Effect of Surface Fluctuations in the Line Shape of Plasma Resonances in Small Metal Clusters

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The line shape of plasma resonances in small sodium clusters ($8 \leq n \leq 20$) is calculated taking into account quadrupole fluctuations of the cluster shape. At room temperatures, an average value of $\Gamma/\omega_M \sim 0.1$ for the damping factor is found. In the case of deformed clusters, these fluctuations are not able to wash out the multipeaked structure associated with the dipole resonance along the principal axes of the cluster.

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The surface-plasma resonance, that is, the collective dipole oscillation of the valence electron cloud against the positive background of the cores, has been observed[1,2] in small sodium clusters. The strong dependence of the cross section on the wavelength and cluster size was successfully interpreted using the experimental static polarizabilities[3] and the ellipsoidal shell model.[4-7] This result underscores the dominant role played by the surface in finite systems, and the fact that dipole motion can directly couple to quadrupole shape distortions (cf., e.g., Figs. 6-21 of Ref. 8). Recently, Bertsch and Tománek[9] have shown that the explicit coupling of the plasma resonance to the atomic vibrations can lead to considerable line broadenings.

In the present Letter we present a detailed analysis of the role surface fluctuations play in the line shape of the Mie resonance in small metal clusters. It will be concluded that fluctuations of the shape at room temperatures (~25 meV) are, for the small clusters under discussion, very important in the determination of the effective cluster shape.

The surface-plasma resonance couples to the quadrupole deformations of the cluster surface leading to a breaking of the dipole strength into three components, corresponding to vibrations along the principal axes of the ellipsoid. The associated radii can be parametrized in terms of the intrinsic quadrupole deformation variables β and γ which measure,[8] in the body-fixed frame of reference, the size of the quadrupole moment of the cluster and its departure from axial symmetry. The values for the three frequencies can then be expressed (classically) in terms of the directional polarizabilities α_κ of the ellipsoid,

$$\omega_\kappa^2 = e^2/m\alpha_\kappa \quad (\kappa = 1,2,3), \tag{1}$$

where the quantities α_κ are related to the average polarizability α_0 (Refs. 3 and 5) via the depolarization factors of the ellipsoid[5,10] through

$$\alpha_\kappa/\alpha_0 = 3D_\kappa^{-1}/\sum_k D_k^{-1}. \tag{2}$$

In keeping with Eq. (1), and generalizing the expression for the photoabsorption cross section of Ref. 11, as done in Ref. 6, one can write

$$\sigma_\kappa(\omega;\beta,\gamma) = 4\pi \frac{Ne^2}{m_e c} \frac{\omega^2\Delta}{[\omega^2 - \omega_\kappa(\beta,\gamma)^2]^2 + \omega^2\Delta^2}, \tag{3}$$

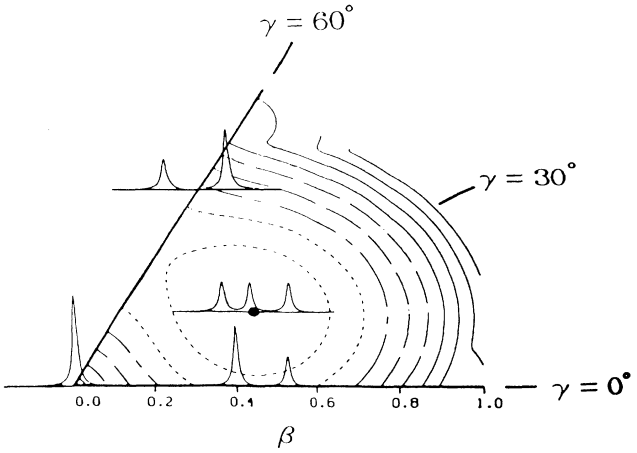

FIG. 1. Potential-energy surface for Na_{12} calculated making use of the Nilsson-Clemenger model. Because of the symmetries of the Hamiltonian, the function $\Phi(\beta,\gamma)$ is shown in the sextant defined by $\beta \geq 0$ and $0° \leq \gamma \leq 60°$. The minimum in the potential is indicated by a solid circle, and corresponds to a triaxial configuration. The contour lines are separated by 1 eV. For illustration we show, at selected values of the parameters (β,γ), the photoabsorption cross section calculated for $T = 25$ meV [cf. Eq. (3)]. An averaging parameter $\Delta = 0.07$ eV was used. Each of the shapes displayed contributed with a weight $Z^{-1}\exp[-\Phi(\beta,\gamma)/T]$ to the thermally averaged value (Ref. 6).

