# Thermal emission of electrons from highly excited sodium clusters

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**Abstract.** Positively charged sodium clusters can be easily ionized by a fs laser pulse of relatively low intensity ($< 10^{10}$ W/cm$^2$), if the laser is in resonance with the plasmon excitation of the cluster. This ionization process was investigated in detail by measuring the kinetic energy distribution of electrons emitted from a size-selected Na$_{93}^+$ as a function of the fs laser intensity. In all cases pure Boltzmann-like energy distributions were observed. A comparison with statistical theory shows that the emission is a purely thermal process. It is different to normal thermionic emission insofar as the electrons are emitted from a hot electron system which is only weakly coupled to a cold ionic background. The results demonstrate purely statistical behaviour of a small fermionic system even for very high excitation energy.

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Thermionic emission from clusters after photoexcitation is a well-known phenomenon [1, 2]. This process is typical for strongly bound clusters such as refractory metal or carbon clusters, as only they can be heated to temperatures high enough for electron emission without undergoing fragmentation. The excitation is typically done using ns laser pulses, and the emission takes place on a nanosecond to microsecond time scale. It is characteristic for this type of emission that the electrons and the ions are in perfect thermal equilibrium. A different type of thermal electron emission has recently been observed for the case of C$_{60}$ clusters [3, 4]. In this case the electron system is heated within a very short time either by the collision of a metastably excited rare gas atom with the cluster or by fs laser irradiation. For not too high excitation energies, electron emission takes place only as long as the energy is still located in the electron system. After transfer of the energy to the ion system, electron emission is not possible any more, as due to the much larger heat capacity of the ions the electron temperature is strongly reduced. We have now studied the same type of phenomenon for the case

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of sodium clusters. Unlike as for C$_{60}$, for these clusters thermal electron emission has not been observed before. Sodium clusters are too weakly bound (binding energy $\sim 1$ eV/atom) to exhibit normal thermionic emission. If they are heated for example by ns laser pulses, they start to evaporate atoms at temperatures far below those necessary for electron emission. As the energy transfer between electrons and ions takes place on a ps-time scale, after absorption of a photon all of the energy is transferred to the ions before the next photon is absorbed, even if a large number of photons is absorbed during a typical 10 ns laser pulse. The situation is different, however, if the clusters are heated by a fs laser pulse. In this case it is possible to excite just the electron system. The optical excitation is especially easy for sodium clusters, which exhibit a strong plasmon resonance close to the energy of the second harmonic of a Ti:sapphire fs laser (3.1 eV). This allows a high excitation to be reached with relatively weak laser intensities, so that no nonlinear high field effects have to be taken into account. The observation of electron emission after fs laser excitation of the plasmon resonance has recently been reported [5]. In that report we interpreted the ionization to be due to the direct coupling between a multiply excited plasmon and a single electron. Although this certainly is a possible mechanism for electron emission, the results as described below show that for the type of laser pulse used thermal electron emission most probably is the dominant emission process.

## 1 Experiment

The experimental setup is similar to the one previously described [5–7]. Cluster ions with a temperature of 105 K are produced in a gas aggregation source and mass-selected in a time-of-flight mass spectrometer. A typical intensity for a size-selected Na$_{93}^+$ is about 5 to 50 clusters per pulse. Two types of measurements can be performed on a cluster of chosen size. Firstly, it can be irradiated by a laser pulse before entering a secondary time-of-flight mass spectrometer. In this case one can measure photofragment distributions and photofragmentation cross-sections. Secondly, the cluster can be injected into a magnetic bottle photo-electron spectrometer, decelerated and then irradiated by a laser pulse. If elec-

trons are emitted, they are collected with high efficiency and their flight time distribution is measured, which can be converted into a kinetic energy distribution.

For the production of the fs laser pulses, a standard configuration is used, which consists of an Ar-ion laser pumped Ti:sapphire oscillator and a Nd:YAG laser pumped regenerative amplifier. The intensity at 800 nm is typically 1 mJ per pulse with a repetition rate of 30 Hz. Frequency-resolved optical gating gives a pulse length of 75 to 110 fs with no visible chirp. After frequency doubling the pulse length is 110–200 fs. The intensity at $h\nu = 3.1$ eV is typically 0.3 mJ. In the case of photoelectron spectroscopy, the laser beam is reduced by apertures to a diameter of 1 mm. The beam is not focussed and should therefore have a flat top profile in the interaction region. This first study was performed on $Na_{93}^+$, which has a closed electronic shell of 92 electrons and is thus spherically symmetric in the nearly free electron (or jellium) model. Its one-photon absorption cross section is about 60 Å$^2$ at $h\nu = 3.1$ eV, as has been measured previously [6].

