Size-Dependent Plasmon Lifetimes and Electron-Phonon Coupling Time Constants for Surface Bound Na Clusters

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In this paper we show that time-resolved analysis of second harmonic generation via femtosecond pump-probe studies can be used to extract simultaneously mean cluster radii, decay times τ_{sp} of localized surface plasmon excitations, and electron-phonon coupling time constants τ_{ep} in large Na_n ($n \approx 10^7$) clusters, bound to insulator surfaces. From the dependence of plasmon lifetime on the mean cluster radius ($5 \leq r_0 \leq 55$ nm) a maximum of $\tau_{sp} = 10$ fs at a mean radius of about 25 nm is observed. Additionally, for Na clusters with mean radii of 30 to 50 nm and bound to a lithium fluoride surface the electron-phonon coupling time constant is found to be $\tau_{ep} \approx 1.1$ ps. [S0031-9007(97)04875-8]

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In large, neutral sodium clusters Na_n ($n > 8$), the oscillator strength for the optical dipole transition is concentrated in a single absorption peak, which has been identified as a collective excitation of conduction band electrons or a "surface plasmon excitation" [1]. A similar observation has been made recently for ionic clusters [2]. This type of giant collective electronic excitation [3] results in strong electromagnetic field enhancement effects [4] and in enhanced electron [5] and atom emission [6]. For clusters bound to dielectrics in the form of rough metallic films, enhancements of their second [7,8] and third order [9] optical nonlinearities have been observed.

As a result of the delocalization of the conduction band electrons, the electronic excitations of large sodium clusters can be described to a good approximation by nearly free electron models, which also makes them of considerable interest for a theoretical treatment. Recently the similarity of the size dependence of the small particle resonance with the wave vector dispersion of flat surface plasmons has been demonstrated for small ($n \leq 93$) ionic Na_n^+ clusters [10]. It is noteworthy that the use of a nonlocal dielectric function in connection with jellium models led to a fairly accurate understanding of coverage-dependent plasmon excitations of flat alkali metal surfaces [11,12], even with respect to their second order nonlinear optical response [13].

Much less is known about the size dependence of surface plasmon excitations in large alkali clusters. Both for a rigorous theoretical treatment and for practical applications, it would be very useful to know the *time constants* of the elementary optical excitations, including the lifetime of the plasmon excitation as well as the electron-phonon relaxation time. These time constants are also of key importance for an understanding of laser-induced desorption or ablation processes from rough metal surfaces [14] and for microstructuring of thin metallic films [15].

Information about the decay time constants for the initial collective excitation of surface bound clusters is obtained more readily from time- instead of frequency-resolved measurements since the spectral width of the surface plasmon resonances is dominated by broadening due to the cluster size distribution and due to chemical interface damping [16]. First time-resolved measurements of plasmon lifetimes of $\tau_{sp} = 40 \pm 7$ fs for surface bound Ag clusters of radius 10 nm, bound to indium tin oxide [17], have recently been complemented by measurements using an array of nanolithographically designed silver posts with radii of about 200 nm, for which $\tau_{sp} = 10$ fs was found on resonance [18]. These results are to be compared with measurements of the spatial decay of nonlocalized, i.e., propagating surface plasmons in metal films, where lifetimes between 10 and 56 fs [19–22] have been deduced, depending on film thickness and surface roughness. Because of strong surface scattering, the lifetimes of *localized* surface plasmons are expected to be smaller compared to those of nonlocalized plasmons.

As for the size dependence of plasmon lifetimes and the values of the electron-phonon coupling time constant τ_{ep} for surface-bound clusters, not much is known experimentally. In the case of thin Au or Ag films, time-resolved thermoreflection methods have revealed hot-electron energy-loss lifetimes of the order of 1 to 2 ps [23], depending on laser fluence and film thickness [24,25] as well as excitation wavelength [26].

