Surface Plasmon Dynamics of Simple Metal Clusters Excited with Femtosecond Optical Pulses

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We report a new mechanism on the dynamics of correlated electrons in simple metal clusters which manifests by a strong electron temperature dependence of the surface plasmon resonance spectral profile. This effect is revealed thanks to a theoretical approach based on the time-dependent local-density approximation at finite electronic temperature, and it should be experimentally observable using pump-probe femtosecond spectroscopy techniques.

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For many years, the study of metallic clusters has been a prolific research field owing to the variety of their physical and chemical properties which make them attractive systems, for instance, as catalysts, as efficient scattering species in bioimaging, or as elementary magnetic recording units. In particular, the investigation of their optical response has lead to interesting findings associated with the resonant excitation of the collective electronic excitations, so-called surface plasmons (SPs). Indeed, unlike in an infinite homogeneous bulk metal, it is possible to couple the plasmon modes with a transverse electromagnetic field due to the symmetry breaking at the boundary of the cluster. Such resonant coupling is in fact responsible for the enhanced light scattering cross section as can be formally described by the Mie theory. In order to properly describe the radiation-matter coupling in metallic clusters, it is necessary to model the electronic transition spectrum leading to any observable such as the polarizability. This description can be carried out with various levels of approximations depending on the size of the cluster, its temperature, and the importance of the local field effects associated with the polarizability of the environment and of the metal itself. In this Letter, we focus on the description of the optical response of clusters at a high electronic temperature T_e, while the ionic temperature T_i is much less, in the framework of the time-dependent local-density approximation (TDLDA) at finite temperature. Such an out of equilibrium situation ($T_i \ll T_e$) can be easily induced in metals using ultrashort optical pulses [1]. A new effect is reported which has the characteristics of an electronic phase transition and which manifests by a nonmonotonous variation of the thermal energy per particle. Correspondingly, the surface plasmon is first redshifted and then blueshifted as T_e increases. Such dynamics of the surface plasmon shows up in the absorption cross section and should be observable with pump-probe femtosecond spectroscopy performed in simple metals.

Before describing our methodology, let us review some preceding works related to the description of the dielectric function of metallic clusters as a function of size and temperature. For clusters with a number of atoms larger than 10^4, it is generally sufficient to consider a Drude model for the valence electrons, taking into account the effect of surface scattering by a frequency damping inversely proportional to the particle diameter [2,3]. If the core electrons are important, as in noble metals, an additional contribution to the dielectric function can be modeled in the manner of Lindhard [4] taking into account the electronic density of states both in the conduction and d bands [5]. For small clusters with typically less than a thousand atoms, the description of the dielectric function requires a more sophisticated approach to take into account the finite size effect on the electronic distribution. Such a task can be carried out in the framework of the density-functional theory with a jellium model in the spirit of the work of Ekardt [6] and taking into account the exchange and correlation in a self-consistent manner. Thus far, this type of approach has been carried out at zero temperature and was successful to describe the linear response of noble metal clusters [7]. More recently, it has been shown that the surface plasmon is strongly damped when it is degenerate with the quasiparticle states associated with the interacting electrons, an effect which is size dependent [8]. The effects of ionic temperature T_i on the optical spectrum of simple metal clusters has been investigated theoretically [9,10] and experimentally [11,12]. It was found that the energy of the surface plasmon ω_{SP} decreases when the lattice temperature increases. This effect is due to the increase of the cluster size with increasing temperature and comes from the fact that the static polarizability is both proportional to the volume of the cluster and inversely proportional to ω_{SP}^2.

The effect of electronic temperature T_e has been taken into account on the interband dielectric function of noble metal particles by considering the temperature dependent density of states at the Fermi level and a damping of the quasiparticles with a temperature and energy dependence of a Fermi liquid [13]. It results in a broadening and a low energy shift of the SP resonance when the electronic temperature increases. The relative amount of broadening and shift depends on the proximity of the SP resonance with respect to the interband transitions as observed in Cu, Ag, and Au nanoparticles using femtosecond optical spectroscopy [13–18]. A self-consistent description of the dynamical screening of the core electrons, taking into account the electronic temperature, has been performed in the plasmon pole approximation [19]. It was shown to induce a size dependent correction in the dielectric function which shows up as a high energy shift of the SP resonance as the temperature T_e increases. This effect is due to the emission of surface plasmons associated with the scattering of the d holes with the conduction electrons.

