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Thermal emission of electrons from highly excited Na_{16}^{+} to Na_{250}^{+}

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Abstract. The electron emission from size-selected sodium clusters excited by a 400 nm femtosecond laser-pulse of moderate intensity ($<10^{10}$ W cm^{-2}) has been studied for cluster sizes Na_n^+ with $n = 16$, 46, 70, 139 and 250. In all cases the kinetic energy distributions show a simple exponential behaviour. Comparison with statistical theory shows that even for the smallest cluster the emission process is purely statistical emission from a thermalized hot electron gas, which takes place on a picosecond timescale after the excitation.

Contents

1. Introduction

Thermionic emission from clusters after photoexcitation is a well known phenomenon [1]–[3]. This process is typical for strongly bound clusters like refractory metal or carbon clusters, as only they can be heated to temperatures high enough for electron emission without undergoing fragmentation. The heating of the cluster is usually achieved by photon absorption from nanosecond laser-pulses, and the emission takes place on a nanosecond to microsecond timescale.

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It is characteristic of this type of emission that the electrons and the ions are in perfect thermal equilibrium.

A different type of thermal electron emission has now recently been observed for C_{60} [4] and for Na_{93}^+ [5]. In these experiments the clusters were heated by the absorption of several photons from a femtosecond laser-pulse, in which case all of the excitation energy is deposited in the electron system. This leads to thermal emission of electrons from the hot electron gas. The timescale on which the emission takes place is determined by the cooling rate of the electron gas. For not too high excitation energies the emission can only take place as long as the energy is located in the electron system. After transfer of the energy to the ion lattice, electron emission is no longer possible as, due to the much larger heat capacity of the ions, the electron temperature is strongly reduced when equilibrium is reached.

Sodium is a special case, as unlike C_{60} it does not exhibit normal thermionic electron emission. Sodium clusters are only weakly bound (binding energy $\sim$1 eV/atom), and therefore in thermal equilibrium will cool by evaporation of atoms at temperatures far below those necessary for electron emission. For this reason in the measured electron spectra a contribution of normal thermionic electron emission can safely be neglected even for strong femtosecond excitation. Another advantage of sodium clusters is the strong plasmon resonance close to the energy of the second harmonic of a Ti:sapphire femtosecond laser (3.1 eV). This allows us to reach a high excitation of the cluster even with relatively weak laser intensities, so that no nonlinear high field effects have to be taken into account.

After having studied the thermal electron emission as a function of laser intensity in detail for the case of Na_{93}^+ [5], we have now studied this phenomenon as a function of cluster size. In the following we will briefly describe the experimental set-up, show the results obtained and compare them to the results of statistical theory.

2. Experiment

For the experiment a new experimental set-up was used, which is similar to the one described earlier [6, 7]. Cluster ions with a temperature of 150–250 K are produced in a gas aggregation source and mass selected in a double reflectron time-of-flight mass spectrometer. Typical intensities for size-selected clusters are about 100–1000 clusters/pulse. The selected clusters are injected into a magnetic bottle photoelectron spectrometer and irradiated by a femtosecond laser pulse. The flight time distribution of the emitted electrons is measured and converted into a kinetic energy distribution.

For the production of the femtosecond laser pulses a standard set-up is used, which consists of a Ti:sapphire oscillator followed by a regenerative amplifier and a multipass amplifier. The pulse energy at 800 nm is typically 4 mJ/pulse at 30 Hz. After frequency doubling, the pulses have an energy of about 1 mJ and a duration of about 200 fs. Before entering the interaction region of the photoelectron spectrometer the laser beam is reduced by apertures to a diameter of 2 mm. The beam is not focused and therefore has a flat top intensity profile in the interaction region. For every cluster size the intensity of the 400 nm laser-pulses was adjusted to a value at which each of the irradiated clusters emits roughly one electron. As the absorption cross section increases with cluster size, the intensities necessary for this varied between 1×10^{10} W cm^{-2} for the smallest and 2.5×10^9 W cm^{-2} for the largest cluster.