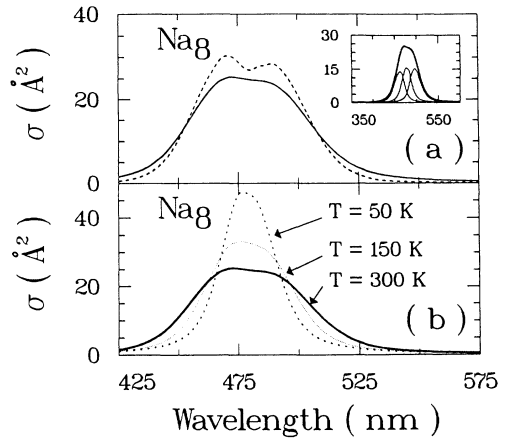

FIG. 2. Photoabsorption cross section associated with Na_8. (a) The total cross section calculated for a temperature of $T=25$ meV, and for two values of the averaging parameter ($\Delta=0.07$ and 0.02 eV) shown with a solid curve and a dashed curve, respectively. Inset: Total photoabsorption cross section for the choice $\Delta=0.07$ eV, together with the single contributions $\kappa=1,2,3$ associated with oscillations along the principal axes of the ellipsoid. (b) The total photoabsorption cross section for the choice $\Delta=0.07$ eV and for three different values of the temperature.

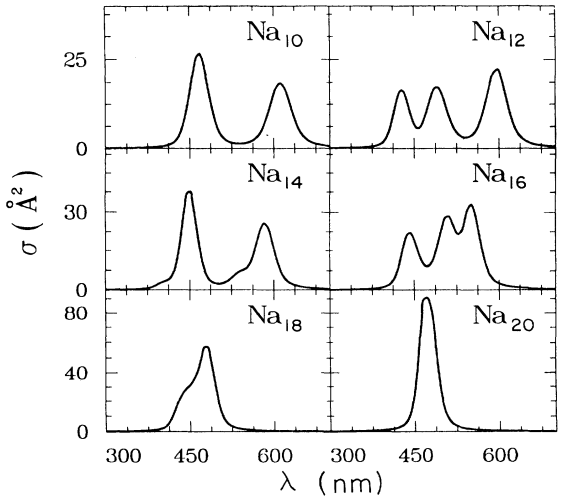

FIG. 3. The results for the total photoabsorption cross section for small sodium cluster, calculated for $T=25$ meV and $\Delta=0.07$ eV. Before the thermal fluctuations are switched on, the whole cluster dipole strength is exhausted at a frequency $\omega_M^2=e^2/m\alpha_0$, where α_0 is the measured average static polarizability (Ref. 5).

where N is the number of valence electrons of the cluster and Δ is an averaging parameter. At finite temperatures, the system will explore the potential-energy surface $\Phi(\beta,\gamma)$ (cf. Sect. A.2.2 of Ref. 7) with a probability

$$P(\beta,\gamma)=Z^{-1}e^{-\Phi(\beta,\gamma)/T}, \tag{4}$$

the quantity Z being the partition function

$$Z=\int d\tau e^{-\Phi(\beta,\gamma)/T}, \tag{5}$$

and $d\tau=\beta d\beta d\gamma$ the volume element.

The average cross section can then be written as[12,13]

$$\langle\sigma(\omega)\rangle=\sum_\kappa\int d\tau\,\sigma_\kappa(\omega;\beta,\gamma)P(\beta,\gamma). \tag{6}$$

In this way one takes into account, in the adiabatic approximation, the coupling of the plasmon resonance to the quadrupole thermal fluctuations of the cluster surface.

Calculations have been carried out for Na_n clusters with $n=8$–20, and the results are displayed in Figs. 1 to 3. The function $\Phi(\beta,\gamma)$ was worked out making use of the extended Nilsson-Clemenger model.[14] An example is shown in Fig. 1, for the case of Na_{12}. The empirical values[3,5] of $\omega_M=(em\alpha_0)^{1/2}$ determined from the experimental static polarizabilities α_0 have been adopted throughout. The averaging parameter Δ is used only for numerical convenience. As shown in Fig. 2(a), the results are independent of its actual value, provided that $\Delta\ll\Gamma$.[15] Here, Γ denotes the total width of the resonance, arising from thermal fluctuations.

The total thermal broadening arises from three independent contributions, associated with each of the three components of the plasmon resonance along the principal axes of the cluster [cf. inset to Fig. 2(a)]. This is also true even in the case of clusters which, like Na_8, display a spherical equilibrium shape. In keeping with this discussion, we define a damping factor as the ratio Γ/ω_M between the total width $\Gamma=(\sum_\kappa\Gamma_\kappa^2)^{1/2}$ and the peak position ω_M of the resonance.

