# Plasmon Enhanced Electron and Atom Emission from a Spherical Sodium Cluster: $Na_{91}^-$

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The photoabsorption cross section of the negatively charged, spherical $Na_{91}^-$ cluster shows a broad collective resonance at $\hbar\omega = 2.65$ eV, the decay of which can lead to two final channels: atom and electron emission. The branching ratio between the two channels was measured to increase linearly with photon energy over the unexpectedly broad energy range of 1.2 eV, which is attributed to the cluster's incipient valence band width. The femtosecond time scales of the processes involved are discussed. [S0031-9007(96)01103-9]

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Alkali clusters show a strong collective resonance in the visible which has attracted a large interest in recent years [1,2]. The resonances have so far been studied experimentally for neutral and positively charged clusters. Only atom emission but no electron emission can occur in these cases, as the threshold for electron emission is higher than the plasmon [3] energy, at least for most of the cluster sizes studied so far. The only exception is a study of photoprocesses in large potassium clusters [4].

For negatively charged alkali clusters, on the other hand, the plasmon resonance is above the threshold for electron ejection. This leads to a huge increase of the cross section for the emission of photoelectrons, as observed earlier for silver aerosols [5]. We have studied photoinduced processes for the negatively charged sodium cluster $Na_{91}^-$, which has 92 valence electrons, giving it a closed shell electronic structure and thus a spherical geometry in the popular shell model for metal clusters [1,2].

Photoemission of electrons from macroscopic surfaces has been studied for a long time [6]. Photoemission from mass selected clusters is a much younger domain [1], due to the experimental problem of an extremely low target density which is at least 15 orders of magnitude below the bulk one. Studying photoemission from free clusters in vacuum has one advantage compared to plane surface studies: Energy is conserved. Globally, this is true of course also for a bulk surface. The energy relaxation into the bulk can be measured in principle [7], but this is not normally done [6]. Photoemission from jellium spheres had already been treated in the seminal Ekardt paper [8].

Photoejection of atoms from plane metal surfaces has a very small probability [6], which can be enhanced by many orders of magnitude to a quantum efficiency (number of atoms emitted per number of photons absorbed) of about $10^{-5}$ for rough surfaces or surfaces covered with clusters [9], while values of the order of unity are reported here.

The process studied is shown schematically in Fig. 1. It can be written as

$$h\nu + Na_{91}^-(T_0)$$
$$\downarrow$$
$$Na_{91}^{-*}(T_0) \xrightarrow{\beta} Na_{91} + e^- \quad (1)$$
$$\xrightarrow{1-\beta} Na_{91}^-(T_0 + \Delta T) \rightarrow Na_{90}^- + Na\ . \quad (2)$$

Here $T_0$ is the initial cluster temperature [3], the asterisk stands for electronic excitation, and $\beta$ is the branching ratio. The photon excites the collective plasmon resonance with a large cross section. Two pathways are open for the plasmon decay: electron emission [Eq. (1)] and relaxation of the energy into the heavy particle degrees of freedom [Eq. (2)]. The latter leads to an increase of the cluster temperature by $\Delta T$ which can, if sufficiently large, cause the emission of an atom [10].

The branching ratio $\beta$ is the relative probability for electron emission: i.e., $\beta = \sigma_1/(\sigma_1 + \sigma_2)$, where $\sigma_1$ and $\sigma_2$ are the cross sections for the two decay processes. In this Letter we present the first experimental data for the collective resonance and for the branching ratio of a negatively charged alkali cluster [11]. It is expected that this experiment can be used as a model case for

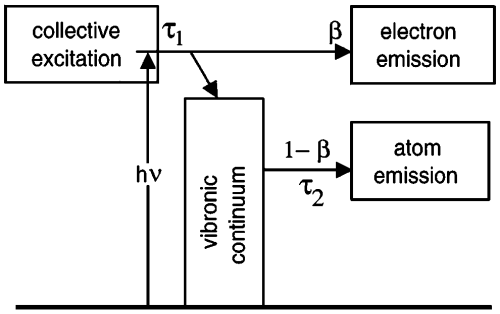


FIG. 1. Schematic of the excitation and relaxation processes. A photon excites a state of definite energy within the plasmon resonance. This state can decay with a time constant $\tau_1$. Either an electron is emitted (branching ratio $\beta$), or via electronic and vibronic relaxation a vibronically excited cluster is produced which decays via atom emission. Estimates of the time constants are $\tau_1 \gtrsim 35$ fs, $\tau_2 \gtrsim 250$ fs.

