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# The intrinsic line width of the plasmon resonances in metal microclusters at very low temperatures: quantal surface fluctuations

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**Abstract.** The line shape of the plasmon resonance in a cold, small sodium cluster ($Na_8$) is calculated taking into account its coupling to the quantal quadrupole fluctuations of the cluster shape. This coupling is found to give rise to a small damping factor ($\Gamma/\hbar\omega_1 \sim 0.03$, where $\hbar\omega_1$ denotes the energy centroid and $\Gamma$ the full width at half maximum of the resonance), and to an asymmetric line shape with Gaussian behaviour in the wings.

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The dipole surface plasmon has been observed in small clusters of alkali atoms [1, 2, 3, 4]. While the mean frequency of the dipole absorption is simply determined by the density of the valence electrons, the line shape is affected by a number of interesting coupling effects involving partly the single-particle degrees of freedom of the electrons (Landau damping) [5, 6, 7, 8] and partly the configurational degrees of freedom of the positive ions. Among the latter effects, the coupling to the quadrupole shape deformations, has been discussed in a number of recent investigations [9, 10]. These studies which treat the quadrupole degrees of freedom as a one dimensional axially symmetric problem, have yielded total line widths which although somewhat too narrow are comparable with those experimentally observed for clusters having closed (spherical) electronic shells.

In the present note we consider the rotationally invariant coupling of the dipole mode to the full set of (five-dimensional) quadrupole shape oscillations. This problem has been studied previously by Le Tourneux [11, 12] in connection with the line broadening of the dipole absorption in atomic nuclei (see also [13]). It will be concluded that the inclusion of the full set of quadrupole oscillations leads to a rather different line shape as compared with the previous analyses as well as a considerably stronger total coupling effect.

After defining the Hamiltonian that describes the coupled motion of dipole and quadrupole quanta, we present a dimensional analysis of the different terms in order to exhibit the order of magnitude of the effects to be expected. Two solutions of the coupled system are then discussed; the first provides an analytic approximation in the limit where the quadrupole frequency is small compared with all the other frequencies in the problem, while the second solution is obtained by "brute force" diagonalization of the dipole-quadrupole coupling.

The Hamiltonian describing the coupling of the dipole surface plasmon and quadrupole shape oscillations is (cf. e.g. [12])

$$H = H_1 + H_2 + H_{\text{coupl}},$$

$$H_\lambda = \hbar\omega_\lambda \sum_{\mu=-\lambda}^{\lambda} c_{\lambda\mu}^\dagger c_{\lambda\mu}, \tag{1}$$

$$H_{\text{coupl}} = K(\alpha_1^{(0)})^2 \alpha_2^{(0)} ((c_1^\dagger c_1)_2 (c_2^\dagger + c_2))_0,$$

where $\hbar\omega_\lambda$ are vibrational frequencies of the dipole surface plasmon ($\lambda = 1$) and of the quadrupole shape oscillations ($\lambda = 2$); $c_{\lambda\mu}^\dagger$ and $c_{\lambda\mu}$ are the boson creation and annihilation operators for the different vibrational modes and the parenthesis notation in the last line indicates the coupling of the tri-linear combinations of boson operators to zero total angular momentum. Note that the quadrupole surface oscillations of the cluster are quite different from the dipole oscillations associated with the plasmon resonance. Indeed, while in the dipole oscillations the electrons are moving in opposite phase with respect to the positive ionic core, in the quadrupole motion the valence electrons oscillate "in phase" with the ionic core. The restoring force for the quadrupole oscillations is still determined by the adiabatic deformation energy of the valence electrons, but the inertia associated with this motion is controlled by the heavy ionic core.

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The coupling term in (1) is the leading order effect appropriate in the limit of small amplitude oscillations [14]. This coupling is expressed in terms of the zero-point amplitudes $\alpha_\lambda^{(0)}$ of the dipole and quadrupole oscillations and of a coupling constant $K$ which can be related [9] to the static restoring force, $C_1$,for the dipole surface plasmon according to

$$K=-\left(\frac{27}{2\pi}\right)^{1/2} C_1 . \tag{2}$$

The relation (2) is obtained most directly by replacing in (1) the dynamic quadrupole amplitudes $\alpha_2^{(0)}(c_{2\mu}^\dagger + c_{2\mu})$ by static $c$-numbers $\alpha_{2\mu}$ which transforms (1) into the hamiltonian for the surface dipole plasmon in a static ellipsoid. The classical result [15] that in this geometry the normal modes of the Mie resonance correspond to oscillations along the three principal axes of the ellipsoid with frequency shifts with respect to the frequency $\omega_1$ in the spherical system,

$$\frac{\delta\omega_{1\kappa}}{\omega_1}=-\tfrac{3}{5}\frac{\delta R_\kappa}{R_0}\,(\kappa=1,2,3), \tag{3}$$

requires the relation (2). Note that in the nuclear problem treated by Le Tourneux [11], the dipole mode is a form of second sound and the relation corresponding to (3) has a coefficient 1 instead of 3/5.

