Observation of Electron Gas Cooling in Free Sodium Clusters

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Free size-selected Na_n^+ ($n = 16$–250) clusters have been studied by femtosecond pump-probe photoelectron and photofragmentation spectroscopy. Thermal electron emission from the hot electron gas was used to monitor the energy transfer from the electronic system to lattice vibrations. The electron-phonon coupling constants determined for the different sizes can be described by the radius dependent function $g(R) = (2.3 + 114\ \text{Å}^2/R^2) \times 10^{16}\ \text{W/m}^3\,\text{K}$. No strong quantum size effect was observed even for the smallest cluster size.

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Electron-phonon coupling is the reason why the electronic system even of a defect-free crystalline metal does not behave like an ideal electron gas. It is responsible for the finite conductivity of metals at not too low temperatures, and causes BCS-type superconductivity. It is therefore of fundamental interest, and has been studied in detail for various bulk materials. The theoretical treatment of the phenomenon has reached a high level; newer calculations are in very good agreement with experiment [1].

An interesting question is whether and how the electron-phonon coupling changes in metal particles. In larger particles (diameters of several nm or more) the presence of a surface should just modify the coupling. It has been shown that surface vibrational modes couple differently to the electrons [2] than bulk modes; furthermore, the reduced electronic screening close to the surface can influence the general electron-phonon coupling [3]. This type of finite size effect is indeed seen in experiments. A number of groups have studied electron-phonon coupling in metal particles with diameters of 2–100 nm. This was mainly done by time-resolved absorption spectroscopy on metal particles in matrices, solutions, or on surfaces [3–6]; additionally, silver islands on graphite have been studied by time-resolved photoelectron spectroscopy [7], and sodium islands on mica by time-resolved second harmonic production [8]. All of the measurements demonstrate a cooling of the laser excited electron gas with decay times on a picosecond time scale. In general, the results can be well described by the simple two-temperature model [9], which assumes different electron system and lattice temperatures and an energy transfer between both proportional to the temperature difference. Although no full agreement about the size dependence of the cooling rates seems to be achieved yet [4], recent comprehensive experiments by Lermé *et al.* [3] have clarified most of the questions concerning matrix and excitation strength influences, and demonstrated a weak increase of the cooling rate with decreasing size for gold and silver particles between 2.2 and 30 nm diameter (about 300 to 8×10^5 atoms per particle). A much stronger effect, however, can be expected to occur in even smaller particles, where the strong discretization of the electron density of states should lead to deviations from extrapolated bulk behavior. Naïvely termed, simple electron relaxation by single phonon creation gets impossible if the average electron energy level spacing is larger than the Debye frequency, which is the case for simple metal particles with less than about 300 atoms [indeed in very small particles like Au_6^- practically infinite lifetimes of some excited states are observed [10]]. This was our motivation to measure electron-phonon coupling in medium sized sodium clusters. Sodium was chosen as it is the best representative of a free electron metal [11].

The measurements make use of the fact that sodium clusters irradiated by a femtosecond laser pulse in resonance with the collective plasmon excitation exhibit thermal electron emission, as has been demonstrated recently [12,13]. Because of the fast decay of the plasmon and strong electron-electron coupling the absorbed energy is redistributed in the electronic system within a very short time (which is not exactly known, but the complete absence of direct multiphoton ionization events in our results indicates time scales $\ll 100$ fs). Absorption of a couple of photons can lead to electronic temperatures of several thousand kelvins, which are high enough for thermal electron emission to occur on a picosecond time scale. This emission can be used to study the cooling of the electron gas in a pump-probe experiment. The cluster is irradiated by two laser pulses of equal strength, from each of which it absorbs some photons. The strength of the pulses is chosen such that each pulse heats the electron gas only to a temperature where the thermal electron emission still is weak. In case of pulse delay times shorter than the electron gas cooling time, energy from both pulses is accumulated in the electron system, which leads to significantly enhanced electron emission due to its strongly nonlinear energy dependence. Measuring the total amount of electron emission as a function of the pulse delay times therefore allows one to directly monitor the energy flow out of the electronic system. One should mention that exactly this technique has been used already more than 20 years ago in time-resolved studies of metal surfaces [14].