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the recent cluster experiments with femtosecond time resolution [12], where also an electronically excited state, like the one at the left hand side of Eq. (1), couples to the two decay channels given by Eqs. (1) and (2). The advantage here is that the electronic energy is known to be that of the one absorbed photon, while in femtosecond experiments it can be difficult to determine the number of photons absorbed.

The apparatus is similar to the one described earlier [13,14]. Briefly, cluster ions of a defined temperature (200 K here) are produced in a gas aggregation source and size selected by a first time-of-flight (TOF) mass spectrometer. After irradiation by a laser the intensity of the unfragmented cluster ($Na_{91}^-$) and of the photofragments ($Na_n^-$, $n \leq 90$) is measured in a second TOF. For photon energies above 3 eV, no cluster fragments have been observed, despite an intensity decrease of the $Na_{91}^-$. Thus in this photon range the absorption of a photon leads always to the ejection of an electron.

For photon energies below 3 eV photofragments like $Na_{90}^-$, $Na_{89}^-$, ... are observed, the intensity of which varies quadratically with laser fluence. This shows that at least two photons are necessary for an atom emission. This can be understood as follows: Absorption of one photon by a $n = 91$ atom cluster leads to an increased temperature of only $T_1 = T_0 + \Delta T \approx 330$ K, as the photon energy is distributed over $3n - 6$ degrees of freedom. Absorption of a second photon accordingly heats the cluster up to $T_2 \approx 460$ K. At this temperature the $Na_{91}^-$ cluster fragments within the 15 $\mu$s time window of our machine.

In order to cast the experimental observations into rate equations, we define the following quantities: $N_0(t)$ is the number of clusters which have *not* absorbed a photon, $N_1(t)$ is the number of clusters which have absorbed *one* photon but did not emit an electron (and also not an atom, because the cluster temperature is still too low). This gives

$$dN_0(t) = -\sigma\phi N_0 dt\,, \tag{3}$$

$$dN_1(t) = [(1 - \beta)\sigma\phi N_0 - \sigma\phi N_1]dt\,, \tag{4}$$

where $\beta$ is the branching ratio defined above, $\phi$ the laser fluence (number of photons per $cm^2$ s), and $\sigma$ the photoabsorption cross section. It is assumed in Eq. (4) that $\sigma$ is independent of the cluster temperature. This should be a good approximation, as the temperature dependence of the optical absorption of sodium clusters of this size range is quite small [15].

For $\beta = 0$, Eqs. (3) and (4) are the standard equations of photodepletion if one photon is not sufficient for photofragmentation [16]. For $\beta \neq 0$, the additional term in Eq. (4) takes the possibility of electron emission into account. For the intensity $N = N_0(\tau) + N_1(\tau)$ of the *remaining* $Na_{91}^-$ clusters after a laser pulse of length $\tau$ one has

$$N/N(0) = 1 - \eta + \eta[N_0(\tau) + N_1(\tau)]/N(0)\,, \tag{5}$$

where $\eta \approx 0.85$ is the geometrical overlap between photon and cluster ion beam, $N(0)$ is the cluster intensity without laser interaction, and the term in the square brackets is found from a solution of the rate equations as

$$[N_0(\tau) + N_1(\tau)]/N(0) = \exp(-\sigma\phi\tau) + (1 - \beta)\sigma\phi\tau\exp(-\sigma\phi\tau)\,. \tag{6}$$

The right hand side of Eq. (6) becomes very small for large laser fluences, so that the overlap $\eta$ entering Eq. (5) can be determined accurately.

For 20 photon energies the ratio $N/N(0)$ was measured as a function of the laser fluence, and values for $\beta$ and $\sigma$ were obtained from a fit by Eq. (5). Note that one can determine values for both $\beta$ and $\sigma$ from the same fit. This is possible because electron emission is a one-photon process, while for atom emission at least two photons have to be absorbed, which leads to a different laser fluence dependence of the two channels. The results for $\sigma$ are given by the bold dots with error bars in the upper part of Fig. 2. The many fine points have been obtained using the fast measuring scheme described earlier [14]. As only ratios of cluster intensities enter Eq. (5), an *absolute* cross section can be obtained by only measuring the laser flux absolutely.