The zero point amplitudes $\alpha_\lambda^{(0)}$ are given in terms of the restoring forces and frequencies by the usual expressions

$$(\alpha_\lambda^{(0)})^2=\frac{\hbar\omega_\lambda}{2C_\lambda}. \tag{4}$$

We consider first a dimensional analysis of the coupled system in order to exhibit the relative order of magnitude of the different terms and the variation of these terms with the parameters describing different clusters. We ignore the effect of Landau damping on the dipole surface plasmon and thus assume a single dipole mode exhausting the full Thomas-Reiche-Kuhn (TRK) sum rule. The frequency of the surface plasmon mode is proportional to the square root of the density of the valence electrons. Thus we have

$$\hbar\omega_1\sim r_s^{-3/2}\,\mathrm{Ry}, \tag{5}$$

and

$$(\alpha_1^{(0)})^2\sim N^{-5/3} r_s^{-1/2}, \tag{6}$$

where $N$ is the number of alkali atoms in the cluster and $r_s$ is the Wigner-Seitz radius in atomic units.

Since we are considering quadrupole shape oscillations of spherical clusters with closed electronic shells, the restoring force is $C_2\sim N\varepsilon_F$ [16] and thus

$$\hbar\omega_2\sim\frac{\mathrm{Ry}}{r_s^2}\,\frac{1}{N^{1/3}}\left(\frac{m}{M}\right)^{1/2}, \tag{7}$$

and

$$(\alpha_2^{(0)})^2\sim\frac{1}{N^{4/3}}\left(\frac{m}{M}\right)^{1/2}, \tag{8}$$

where the electron and ionic masses are $m$ and $M$ respectively. The large mass involved in the shape oscillations implies that $\hbar\omega_2$ is in most cases small compared with the other energies involved in the problem and that the amplitude $\alpha_2^{(0)}\ll 1$, ensuring the adequacy of the first order approximation for the coupling term appearing in (1).

The width $\Gamma$ of the dipole absorption resonance associated with transitions from the ground state $|n_1=n_2=0\rangle$ can be estimated from the dispersion in energy of the complete set of dipole states which exhausts the TRK sum rule:

$$\begin{aligned}\Gamma^2&\sim\langle n_1=1\,n_2=0\,|\,(H-\hbar\omega_1)^2\,|\,n_1=1\,n_2=0\rangle\\&=\tfrac{1}{3}K^2(\alpha_1^{(0)})^4(\alpha_2^{(0)})^2,\end{aligned} \tag{9}$$

from which we find

$$\frac{\Gamma}{\hbar\omega_2}\sim\frac{r_s^{1/2}}{N^{1/3}}\left(\frac{M}{m}\right)^{1/4}. \tag{10}$$

For the $Na_8$ cluster the relation (10) implies $\Gamma$ more than an order of magnitude larger than $\hbar\omega_2$.

For dipole absorption associated with clusters having temperatures $T\gg\hbar\omega_2$, the estimate (9) is multiplied by a factor of the order of the number of thermally exited quadrupole quanta in the initial state

$$\langle n_2\rangle_T\sim\frac{T}{\hbar\omega_2}, \tag{11}$$

and thus

$$\Gamma\sim\hbar\omega_1\sqrt{\frac{T}{C_2}}\sim\hbar\omega_1\sqrt{\frac{T}{N\varepsilon_F}}. \tag{12}$$

Since coupling to the density fluctuations of the positive ions (bulk resistivity [17]) gives an additional damping width of order $T$, this contribution to the total damping width will dominate over the contribution (12) in the case of large clusters and high temperatures. Therefore, in the present work we are especially considering small clusters ($N\lesssim 100$) and low temperatures ($T\ll 10^3$ K).

The estimate (10) implies that it should be a useful approximation to consider the quadrupole shape of the cluster to be constant during the damping process of the dipole mode. Such an approximation is obtained by replacing the quantal operator $(c_2^\dagger + c_2)$ in (1) by a $c$-number amplitude; the dipole line shape then directly reflects the probability distribution of this amplitude in the ground state ($n_1=0$) configuration. The resulting line shape has been given in [11] and can be written as

$$\begin{aligned}P(E)=&\left(\frac{\sqrt{40}}{9}\right)\left(\frac{1}{\hbar\omega_1\alpha_2^{(0)}}\right)\\&\times((3y^2-1)\exp(-y^2)+2\exp(-4y^2)),\end{aligned} \tag{13}$$