In the present paper, τ_{sp} and τ_{ep} for large, surface-bound Na clusters are measured as a function of mean cluster radius r_0 using a femtosecond pump-probe technique which relies on second harmonic generation (SHG) at the surface of the Na clusters [27]. Although, in principle, a SH signal is also expected far off the surface plasmon resonance due to the nonvanishing value of $\chi^{(2)}$, it is well known from numerous optical experiments on rough metal films [28,29] that the excitation of surface plasmons enhances the nonlinear signal intensity by several orders of magnitude. Given the detection efficiency of the present apparatus we observe a signal *only* if surface plasmons are excited, and hence the duration of the

SH signal provides a direct measurement of τ_{sp} [17], whereas the absolute magnitude is used to determine the size distribution of the clusters on the surface [8]. Finally, electron-phonon coupling time constants τ_{ep} are measured analogous to the commonly used linear time-resolved thermoreflection pump-probe technique [23]. The advantage of the present nonlinear method over the linear approach [30] is a several orders of magnitude larger change in reflectivity since, with laser energies near the interband transition threshold at $\lambda = 570$ nm, the SH signal is expected to be sensitive to transient changes in electron temperatures [31,32].

The experimental setup consists of an ultrahigh vacuum surface apparatus [9] and a pulsed femtosecond laser source [33] with a pulse duration of 50 fs (sech^2), a wavelength of 570 nm, and pulse energies of 10 nJ at a repetition rate of 10 Hz. Focused to a Gaussian beam waist of 45 μm, the total irradiance of the samples is about 2 GW/cm^2. In order to obtain time-resolved signals the initial laser pulses are split into two pulses and are mutually time delayed using a translator stage with micrometer precision. Both p-polarized pulses are then focused by a common lens onto the sample surface. The reflected SH radiation is detected by a photomultiplier after passing through a combination of a color glass filter (Schott UG5) and a monochromator to suppress the fundamental radiation. Part of the incoming light of both beams is directed onto a beta-barium-borate (BBO) crystal. The resulting SH signal serves as a reference, providing accurate values of incident pulse energy and pulse length. As discussed below, clusters grow on the surface following evaporation of Na atoms from an Na dispenser (SAES getters) in ultrahigh vacuum ($p_0 \approx 10^{-11}$ mbar) onto cleaved mica or lithium fluoride substrates at 150 K surface temperature [6].

The intensity of the SH signal, generated by the clusters, is related to the incident laser intensity I, the second order nonlinear susceptibility of the clusters $\chi^{(2)}$, and the field enhancement factors via [34]

$$I(2\omega) \propto I^2(\omega)|\chi^{(2)}|^2 Q^2(\omega) Q(2\omega) r_0^4 . \qquad (1)$$

Here, the factors Q describe the averaged local electric field at the cluster surface in units of the geometrical cross section. They depend on the mean cluster radius r_0 and can be calculated accurately for spherical clusters using Mie theory [35] or for elliptical clusters using T-matrix theory [36]. The second order nonlinear susceptibility is predicted to be size independent for large clusters with $r_0 > 5$ nm [27], in agreement with findings for $\chi^{(3)}$ [37].

Recently we have shown that it is possible to obtain values of r_0 *in situ* by monitoring the total SH yield as a function of Na deposition time and fitting the change in signal intensity to calculated values [8]. It is well known [38] that metal clusters, adsorbed on a dielectric at 150 K surface temperature, obey a Volmer-Weber growth mode. Taking advantage of previous electron microscopy measurements of size distributions for lithium cluster films [39], we parametrize the Na size distribution in the form of an asymmetric Gaussian distribution, for which the half-width is constant with increasing r_0. In the fitting routine [grey lines in Figs. 1(b) and 3(b)] an effective increase in large axis dimension as a function of deposition time has been included [8], since Na clusters on mica form oblate ellipsoids instead of spheres with an axial ratio of 2:1 for small clusters [40], increasing to 5:1 for clusters with average radius 40 nm [6].