Examples of photoelectron kinetic energy distributions measured for different cluster sizes are shown in figure 1. Almost perfectly exponential distributions are obtained in all cases. We

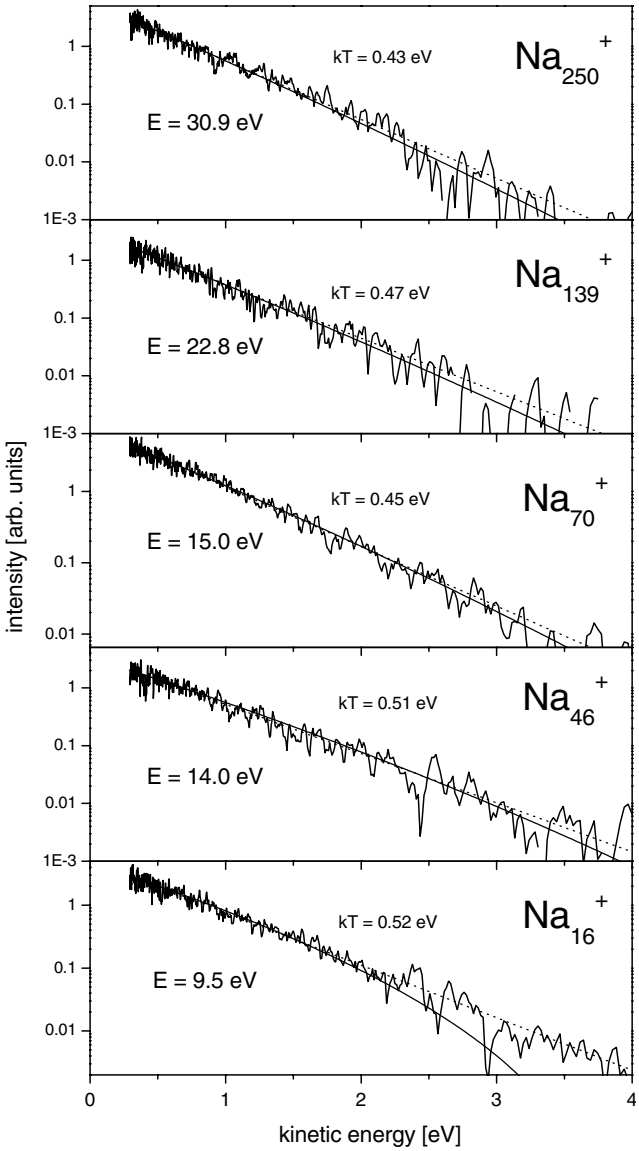

Figure 1. Kinetic energy distribution of electrons emitted from size-selected sodium clusters after the excitation by a femtosecond laser-pulse (wavelength 400 nm, duration 200 fs). In all cases a laser intensity was used at which each cluster emits roughly one electron. The spectra have been fitted with simple Boltzmann distributions (dotted lines) and with the Weisskopf model as given in equation (1) (solid lines).

have not observed any structure (apart from noise) in these spectra even for laser intensities up to 5×10^{10} W cm^{-2}. In particular, above threshold ionization (ATI) patterns as reported in [4] for C_{60} were never seen.

In order to demonstrate the exponential form of the spectra and to obtain the mean energy of the electrons, the spectra have been fitted with simple Boltzmann distribution functions, as indicated in figure 1 by the dotted lines. The corresponding temperatures (mean kinetic energies)

are given above the curves. It turns out that in all cases the mean energy of the electrons is close to 0.5 eV, with a weak decrease of the values with increasing cluster size. Furthermore the spectra have been fitted using a more realistic statistical model, as will be explained in the next section.

3. Theory

We have recently demonstrated [5] that the thermal electron emission from Na_{93}^{+} can be well described by statistical theory, namely the Weisskopf formalism [8]. In this model the electron emission rate is given by (adopted from [9])

$$k(E,\varepsilon) = \frac{2m_e\sigma(\varepsilon)}{\pi^2\hbar^3}\varepsilon\frac{\rho(E-\phi-\varepsilon)}{\rho(E)}. \tag{1}$$