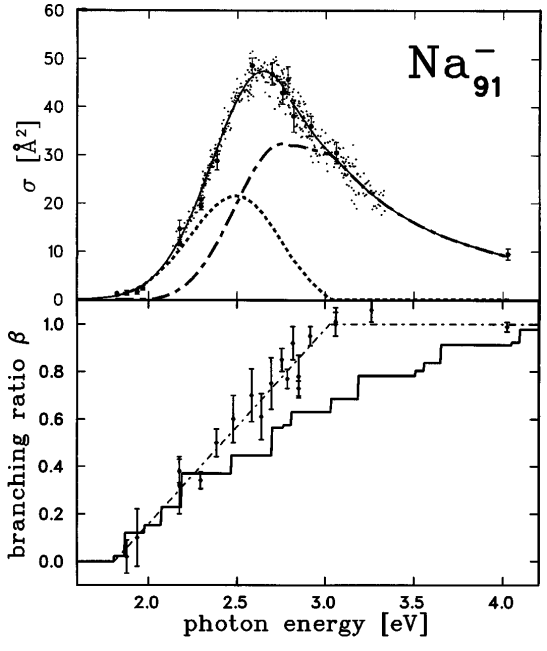


FIG. 2. The photoabsorption cross section for $Na_{91}^-$ as a function of photon energy is given in the upper part. The branching ratio $\beta$, shown in the lower part, was used to decompose it into the partial cross sections for vibrational excitation (dashed line) and plasmon enhanced electron emission (dot-dashed line). The staircaselike line has been calculated from the model discussed in the text.

An independent check on this data treatment is possible. The intensity of the photofragments was measured as a function of photon flux at 540 nm (2.3 eV). Indeed a quadratic variation is observed at low fluences and a fit gives—within experimental error—the same values for $\beta$ and $\sigma$ [17].

The photoabsorption cross section shown in Fig. 2 features one broad asymmetric maximum. Its position, width, and oscillator strength are compared in Table I to values of the positively charged cluster $Na_{93}^{+}$ which has the same number of valence electrons [14,17]. The width of the negatively charged Na cluster is a factor of 1.8 wider. This is due to the following two effects: (1) The potential is softer in the vicinity of the collective resonance for the $Na_{91}^{-}$, which leads to a broader resonance [18], and (2) the open electron emission channel gives an extra escape width. A similar broadening has been observed for $Ag_n^{-}$ clusters [19]. The resonance of the negatively charged cluster is red shifted in agreement with theoretical results [18]. The oscillator strength [1,2] is smaller than that of the positively charged ones. The position and (to a lesser degree) the width of the resonance are in good agreement with two unpublished calculations [20,21].

The experimental branching ratio $\beta$ is shown in the lower part of Fig. 2. Within experimental error, it increases linearly from threshold ($1.81 \pm 0.05$ eV) to 100% at about 3 eV. Thus electron and atom emission compete with each other over an energy range of $\delta = 1.2 \pm 0.11$ eV. Sodium is the best example of a free electron metal. Its electron-phonon coupling is very weak. Thus one could expect naively that electron emission will be dominant shortly above threshold which is in contradiction with the experimental results. A similar linear increase of a branching ratio can be deduced from the data given in Fig. 6 of Ref. [4].

We will argue now that the large unexpected value for $\delta$ is due to the finite width $W$ of the incipient sodium conduction band [3]. Figure 3 shows schematically the jellium potential for $Na_{91}^{-}$. The plasmon can be described as a coherent superposition of electron-hole states [2], whose energies are given schematically by the horizontal lines. If the excited electron comes from the highest occupied levels (process a in Fig. 3) it can leave the cluster

TABLE I. Comparison of the plasmon parameters of the 92 valence electron clusters $Na_{91}^{-}$ and $Na_{93}^{+}$. For the negatively charged cluster studied here, the maximum of the resonance is red shifted, its width $\Gamma$ is larger, and the oscillator strength $f$ smaller. The values of $f$ given are only lower limits to the true ones, as the data have been measured and integrated over a limited energy range only (up to 3.7 and 4 eV for positively and negatively charged clusters, respectively).

