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Effects of motional narrowing on the plasmon resonance in small metal clusters

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Abstract. A model accounting for the time dependence of shape fluctuations in metal microclusters and their effect on the damping width of the plasmon resonance is discussed. An estimate of the relaxation time of the quadrupole shape is given, and calculations demonstrating the effects of time-dependent thermal fluctuations on the plasmon in K_9^+ are presented.

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An important mechanism in the damping of the plasmon resonance in metal microclusters is the coupling of the resonance to the quadrupole distortion of the cluster surface [1–5]. While it is true that the plasmon frequency does not depend on the size of the cluster, aside from corrections due to electron spill out, the directional polarizabilities, α_k, are strongly dependent on the intrinsic quadrupole deformation parameters, β and γ, characterizing the quadrupole moment of the ellipsoid and its departure from spherical symmetry. This dependence splits the plasmon frequency into three components [6]

$$\omega_k^2(\beta,\gamma)=\frac{e^2}{m\alpha_k(\beta,\gamma)}, \tag{1}$$

with $k=1,2,3$ and corresponding to vibrations along the principal axes of the ellipsoid. The total photo-absorption cross section can be written as

$$\sigma(\omega;\beta,\gamma,\Omega)=\sum_k \frac{4\pi f_k(\Omega)\,N e^2}{mc}\,\frac{\omega^2\Gamma}{(\omega^2-\omega_k(\beta,\gamma)^2)^2+\omega^2\Gamma^2} \tag{2}$$

where f_k is the fraction of the total strength carried by the vibration along the k^{th} axis, and is in principle a function of the Euler angles, $\Omega=(\phi,\theta,\psi)$, that define the orientation of the cluster relative to a fixed reference frame. The quantity N is the number of delocalized electrons in the cluster and Γ is the intrinsic width of the plasmon arising from relaxation processes different from those associated with fluctuations of the surface. In particular, with the finite mean-free path of the electrons due to collisions with lattice phonons (resistivity).

At finite temperatures, the system will explore the ensemble of shapes of the system, and a weighted average should be carried out over parameters β, γ, and Ω of the photoabsorption cross section (2) before the quantity can be compared with experiment. At low temperatures, the shape degrees of freedom can be treated in the adiabatic approximation. In this case, the probability that the system has a definite shape and orientation is given by the Boltzman factor determined by the free energy, F, and the temperature T of the ionic system, that is [4, 7]

$$\sigma(\omega)=\int \mathrm{d}\tau\, p(\beta,\gamma,\Omega)\,\sigma(\omega,\beta,\gamma,\Omega), \tag{3}$$

where the probability

$$p(\beta,\gamma,\Omega)=Z^{-1}\exp(-F(T,\beta,\gamma,\Omega)/T),$$

with

$$Z=\int \mathrm{d}\tau \exp(-F/T),$$

and

$$\mathrm{d}\tau=\beta^4\,\mathrm{d}\beta\,\sin(3\gamma)\,d\gamma\,\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi\,\mathrm{d}\psi.$$

As the temperature increases, the cluster shape may fluctuate so rapidly that the system may not have enough time to perceive the sampling of all the variety of deformations (cf. also [8, 9]). In this limit, the system "hops" from one deformation to another with a characteristic time $\tau_h=\hbar/\lambda$ that is shorter than the inverse of the spread in frequencies, $\Delta\omega$, induced by the thermal fluctuations,

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leading to a narrowing of the line shape of the plasmon. The parameter that defines the transition from the adiabatic to motionally narrowed regimes is the ratio $\hbar\Delta\omega/\lambda$. If this ratio is larger than unity, the adiabatic picture is valid, whereas values less than unity are typical of motional narrowed situations.

In the present paper, we study the conditions for the existence of motional narrowing of the plasmon resonance in small metal clusters, in particular the K_9^+ ionic system, where some experimental information is available [10]. We also present an estimate of the relaxation time of the quadrupole degree of freedom based on molecular-dynamic simulations.

