Energy Dissipation in Small Clusters: Direct Photoemission, Dissociation, and Thermionic Emission

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The competition between electron emission and unimolecular dissociation following the absorption of a single photon is studied for small clusters of various elements. Electron emission results from either direct photoemission, observed as a series of peaks in the spectrum, or thermionic emission, giving rise to a continuous background. Depending on the energetics involved, thermionic emission is in competition with evaporation of atoms. These results are compared to the corresponding events observed for solids, where the dominant decay products are inelastically scattered photoelectrons. [S0031-9007(96)01663-8]

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The absorption of a photon of energy $h\nu$ by an atom in a cluster or a solid, in general, results in the creation of an excited electronic state. This state can lead directly to the emission of a photoelectron, whereby all the excess energy is carried away by the emitted electron [1]. Alternately, the excited electron may transfer part or all of its energy through scattering processes to other electrons or phonons [1]. With much smaller probability, the excited state decays via the emission of a photon, atom, or ion. For solids, the dominant process observed is the emission of inelastically scattered electrons, together with the direct photoemission. The thermalization process, whereby energy is shared by many electrons or photons, generally does not result in emission of any secondary particles.

In small clusters these series of events are quite different. Just as in solids, the excited electronic state can decay by the emission of a photoelectron. The other decay channels, however, lead to different results. Because of the finite size of the system, inelastic scattering processes of the outgoing photoelectron are much less likely than in a solid. Thermalization, on the other hand, results in the distribution of energy over a finite number of degrees of freedom. The main difference to the solid, however, is that the total energy remains localized over a very limited number of atoms, resulting in a considerable "temperature" of the cluster. The hot clusters are metastable with only a limited possibility for energy release. Since the energy remains localized, processes with a long time scale or small probability may take place, such as evaporation of atoms [2–7], thermionic emission (TE) of electrons [6–13], or, on a very long time scale, radiative cooling [14].

In a recent publication [15], we presented the first results on the kinetic energy distribution of photoelectrons emitted from size-selected W_n^- clusters following single photon absorption. These clusters have stored a well defined internal energy (≈photon energy). The photoelectron spectra (PES) exhibit a smooth emission signal with an intensity I, which increases exponentially towards low kinetic energy E_{kin}. This can be fitted by a Boltzmann function

$$I \sim e^{-E_{\mathrm{kin}}/kT},$$

with a temperature T corresponding to the photon energy $h\nu$ divided by the number of internal degrees of freedom $(3n - 6)$. This emission signal is assigned to TE, and the corresponding temperature of the photoexcited clusters is the photon energy divided by the number of vibrational degrees of freedom.

Here we extend these studies to a broad range of clusters of different elements to systematically study the energy dissipation. The spectra show contributions from three different processes: direct emission features, the TE signal, and inelastic scattered electrons. At first glance, the features in the photoemission spectra of clusters and solids are quite similar. Our analysis, however, shows that the underlying processes leading to the emission of these electrons are quite different. Essentially, the background of inelastic scattered electrons dominating PES of solids is replaced by the TE signal for the smallest clusters. Additionally, clusters with a threshold energy for unimolecular dissociation (= dissociation energy E_D) smaller than the threshold for electron emission [= electron affinity (EA)] show no TE signal. The energy dissipation depends crucially on the balance between E_D and EA: For most materials the spectra of the clusters either exhibit a TE signal (W, Pd, Pt, ...) or do not show TE (Na, Ga, ...). For carbon clusters the appearance of the TE signal is size dependent. In addition, we will show that chemisorption of a molecule "quenches" the TE signal, if the energy to remove the molecule from the cluster is smaller than EA, thus confirming our simple picture.

The spectra are obtained using photoelectron spectroscopy of negatively charged clusters [16]. This technique allows mass separation of the clusters by standard methods prior to the experiment. The energies involved refer to negatively charged clusters. The negatively charged clusters are produced using a laser vaporization source and are cooled down to approximately room temperature in a seed gas (He). The anions are accelerated in a pulsed electric field, and, depending on the time of flight, the clusters separate into a chain of bunches of defined cluster size. The kinetic energy of electrons detached from a selected bunch is measured in a "magnetic bottle" time-of-flight electron spectrometer. The photon flux of the detachment laser is kept as low as possible to ensure contributions from single photon events only.