In the following, we focus on the influence of the electronic temperature T_e on the valence electrons of simple metal clusters. In order to unravel the specificity of a hot nonequilibrium distribution of valence electrons on the dynamical optical response of clusters, we consider alkali clusters, for which the influence of the core electrons can be neglected.

The bulk longitudinal dielectric function is one of the most important quantities in discussing the dynamical properties of a quantum many-electron system in a linear regime. In the linearized time-dependent Hartree theory [this approximation is also referred to as the random phase approximation or the self-consistent-field method] [20,21], the longitudinal dielectric function of a three-dimensional homogeneous electron gas reads

$$\varepsilon_l(\vec{q};\omega) = 1 - V(q)\chi^0(\vec{q};\omega), \tag{1}$$

where $V(q) = 4\pi e^2/q^2$ and $\chi^0(\vec{q};\omega)$ are, respectively, the Fourier transform of the Coulomb potential and the noninteracting retarded density correlation function. The latter is given by

$$\chi^0(\vec{q};\omega) = \lim_{\eta\to 0^+}\frac{2}{(2\pi\hbar)^3}\int\frac{n_F(\vec{p}) - n_F(\vec{p}+\hbar\vec{q})}{\epsilon_{\vec{p}} - \epsilon_{\vec{p}+\hbar\vec{q}} - \hbar\omega - i\eta}d^3\vec{p}, \tag{2}$$

where $n_F(\vec{p}) = 1/(e^{\beta(\epsilon_{\vec{p}}-\mu_F)}+1)$ is the Fermi-Dirac distribution function which depends on $\vec{p}$ only through the electronic energy $\epsilon_{\vec{p}} = p^2/2m$, $\beta = 1/k_B T_e$, and μ_F is the Fermi chemical potential. In the above formula, the variable η has been originally introduced by Lindhard for causality requirements [22].

The condition for plasma oscillation in the electron gas is given by $\varepsilon_l(\vec{q};\omega_r) \equiv \varepsilon_l'(\vec{q};\omega_r) + i\varepsilon_l''(\vec{q};\omega_r) = 0$. Generally, this condition cannot be fulfilled with real values of ω. However, in the long-wavelength limit, there are approximate solutions obtained from $\varepsilon_l'(\vec{q};\omega_r) = 0$. Thus, for any temperature one has

$$\omega_r = \omega_p\left\{1 + \frac{1}{2}\frac{q^2\langle v^2\rangle_F}{\omega_p^2} + \vartheta(q^4)\right\}, \tag{3}$$

where $\langle v^2\rangle_F = [2/(2\pi\hbar)^3]\int v^2 n_F(\vec{p})d^3\vec{p}\; d^3\vec{r}$ and $\omega_p = \sqrt{4\pi\rho_0 e^2/m}$ is the bulk plasma frequency. At $T_e = 0$ and $T_e \gg T_F$, one has $\langle v^2\rangle_F = \frac{3}{5}v_F^2$ and $\langle v^2\rangle_F = 3k_B T_e/m$, respectively. The corresponding formulas (3) are the ones which are currently found in textbooks of solid-state physics (Fermi-Dirac statistics) and plasma physics (Maxwell-Boltzmann statistics). The shift of the resonance frequency due to the temperature is given by

$$\Delta\omega_r(T_e) \equiv \omega_r(T_e) - \omega_r(0) = \frac{q^2}{m\omega_p}\varepsilon_{\mathrm{th}}(T_e), \tag{4}$$

where $\varepsilon_{\mathrm{th}}(T_e)$ is the *thermal energy per particle* of the electronic gas. Thus, in the bulk, the plasma resonance is always blueshifted with increasing temperature.