As shown in Fig. 2(b), Γ displays a clear dependence

TABLE I. Parameters characterizing the shape of the Na_n clusters, and the thermal broadening of the photoabsorption cross-sectional peaks. The equilibrium values of the deformation parameters associated with the minimum in the potential-energy surface $\Phi(\beta,\gamma)$ (cf. Fig. 1) are indicated by β_0 and γ_0. They are listed in the second and third columns, respectively. The thermal fluctuations associated with these quantities, as measured by the square root of their second moments obtained by replacing σ_κ in Eq. (6) with $(\beta-\beta_0)^2$ and $(\gamma-\gamma_0)^2$, respectively, are shown, for $T=25$ meV, in columns four and five. The last two columns list the damping factor $\Gamma/\omega_M=(\Sigma_\kappa\Gamma_\kappa^2)^{1/2}/\omega_M$ as well as the values of ω_M.

n	β_0	γ_0 (deg)	$\Delta\beta$	$\Delta\gamma$ (deg)	Γ/ω_M	ω_M (eV)
8	0.00	0.0	0.06	18.3	0.10	2.6
10	0.46	0.0	0.07	5.7	0.13	2.4
12	0.50	25.5	0.06	8.0	0.14	2.4
14	0.45	0.0	0.06	15.0	0.11	2.5
16	0.34	39.6	0.06	11.5	0.12	2.5
18	0.00	0.0	0.06	16.6	0.12	2.7
20	0.00	0.0	0.03	18.3	0.08	2.6

with cluster temperature. This dependence can be parametrized as $\Gamma \sim \sqrt{T}$ (cf. also Refs. 9 and 12). The observed damping ratio[2] of 0.12 ± 0.02 can be accounted for within the framework of the present model, assuming a cluster temperature of ~ 25 meV (~ 300 K). Although considerable uncertainty is ascribed to this value, the assumption that the light Na clusters treated in this paper are at room temperature seems to be consistent with the present experimental evidence.[16]

In Table I we collect the main parameters characterizing the calculated photoabsorption cross sections for the different Na_n clusters. In all cases a temperature of 25 meV was used. The resulting average of the damping factor is $\Gamma/\omega_M \sim 0.11 \pm 0.02$. This value compares well with the available experimental information.[1] As seen from Fig. 3, although thermal fluctuations at room temperature are sizable, they are not strong enough to wash out the fingerprints of, for example, triaxial cluster shapes ($n = 12$ and 16) as evidenced by the three peaks in the associated photoabsorption cross sections. While two-peak structures have been clearly identified in the nuclear case (cf., e.g., Ref. 9), no three-peak response function has been observed, not even at zero temperature, in keeping with the fact that the typical value of the damping factor is, in the nuclear case, ~ 0.4.

We conclude that the coupling between the plasmon resonance and the quadrupole surface thermal fluctuations provide, at room temperature, an important damping mechanism in small sodium clusters.

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[14]Results obtained making use of the Nilsson-Strutinsky method did not change in any appreciable way the results displayed in Fig. 1. [J. M. Pacheco, M. Brack, and R. A. Broglia (to be published)].

[15]One has to use values of $\Delta \approx 0.2$ eV to increase the damping factor Γ/ω_M by 10%.

[16]The average internal temperature of clusters in a seeded beam results from a competition between carrier-gas cooling and heat of cluster condensation. It is known spectroscopically that the vibrational temperature of the sodium trimer is ~ 50 K for moderate expansion ratios. See M. Broyer *et al.*, J. Phys. Chem. **91**, 2626 (1987). Under comparable conditions, the potassium dimer temperature was ~ 140 K, while the translational temperature of both carrier and seed gas was ~ 10 K. Carrier-gas cooling of vibrations in alkali halide molecules for moderate expansion ratios produce vibrational temperatures $\sim \frac{2}{3}$ of the source temperature. See H. Bennewitz and G. Buess, Chem. Phys. **28**, 175 (1978). Sodium cluster temperatures for $n > 3$ are not known, but it has been assumed that carrier cooling would be significantly less effective for the larger sodium clusters $n = 8$–20 than for the sodium trimer under comparable conditions, and T would be an appreciable fraction (say $\frac{1}{3}$) of the source temperature. See W. de Heer *et al.*, Phys. Rev. Lett. **59**, 1805 (1987). These and other considerations suggest that $200 < T < 400$ K. Until more precise data are available, $T = 300$ K is taken as a reasonable estimate.