In Fig. 1(a) the total SH signal intensity $G^{(2)}(\tau)^{\text{Na}}$ is shown as a function of time delay between the two laser pulses for Na clusters of $r_0 = 20$ nm, which are adsorbed on mica. The SH autocorrelation function $G^{(2)}(\tau)$ of the laser with a half-width of 50 fs (sech^2) is also shown as measured in a BBO crystal. As noted above, the observed SH signal intensity is governed by the surface plasmon excitation in the clusters. Let us assume that the plasma oscillations can be described by a damped harmonic oscillator which is driven by the femtosecond laser field. Then the measured curve corresponds to the intensity autocorrelation of the convolution of the temporal intensity profile of the laser pulse (given by a sech^2 function) and the exponential decay time of the plasmon excitation. Since $G^{(2)}(\tau)$ is measured simultaneously with $G^{(2)}(\tau)^{\text{Na}}$, the only fit parameter to the measured curves in Fig. 1(a) is the plasmon lifetime, which is $\tau_{sp} = 8$ fs for the present example.

The reproducibility of the data has been controlled by measuring the half-width of the autocorrelation curve on the Na clusters for given r_0 as a function of laser pulse length. With increasing laser pulse length the half-width of the SH curve from the Na clusters also increases, but all of the measured curves can be reproduced using the same value of τ_{sp}. These measurements show that

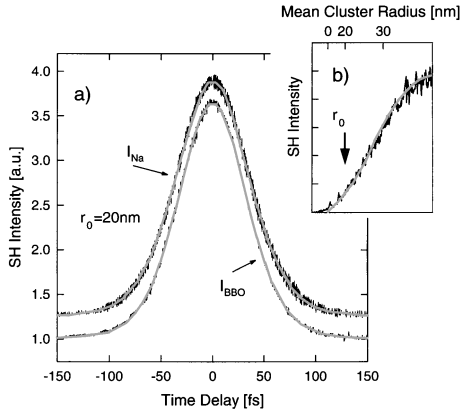

FIG. 1. (a) Simultaneously measured second harmonic collinear autocorrelation curves from a Na cluster film with mean radius of $r_0 = 20$ nm, adsorbed on mica, I_{Na}, and from a BBO crystal, I_{BBO}. Pump and probe laser energy 8 nJ. The grey lines through the data points are calculated autocorrelation functions, resulting in a laser pulse length of 50 fs and a plasmon lifetime of 8 fs. (b) Measured total SH signal as a function of mean cluster radius. The grey line is a theoretical curve [8], which allows the assignment of mean cluster radius r_0 to the measured SH intensities.

broadening effects of the femtosecond pulses due to the optical components are well taken into account by the reference measurements in the BBO crystal. The resulting accuracy of the measured plasmon lifetime is $\tau_{sp} \pm 1$ fs.

From correlation measurements such as the one shown in Fig. 1(a) and determining r_0 from the total SH intensity we deduce $\tau_{sp}(r_0)$ for Na clusters deposited on mica (Fig. 2). As seen, there is a pronounced maximum for clusters of an average radius of 22 nm, with lifetimes decreasing both for smaller and for larger cluster radii. The maximum value of about 10 fs agrees with the value found for the surface plasmon resonance of nanostructured silver posts [18].

The size dependence in Fig. 2 can be understood by realizing that, for small clusters, surface scattering is the dominant damping mechanism. Since the ratio of the surface scattering probability (proportional to the area of the cluster) to the number of scattering electrons (proportional to the volume) scales with $1/r_0$, the plasmon lifetime is expected to be [41]

$$\tau_{sp} = \left(\frac{v_F}{\bar{l}} + \frac{A v_F}{r_0} \right)^{-1}, \qquad (2)$$

where v_F is the Fermi velocity, $\bar{l}$ the mean free path of the electrons in bulk Na [42], and A is a size parameter that takes into account electron screening and surface roughness [43] and varies between about 0.38 and $4/\pi$ [41]. For large clusters, retardation effects (radiation damping, excitation of higher multipole plasmons) are expected to broaden the plasmon resonances, i.e., shorten the lifetime with increasing r_0 ("extrinsic" or electrodynamic size effects). The resulting size dependence of the dipole resonance can be readily calculated via classical Mie theory using the experimentally determined dielectric function of Na and thus including damping by interband transitions [8].

