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Size dependence of dipole and quadrupole plasmon resonances in light induced sodium clusters

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ABSTRACT

The dependence of the optical properties of large sodium clusters as a function of their size is studied. Clusters are light induced allowing observation of the smooth change of their sizes as a result of the spontaneous nucleation process. We combine the formalism of the classical Mie scattering theory for spheres of arbitrary large size and the concept of the collective electron oscillations (plasmons). The maxima in normalized intensities of light scattered by single cluster we attribute to resonant excitation of dipole and quadrupole plasmon oscillation respectively. We show that plasmon resonances take place for different cluster sizes when excited with different wavelength. We compare these results with expectations resulting from solving the problem of eigenfrequencies of free-electron sphere with the dielectric function described within the Lorentz-Drude model.

Keywords: Free-electron clusters, alkali nano-spheres, plasmon modes, Mie theory, light scattering, nucleation from vapour phase.

1. INTRODUCTION

Optical properties of metal clusters differ from both the optical properties of atomic vapors and of the bulk metal. One of directions of cluster studies concerns with change of electronic and optical properties of metal clusters with size. In this paper we study the change of the scattering properties of sodium clusters with cluster size in the context of possible excitation of plasmon oscillations (i.e. collective free-electron harmonic motion). Sodium clusters are light induced[1,2] giving the unique opportunity of observing the smooth change of their sizes as a result of the spontaneous nucleation process in supersaturated vapor. The process of cluster formation is initiated by laser light interacting with saturated sodium vapour. Supersaturation is due to light induced dissociation of Na_2 molecules present in the vapor. We measure the intensities of the probe laser beam scattered elastically under the right angle to the incoming beam, with polarization parallel and perpendicular to the observation plane. The measurement is performed for several wavelengths of the probe light scattered by clusters growing with time. The cluster nucleation mechanism and experimental set-up is described in more details in[1,2] .

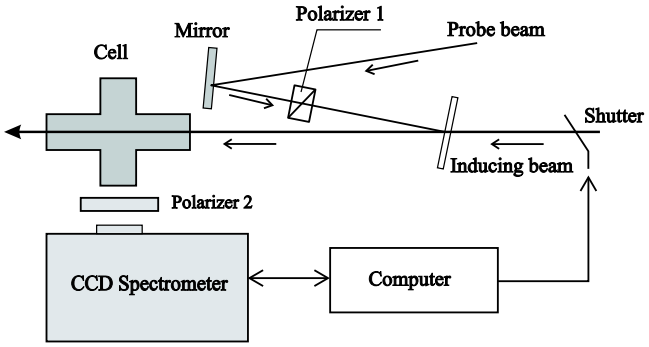

Figure 1. Scheme of the experimental set-up

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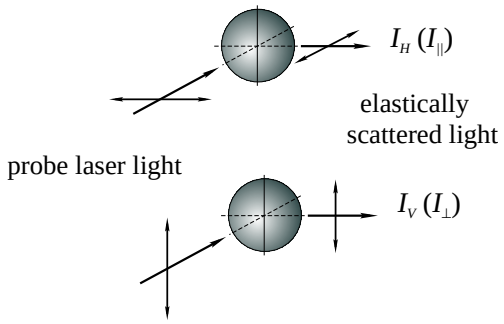

Figure 2. Polarization geometry of the scattering experiment

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2. EXPERIMENTAL RESULTS

The experimental shame is sketch in Fig. 1. The probe beam of the argon-krypton laser is linearly polarized under 45 degree in respect to the observation plane defined by the direction of the probe beam and the chosen direction of observation. We measure intensities $I_H(t)$ and $I_V(t)$ of the scattered probe light beam in two polarization geometries: the polarization of the incident and the detected light beam perpendicular to the fixed plane of observation, (V geometry), and the polarization of the incident and the detected beams parallel to the plane of observation (H) (see Fig. 2). The example of experimental data is shown in Fig. 3a. Zero time corresponds to switching on the inducing laser light at 488nm which initiates cluster growth. The experimental signals are taken at temperature of 400^oC, at helium gas pressure of 600Torr, with inducing and probe laser power of 100mW and 2.3mW respectively. The scattered intensities $I_V(t)$ and $I_H(t)$ of the light wave at the corresponding wavelengths λ: 403.4nm, 457.9nm, 496.5nm, 514.5nm, 568.2nm and 647.1nm of the probe beam show maxima, however the maximum in $I_V(t)$ appear earlier (so it corresponds to smaller clusters), than the maximum observed in $I_H(t)$. Signals at both polarizations stabilize with time, due to cluster size and concentration stabilization.