A typical photofragment distribution is shown in Fig. 1. A high intensity of doubly and some triply charged clusters are observed. This is in contrast to the observations for nanosecond laser pulses, where no ionization occurs at this wavelength, even if the laser intensity is high enough to totally fragment the cluster. Examples of photoelectron kinetic energy distributions measured for different laser intensities are shown in Fig. 2. Almost perfectly exponential distributions are obtained in all cases. The only influence of the laser intensity is that for stronger laser pulses one obtains higher electron intensities and a higher mean kinetic energy. No structure (apart from noise) was observed in the spectra for laser intensities between $1 \times 10^9$ W/cm$^2$ and $5 \times 10^{10}$ W/cm$^2$, that is ATI (above threshold ionization)-like patterns as reported in [4] for $C_{60}$ were never seen.

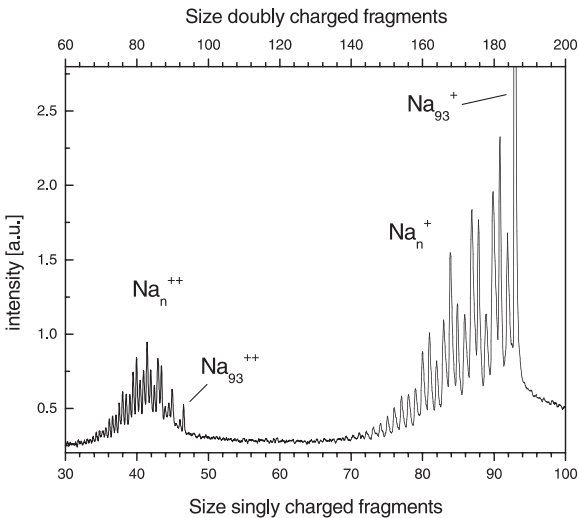An obvious explanation for the observed exponential (Boltzmann-like) energy distribution would be a thermal electron emission process. This possibility will be discussed in the next section.
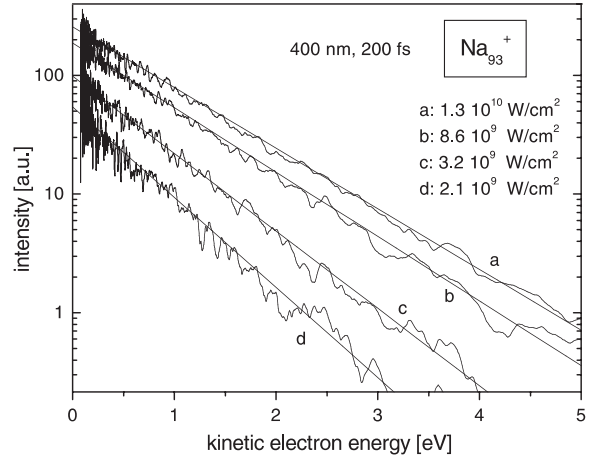


**Fig. 2.** Kinetic energy distributions of electrons emitted from size-selected $Na_{93}^+$ clusters irradiated by 400 nm fs laser pulses of different intensities. The pulses had a temporal width of 200 fs (FWHM)

## 2 Theory

In order to check whether the observed electrons were thermally emitted, we simulated the electron intensity and kinetic energy distribution using a statistical theory for thermal emission, namely the Weisskopf formalism [8]. In this formalism the electron emission rate is given by (adopted from [3]):

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

Here $E$ is the inner energy of the electron system, $\varepsilon$ the kinetic energy of the electron, $m_e$ the electron mass and $\phi$ the ionization potential. The factor 2 accounts for the spin degeneracy. The multi-particle level density $\varrho$ is given by

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

$g(E_f)$ being the single particle level density at the Fermi energy:

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

where $N$ is the number of valence electrons and $E_f$ the Fermi energy. For the capture cross section $\sigma$, the classical geometrical cross-section is used:

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

where $V(r_0)$ is the potential close to the surface ($Z$ is the cluster charge before ionization; the image charge is neglected):

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

For the calculation of $r_0$, the bulk density of sodium was used ($r_0 = \sqrt[3]{93} \times 2.1$ Å). In order to calculate the total electron emission probability and the distribution of the kinetic



**Fig. 1.** Typical photofragment distribution produced by irradiation of size-selected $Na_{93}^+$ clusters with a fs laser pulse (400 nm, 200 fs, $\approx 4 \times 10^9$ W/cm$^2$). The intensity distribution of the fragments, showing a maximum about every three atoms, is due to the low binding energy of the sodium atoms ($\approx 1$ eV/atom): for every absorbed photon, about three atoms are evaporated

energies, one has to know the time dependence of the inner energy $E$. The electron gas is heated by photon absorption, and cooled by energy transfer to the ion system. Assuming a constant optical absorption cross section $\sigma_o$ and a linear coupling to the ions with a characteristic time $\tau_e$, the inner energy follows the simple differential equation

$$\frac{\mathrm{d}}{\mathrm{d}t} E(t) = \sigma_o p(t) - \frac{1}{\tau_e} E(t) \ . \tag{6}$$

The laser intensity $p(t)$ is assumed to have a Gaussian temporal profile:

$$p(t) = \frac{p_0}{\tau_L \sqrt{2\pi}} \exp\left(-\frac{(t-t_0)^2}{2\tau_L^2}\right) \ . \tag{7}$$

The inner energy is then given by

$$E(t) = \frac{E_0}{2} \exp\left(\frac{\tau_L^2}{2\tau_e^2} + \frac{t_0 - t}{\tau_e}\right) \left[1 - \mathrm{erf}\left(\frac{\tau_L^2 - (t-t_0)\tau_e}{\sqrt{2}\tau_L\tau_e}\right)\right] , \tag{8}$$

with $E_0 = \sigma_o p_0$. This is only true if no electron emission occurs; otherwise the energy loss due to the emission has to be taken into account. We thus define internal energies for each charge state (singly charged, doubly charged, ... ) by

$$
\begin{aligned}
E_1(t) &= E(t) \\
E_2(t) &= E_1(t) - \phi_1 - \bar{\varepsilon}_1 \\
E_3(t) &= E_2(t) - \phi_2 - \bar{\varepsilon}_2 \\
&\vdots
\end{aligned}
\tag{9}
$$

where $\phi_i$ is the ionization potential of the $i$th charge state and $\bar{\varepsilon}_i$ is the average kinetic energy of the $i$th emitted electron. Integrating (1) over the electron energy, one obtains the total electron emission rates for the different charge states:

$$
\begin{aligned}
K_i(t) &= \int_0^{E_i(t)-\phi_i} k_i(E_i(t), \varepsilon) \mathrm{d}\varepsilon \\
&= \int_0^{E_i(t)-\phi_i} \frac{2m_e \sigma_i(\varepsilon)}{\pi^2 \hbar^3} \varepsilon \frac{\varrho(E_i(t) - \phi_i - \varepsilon)}{\varrho(E_i(t))} \mathrm{d}\varepsilon \ .
\end{aligned}
\tag{10}
$$

Using this, one can write down the coupled differential equations for the population of the different charge states:

$$
\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t} N_1(t) &= -K_1(t) N_1(t) \\
\frac{\mathrm{d}}{\mathrm{d}t} N_2(t) &= K_1(t) N_1(t) - K_2(t) N_2(t) \\
\frac{\mathrm{d}}{\mathrm{d}t} N_3(t) &= K_2(t) N_2(t) - K_3(t) N_3(t) \\
&\vdots
\end{aligned}
\tag{11}
$$

with the initial values $N_1(0) = 1$ and $N_{i \neq 1}(0) = 0$. The intensity of electrons emitted from each charge state is then

$$I_i = 1 - \sum_{j=1}^{i} N_j(\infty) \ , \tag{12}$$

and the total electron intensity is

$$I_{\mathrm{tot}} = \sum_{j=1}^{\infty} I_j. \tag{13}$$

The kinetic energy distributions of the electrons emitted from charge state $i$ and the total distribution are given by

$$
\begin{aligned}
f_i(\varepsilon) &= \int_0^{\infty} N_i(t) k_i(E_i(t), \varepsilon) \mathrm{d}t, \\
f_{\mathrm{tot}}(\varepsilon) &= \sum_{j=1}^{\infty} f_j(\varepsilon) \ .
\end{aligned}
\tag{14}
$$

