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Observation of strong optical absorption at the surface of small particles

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Abstract

Experiments are presented in which strong optical absorption at the surface of small metal particles is been observed. This was accomplished by the following method. Na clusters with rough surfaces were prepared on a transparent substrate. They provide the possibility of localized electronic excitations in the surface region in addition to the well-known plasmon–polaritons in the bulk. The particles were irradiated with pulsed laser light and their temperature rise was derived from measurements of the kinetic energy distribution of thermally desorbed Na dimers. From the temperature increase, the heat generated in the particles during decay of both surface and bulk excitations was calculated and taken as a measure of the total absorption cross-section. Separation of the bulk and surface contributions was achieved by repeating the experiments after removal of the surface roughness by annealing. We find that the surface contributes as much as 32% to the total optical absorption at $\lambda = 532$ nm for Na clusters of a mean radius R of 21 nm. © 1997 Elsevier Science B.V.

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Since the pioneering work of Gustav Mie in 1908 [1], the interaction of small particles with light has been investigated in a large variety of experimental and theoretical studies (see, e.g., Refs. [2,3]). The optical spectra of such systems with reduced dimensions are characterized by broad resonances, the positions of which depend on the electron density in the particle¹, its size, and the dielectric properties of the surrounding

medium. Today, Mie resonances are often denoted as surface plasmons, i.e. collective oscillations of the electrons in the particle.

The Mie theory treats the particles as spheres and assumes a sharp surface boundary. Often, however, these conditions are not fulfilled. For example, adsorbed clusters are not spherical because of interaction with the substrate: rather, they resemble rotational ellipsoids [4]. Furthermore, the surface of small particles can be composed of atoms located at different binding sites with low coordination numbers, i.e. they exhibit pronounced roughness on an atomic scale. As a result, the assumption of a sharp edge is no

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¹ The terms “small particle” and “cluster” will be used synonymously in this paper.

longer always justified and new, additional channels for the absorption of light in the surface layer come into play. Recent experimental (see, e.g., Refs. [5–7]) and theoretical work [8] has indeed shown that the electronic properties of the surface can be critical. Their special role manifests itself, for example, in thermal and non-thermal desorption of atoms and dimers [9–11] or in optical second-harmonic generation [12]. Electronic resonances localized in the surface region can be particularly important if they overlap spectrally with surface plasmon excitation. In such a case, they are driven with an exceptionally high rate, since simultaneous excitation of the plasmon is accompanied by a large enhancement in the electric field at the surface [2,3].

The present paper reports the observation of strong optical absorption at the surface of small metal particles, and describes a method of separating surface absorption experimentally from absorption of light in the interior of the clusters.

The method applied here to separate the surface and volume contributions of the total optical absorption was as follows. Small metal particles were prepared by the deposition and nucleation of atoms on a transparent substrate held at a low temperature T_0 which was typically below 100 K. It is known from desorption experiments that clusters generated under such conditions have rough surfaces with special electronic properties [9,10]. The particles were irradiated with pulsed laser light, which stimulates electronic excitations at their surfaces and in the bulk. During the decay of these excitations, the absorbed energy is converted into heat. This causes a temperature rise $\Delta T = T_1 - T_0$ which is accompanied by thermal desorption of atoms from the surface of the particles. Their time-of-flight distribution was determined, and serves as a measure of T_1 [13]. The exact value of T_1 was obtained by fitting a Maxwellian to the experimental time-of-flight data (see, e.g., Refs. [14,15]). T_0 also being known, the temperature rise $\Delta T = T_1 - T_0$ can be computed and this allows us to determine the released heat, i.e. the photon energy E_{abs} absorbed by the clusters. Separation of volume and surface contributions was accomplished by repeating the experiments after removal of the surface roughness by heating

and annealing for at least several minutes. The temperature rise induced by the laser light, on the other hand, lasts for a period of time which is too short for mass transport by diffusion and subsequent annealing of the roughness to occur [16].