The metallic clusters are described in the spherical background jellium model which is known to be a very good approximation for closed-shell simple metal clusters. This model consists of replacing the real ionic core potential by the potential of a constant positive background corresponding to a uniformly distributed charge density [6]. The electronic system is assumed to be at a thermal equilibrium with a temperature T_e. In the Kohn-Sham (KS) formulation of the density-functional theory at finite temperature within the grand-canonical ensemble [23,24], the ground-state electronic density ρ of an N-electron system is written, in terms of single-particle orbitals and energies φ_i and ε_i, as

$$\rho(\vec{r}) = \sum_{k=1}^{N} f_k\rho_k(\vec{r}) = \sum_{k=1}^{N} f_k|\varphi_k(\vec{r})|^2, \tag{5}$$

where $f_k = [1 + \exp\{(\varepsilon_k - \mu)/k_B T_e\}]^{-1}$ are the Fermi occupation numbers and μ is the chemical potential. These orbitals and energies obey the Schrödinger equation:

$$[-\tfrac{1}{2}\nabla^2 + V_{\mathrm{KS}}(\vec{r})]\varphi_i(\vec{r}) = \varepsilon_i\varphi_i(\vec{r}), \tag{6}$$

where $V_{\mathrm{KS}}(\vec{r})$ is the effective single-particle potential:

$$V_{\mathrm{KS}}(\vec{r}) = V_{\mathrm{jel}}(\vec{r}) + V_{\mathrm{H}}[\rho(\vec{r})] + V_{\mathrm{xc}}[\rho(\vec{r})], \tag{7}$$

$V_{\mathrm{jel}}(\vec{r})$, $V_{\mathrm{H}}[\rho(\vec{r})]$, and $V_{\mathrm{xc}}[\rho(\vec{r})]$ being, respectively, the jellium, the Hartree, and the exchange-correlation potentials. For the latter, we have used the form of Gunnarsson and Lundqvist [25]. The chemical potential is determined self-consistently by requiring the conservation of the total number of electrons from Eq. (5). By analogy with the bulk case, the shift of the resonance frequency (volume and surface plasmons) due to the temperature is controlled by $\Delta\kappa \equiv \kappa(T_e) - \kappa(0)$ with $\kappa \equiv K/N$ and where K is the kinetic energy of a noninteracting electron gas of density $\rho(\vec{r})$. In order to calculate K, we note that from (6) we have

$$U = \sum_i f_i\varepsilon_i = \sum_i f_i\left\langle\varphi_i\left| -\frac{1}{2}\nabla^2 + V_{\mathrm{KS}}(\vec{r})\right|\varphi_i\right\rangle,$$

leading to

$$K = U - \int V_{\mathrm{KS}}(\vec{r})\rho(\vec{r})\,d\vec{r}, \tag{8}$$

where U is the total internal energy.

The optical response of the valence electrons is treated quantum mechanically. In the usual first-order TDLDA, the induced electronic density $\delta\rho(\vec{r};\omega;T_e)$ is related to $V_{\rm ext}(\vec{r}\,';\omega)$, the Fourier transform (with respect to time) of the external potential associated to the electric field of the laser, by [26]

$$\delta\rho(\vec{r};\omega;T_e) = \int \chi(\vec{r},\vec{r}\,';\omega;T_e)V_{\rm ext}(\vec{r}\,';\omega)\,d\vec{r}\,', \qquad (9)$$

where $\chi(\vec{r},\vec{r}\,';\omega;T_e)$ is the retarded density correlation function which is deduced from the noninteracting retarded density correlation function χ^0 via a Dyson-type integral equation:

$$\begin{aligned}\chi(\vec{r},\vec{r}\,';\omega;T_e) =& \chi^0(\vec{r},\vec{r}\,';\omega;T_e) + \iint \chi^0(\vec{r},\vec{r}\,'';\omega;T_e)\\ &\times K_r(\vec{r}\,'',\vec{r}\,''';\omega)\chi(\vec{r}\,''',\vec{r}\,';\omega;T_e)\,d\vec{r}\,''\,d\vec{r}\,''',\end{aligned}$$

with K_r the residual interaction.

At finite electronic temperature, the grand-canonical noninteracting retarded density correlation function reads [27]

$$\begin{aligned}\chi^0(\vec{r},\vec{r}\,';\omega;T_e) = \frac{1}{Z_G}\sum_{n,N}\exp\left\{-\frac{1}{k_BT_e}[E_n(N) - N\mu]\right\}\\ \times \chi^0_{n,N}(\vec{r},\vec{r}\,';\omega;T_e), \qquad (10)\end{aligned}$$

where Z_G is the grand-canonical partition function, $E_n(N)$ is the energy of the state $|nN\rangle$ having N electrons, and

$$\begin{aligned}\chi^0_{n,N}(\vec{r},\vec{r}\,';\omega;T_e) = \sum_m \frac{\langle nN|\hat{n}(\vec{r})|mN\rangle\langle mN|\hat{n}(\vec{r}\,')|nN\rangle}{\omega - [E_m(N) - E_n(N)] + i\delta}\\ - \frac{\langle nN|\hat{n}(\vec{r}\,')|mN\rangle\langle mN|\hat{n}(\vec{r})|nN\rangle}{\omega + [E_m(N) - E_n(N)] + i\delta}.\end{aligned}$$