2.1. Determination of cluster size and relative concentration dynamics

We use the full Mie scattering theory (retardation included) to interpret experimental intensities $I_V(t)$ and $I_H(t)$ of light scattered by a cloud of growing clusters. The Drude dielectric function of the free-electron plasma is used to describe material properties of sodium particles (see e.g.[3]). $I_{||}(R)$ and $I_\perp(R)^2$ are calculated intensities (see Fig. 3 b) scattered per single cluster of radius R in direction perpendicular to the incoming light wave. $I_{||}(R)$ and $I_\perp(R)$ dependence on cluster radius R resulting from the Mie theory is illustrated in Fig. 3b. We fit the intensities $I_{||}(R)$ and $I_\perp(R)$ of the light wave at the corresponding wavelength and polarization to the $I_V(t)$ and $I_H(t)$ experimental intensities scattered by a cloud of clusters of relative concentration $N(t)$ and radius $R(t)$ being the fit prameters. The fitting procedure is strongly improved in respect to the previous one[2] . It allows us to determine the the dynamic parameters of the nucleation process: the cluster radius $R(t)$ and the relative concentration $N(t)$ changing by orders of magnitude (see Fig. 4). From time dependence of $N(t)$ and $R(t)$, we can derive experimental intensities scattered per unit surface of a single cluster: $I_V(R)/N(R)R^2$ and $I_H(R)/N(R)R^2$.

2.2. Size dependence of dipole and quadrupole plasmon resonance frequency

To interpret the maxima appearing in $I_V(R)/N(R)R^2$ and $I_H(R)/N(R)R^2$ for given wavelength, we use the concept of plasmons (collective free-electron oscillations). The resonant frequencies $\omega_l(R)$ of the multipolar plasmon modes of polarity l, $l = 1, 2, 3...$(see Fig. 5, solid lines) are solutions of the eigenmode problem of the metal sphere.[4] The plasmon resonance frequencies are due to the TM mode of the field (i.e. the mode of the field resulting from the wave equation in spherical coordinates with the nonzero radial component of the electric

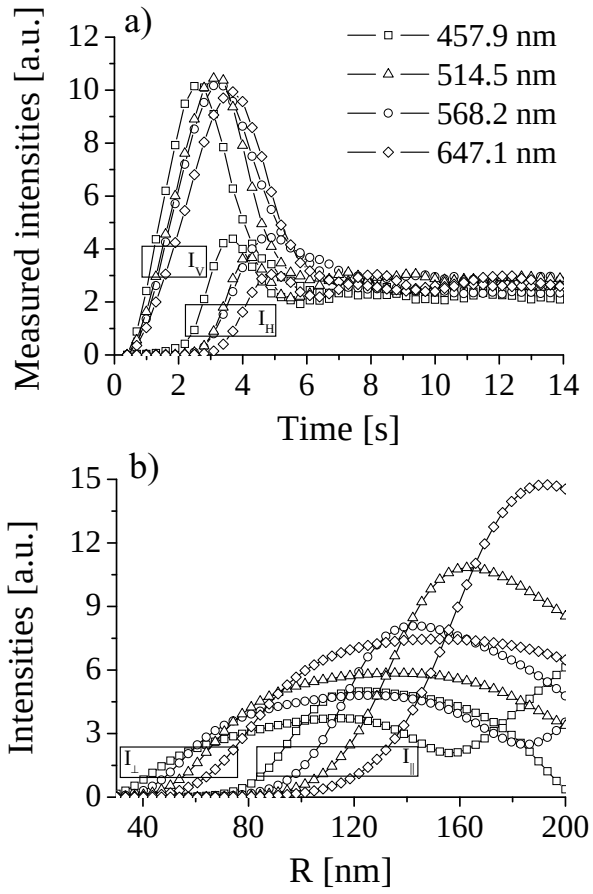

Figure 3. a) Intensities $I_V(t)$ and $I_H(t)$ scattered by a $N(t)$ growing clusters of mean radius $R(t)$. Solid lines are for eye guiding. b) $I_{||}(R)$ and $I_{\perp}(R)$ intensities scattered per single cluster of radius R resulting from the Mie theory.