The different experimental quantities are connected to each other by the following relations:

$$E_{\text{abs}} = c \cdot M \cdot \Delta T, \quad (1)$$

where M is the mass of the heated material and c is its specific heat. The energy E_{abs} absorbed per laser pulse is also related to the laser fluence ϕ (measured in mJ cm^{-2}) and the absorption cross-section σ (measured in cm^2):

$$E_{\text{abs}} = \sigma \cdot \phi \quad (2)$$

σ is either the sum σ_{tot} of the cross-sections for absorption of light at the rough surface σ_{sur} and in the volume σ_{vol} of the particles, or is identical to σ_{vol} if the surface roughness has been removed. Combining Eq. (1) and Eq. (2) the temperature rise can be written as follows:

$$\Delta T = [(\sigma_{\text{sur}} + \sigma_{\text{vol}})\phi] / (c \cdot M). \quad (3)$$

The separation of the total absorption into additive volume and surface terms assumes that absorption due to surface roughness comes into play in addition to plasmon-polariton excitation of the non-localized conduction electrons. This is justified here, since surface roughness makes possible additional excitation of special localized electronic states, which, as mentioned above, have already been found to play an essential role in the non-thermal desorption of atoms and dimers [5–8]. The physical nature of these states is currently under investigation, and seems to be associated with, for example, binding sites similar to adatoms on terraces and at steps.

Eq. (3) implies that the validity of the approach outlined above can be tested by verifying the linear dependence of the temperature rise ΔT on the laser fluence ϕ . Repetition of the measurements for different values of the fluence ϕ gives the following ratios k_{tot} and k_{vol} , which were determined experimentally (see below):

$$k_{\text{tot}} = \Delta T / \phi = \sigma_{\text{tot}} / (c \cdot M) \quad \text{and} \quad k_{\text{vol}} = \sigma_{\text{vol}} / (c \cdot M) \quad (4)$$

for clusters with and without surface absorption, respectively. We therefore obtain

$$k_{\text{tot}}/k_{\text{vol}} = (\sigma_{\text{sur}} + \sigma_{\text{vol}})/\sigma_{\text{vol}}, \quad (5)$$

and for the surface absorption cross-section [17],

$$\sigma_{\text{sur}} = (k_{\text{tot}}/k_{\text{vol}} - 1)\sigma_{\text{vol}}. \quad (6)$$

In our experiments, small sodium particles adsorbed on quartz substrates served as a model system. Na clusters lend themselves naturally for experiments along the lines described above for several reasons. First, the surface of Na clusters offers a considerable roughness if they are prepared at liquid-nitrogen temperature [9,10]. Secondly, it is known from our earlier experiments that the rough particle surface (at $T=80$ K) can be planarized and smoothed effectively by annealing [10]. Finally, we have found that Na dimers evaporate from the surface of the particles at a higher rate than atoms in the low laser-fluence regime [10,16]. Therefore, in contrast to the general outline of the method described above, the signal-to-noise ratio of the time-of-flight data was optimized using the thermal evaporation of dimers rather than atoms to determine the temperature increase of the clusters.

The principal advantage of the method presented here as compared to optical extinction measurements is that it allows one to determine absorption directly. In contrast, extinction is influenced by scattering of light, which makes it difficult or impossible to distinguish absorption at the surface from absorption in the volume. We estimate that scattering of light contributes as much as 50% of the total optical extinction for clusters of the size studied here [2]. In principle, optical absorption can also be measured directly by photothermal methods [18], which, however, can hardly be applied to the samples studied here under ultra-high vacuum conditions.