In order to evaluate these functions numerically, one has to make an assumption about the ionization potentials for the different charge states. For $Na_{93}^+$ the ionization potential $\phi_1$ was measured by determining the photoionization probability as a function of laser wavelength. A value of $4.65\,\mathrm{eV}$ ($\pm 0.15\,\mathrm{eV}$) was found. The other ionization potentials were calculated using

$$\phi_i = 2.35\mathrm{eV} + \frac{(i+1/2)e}{4\pi\varepsilon_0 \sqrt[3]{93} r_e} \ , \tag{15}$$

with $r_e = 2.07\,\text{Å}$ (fitted to $\phi_1$). The absorption cross-section, which is not precisely known for the excited cluster or for the higher charge states, has been used as a fitting parameter to adjust the calculated curve to the measured ones. For the lifetime of the electron system excitation, a value of $\tau_e = 2500\,\mathrm{fs}$ was used, which is in accordance with preliminary results of pump–probe experiments started recently.

Some examples of calculated kinetic energy distributions are plotted in Fig. 3. The curves are calculated for different total amounts of energy absorbed by the electron system. Like the measured ones, the curves are almost perfectly exponential, although each curve is a superposition of different distributions, as the electrons are emitted from clusters with
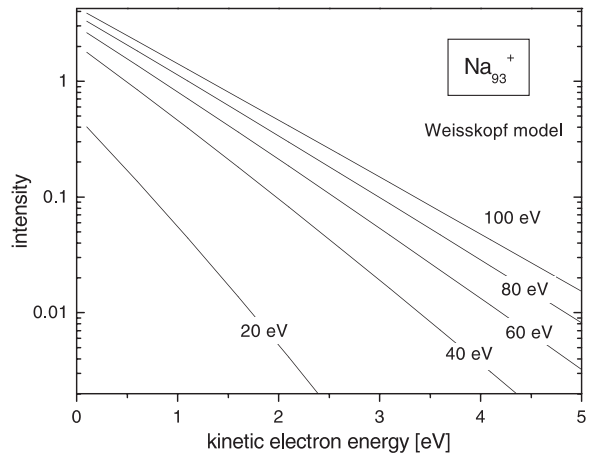


**Fig. 3.** Kinetic energy distributions of electrons emitted from size-selected $Na_{93}^+$ clusters as calculated using the Weisskopf formalism (see text for details). The parameter given is the total amount of energy absorbed by the cluster from a 200 fs laser pulse. An electron cooling rate of $(2.5\,\mathrm{ps})^{-1}$ was assumed

a broad range of temperatures and charge states. With increasing internal energy, the electron intensity strongly increases. The mean kinetic energy, however, seems almost to saturate for higher inner energies. This is due to two reasons: Firstly, this is simply an effect of the heat capacity of the electron system, which increases with temperature. A given increase in the internal energy leads to a smaller increase in the temperature if the system is already hot. Secondly, it is due to the steeply rising electron emission probability: for strong excitation the cluster actually cools by electron emission during the excitation process.

## 3 Comparison with experiment

The photoelectron spectra measured for different laser intensities were fitted with simple exponential functions, using the two parameters intensity and mean energy. The results are shown in Figs. 4 and 5. In Fig. 4 the measured intensities are compared to the simulated intensities $I_i$ and $I_{tot}$, which are plotted as a function of the total absorbed energy. The $x$ and $y$ axes of the experimental and theoretical results are adjusted to get a good fit of the data. The obtained relationship between absorbed energy and laser intensity determines the average absorption cross section of the excited cluster. From the fit a value of $\approx 50$ Å$^2$ is obtained, which is in good agreement with previous measurements [6]. In Fig. 5 the measured mean kinetic energies of the electrons are compared to the mean energies of the calculated distributions $f_{tot}(\varepsilon)$. The same relationship between absorbed energy and laser intensity as determined from Fig. 4 was used, so no adjustment was done.