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The experimental setup is the same as used in earlier studies [11,12]. Positively charged sodium clusters of about 200 K temperature are produced in a gas aggregation cluster source and inserted into a double reflectron time-of-flight mass spectrometer equipped with a magnetic bottle type photoelectron spectrometer. Here either photofragmentation or photoelectron spectroscopy can be performed on the size-selected clusters. For the excitation a Ti:sapphire oscillator combined with a regenerative and a multipass amplifier is used. It produces 800 nm pulses at 30 Hz, which after frequency doubling have an energy of about 0.5 mJ and a duration of 200 fs. They are split into two pulses of variable delay time in a standard Michelson interferometer setup. In one of its arms a half-wave plate serves to rotate the polarization of one of the pulses by 90° in order to avoid interference effects for short delay times.

Typical results are shown in Fig. 1. One can see the total electron intensity as a function of pulse delay time for two cluster sizes, Na_{16}^+ and Na_{139}^+. Both curves are very similar; electron emission is maximal for zero delay, that is for perfect overlap of the two pulses, and falls off with increasing delay. This decrease is symmetrical with respect to time zero as pump and probe pulse are identical. In order to obtain an estimate for the decay time the curves have been fitted with simple exponential functions $I(\Delta t) = A\exp(-|\Delta t|/\tau) + Y_0$. For τ values of about two picoseconds are obtained. These decay times are not constants, but depend on the excitation strength, as is demonstrated in Fig. 2. Here the normalized delay curves of Na_{70}^+ are shown for two different laser intensities; clearly different decay times can be observed. This well-known excitation dependence of the electron cooling rate is a direct consequence of the temperature dependence of the electron system heat capacity [4].

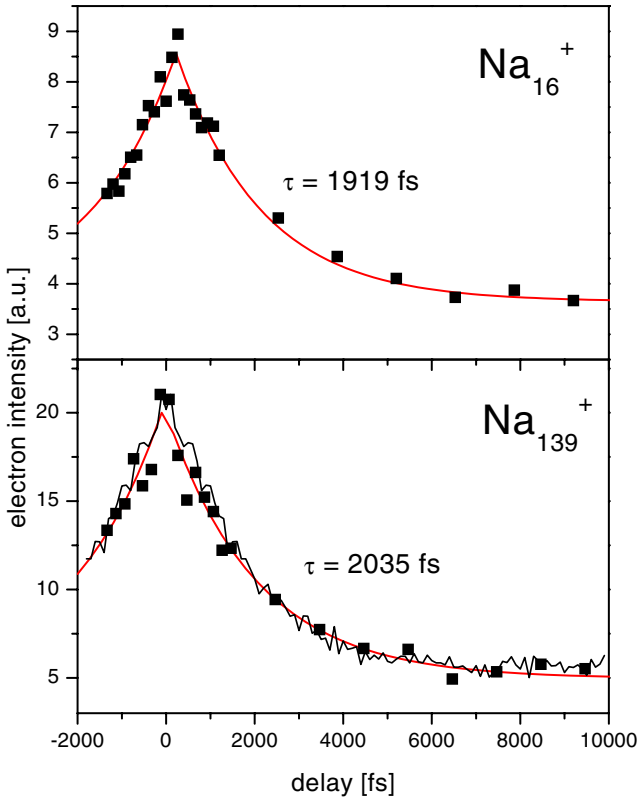

FIG. 1 (color online). Photoelectron intensity emitted from Na_{16}^+ and Na_{139}^+ irradiated by two femtosecond laser pulses (400 nm, 200 fs) as a function of the delay time Δt between the pulses. The thick lines indicate an exponential fit; in the lower graph the thin line indicates the result of the simulation described in the text.