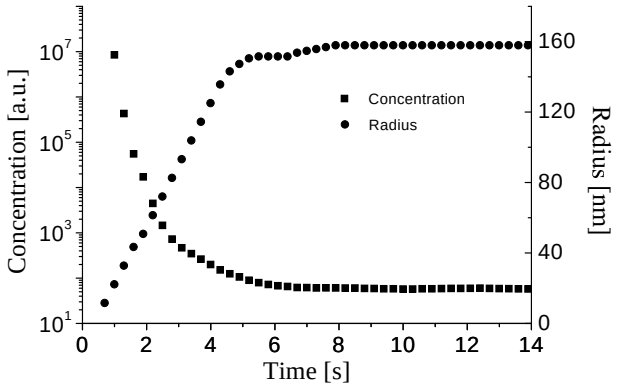

Figure 4. Relative concentrations N and sodium droplet radius R as a function of time resulting from the fitting procedure (example of the data).

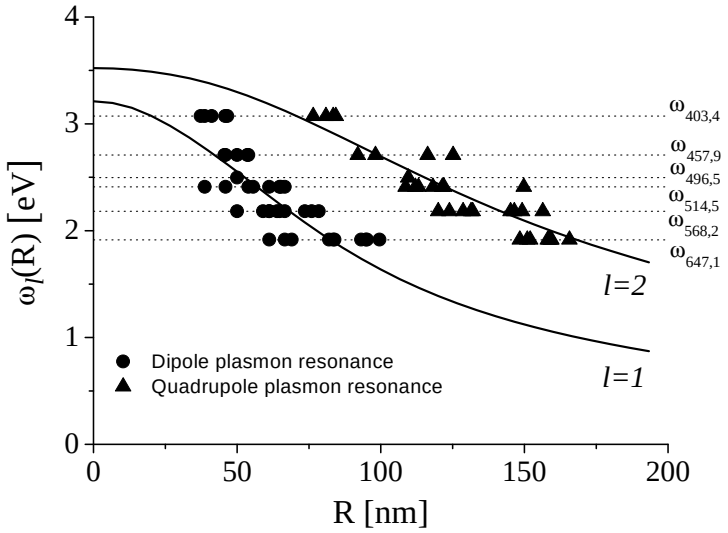

Figure 5. Coordinates of the dipole (dots) and the quadrupole (triangles) plasmon resonances derived from $I_V(R)/N(R)R^2$ and $I_H(R)/N(R)R^2$ dependencies. Solid lines illustrate the dipole $\omega_{l=1}(R)$ and the quadrupole $\omega_{l=2}(R)$ plasmon frequencies as a function of cluster size resulting from solving the eigenvalue problem.[4]

field). The resonance in given observable at given multipolarity l takes place, when the sphere radius R is large enough to ensure the matching of the light frequency ω, and the plasmon resonance frequency $\omega_l(R)$: $\omega = \omega_l(R)$.

In[4] we have shown, that it is the TM mode only, which contributes to the maxima appearing in $I_{||}(R)/R^2$ and $I_{\perp}(R)/R^2$ Mie intensities in spite that in spherical geometry of the cluster problem always both the TM and the TE contribute in every order of l. The TM mode with $l = 1$ is responsible for the maximum in $I_{\perp}(R)/R^2$, while the maximum in $I_{||}(R)/R^2$ is due to the TM mode contribution in $l = 2$. The maximum in $I_{\perp}(R)/\pi R^2$ we attributed to the dipole surface plasmon oscillation at the corresponding frequency $\omega_{l=1}(R)$, while the maximum in $I_{||}(R)/\pi R^2$ we attributed to quadrupole plasmon oscillation at the frequency $\omega_{l=2}(R)$[4] . The smaller the frequency of the light field ω (the longer the wavelength λ), the larger the cluster size enabling the resonant excitation of plasmon with given multipolarity l. Fig. 5 illustrates how the maxima in $I_V(R)/N(R)R^2$ and $I_H(R)/N(R)R^2$ dependencies change with the light wave frequency ω_λ and how they match the expected dipole and quadrupole plasmon resonance frequencies resulting from the eigenvalue problem for the sodium sphere. As far as we know, these data are the only experimental data illustrating the dependence of the plasmon resonance frequency on cluster size in the range of few tens up to few hundreds nanometers.

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