Both measured distributions are reproduced well by the calculated functions. There is some deviation between the measured and the calculated curves for the lowest and for the highest laser intensities. The deviation at the low intensities could be due to spatial or shot-to-shot laser intensity varia-
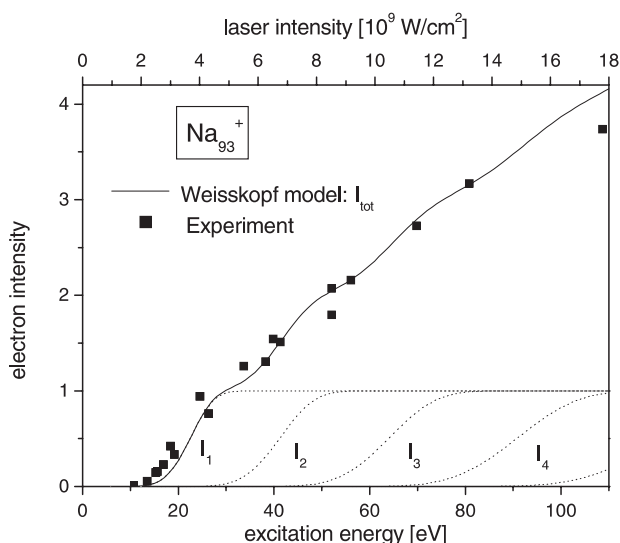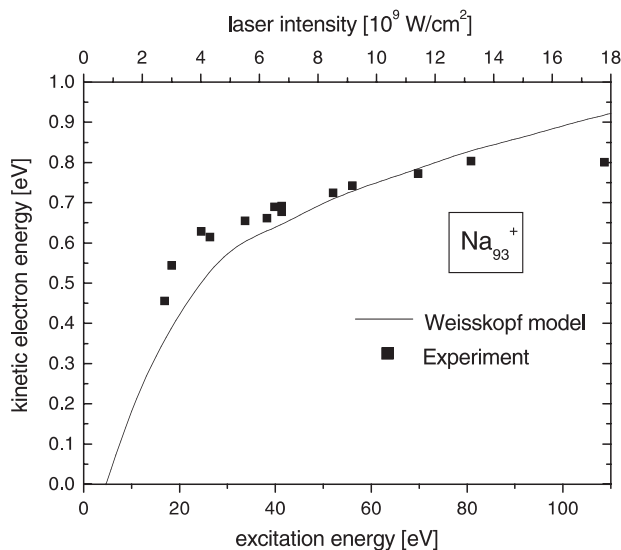


**Fig. 5.** Mean kinetic energy of photoelectrons emitted from Na$_{93}^+$ clusters irradiated by a 400 nm fs laser pulse: measured values compared to calculated ones (see text for details)

tions, which because of the steeply rising ionization probability tend to shift the distributions towards lower intensities. The deviation for the high intensity could be due to the fact that the calculated ionization potentials for the higher charge states are not correct. A second possible reason would be that the absorption cross-section becomes smaller for high excitation energies, due to a broadening of the absorption profile, which would lead to a lower value of the absorbed energies at the highest laser intensities.

In any case the results show that the observed electron emission can be safely interpreted as thermal emission from a hot electron gas. No significant deviation from thermal behaviour occurs even for the highest excitation energy of about 100 eV, which is more than 1 eV per electron.

From these results one can conclude that in order to unambiguously detect direct electron emission via a multiply excited plasmon as postulated in [5], one has to use much shorter laser pulses. Only then it is possible to multiply excite the plasmon and still keep the total absorbed energy below $\approx 20$ eV, the point at which thermal electron emission massively sets in.

## 4 Summary

The electron emission from size-selected cold Na$_{93}^+$ clusters after fs laser pulse excitation of the plasmon resonance was characterized by measuring the photoelectron spectra. The results are in very good agreement with model calculations, which assume thermal electron emission from a hot electron gas. As the cooling rate of the electron gas has a strong influence on the ionization probability, this type of thermal electron emission can be used to measure the coupling between electrons and ions in free, mass-selected sodium clusters. Such experiments are underway.

**Fig. 4.** Measured photoelectron intensities compared to calculated intensities. The experimental values are given as a function of the measured laser intensity (*upper scale*), while the calculated ones are plotted as a function of the total energy absorbed. $I_i$ is the calculated intensity of the $i$th electron emitted from the cluster. $I_{tot}$ is the sum of these contributions

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