Figure 1 shows photoelectron spectra of W_n^- clusters with $n = 1, 4, 6,$ and 9. The spectrum of W_n^- exhibits a multitude of narrow features, which are assigned to transitions from the electronic ground state of the anion into various states of the neutral atom. All features marked in black correspond to direct photoemission. The widths reflect the experimental resolution [16]. The spectra of the clusters show evidence for three different contributions: direct photoemission (black), TE (hatched), and inelastic scattered electrons (white). The graphical separation into these three channels should be taken as a qualitative suggestion and is not based on an exact deconvolution. Direct emission gives rise to pronounced peaks at relatively high kinetic energies, which are assigned to photoemission from d-derived orbitals. These will develop into the d-density of states of the bulk valence band close to the Fermi energy [17]. The low energy range is dominated by the TE signal (hatched). Since the photon energy is constant, the temperature T decreases with cluster size corresponding to a steeper decrease of the exponential function fitted into each spectrum using the calculated temperature (Fig. 1). The agreement of the experimental data with both the exponential functions *and* the observed cluster size dependence strongly supports the assignment to TE.

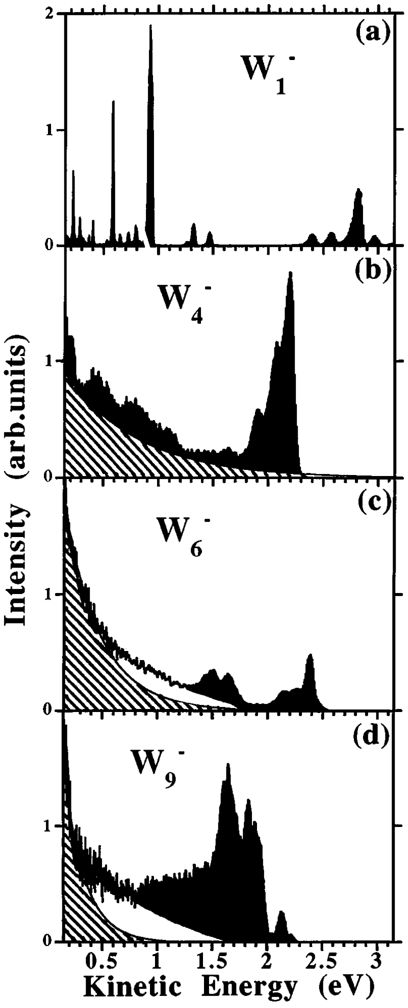

FIG. 1. Photoelectron spectra of W_1^-, W_4^-, W_6^- and W_9^-. The photon energy is $h\nu = 4.0$ eV. For a discussion of the marked features, see text.

The spectrum of W_4^- is composed of the exponential TE signal (hatched) and the structured direct emission signal (black). The spectra of the larger W_n^- clusters (Fig. 1c, d) cannot be completely reproduced by the sum of the direct emission and the TE signal, but an additional unstructured contribution appears (white). This contribution increases in intensity with increasing cluster size. We tentatively assign it to inelastic scattered photoelectrons, which finally will be the largest contribution to the photoelectron spectrum of bulk materials [1].

Figure 2 displays examples of photoelectron spectra of clusters showing a strong TE signal (Pt_5^-, Pd_8^-, C_{10}^-, C_{14}^-, Pt_3^-) as well as no TE signal (Na_7^-, Ga_7^-, C_7^-, C_9^-, $Pt_3(CO)_6^-$). For most elements the spectra show either a strong (e.g., Pt_n^-) or no (e.g., Ga_n^-) TE signal for all clusters independent of their size. This can be explained by the difference in threshold energies necessary for electron emission and unimolecular dissociation (E_D). The threshold for electron emission is the ionization potential of the anion: the electron affinity EA. The threshold for unimolecular dissociation is the minimum energy necessary for the lowest energy fragmentation process of the type $X_n^- = X_{n-m}^- + X_m$. In most cases the lowest energy fragmentation channel corresponds to the evaporation of single atoms ($m = 1$). The time constants for both cooling mechanisms depend exponentially on the energy difference between the internal energy $E_{\text{int}}(\approx h\nu)$ and the thresholds EA and E_D. At a given E_{int} the process with the lower threshold will be the faster one. EA(n) and $E_D(n)$ are size dependent and in many cases not known. However, $E_D(n)$ can be estimated from the heat of vaporization ΔH_{vap}^0 of the bulk materials [18]. EA(n) corresponds roughly to the vertical detachment energies VDEs(n), which can be extracted