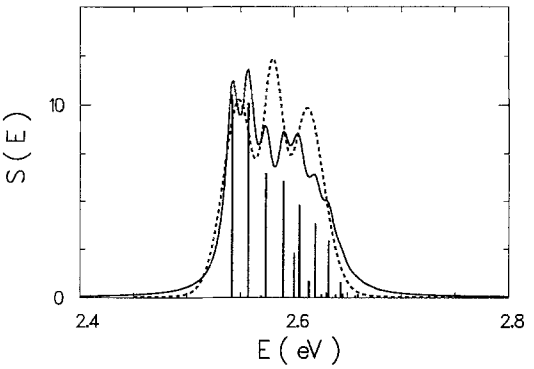


**Fig. 1.** The strength function associated with the plasmon resonance of $Na_8$ at zero temperature. The results of the diagonalization of the hamiltonian defined in (1) in a basis including all states up to 40 quadrupole phonons are shown as a set of vertical lines, representing the oscillator strength for the excitation of the dipole phonon resonance. The continuous line corresponds to distributing the oscillator strength $f_i$ over a Lorentzian line $S(E)=2f_iE^2\Delta_E/(\pi((E^2-E_i^2)^2+E^2\Delta_E^2))$, where the averaging parameter $\Delta_E$ was taken to be 0.015 eV, the minimum value to smooth the resulting strength distribution. It is noted that the FWHM obtained from the strength function is not affected by this small value $\Delta_E$. The result of the adiabatic approximation given by (13) is displayed with a dashed curve

where

$$y=\frac{\sqrt{10\pi}}{3}\left(\frac{E-\hbar\omega_1}{\hbar\omega_1\alpha_2^{(0)}}\right). \tag{14}$$

The line shape implied by (13) exhibits three peaks (see Fig. 1) since the phase space for the five-dimensional quadrupole motion is dominated by triaxial shapes. The line shape in (13) is Gaussian, due to the fact that the dipole-quadrupole coupling in (1) leads to a time dependent problem in which the strength of the coupling (proportional to the quadrupole amplitude) increases linearly in time. Thus the probability of the unperturbed dipole mode decays as a Gaussian function in time which, by a Fourier transform, leads to a Gaussian function in energy.

Since the probability distribution of quadrupole fluctuations at non-zero temperature has the same Gaussian dependence on the five quadrupole amplitudes as does the zero point motion in the quantum ground state, the result (13) can also be employed for $T\gg\hbar\omega_2$ by replacing

$$\alpha_2^{(0)}\to\sqrt{\frac{T}{C_2}}. \tag{15}$$

In order to further explore the line shape implied by the dipole-quadrupole coupling we have carried out a numerical evaluation of the spectrum implied by the Hamiltonian defined in (1). Using a basis with all states up to $n_2=40$ quadrupole phonons the Hamiltonian (1) was diagonalized. The dipole absorption spectrum intensities associated with the resulting eigenstates $|i\rangle$ (proportional to $|\langle I=1n_1=1n_2=0|i\rangle|^2$) is plotted in Fig. 1 for the assumed parameters:

$$\begin{aligned}\hbar\omega_1&=2.58\text{ eV},\\ \hbar\omega_2&=1.3\ 10^{-2}\text{ eV},\\ C_2&=15.8\text{ eV}.\end{aligned} \tag{16}$$

These values have been selected to be representative for describing the cluster $Na_8$ [1, 4]. The quadrupole restoring force $C_2$ has been calculated by summing the independent particle energies of electrons moving in a modified harmonic oscillator potential of the Clemenger-Nilsson model (for details, cf. [18]), expanding around the spherical configuration [19]. The quadrupole frequency is then obtained by assuming that the oscillator sum rule for the mass quadrupole operator is exhausted in the single quadrupole surface mode.

It is seen from Fig. 1 that the line width obtained from the detailed diagonalization is qualitatively in good agreement with the prediction of the adiabatic approximation, but the details of the line shape are poorly reproduced by the approximate solution even though the quadrupole frequency is more than two orders of magnitude smaller than the dipole frequency and one order of magnitude smaller than the resulting line width. The marked asymmetry of the line shape obtained from the numerical diagonalization is another effect of order $\hbar\omega_2/\Gamma$ that goes beyond the adiabatic approximation. The longer tail on the high energy side apparently reflects the fact that the amplitude of quadrupole motion is increasing with excitation energy and is therefore larger on the high energy side of the line.

We conclude that the coupling of the dipole surface plasmon to the quadrupole surface oscillations of small metallic clusters at low temperatures appears to provide a line width similar to the observed value [3], and that this coupling predicts an asymmetric line shape with a high energy tail that is more extended than on the low energy side. The dipole-quadrupole coupling yields a line shape in which the wings of the resonance have Gaussian form.

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