Here E is the inner energy of the electron system, ε the kinetic energy of the electron, m_e the electron mass and ϕ the ionization potential. The factor of two accounts for the spin degeneracy. The multiparticle level density ρ is given by

$$\rho(E) \propto \exp(2\sqrt{aE}) = \exp\left(2\sqrt{\frac{\pi^2}{6}g(E_f)E}\right), \tag{2}$$

where $g(E_f)$ is the single-particle level density at the Fermi energy, which in the free electron model is given by

$$g(E_f) = \frac{3N}{2E_f}. \tag{3}$$

(N, number of valence electrons; E_f, Fermi energy). For the capture cross section σ the classical geometrical cross section is used:

$$\sigma = \sigma_0(1+V/\varepsilon) = \pi r_0^2(1+V/\varepsilon), \tag{4}$$

where V is the potential energy of an electron close to the surface (Z is the cluster charge before ionization; the image charge is neglected):

$$V = \frac{(Z+1)\mathrm{e}^2}{4\pi\varepsilon_0 r_0}. \tag{5}$$

For the calculation of r_0 the bulk density of sodium was used ($r_0 = \sqrt[3]{N+1}\,2.1$ Å). The ionization potentials of the positively charged clusters were calculated using

$$\phi_i = 2.75\ \mathrm{eV} + 1.4\frac{\mathrm{e}}{4\pi\varepsilon_0(r_0 + 1\ \text{Å})} \tag{6}$$

which is a fit to the results of a recent ultraviolet photoelectron spectroscopy study of positively charged sodium clusters [10].

It is not obvious that equation (1) leads to exponential kinetic energy distributions. This can be seen more easily by insertion of equations (2) into (1) and an expansion of the square root in the exponent in ε. For the case of small ε equation (1) can then be approximated by

$$k(E,\varepsilon) \approx \frac{2m_e\sigma_0 V}{\pi^2\hbar^3}\exp\left[2\sqrt{a}\left(\sqrt{E-\phi}-\sqrt{E}\right)\right]\exp\left[-\varepsilon/\sqrt{(E-\phi)/a}\right]. \tag{7}$$

With the approximation for the temperature of a free electron gas [11]

$$k_B T_E = \sqrt{E/a} \tag{8}$$

and for the case $\phi \ll E$ the rate then gets the more familiar form

$$k(E, \varepsilon) \approx \frac{2m_e\sigma_0 V}{\pi^2\hbar^3} e^{-\phi/k_B T_E} e^{-\varepsilon/k_B T_{E-\phi}}. \tag{9}$$

An interesting (and well known) consequence which can be seen here is that the electron emission from an electron system with energy E leads to a Boltzmann-like kinetic energy distribution with a temperature which corresponds to the electron system energy after the emission, that is to $E - \phi$.

We have now fitted the spectra of figure 1 with the kinetic energy distribution as given by equation (1) by adjusting the slopes of the measured and the theoretical curve in the energy interval between 0.5 and 1.5 eV.

The resulting fit curves are shown in figure 1, together with the obtained values of the excitation energy E. It turns out that in all cases, but especially for Na_{16}^+, at the highest kinetic energies the Weisskopf model actually gives a worse fit than the simple Boltzmann distribution. This is astonishing at first sight, as the Weisskopf formula should be the better model. It takes into account the finite excitation energy of the cluster, and therefore does not allow kinetic energies of the electrons larger than $E - \phi$. The Boltzmann distribution, however, gives finite probabilities for any kinetic energy, which is in contradiction to the conservation of energy. There are two reasons why the predicted curvature of the kinetic energy distribution is not observed here. First the numbers of photons which are absorbed by the clusters vary statistically, which leads to a broad distribution of excitation energies. Second the electron system starts to cool directly after the absorption of the first photon by transfer of energy to the ion lattice, which means that when the electron emission takes place the excitation energy of the electron system is already lower than the total amount of energy absorbed.

For these reasons the electrons are emitted from clusters with quite a broad distribution of energies, which smears out the details of the spectra and leads to the observed almost perfect exponential form. A second consequence of this is that we do not obtain integer multiples of the photon energy for the excitation energy, but just an average value.