At this point, we give a rough estimate of the parameters $\Delta\omega$ and λ that govern the transition between the adiabatic and motionally narrowed regimes. First, the spread in frequencies $\Delta\omega$ can be estimated by assuming that the free energy is harmonic, i.e. $F=\frac{1}{2}C\beta^2$, and neglecting non-axially symmetric shapes, giving [9, 11]

$$\Delta\omega\approx 0.35\sqrt{\frac{T}{C}}\hbar\omega_D. \tag{4}$$

The restoring parameter C can be estimated within the framework of the spheroidal shell model [3, 12, 13], giving $C\approx 11$ eV for K_9^+ (cf. also [6]). The observed centroid energy $\hbar\omega_D\approx 2$ eV then leads to a spread in frequencies $\Delta\omega\approx 0.21\sqrt{T_{\mathrm{eV}}}$ (eV), where T_{eV} is the temperature measured in eV.

In order to estimate the hopping width λ, we note that this quantity is essentially the relaxation time of the quadrupole shape degree of freedom, i.e. the time it takes the system to loose all memory of its initial configuration. In this regard, we have evaluated the Fourier transform of the correlation function of the quadrupole degree of freedom using a molecular dynamics simulation [14] to describe the dynamical properties of a K_9^+ cluster. This technique is based on integrating the classical equations of motion of the ionic system starting from the Hamiltonian

$$H=\sum_{i=1}^{8}\frac{\mathbf{P}_i^2}{2m}+V(\{\mathbf{r}_i\}),$$

where $V(\{\mathbf{r}_i\})$ is a general type potential of the ion coordinates. We have used a two-body phenomenological Morse-type potential that permits the study of anharmonic effects in the dynamical properties, i.e.

$$V(\{\mathbf{r}_i\})=\sum_{j>i}V_{ij}(r_{ij}),$$

$$V_{ij}(r_{ij})=D\{\exp[-2\alpha(r_{ij}-r_0)]-2\exp[-\alpha(r_{ij}r_0)]\}.$$

The parameters D, r_0 and α were obtained by fitting the cohesive energies, the mean distances between ions, and the fragmentation energies of clusters with 6 atoms to the results of an ab-initio calculation [15]. The Hamiltonian was integrated using time steps of 10^{-15} s for a total time of 20×10^{-12} s. The ground-state configuration was obtained by using the annealing technique while starting from a bcc Potassium crystal. This technique consists of raising the cluster to a suitable temperature so that memory of the initial crystaline state is lost. The system is then slowly cooled to a temperature of 0 K. The parameter that defines the slowness of this process is the cooling ratio $R=\dfrac{\Delta T}{\Delta t}$ where ΔT is the temperature difference between the steps in the cooling function. Here the value $R=10^{12}$ K/s was used. This procedure has been tested by calculating energies and configurations of 7, 8, and 13 atom Na-clusters, where it is possible to compare the results with ab-initio calculations. The configurations obtained at $T=0$ are in good agreement with those reported in [16], that is the energies and interatomic distances are reproduced to within 5%. The parameters resulting from this fitting procedure for potassium clusters are $D=0.28$ eV, $r_0=9.0$ Å, and $\alpha=1.5$ Å [17].

At finite temperature, the behaviour of the cluster was investigated by raising the temperature of the cluster via small, incremental steps in the total energy. The system was then allowed to evolve to the equilibrium state for a time of 5 ps, and followed for 20 ps. The temperature range observed was 50–1000 K.

The density of total vibrational states at each temperature was evaluated from the Fourier transform of the velocity correlation function

$$\rho_{\mathrm{vib}}(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{i\omega t}\sum_{ij}\mathbf{v}_i(t)\cdot\mathbf{v}_j(0), \tag{5}$$

where $\mathbf{v}_i(t)$ is the velocity of the i^{th} ion at time t. In addition, the quadrupole frequency response was evaluated from the correlation function of the quadrupole coordinate associated with the cigar-like (prolate) shape, i.e. $Q=2z^2-x^2-y^2$. The quadrupole degree of freedom exhibits features very similar to the total vibrational spectrum accounting for the most relevant structures in the phonon density of states (DOS). In Fig. 1, the DOS for various temperatures are shown. With increasing temperature, the cluster shows two distinct phases. At low temperatures (<550 K), the cluster exhibits solid-like behaviour, with no diffusion of the ions inside the cluster. The density of states is characterized by well defined peaks associated with the normal modes of the cluster that tend to merge at ≈ 400 K due to the anharmonicity of the potential. For temperatures above 750 K, the system is in a liquid-like phase, with active diffusive processes occurring. These diffusive processes are responsible for the peak in the DOS at zero frequency.