The experimental arrangement has been described in detail elsewhere [4,7], and basically consists of an ultra-high vacuum system with the sample, two pulsed lasers for exciting the clusters and photoionizing the evaporating dimers, and a time-of-flight mass spectrometer. A thermal atomic beam of Na atoms with a constant flux is directed onto the quartz substrate in order to deposit a

predetermined coverage onto the surface held at $T_0=80$ K. The flux of the beam (i.e. the Na coverage reached after a certain deposition time) is determined with a quartz crystal microbalance. In all experiments reported in the present paper, the coverage was 1.1×10^{16} atoms cm^{-2} . This corresponds to an average particle size of $R_{\text{av}}=21$ nm [7,16]. The temperature of the sample was measured with a thermocouple and could be raised by an electrical heater incorporated in the substrate holder. After preparation the clusters were irradiated with p-polarized light from a Nd:YAG laser at $\lambda=532$ nm with a pulse duration of 7 ns. At a distance of 21 mm in front of the substrate, the dimers desorbed from the metal surface were ionized with the light of an excimer laser operating at $\lambda=248$ nm. The corresponding photon energy lies only a little above the ionization threshold of Na_2 . Therefore, "soft" ionization of the desorbed dimers is accomplished and there is only very little dissociation into monomers [10]. By varying the delay time between the two laser pulses used for desorption and ionization, the time-of-flight distribution of the desorbed Na dimers for a given fluence of the laser light were determined. Subsequently, the sample was re-prepared and the procedure repeated for a new value of the fluence, and so forth. It should be noted that the experimental conditions were chosen such that the desorbed species did not suffer collisions in front of the surface, and thus the kinetic energy distributions unambiguously reflect the surface temperature values.

As an example, Fig. 1a displays time-of-flight distributions of Na dimers desorbed by p-polarized laser light with $\phi=10$ and 20 mJ cm^{-2} . Desorption was stimulated from the particle surface as prepared at $T_0=80$ K, i.e. with roughness and optical absorption in the surface layer. The time-of-flight spectra are characterized by a maximum which is located at 33 μs for $\phi=10$ mJ cm^{-2} and at 26 μs for $\phi=20$ mJ cm^{-2} . Different fluence values do not change the shape of the distributions noticeably. The dashed lines in the spectra are Maxwellians which were fitted to the experimental data. Since the desorption signal generated by pulsed laser ionization measures the density of the desorbed species, this Maxwellian reads as follows