In order to get information about the degree of the excitation the mean excitation energies which have been obtained by the fitting have been divided by the number of electrons in the respective cluster and plotted in figure 2 as a function of the cluster size. One can see a steep increase of the energy per electron with decreasing cluster size. This is the direct consequence of the prediction of the Weisskopf model that the kinetic energies of the emitted electrons reflect the temperature of the system after the emission $T_{E-\phi}$. As this temperature is about the same for all cluster sizes, that is

$$k_B T_{E-\phi} = \sqrt{(E - \phi)/a} \approx \text{const}, \tag{10}$$

and as a is proportional to N, the energy per electron before the emission is given by

$$E/N \approx \text{const} + \phi/N \tag{11}$$

which leads to the strong increase of the energy for the small clusters. In fact for Na_{16}^+ a value of 0.63 eV is obtained, which corresponds to a temperature of about 11 000 K, whereas for Na_{250}^+ we get only 0.12 eV, which corresponds to about 2600 K.

In order to check whether this strong size dependence is correct we have tried to obtain the excitation energies in a different way. As mentioned above, in the experiment the laser intensity was adjusted for each cluster so that roughly one electron per cluster is emitted. The time during which an emission takes place is determined by the cooling time of the electron gas. As the

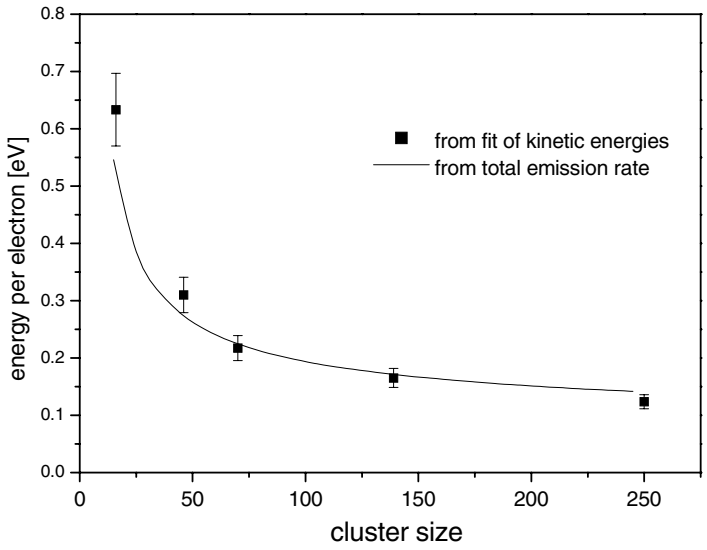

Figure 2. Excitation energy of the electron system *before* the electron emission as obtained from the fit of the kinetic energy distribution in figure 1 (points) and from the total electron emission rate (solid curve). The good agreement of the two data sets demonstrates the purely statistical nature of the electron emission process.

energy transfer between the electrons and the ion lattice for simple metals has time constants in the picosecond range [12, 13], we can make the rough assumption that for all clusters the emission takes place within 1 ps. From this one can get now a crude estimate for the excitation energy of the electron gas by setting the integrated rate of equation (1) equal to the rate 1 electron ps^{-1}:

$$K(E) = \int_0^\infty k(E, \varepsilon)\, \mathrm{d}\varepsilon = (1\ \mathrm{ps})^{-1}. \tag{12}$$

Solving this for E gives the excitation energy as a function of the cluster size, which is indicated in figure 2 by the solid curve. This curve is in very good accordance with the values obtained from the fit of the kinetic energy distributions. This demonstrates that the Weisskopf model gives a complete description of the electron emission from the highly excited sodium clusters, which means that even in the case of a cluster as small as Na_{16}^+ the emission is a purely statistical process. This is of course only true for the photon energy and the laser intensity used. Absorption of photons with energies larger than the ionization potential naturally leads to direct electron emission as e.g. observed in [10], and it can be expected that the use of much more intense femtosecond laser-pulses will also lead to direct (multiphoton-) ionization processes.

4. Summary

Irradiation of sodium clusters with femtosecond laser-pulses of moderate intensity in resonance with the plasmon resonance leads to thermal emission of electrons. We have measured the kinetic energy distributions of the electrons for size-selected Na_n^+ with n from 16 to 250. The results can be consistently described by the Weisskopf model, which demonstrates that even in the case of Na_{16}^+ the excited electron system behaves like a free electron gas in thermal equilibrium.

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