A rough estimate of the relaxation width of the quadrupole degree of freedom may be obtained the full-width-at-half-maximum (FWHM) of the density of quadrupole states displayed in Fig. 1. Generally, the quadrupole density of states is characterized by a large bump centered at ≈ 4 THz (≈ 15 meV), whose FWHM increases with temperature and ranges from 15 to 30 meV, and may be roughly parameterized as $0.1\sqrt{T_{\mathrm{eV}}}$ meV. We note that this value of λ is approximately a factor of two smaller than the estimate of $\Delta\omega$ given by (4), indicating that the effects of large-amplitude fluctuations of the

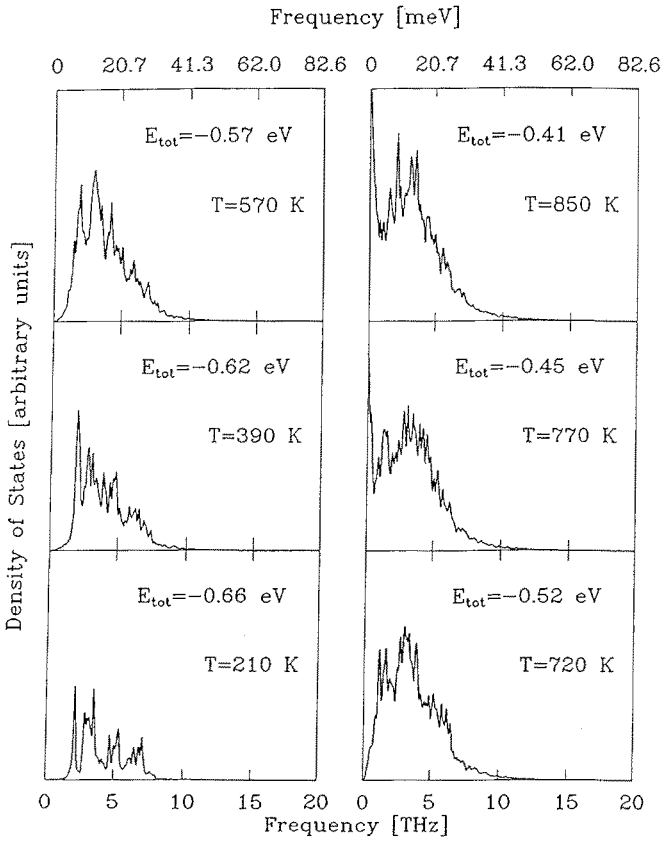

Fig. 1. The density of vibrational states at various temperatures for a K_9^+ cluster as calculated from the Fourier transform of the velocity autocorrelation function (5) obtained by a molecular-dynamics simulation

cluster shape may be adiabatic or possibly transitional between the adiabatic and motionally narrowed regimes.

At this point, we have qualitatively discussed the effects of time-dependent thermal fluctuations on the plasmon resonance within the framework of the relaxation width λ and the spread in plasmon frequencies $\Delta\omega$. In the remaining part of this work, we describe a model that gives a detailed description of the plasmon resonance that includes large-amplitude thermal fluctuations and their time dependence.