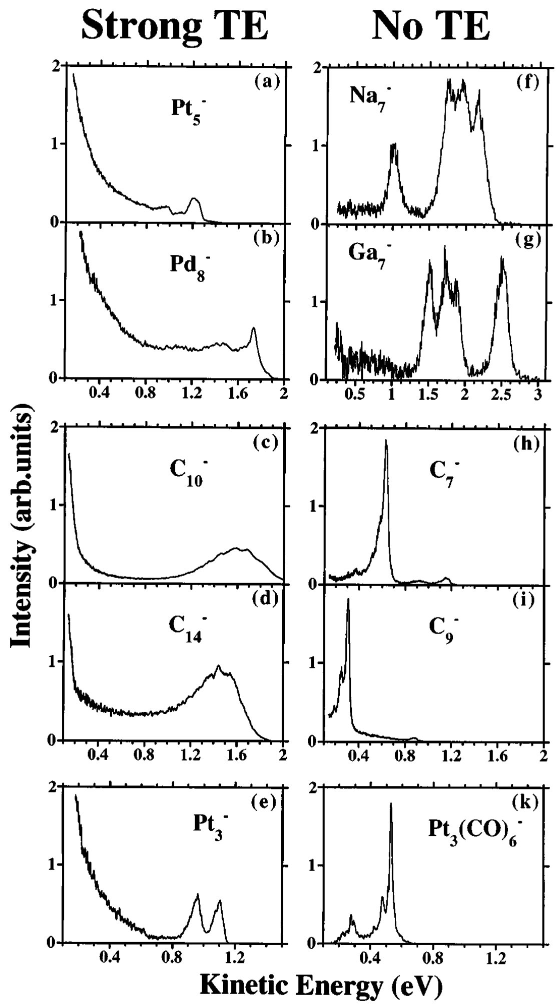

FIG. 2. Examples of photoelectron spectra of clusters with a strong TE signal [(a) Pt_5^-, (b) Pd_8^-, (e) Pt_3^-], with no TE signal [(f) Na_7^-, (g) Ga_7^-, (k) $Pt(CO)_6^-$], and a size dependent TE signal [strong TE: (c) C_{10}^-, (d) C_{14}^-; no TE : (h) C_7^-, (i) C_9^-]. The photon energies are $h\nu = 4.0$ eV (Pt_5^-, Pd_8^-, Ga_7^-, C_n^-), $h\nu = 3.49$ eV (Na_7^-), and $h\nu = 3.0$ eV (Pt_3^-, $Pt_3(CO)_6^-$].

directly from the electron spectra [19]. The difference between VDEs(n) and EA(n) corresponds to the one between the vertical and the adiabatic ionization potential of a neutral molecule and is small, if the ground state geometries of the neutral and anion are similar. For comparison with ΔH_{vap}^0 we take the value ⟨VED⟩, which is the average of the VDEs of the clusters with $n = 3 - 15$. In Fig. 3 each element studied corresponds to one data point with a certain ⟨VDE⟩ and ΔH_{vap}^0. The straight line serves as a guide to the eye separating the elements showing no (open circles) and strong TE signals (filled circles). This strong correlation supports the model of competing cooling channels.

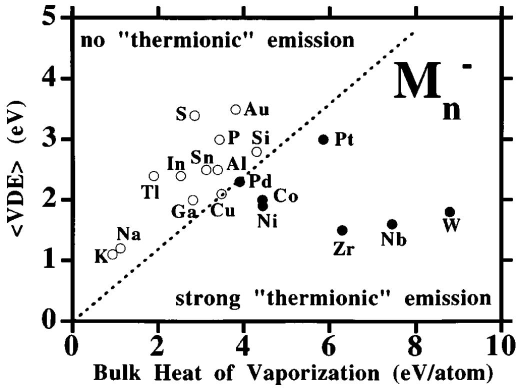

FIG. 3. The vertical detachment energies of elemental clusters M_n^- averaged on the cluster sizes $n = 3 - 15$ ⟨VDE⟩ [19] and the bulk heat of vaporization [18] of various elements. The position of the elements in the diagram corresponds to the two values of the energies. Open circles represent elements with no TE signal, the ones marked by filled circles display an intense TE signal. The dotted line separates the two areas as a guide to the eye corresponding to a constant ratio of the two energies.