In order to evaluate our results we have fitted them using the two-temperature model [9], which assumes that the energy transfer between the electron system and the lattice is proportional to their temperature difference:

$$c_e(T_e)\dot{T}_e = -g(T_e - T_i) + h\nu\sum_n \delta(t - t_n). \quad (1)$$

$$c_i\dot{T}_i = g(T_e - T_i). \quad (2)$$

Here T_e and T_i are the temperatures of the electronic and the ionic system, $c_e(T_e)$ and c_i are the respective heat capacities, and g is the electron-phonon coupling constant. For the ions the heat capacity is taken to be the Dulong Petit value ($c_i = 3N_{At}k_B$), whereas the value for the electron gas is calculated from the temperature dependence of the energy of an ideal electron gas:

$$E(T) = \frac{3N_{el}}{2E_F^{3/2}}\int_0^\infty E^{3/2}\left[\exp\left(\frac{E-\mu}{k_BT}\right) + 1\right]^{-1} dE. \quad (3)$$

For the Fermi energy the bulk value $E_F = 3.1$ eV is used. The energy of the electron system is increased by photon absorptions at the times t_n. These times are assumed to obey classical statistics, which means that the conditional probability for a photon absorption at time t_n after a photon absorption at time t_{n-1} is given by:

$$P(t_n|t_{n-1}) = \sigma\phi(t_n)\exp\left[-\int_{t_{n-1}}^{t_n}\sigma\phi(t)dt\right]. \quad (4)$$

The laser intensity $\phi(t)$ is modeled by two Gaussians with a width of 200 fs and variable delay time Δt. The product

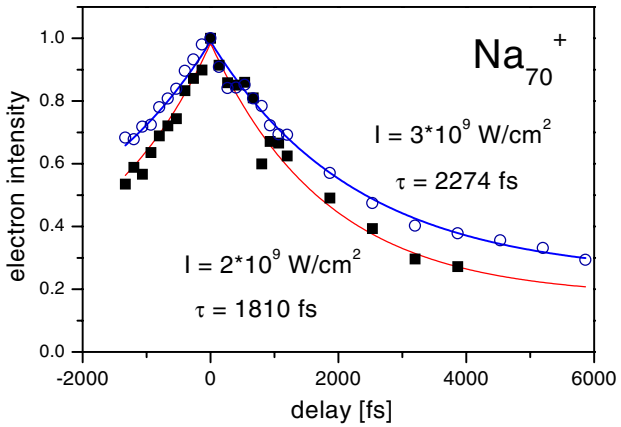

FIG. 2 (color online). Pump-probe photoelectron intensity emitted from Na_{70}^+ for two laser intensities (per pulse). Note the faster decay for weaker excitation.

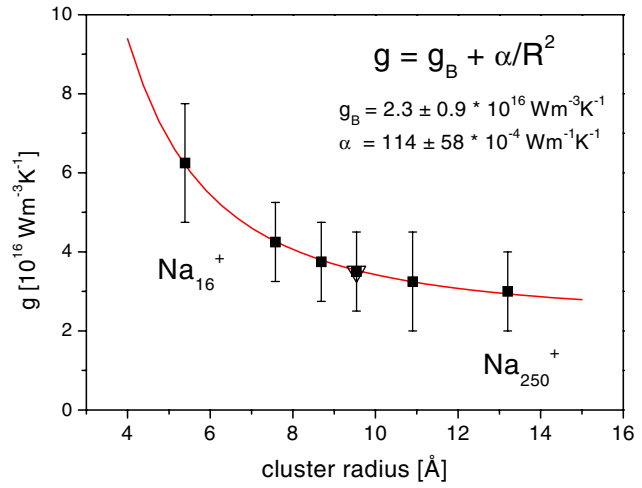

FIG. 4 (color online). Measured size dependence of the electron-phonon-coupling constant. For Na_{93}^{+} the result obtained from the microcaloric experiment is given as well (open triangle). The line indicates a fit with a tentative fit function.

of total laser fluence and cluster absorption cross section σ is used as a fitting parameter, as described below. In order to simulate the measured results, Eqs. (1) and (2) are integrated numerically. Photon absorption events are generated from random numbers in accordance with Eq. (3). From the resulting time dependent electron temperature the electron emission rate $k(E, \varepsilon)$ [$E(T_e)$ being the electron system energy, ε the kinetic electron energy] is calculated using the Weisskopf model, which is described in detail in [12]. Random numbers are used to generate electron emission events in accordance with this calculated rate. Each electron emission reduces the electron system energy by the ionization potential and the electron kinetic energy. The results (number and kinetic energies of the emitted