For a description of the effects of time-dependent fluctuations, we make use of the model for the absorption line shape $I(E)$ described in [18]. The photo-absorption cross section is taken as

$$\begin{aligned}\sigma(E)&=\sigma_0 I(E)\\&=\frac{\sigma_0}{\pi}\sum_k f_k \operatorname{Re}\int_0^\infty \mathrm{d}t\, \mathrm{e}^{-st}\operatorname{Tr}\{\rho_i d_k^\dagger(0)\, U(t)\, d_k(0)\},\\&=\sigma_0\sum_k f_k \operatorname{Re}\operatorname{Tr}\{\rho_i d_k^\dagger(0)\, U(s)\, d_k(0)\},\end{aligned}\tag{6}$$

where $s=\mathrm{i}E/\hbar+\frac{1}{2}\Gamma/\hbar$, with Γ being the intrinsic width of the plasmon, ρ_i is the density of initial states, d_k is the dipole-transition operator, $f_k=1/3$, and $U(s)$ is the Laplace transform of the time-developement operator $U(t)=\exp\left(\mathrm{i}\int_0^t \mathscr{H}^X(t')\,\mathrm{d}t'\right)$, where $\mathscr{H}^X$ is the Liouville operator associated with the Hamiltonian H with matrix elements

$$(i'f'|\mathscr{H}^X|if)=[\delta_{ff'}\langle i'|H|i\rangle-\delta_{ii'}\langle f|H|f'\rangle].$$

To evaluate (6), we follow closely the discussion of [18], making use of five assumptions. First, the complicated many-body Hamiltonian describing the small metal cluster is assumed to be separable into two parts. The first describes the subsystem of interest and encompasses all the relevant degrees of freedom of the plasmon resonance. In the second part, all other degrees of freedom, i.e. the quadrupole deformation and orientation of the system, are attributed to a heat bath, which couples weakly to the subsystem of interest. In this limit, ρ_i factors into two parts $\rho_i=\rho_S^i\rho_B$, where ρ_S^i refers to the subsystem and ρ_B refers to the heat bath. Secondly, we assume that the time evolution operator $U(t)$ represents a stationary Markovian process in which each state of the heat bath has a mean lifetime $\hbar/\lambda$. Thirdly, the transitions between the various heat bath states are taken to be governed by a Kubo-Anderson process [19], that is, the probability of making the transiton to a new heat bath state is independent of the initial state. As for the fourth, we assume the plasmon resonance to correspond to collective vibrations along the intrinsic axes of the system, and define the subsystem Hamiltonian as [20]

$$H=\tfrac{1}{2}\sum_k E_k(\alpha_k^\dagger a_k+a_k a_k^\dagger),\tag{7}$$

where $a_k^\dagger$ and a_k are the creation and annihilation operators, respectively, of the plasmon resonance in the intrinsic frame, and $E_k=\hbar\omega_k$ at each deformation and orientation is given by (1). Finally, we assume that photo-absorption occurs only from the ground state, i.e. $\rho_S^i=\delta_{0i}$.

Making use of these assumptions, $\sigma(E)$ may be written as

$$\begin{aligned}\sigma(E)=\sigma_0\sum_k f_k\sum_{ff'}&\langle 0|d_k^\dagger(0)|f\rangle\langle f'|d_k(0)|0\rangle\\&\cdot(0f'|[1-\lambda\langle U_0(s+\lambda)\rangle]^{-1}\langle U_0(s)\rangle|0f),\end{aligned}\tag{8}$$

with

$$\langle U_0(s)\rangle=\int \mathrm{d}\tau\, p(\tau)\, U_0(s;\tau),\tag{9}$$

where, as in (3), $p(\tau)=Z^{-1}\mathrm{e}^{-F/T}$ and

$$U_0(s;\tau)=(s-\mathrm{i}\mathscr{H}^X(\tau))^{-1}.$$

Finally, since time-dependent fluctuations can cause changes in the orientation of the system, it is necessary to evalute (8) in a fixed reference frame so that the various intrinsic shapes and orientations may be defined relative to one another. Towards this end, we define creation and anhilation operators $\alpha_k^\dagger$ and α_k in the fixed reference frame. In terms of the intrinsic operators, we have

$$\alpha_l^\dagger=\sum_k R_{kl}^{-1}\, a_k^\dagger=\sum_k R_{lk}\, a_k^\dagger,$$

$$\alpha_l=\sum_k R_{kl}^{-1}\, a_k=\sum_k R_{lk}\, a_k,$$

where $R_{l,k}$ is the standard rotation matrix for a three component vector [21]. The Hamiltonian may then be written as