In the above expression, $\hat{n}(\vec{r})$ is the particle density operator defined from the wave field operators by $\hat{n}(\vec{r}) = \hat{\psi}^+(\vec{r})\hat{\psi}(\vec{r})$ with $\hat{\psi}^+(\vec{r}) = \sum_k \hat{a}_k^+\varphi_k^*(\vec{r})$ and $\hat{\psi}(\vec{r}) = \sum_k \hat{a}_k\varphi_k(\vec{r})$. In order to produce numerically tractable results, we have added a small imaginary part to the probe frequency, so $\omega \longrightarrow \omega + i\delta$.

The quantity which is directly related to an experimental determination of the plasmon shift is the differential transmission usually defined in femtosecond spectroscopy by

$$\frac{\Delta T}{T}(\omega;T_e) = \frac{3}{2\pi R^2}[\sigma(\omega;T_0) - \sigma(\omega;T_e)], \qquad (11)$$

where R is the radius of the metallic particle. The variation of temperature from T_0 to T_e is induced by a pump pulse which can be delayed with respect to the probe (dynamical measurements). $\sigma(\omega;T_e) = [4\pi\omega/c]\Im[\alpha(\omega;T_e)]$ is the photoabsorption cross section calculated from the frequency dependent polarizability at temperature T_e given by

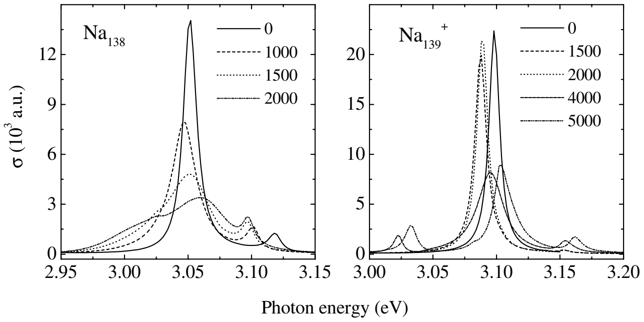

FIG. 1. TDLDA photoabsorption cross sections of Na_{138} and Na_{139}^+ as a function of the photon energy for different values of the electronic temperature.

$$\alpha(\omega;T_e) = \int \delta\rho(\vec{r};\omega;T_e)V_{\rm ext}(\vec{r};\omega)\,d\vec{r}. \qquad (12)$$

Because of the problem of mass selection, most of the experiments on free mass-selected clusters are carried out with charged species. We have computed the optical spectrum for two isoelectronic free closed-shell sodium clusters having 138 valence electrons. The results are presented in Fig. 1. The oscillator strengths in the photon energy range shown in the figure are 73% and 84% for Na_{138} and Na_{139}^+, respectively. Thus, due to the presence of the surface plasmon resonance, almost all the oscillator strength is concentrated in this small energy range (0.2 eV). Furthermore, it does not change in the electronic temperature range considered in this work. Additional quasiparticle states are also present in this energy range. They will be ignored in the following since they do not reflect the collective behavior of the confined electronic system. For the two species, we observe the same striking evolution with increasing temperature: a redshift of the SP up to a certain temperature, T_e^{tr}, followed by a blueshift of the resonance. The value of T_e^{tr} depends on the cluster charge. Indeed, we have approximately $T_e^{tr} \simeq$ 1000 K and 2500 K for Na_{138} and Na_{139}^+, respectively.

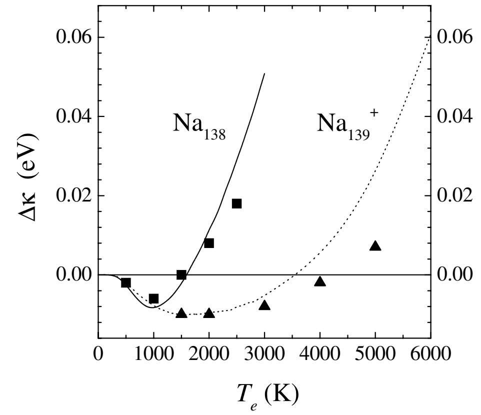

FIG. 2. Specific thermal energies of Na_{138} and Na_{139}^+ versus temperature. Full squares and triangles indicate the energy shifts deduced from the photoabsorption spectra (see Fig. 1).