The dashed line in Fig. 2 represents calculated plasmon lifetimes, including intrinsic and extrinsic damping mechanisms as well as $A = 0.45$, taken from density functional calculations for Na spheres [44]. The contribution of clusters of different sizes to a given value of $\tau_{sp}(r_0)$ has been taken into account by calculating $G^{(2)}(\tau)^{Na}$ for monodisperse clusters, summing it up for given r_0, weighted by the field enhancement factors according to the cluster size distribution, and then recalculating $\tau_{sp}(r_0)$. For small cluster radii the agreement between measurements and classical size effect is fair, although a value of $A = 1$ (solid line) provides a somewhat better agreement between experiment and theory. Of course, for very small clusters of the order of 1 nm this calculation certainly would be too simple [45] and would require a quantum treatment [46]. For large cluster radii the measured lifetimes are somewhat smaller than the theoretical ones which might be due to cluster-cluster interactions, which have not been taken into account. According to T-matrix calculations [47], such interactions have an influence on the local fields for distances between neighboring clusters smaller than four times their radius. This would be the case for clusters with $r_0 \geq 34$ nm for the experimental data of Fig. 2.

Next we present, as a typical example of pump-probe measurements, the relative change in reflected SH signal intensity as a function of pump-probe delay for Na clusters with $r_0 = 38$ nm [Fig. 3(a)]. The clusters were adsorbed on lithium fluoride at 150 K. As seen, the temporal overlap of pump and probe pulses results in a decrease of signal intensity with a time constant given by the laser pulse width of 50 fs. The subsequent exponential recovery of the signal is due to electron-phonon collisions [23] and is measured to be independent of cluster size for radii between 30 and 50 nm. The temporal half-width of the electron-phonon relaxation time is $\tau_{ep} = 1.1(1)$ ps, which is comparable to the values obtained for thin metal films [24], but is at variance with recent observations for gold colloidal nanoparticles (12–18 nm diameter), where considerably longer electron-phonon relaxation times of $\tau_{ep} = 7$ ps were found [48]. Apparently, since the clusters are adsorbed on an insulating surface and the dominant mode of energy exchange between adsorbate and substrate is via phonons, they behave more like rough films instead of isolated clusters on the time scale of picoseconds.

In summary, using cluster-size dependent, electromagnetic field enhanced SHG we have measured for the first

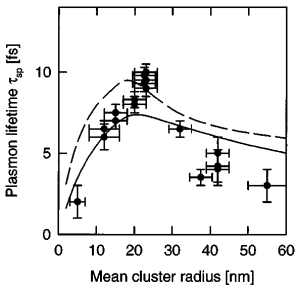

FIG. 2. Measured plasmon lifetimes as a function of mean cluster radius for Na clusters adsorbed on mica. The lines are from calculations including both intrinsic and extrinsic size effects with $A = 1$ (solid line) and $A = 0.45$ (dashed line); see text.

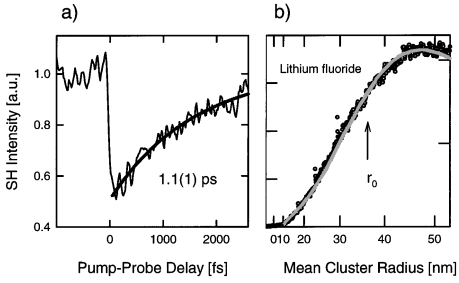

FIG. 3. (a) Measured SH intensity in the reflected probe beam direction as a function of time delay between pump (123 nJ) and probe (57 nJ) pulses, obtained from a cluster film with mean radius $r_0 = 38$ nm, adsorbed on lithium fluoride. The grey line corresponds to a temporal half-width of 1.1(1) ps. (b) Same as Fig. 1(b), but for Na clusters adsorbed on lithium fluoride.

time the absolute values and the size dependence of τ_{sp}, as well as, τ_{ep} for Na clusters adsorbed on dielectric surfaces. We expect to observe quantum size effects in future experiments by using clusters with smaller radii but larger surface densities (e.g., grown on a substrate with higher defect density such as boron nitride). The measurements indicate that, on the femtosecond time scale, adsorbed, large Na clusters behave similar to free clusters in terms of their collective electronic excitations, whereas they are reminiscent of rough metallic films on the picosecond time scale. This finding implies that one can make use of the experimental advantages of surface bondage (i.e., high cluster density and well defined temperature) while being able to treat the systems by an *ab initio* theoretical approach.

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