$$H=\tfrac{1}{2}\sum_{k}\sum_{ll'}\omega_k R_{kl} R_{kl'}(\alpha_l^\dagger \alpha_{l'}+\alpha_l \alpha_l^\dagger),$$

while the transition operators are given by

$$d_k=\frac{1}{\sqrt{2}}(\alpha_k^\dagger+\alpha_k).$$

The free energy used to define the relative probability of the each shape and orientation for the K_9^+ cluster was evaluated using the spheroidal Nilsson-Clemenger model [3, 12] with the parametrization of [13]. As mentioned above, this cluster is spherical in the ground state, and exhibits a free energy that is essentially harmonic in the deformation parameter β, i.e. $F=\frac{1}{2}C\beta^2$, with $C \approx 11$ eV.

Before describing the results of our calculations, we note that it is possible that the hopping widths for the deformation variables β and γ and the orientation angles Ω may be different. At present, no clear information on this possibility exists, and we have performed calculations for two limiting cases. In the first, we assume that all hopping widths are the same (unrestricted hopping), and, in the second, the relaxation time for orientation fluctuations is assumed infinite, namely that time-dependent fluctuations occur only in the β and γ variables (restricted hopping). As a practical point, the restricted hopping situation is evaluated by not treating the Euler angles as stochastic variables in (9), thereby integrating over only β and γ for $\langle U_0(s)\rangle$. This gives an effective cross section $\sigma(E, \Omega)$. However, since the free energy of the cluster is independent of the intrinsic orientation, $\sigma(E, \Omega)$ is also independent of Ω due to the sum over all intrinsic axes k. Therefore, $\sigma(E)=8\pi^2\sigma(E, \Omega)$.

At this point, we note that many of the parameters that enter into the calculation of $\sigma(E)$ are somewhat uncertain (including the relaxation width λ). Therefore, we focus our discussion on the overall effects, with the intent on giving a description of what may be expected from time-dependent thermal fluctuations of the cluster shape. Towards this end, we present the results of calculations as a function of temperature assuming two different temperature dependences for the relaxation width: (i) $\lambda=0.1\sqrt{T}$ and (ii) $\lambda=T$. The intrinsic width is due to collisions between the electrons and lattice phonons, and in keeping with this assumption, we have used $\Gamma=2T$, where the proportionality factor was obtained from the dependence of the electronic resistivity with temperature in bulk potassium [22]. Finally, the plasmon frequency for the spherical shape, $\omega_0=\sqrt{e^2/m\alpha_0}=1.93/\hbar$ eV and the overall normalization strength $\sigma_0=7.38$ Å^2 eV were taken from experimental data [10].

Shown in Figs. 2 and 3 are the cross sections for $T=200$ K a, 400 K b, 600 K c, and 800 K d for $\lambda=0.1\sqrt{T}$ and $\lambda=T$, respectively. The long dashed line represents the adiabatic situation, while the short dashed and solid lines represent the unrestricted and restricted hopping situations, respectively. We note that the primary difference between the adiabatic and restricted hopping results is that at low temperatures the restricted hopping situation yields three distinct peaks that gradually become unresolvable at higher temperatures because of the increasing intrinsic width. On the other hand, the

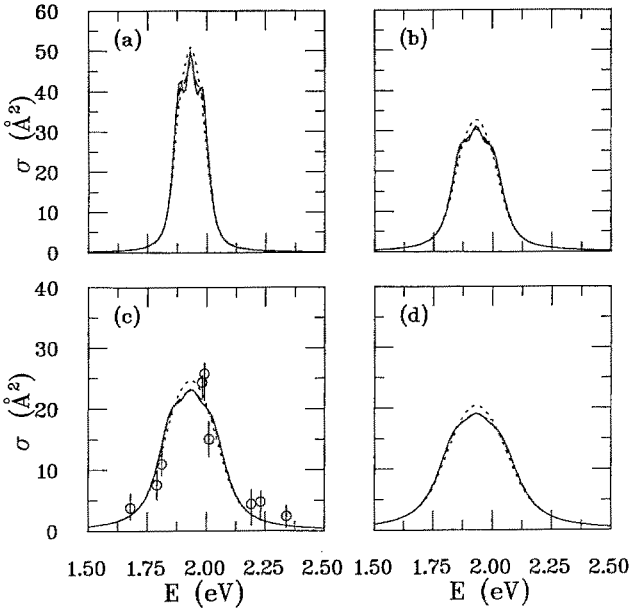

Fig. 2. The photo-absorption cross sections for the K_9^+ cluster with $\lambda=0.1\sqrt{T}$ at $T=200$ K **a**, 400 K **b**, 600 K **c**, and 800 K **d**. The *long dashed line* represents the adiabatic situation. The *short dashed* and *solid lines* represent the unrestricted and restricted hopping situations, respectively

