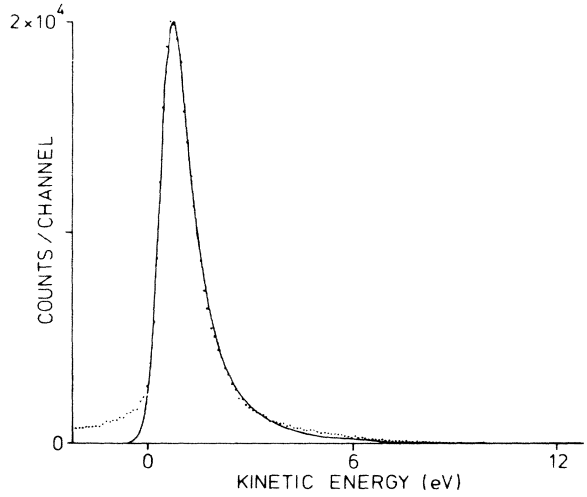

FIG. 1. Electron kinetic energy distribution resulting from the CCl_4-cluster bombardment of a copper surface.

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apart from the points below the work function, is obtained for $T_S \approx 5000$ K. For CCl_4 clusters in He this seems to be a general temperature not much affected by the stagnation pressure or by the nature of the metal.

Obviously, the kinetic energy of the clusters must be transferred to the metal surface to obtain electron emission. Scattering of molecules off surfaces usually leads to their rotational or vibrational excitation, as for instance happens with NO[2] or I_2[3] scattered from LiF, or pyrimidine, a ten-atom molecule, from a CdS surface.[4] Electron emission was not reported in these cases, but it may not have been looked for. In any case all masses studied seem to be too low to have the kinetic energy required to overcome the work function.

Why should clusters of neutral molecules transfer their energy to a surface? It should first be noted that calculations of the energy loss of small molecules colliding with a surface have yielded transfers of about 1% at the energies involved here.[5] This probably finds its cause in the high internal frequencies of small molecules, which do not match the inverse collision time. The van der Waals bonds holding the cluster together have much lower typical frequencies than either the intramolecular or the frequencies of the metallic or covalently bonded surface.[6] Therefore, the cluster behaves much like a soft football hitting a brick wall. If we take the interaction distance between cluster and surface to be about 1 Å, the force on a cluster at a velocity of, say, 1600 m/s contains frequency components up to 1.6×10^{13} s^{-1}, which is considerably higher than typical van der Waals frequencies but just barely enough to excite lattice frequencies.[6] Therefore, the "phonons" of the van der Waals clusters can be highly excited, absorption of the impact energy occurs, the collision is inelastic, and the clusters will be deformed on impact. On the other hand, the deformation of the target surface will be limited, since its phonon frequencies are higher.

Consistent with this model is our failure to observe specular reflection of clusters under conditions where we did see specular reflection of the He beam. All we could see was the rise of the CCl_4 concentration upon impact and its subsequent removal by the pumps as monitored by the quadrupole mass spectrometer through ionization by its electron-impact ionizer.

If we assume that all kinetic energy is transferred to the first layer of the surface, an estimate of the ensuing temperature can be made. The question then arises whether the electronic or the nuclear motion, or possibly both, are affected by the collision. Since the repulsion is governed by the electrons and the Pauli principle, it seems most reasonable to use the electronic specific heat of, for instance, free electrons: $c_v^{el} = \pi^2(T/T_F)k_B$, where T is the temperature, $k_B T_F$ the Fermi energy, and k_B the Boltzmann constant. The kinetic energy of each CCl_4 molecule in a cluster at 1600 m/s amounts to $E_k = 2.50$ eV. With a radius of 3.57 Å for CCl_4 as obtained from appropriate atomic and van der Waals radii we find that each CCl_4 molecule covers on average $n = 6.4$ atoms of copper to which the energy is imparted. From the equality $E_k/n = \int_{T_0}^{T_S} c_v^{el}\, dT$, with a Fermi energy of 7 eV we find $T_S \approx 6500$ K, which in view of the severe approximations is in satisfactory agreement with the experimental result of 5000 K. Of course, for silicon the free-electron approximation is really poor, but for the high temperatures involved, it may not be unreasonable. It should be noted that the relative yields are in the order of the densities of states at the Fermi surface, lending somewhat more credence to our model. It may also explain why "dirtier" surfaces have somewhat more emission: "Dirt" usually increases this density of states.

A similar calculation using the lattice specific heat $c_v^l = 3k$ yields 1600 K, which indicates that indeed the nuclei of the surface play a minor role in the emission process.

Some electron emission appears to occur at energies lower than the work function, as well as at energies considerably exceeding the values expected from thermionic emission. These signals are probably misleading. Any metallic surface in our instrument will emit electrons when impacted by a cluster. Electrons entering our analyzer from objects other than our target are not analyzed properly and are most likely responsible for these spurious results.

In summary, when neutral clusters of molecules with kinetic energies exceeding the work function of metals or semiconductors collide with their surfaces, electrons are emitted. Their energy distribution is indicative of a purely electronic process. Although the name has in the past been used for a somewhat different phenomenon,[7] we suggest that the cluster-induced electrons be called "exoelectrons."

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