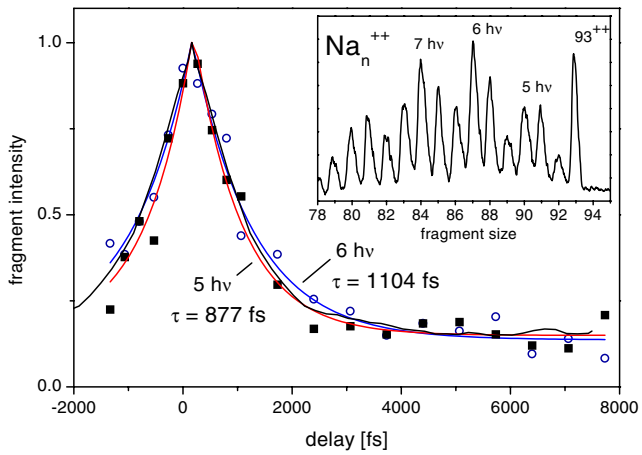

FIG. 3 (color online). Pump-probe intensities of doubly charged photofragments of Na_{93}^{+}: summed intensities of $Na_{90}^{2+}/Na_{91}^{2+}$ (squares), and $Na_{87}^{2+}/Na_{88}^{2+}$ (circles). The thick lines are exponential fits; the thin line is the result of a simulation for the six photon fragment group $Na_{87}^{2+}/Na_{88}^{2+}$. The inset shows an example mass spectrum of the fragments.

electrons) are averaged over many such Monte Carlo runs at each time step of a delay curve. The coupling constant g is then varied until the measured and the simulated delay curves exhibit the same decay times. As mentioned above, the decay time (and therefore the fitted value of g) depends on the total excitation energy, which is not exactly known due to the unknown absorption cross section of the electronically heated cluster. In principle, the excitation energy can be obtained from the measured kinetic energy distributions of the electrons. This nevertheless leads to quite an uncertainty as the average kinetic energy only weakly depends on the amount of excitation [12,13]. It turned out that the ratio of electron intensities for zero and very large delay times $\beta = (A + Y_0)/Y_0$ is much more sensitive to the excitation strength. Therefore, in the simulations the average amount of energy absorbed was varied until the simulated β was the same as the measured one.

Examples of simulated curves as obtained from these calculations are shown in Figs. 1 and 3. The good agreement between the simulated and the experimental curves demonstrates the overall correctness of the model; most importantly, it demonstrates that the assumption of a temperature independent coupling constant g is reasonable.

Obtaining the total excitation energy from the ratio β of course strongly relies on the correctness of the Weisskopf model for the description of the electron emission. So an at least partly independent test of the whole model is highly desirable. For this reason we have done a second experiment, a ''microcaloric'' determination of the electron-phonon coupling. As has been demonstrated earlier, one can use the modulation visible in photofragment distributions of sodium clusters to determine the number of photons they have absorbed during the excitation [15]. This works not only for singly charged fragments, but for doubly charged ones as well, as is demonstrated in Fig. 3, where a mass spectrum of doubly charged fragments produced from Na_{93}^{+} irradiated by a 400 nm femtosecond laser pulse is shown. One can observe groups of fragments with a spacing of about three atoms, which is the ratio of the photon energy of 3.1 eV and the binding energy of sodium atoms of about 1 eV/atom. Based on previous temperature dependent experiments [15] one can identify the first fragment group (sizes $Na_{90}^{2+}/Na_{91}^{2+}$) as being produced from clusters which have absorbed exactly five photons during the excitation, whereas the second group ($Na_{87}^{2+}/Na_{88}^{2+}$) results from the absorption of six photons. So the intensities of these doubly charged fragments indicate the probability of the emission of exactly one electron after the absorption of a well-defined amount of energy. Measuring the fragment group intensities in a pump-probe experiment as a function of the delay time between the laser pulses yields similar curves as the measurements of the total electron intensity. They can be fitted in the same way, with the one important difference that here only one free parameter is used, the electron-phonon coupling constant. In Fig. 3 two pump-probe curves are shown, for five and six photon

absorption, respectively. One can see that the decay times are much shorter than for the results presented in Figs. 1 and 2; this is due to the fact that in the electron emission measurements a stronger average excitation was used for intensity reasons. Accordingly, the six photon curve exhibits a slower decay than the five photon one. Fitting these curves with the model described above (doing the Monte Carlo simulation, but keeping just the results for a specified total number of photons absorbed) an electron-phonon-coupling constant of $g = 3.5 \times 10^{16}$ W/m^3 K for Na_{93}^+ is obtained, which within the experimental uncertainty is exactly the value obtained from the electron intensity measurements. This agreement gives strong evidence that the modeling used is indeed adequate.