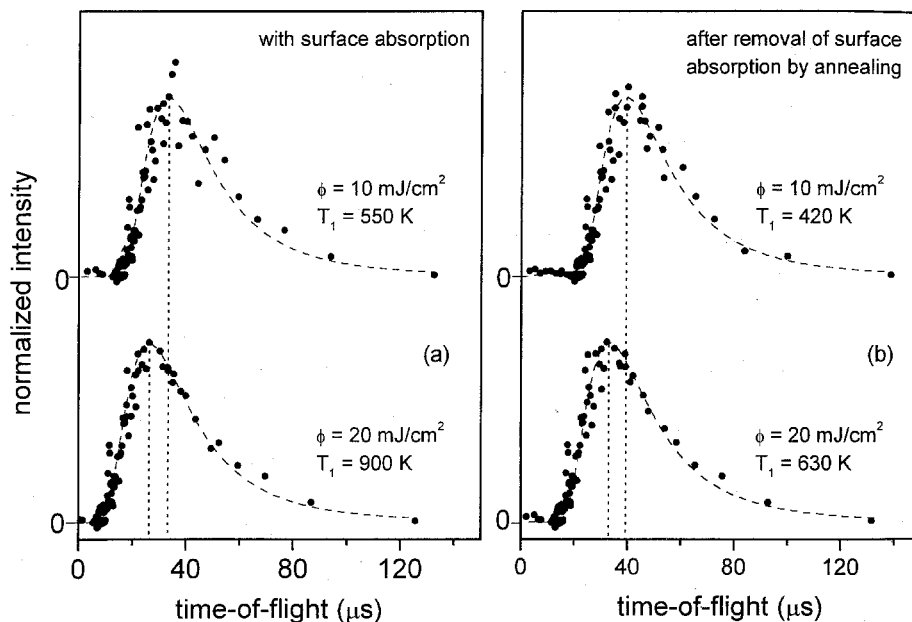


Fig. 1. Time-of-flight spectra of Na dimers desorbed with laser light of $\lambda=532$ nm from the surface of small metal particles (a) with and (b) without surface absorption. The total coverage of sodium was 1.1×10^{16} atoms cm^{-2} , which corresponds to an average particle size of 21 nm. The fluence of the Nd:YAG laser was set to values of 10 and 20 mJ cm^{-2} . The solid line corresponds to a fit by Eq. (7), from which the cluster temperatures T_1 quoted in the figure were deduced. See text for details.

[14,15]:

$$n(t) = Ct^{-4} \exp[-2(t_m/t)^2], \quad (7)$$

where $n(t)$ denotes the density of the desorbed dimers at time t in the ionization region, and $t_m = L(m/4k_B T_1)^{1/2}$ is the flight time which corresponds to the maximum of the distribution. C denotes a constant which includes experimental parameters such as the distance $L=21$ mm between the surface and the ionization region. As can be seen from Fig. 1, the Maxwellians describe the experimental data very well and allow us to extract the translational temperatures T_1 of the desorbed dimers from the fits. Furthermore, the integral desorption rate increases exponentially as a function of fluence.

As mentioned above, the experiments were repeated after annealing the samples (i.e. after removal of the surface roughness). For this purpose, Na was first deposited on the substrate at $T_0=80$ K as outlined above. Subsequently the sample was annealed for 5 min at $T=140$ K and

then cooled to the initial temperature of 80 K at which the time-of-flight spectra were recorded. It is known from our earlier experiments that annealing at this temperature does not shift the peaks in the optical spectra, i.e. the geometrical shape of the clusters and the optical absorption in the volume remain constant [7]. Fig. 1b displays two examples of time-of-flight distributions recorded for the same fluence values of laser light as in Fig. 1a. The maxima of the distributions are now located at 38 μs for $\phi=10$ mJ cm^{-2} and at 31 μs for $\phi=20$ mJ cm^{-2} . The longer most probable flight times of the dimers as compared to Fig. 1a reflect the smaller temperature rise of the clusters after the removal of surface absorption. Again, temperature values of T_1 were obtained by fitting the measured distributions to Maxwellians.

In order to determine the temperature rise ΔT of the particles with and without surface absorption of light, $T_0=80$ K was subtracted from all determined values of T_1 . The results are compiled in Fig. 2, which shows the temperature increase

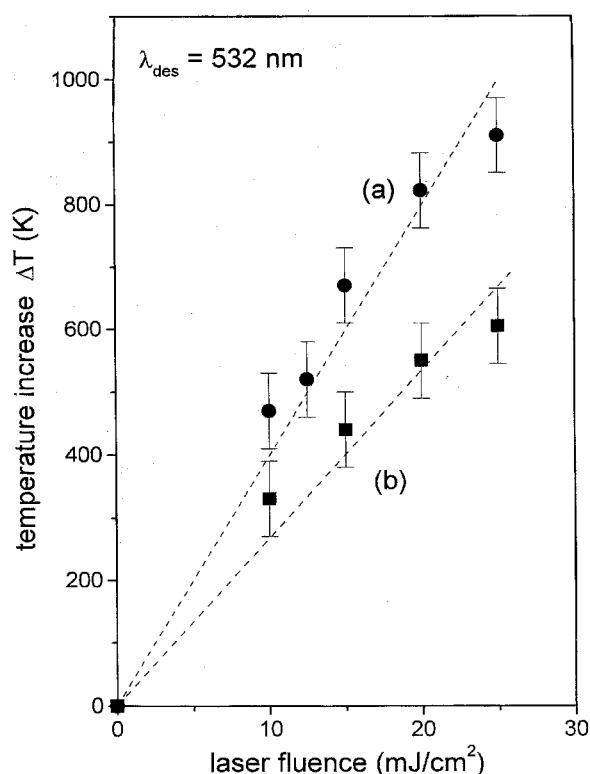


Fig. 2. The temperature rise ΔT of small Na particles following absorption of laser light with $\lambda = 532$ nm as a function of laser fluence. The values of trace (a) were obtained from measurements of the translational energy distributions of Na dimers desorbed from clusters with rough surfaces, the results compiled in trace (b) from measurements after annealing ($T = 140$ K, $t = 5$ min) of the cluster surface (i.e. after smoothing and removal of surface absorption).