| Cluster | $E_{max}$ (eV) | $\Gamma$ (eV) | $f$ |
|---|---|---|---|
| $91^{-}$ | 2.65 | 0.92 | 47.5 |
| $93^{+}$ | 2.77 | 0.51 | 75 |

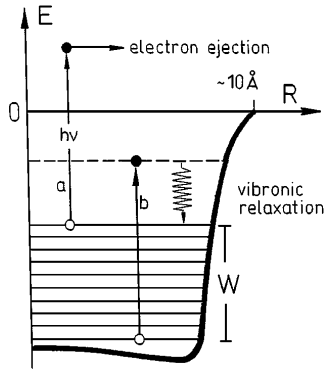


FIG. 3. The thick line shows schematically the potential for the sodium valence electrons. The horizontal lines indicate the filled electronic orbitals. The decay of the plasmon has produced electron-hole pairs. The photon energy is sufficient only to raise weakly bound electrons into the continuum so that they can escape from the cluster (process a). For a strongly bound electron (b) this channel is closed. The picture should not be taken too literally; it gives only the first step of the complicated many-electron processes. For $Na_{91}^{-}$ the well depth is about 5 eV, the width of the incipient conduction band $W \approx 2.5$ eV, and the cluster radius about 10 Å.

if its mean free path is larger than the cluster radius. But if the electron comes from a deep level (b) its energy is not sufficient to leave the cluster. We have modeled this process, taking the energies from an unpublished TDLDA calculation [20], neglecting all matrix element and density of states effects, and assuming that an electron excited to an energy above its angular momentum barrier has a 100% probability of leaving the cluster (see Fig. 3). Only the angular momentum barrier of the outgoing electron and energy conservation go into the calculation [22]. The result is shown by the staircaselike line in Fig. 2. Each step is caused by the opening of a channel for an electron with angular momentum $\ell$ going into continuum states $\ell + 1$ and $\ell - 1$. The threshold energy was obtained by extrapolating the experimental branching ratio to $\beta = 0$.

Up to $\beta \approx 0.6$ this highly simplified model gives a good representation of the data. Although the agreement is surprisingly good, we do not expect this calculation to be very realistic, but it is sufficient to show that *(1) a single particle picture might be sufficient for a rough description of the branching ratio, and (2) the relative broad transition range ($\delta \approx 1.2$ eV) from pure atom emission to pure electron emission can come from the cluster bandwidth W.* If this simple picture would be correct, one would have $\delta \approx W$, which is about 2.5 eV for $Na_{91}^{-}$ [20]. We conjecture that part of this difference is due to intraband Auger processes.

We conclude by giving some estimates of the relevant time scales, which have been of much interest recently due to the availability of lasers with femtosecond time resolution. The relaxation of the excited electron and hole is a complicated many-body problem whose treatment has a long history [23–25]. As we are not aware of any

attempt to study it for a cluster, we will use the bulk data without any correction for finite size effects. According to the accepted picture, the collective plasmon resonance decays by transferring its energy to one electron, or in other words it excites an electron-hole state [2]. From femtosecond laser experiments (1 fs $= 10^{-15}$ s) the relaxation time $\tau_1$ for this process (see Fig. 1) is 30 to 40 fs [24]. The electronic escape time can be estimated as (cluster radius)/(Fermi velocity) $\approx$ 1 fs.

If the electron does not leave the cluster it will start a collisional relaxation cascade, which has been modeled several times [23]. At each step the number of excited electrons goes up by a factor of 2, the mean energy decreases by a factor of 2, and the relaxation time increases by a factor of 4 [24,25]. After four to five collisions it is on the order of the electron-phonon coupling time $\tau_2 \approx 0.25$ to 1 ps, a value which is in agreement with fs-laser experiments of several groups [24,25].

In summary, the collective resonance of the spherical $Na_{91}^-$ cluster shows a broad, asymmetric line shape. The branching ratio for electron emission versus relaxation of the electronic energy into heavy particle motion rises linearly with photon energy from threshold over 1.2 eV until it reaches 100%. This slow increase is attributed to the cluster's valence band width. The time scales for the processes involved have been discussed. They are in qualitative agreement with the experimental data.

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