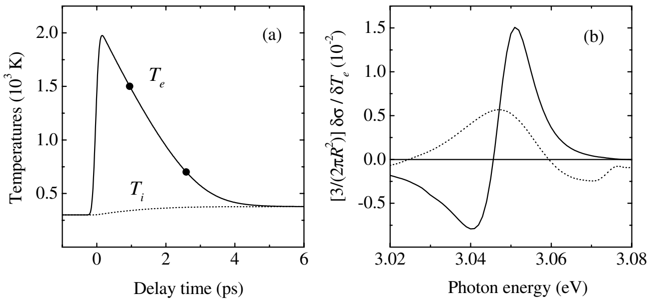

FIG. 3. (a) Time evolution of the electronic and ionic temperatures of Na_{138}. (b) $[\delta\sigma/\delta T_e](\omega; T_e)$ as a function of probe energy, corresponding to the two dots in (a). Dotted line: $t = 0.95$ ps, $T_e = 1500$ K; full line: $t = 2.59$ ps, $T_e = 700$ K. In the two temperature model, the pulse duration is 100 fs and the energy density 100 $\mu\mathrm{J/cm}^2$.

We show in Fig. 2 the KS thermal energy per particle of Na_{138} and Na_{139}^+ as a function of the temperature. According to the optical spectra of Fig. 1, it is clearly seen that the nature (red or blue) and the magnitude of the spectral shift of the SP are directly related to $\Delta\kappa$. Therefore, the changes of the optical spectrum with temperature, and, in particular, the frequency shift of the SP, may be explained qualitatively and quantitatively from the KS ground-state properties. We have checked that this finding is very general and holds for different cluster sizes, cluster charges, and cluster metal elements.

As discussed before, in order to observe the above SP dynamics, it is important to be in a highly nonequilibrium regime $T_i \ll T_e$. This can indeed be investigated using the techniques of time-resolved pump-probe spectroscopy. This is illustrated in Fig. 3 in the context of the two temperature model. In such a model, the electronic bath at temperature $T_e(t)$ is coupled to the lattice at temperature $T_i(t)$ via an effective electron-phonon interaction. In Fig. 3(a), we have represented $T_e(t)$ for sodium, taking into account the KS electronic specific heat of Na_{138} and the bulk lattice specific heat [28]. Figure 3(b) shows the derivative of the differential transmission spectra with respect to the temperature T_e ($\propto [\delta\sigma/\delta T_e] \times (\omega; T_e)$) associated to the two dots in Fig. 3(a). Such an effect should be easily observable with a probe obtained from a continuum generation. Indeed, it corresponds to a very large spectrotemporal variation which should not suffer drastically from fluctuations in the cluster sizes. It is worth mentioning that it is an experimental way to directly investigate the correlation properties of the electrons confined in the cluster. The mechanism associated with the behavior of the SP dynamics (and the specific kinetic energy) results from the redistribution of the electrons among the available unoccupied cluster states as the temperature increases. The associated spatial modification of the density leads to a redshifted SP. As the temperature further increases, the electrons become more and more sensitive to bulklike extended states leading to a blueshift as expected for homogeneous bulk metals.

In conclusion, we have shown that the dynamics of the surface plasmon in alkali metal clusters displays a nonmonotonous spectral shift when the electronic temperature increases. The physical picture underlying this effect is that the optical response of the cluster gradually goes from a quantum behavior to a semiclassical one when the temperature increases. At low temperature, electronic shell effects are important and the spillout of the electronic density leads to a redshift of the surface plasmon resonance. At higher temperature, the density of states of the cluster displays a continuumlike behavior. It leads to a blueshift of the surface plasmon as can be obtained with a semiclassical description of the electron dynamics using a hydrodynamical-like model [29].

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[29] As it will be published elsewhere, the Bloch linearized hydrodynamical model of a spatially inhomogeneous electron gas leads to a monotonous blueshift of the surface plasmon resonance as a function of the temperature.