ΔT as a function of laser fluence for the cluster surface as prepared initially (trace (a)) and after smoothing (trace (b)). We first notice that the temperature increase indeed depends linearly on the laser fluence, as expected from Eq. (3). Furthermore, the temperature rise obtained after annealing (i.e. without surface absorption) is substantially lower.

Eq. (4) now allows us to compute the slope of the temperature increase with and without optical absorption by the cluster surface. We obtain

$$k_{\text{tot}} = \Delta T / \Delta \phi = (\sigma_{\text{sur}} + \sigma_{\text{vol}}) / (cM)$$

$$= 990 \text{ K} / 25 \text{ mJ cm}^{-2} = 39.6 \text{ K cm}^{-2} \text{ mJ}^{-1},$$

and

$$k_{\text{vol}} = \Delta T / \Delta \phi = \sigma_{\text{vol}} / (cM)$$

$$= 670 \text{ K} / 25 \text{ mJ cm}^{-2} = 26.8 \text{ K cm}^{-2} \text{ mJ}^{-1},$$

from which the ratio $k_{\text{tot}}/k_{\text{vol}} = (\sigma_{\text{sur}} + \sigma_{\text{vol}}) / \sigma_{\text{vol}} = 1.48$ (Eq. (5) and finally

$$\sigma_{\text{sur}} / (\sigma_{\text{sur}} + \sigma_{\text{vol}}) = 0.32$$

are obtained. In other words, the cluster surface contributes as much as about 32% to the total optical absorption.

If the cluster size exceeds several nm, the rough surface layer is negligibly small as compared to the total volume of the particles. Therefore, at first glance, it is quite surprising that the surface contributes as much as about one third to the total optical absorption. However, the restricted volume of the surface (i.e. the limited number of binding sites at which excitation with $\lambda = 532$ nm can be accomplished) is obviously overcompensated by the enhancement of the electric field due to simultaneous surface plasmon excitation. This enhancement can easily amount to a factor of several hundred. Therefore, the strong surface absorption observed here is due to a very delicate interplay between localized and collective electron excitations. Of course, the same effect should play a role at larger metal coverages on the substrate (i.e. under conditions where the particles have grown together and form a rough film). In such a case, however, the whole volume of the film up to a thickness which corresponds to the penetration depth of the light contributes to the total optical absorption, and the relative importance of the surface is diminished.

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- [17] In principle, two channels for energy loss exist: thermal radiation and conduction of heat into the quartz crystal. Both can be taken into account by an additional term $\Delta E_Q(\Delta T)$ in Eq. (1). Thermal radiation grows with T^4 and, if it were essential here, would manifest itself in a deviation from the linear dependence of the temperature increase on the laser fluence (Eq. (1)). Such deviations, however, are not observed experimentally (see Fig. 2), and we conclude that thermal radiation does not constitute a substantial channel for loss of heat. On the other hand, heat losses into the quartz substrate depend linearly on the induced temperature difference ΔT and therefore leave the linear dependence of Eq. (1) untouched. Such losses, however, play an equal role with and without surface absorption of the clusters and therefore cancel out if the ratio $k_{\text{tot}}/k_{\text{vol}}$ is computed in order to obtain the surface absorption as the percentage of the volume absorption of the clusters. For this reason and for simplicity, $\Delta E_Q(\Delta T)$ has been omitted in the equations.
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