The final results for the electron-phonon coupling constants obtained are shown in Fig. 4. The error bars do not reflect the statistical error of the measurements, which is much smaller, but the uncertainty caused by the simultaneous determination of excitation energy and coupling constant. To our knowledge no rigorous theoretical prediction for the analytical form of the size dependence exists yet. It has been shown that electron-surface-phonon coupling exhibits a predominant $1/R$ and a weaker $1/R^2$ dependence [2] (R being the cluster radius); the correct adding of surface and bulk terms, however, is still under debate [3]. Here we simply rely on the fact that for large sizes the coupling constant must converge to the bulk value, and tentatively use the fitting function:

$$g = g_B + \alpha/R^2. \tag{5}$$

The fit (see Fig. 4) yields values of $g_B = 2.3 \times 10^{16}$ W/m^3 K and $\alpha = 114 \times 10^{-20}$ W/m K. No direct measurement of the bulk value exists to which this result could be compared. Nevertheless an estimate for the bulk coupling constant can be obtained from the so-called electron-phonon spectral function $\alpha^2F(\omega)$ [16]:

$$g_B = \frac{3\hbar}{\pi k_B}\gamma 2\int_0^\infty \alpha^2F(\omega)\omega d\omega. \tag{6}$$

The spectral function can be obtained from calculations or measured point-contact spectra [1]; from the experimental data one obtains $\int_0^\infty \alpha^2F(\omega)\omega d\omega = 1.2 \times 10^{25}$ s^{-2}. Together with the measured value of the electron heat capacity coefficient $\gamma = 1.38$ mJ/mol K^2 [17] this leads to a value of the bulk electron-phonon coupling constant of $g_B = 1.0 \times 10^{16}$ W/m^3 K that is only a factor of 2 smaller than the extrapolation of our results. Given all uncertainties of both our data and the ''experimental'' bulk value, this is a rather good agreement. Note that sodium exhibits an electron-phonon coupling somewhat weaker than that of noble metals [Au: $g_B = 3.0 \times 10^{16}$ W/m^3 K; Ag: $g_B = 3.5 \times 10^{16}$ W/m^3 K [18]] and significantly weaker than that of the ''free'' electron metal aluminum [Al: $g_B = 24.5 \times 10^{16}$ W/m^3 K [19]].

So although the experiments are done on very small systems, and in an extremely high excitation regime (with pump pulse induced intermediate electronic temperatures of up to 7500 K and lattice temperatures of up to 1100 K) an electron lattice energy transfer is observed which is not very different from that of the bulk, and probably converges smoothly to it with increasing size. One reason why the smallness of the systems does not lead to dramatically different behavior might actually be the high temperatures involved, which can completely mask the discreteness of the density of states. It has, e.g., been shown by RPA calculations that the density of the excited states of a Na_{20} cluster is about 200 (eV)$^{-1}$ already at an excitation energy of 3.1 eV [20]. A much higher value can be expected for a Na_{16}^+ at its typical excitation energy of 6.2 eV (absorption of two photons). So here relaxation in steps of the small phonon energies is certainly possible. One should note, however, that this implies that multiparticle state relaxation takes place instead of single particle one. At much lower excitation energies the discreteness even of the multiparticle density of states will be appreciable and should influence the electron-phonon coupling; this will be tested in forthcoming experiments.

In conclusion, we have studied electron-phonon coupling in sodium clusters as a function of size. Surprisingly even for the smallest size (Na_{16}^+) no deviation from the simple two-temperature model was found. Accordingly, the determined coupling constants seem to exhibit a smooth convergence towards the bulk value. No significant influence of the strongly discretized electronic density of states of the clusters was found, which is probably due to the strong excitation necessary in this type of experiment.

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