In order to support this simple model we compare the bare Pt_3^- cluster with its CO saturated counterpart $Pt_3(CO)_6^-$. The energy necessary to desorb a single chemisorbed CO molecule from a $Pt_3(CO)_6^-$ cluster is about 1 eV [22]. In contrast, the ΔH_{vap}^0 for Pt is 5.85 eV [18]. The EA of $Pt_3(CO)_6^-$ is 2.4 eV, whereas the EA of Pt_3^- is 1.87 eV [23]. The spectrum of $Pt_3(CO)_6^-$ [Fig. 2(k)] shows no TE signal in contrast to bare Pt_3^- [Fig. 2(e)]. The narrow peak in Fig. 2(k) corresponds to the transition from the electronic ground state of $Pt_3(CO)_6^-$ into the neutral electronic ground state. The smaller features are assigned to vibrational fine structure [24]. The spectrum shows no unstructured emission signal. We conclude that, in agreement with the model proposed above, $Pt_3(CO)_6^-$ "cools" by evaporation of a chemisorbed CO molecule explaining the disappearance of the TE signal.

So far, we observe only for one element a size-dependent existence of a TE signal. The small carbon clusters, which form chain isomers [25], show no TE signal [C_7^-, C_9^-, Figs. 2(h) and 2(i)]. The larger clusters have ring structures [25] and display a strong TE signal [C_{10}^-, C_{14}^-, Figs. 2(c) and 2(d)]. The carbon ring isomers exhibit relatively low VDEs (≈2.5 eV), while the VDEs of the chain isomers are considerably higher (≈3.5 eV). The observation of TE for C_n^- clusters with lower VDEs supports our general picture. However, the dissociation energies of the C_n^- clusters with $n = 5 - 10$ are estimated to be larger than 4.5 eV [26] and, accordingly, TE is expected to appear in all these spectra. Possible explanations for this discrepancy are an overestimation of the cluster binding energies [26] or possible additional effects, which have been neglected so far. E.g., the appearance of the TE signal requires the existence of a fast thermalization mechanism with a probability comparable to the one of direct photoemission. If the fast thermalization is hampered by, e.g., symmetry restrictions, the TE signal might be very weak.

However, such considerations are beyond the scope of the present paper.

In small clusters, thermalization always results in TE [if EA $(n) < E_D(n)$] and, therefore, the intensity ratio of the photoemission signal (direct and inelastic) and the TE signal corresponds roughly to the ratio between photoemission and thermalization. From our W_n^- spectra, we find ratios in the order of 1:1. This observation agrees with the finding of fast electronic relaxation processes in small metal clusters using resonant two-photon ionization spectroscopy [27]. Therefore, even in clusters with a few atoms only electronic relaxation is very effective. However, a quantitative determination of the time scales of relaxation and thermalization processes is only possible using time-resolved spectroscopy in the femtosecond time regime.

The ratio between thermalization and direct photoemission should be similar in solids. For these, however, the thermalization energy does not lead to electron emission. For a tungsten metal surface the probability for electron emission after the interaction with a photon (quantum yield) is of the order of 10%–20% (at $h\nu \approx 20$ eV) [28]. However, the quantum yield cannot be directly compared to the ratio between thermalization and direct emission because it also depends on additional bulk properties such as surface reflectivity and the mean free paths of photons and electrons.

In comparison with solids and surfaces we find that the processes leading to the emission of particles (electrons and atoms) and their time scales are completely different. In contrast to free clusters, only highly vibrationally and/or electronically excited atomic or molecular species can "escape" from a surface [1]. Very efficient relaxation processes dissipate energy quickly for lower excitations, and the atom or molecule is no longer able to leave the surface. Therefore, for a solid or surface, an ejection is observed only if it leads to the final state (e^-, ion or atom evaporation) within a very short time. For clusters, events on a long time scale are observed even if a complicated redistribution of energy is necessary. Thus the finite size of the particle results in the observation of slow processes such as thermal emission and unimolecular dissociation following photoexcitation.

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