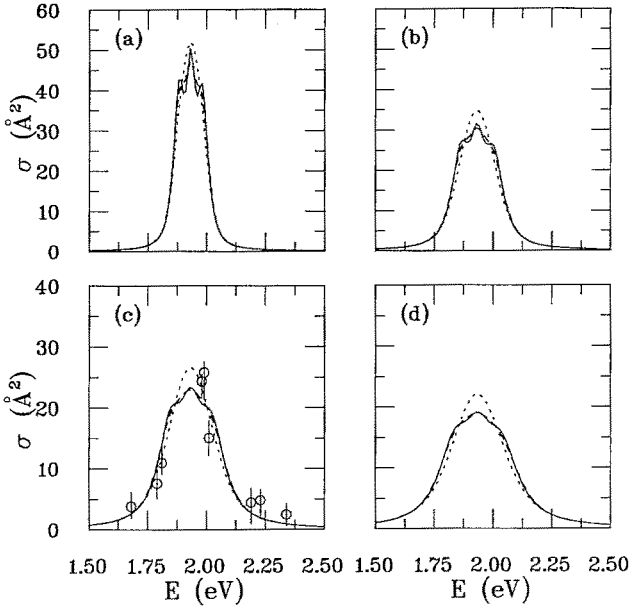

Fig. 3. The photo-absorption cross sections for the K_9^+ cluster with $\lambda=T$ at $T=200$ K **a**, 400 K **b**, 600 K **c**, and 800 K **d**. The *long dashed line* represents the adiabatic situation. The *short dashed* and *solid lines* represent the unrestricted and restricted hopping situations, respectively

cross section in the unrestricted hopping situation exhibits only one peak. The reason for this is that changes in the orientation transfer the plasmon vibration onto another axis, and if λ is larger than the frequency shift caused by the deformation (1), the system responds to an external probe with a frequency that is the average of the fundamental modes [9, 18].

Also shown in Figs. 2c and 3c are the experimental photo-absorption cross section for the K_9^+ cluster [10], where the best overall agreement is obtained with the unrestricted motionally narrowed picture at $T=600$ K with $\lambda = T$. We note, however, that since the experimental errors are quite large and that the temperature of the cluster is uncertain, ranging between 300 and 700 K, reasonable agreement with experiment can be achieved with either the 400 or 800 K theoretical spectra by increasing or decreasing the intrinsic width accordingly. In this light, it is clear that a conclusive determination of the existence or not of motional narrowing in the plasmon of metal clusters cannot be made from one measurement. Such a test requires the analysis of a comprehensive set of high-resolution optical response data for a wide range of well controlled temperatures.

Finally, by comparing the results displayed in Figs. 2 and 3, it is clear that the observed cross sections strongly affected by the relaxation width λ. With larger values of λ giving more dramatic effects. Unfortunately, the observed cross section is also strongly affected by the intrinsic width Γ, which if it increases with temperature, as suggested by electrical resistivity, tends to disguise the effects of motional narrowing, although, in all cases the adiabatic and restricted hopping situations lead to flater cross sections due to the presence of the three underlying peaks.

We conclude by noting that time-dependent thermal fluctuations of the surface of a small metal cluster may affect the observed plasmon resonance. Molecular-dynamics simulations give relaxation widths for the quadrupole degree of freedom that are within a factor of two of the expected spread in frequencies caused by the thermal fluctuations. Detailed calculations of the photo-absorption cross section indicate that the effects of time-dependent fluctuations may be observable provided that high-resolution data over a wide range of temperatures are available.

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