Collective Dipole Oscillations in Small Sodium Clusters

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Photoabsorption cross sections of small neutral sodium clusters composed of $N=2-40$ sodium atoms are measured by longitudinal-beam-depletion spectroscopy at several wavelengths of visible light. Absorption occurs via coupling of photons to collective oscillations of the valence electrons. The cross section is strongly size and wavelength dependent. Good agreement is found with predictions based on an extended Clemenger-Nilsson shell model and the experimental static polarizabilities.

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Presently available data on optical spectra of metal microclusters are meager and primarily concern alkali-metal dimers and trimers.[1] Heretofore no values of cross sections, except for dimers, were available. Our results indicate that the optical spectrum for clusters larger than the tetramer is dominated by the collective resonances of the valence electrons. Neutral sodium clusters $N=2-40$ are studied at several wavelengths between 450 and 600 nm. The results are analyzed in terms of an ellipsoidal-shell model[2,3] which has proven to be very successful for the description of the properties of metal clusters. For example, it is well known that spherical-shell closings occur in alkali and other metal clusters for electron numbers $N=2,8,20,40,\ldots$, resulting in observed features in the abundances and ionization-potential curves. Enhanced polarizabilities for the open-shell clusters are also observed[4] and are known to be related to ellipsoidal shapes of the open-shell clusters. In this work the cluster shapes from the extended ellipsoidal-shell model are used to calculate the resonance frequencies and the photoabsorption cross sections. They are in good agreement with experiment. Since the resonance frequencies are uniquely related to the relative lengths of the ellipsoidal axes, measurement of the frequencies gives a direct measure of the cluster geometries.

The experimental apparatus has been described elsewhere.[2] The clusters are produced in a supersonic expansion of a mixture of sodium vapor (50 Torr, 920 K) and argon (300 kPa) through a 0.0076-cm-diam nozzle into vacuum. A skimmer (0.04-cm-diam aperture) 0.6 cm downstream and a rectangular slit (0.1×0.1 cm^2) 77 cm downstream from the nozzle collimate the molecular beam with an angular divergence of less than 1 mrad. The beam enters the detector via a 0.2-cm-wide$\times$0.3-cm slit, 2 m downstream from the nozzle, and the clusters are photoionized with filtered light from a uv arc lamp. Mass-sensitive detection is accomplished with a quadrupole mass analyzer in conjunction with a Daly ion detector. The detected signals are converted into digital pulses for storage and further processing by a microcomputer. A window in the detector chamber is installed so that laser light illuminates the cluster beam along its entire length from detector to source.

In the present experiment a flashlamp-pumped dye laser provides 1-μs pulses with $\simeq$1 mJ per pulse and a 22-Hz repetition rate. The light is attenuated to about 0.1 mJ and expanded to produce a collimated beam with a diameter of 0.8 cm. The intensity of the laser light is monitored near the output of the laser and also at the cluster-beam axis inside the vacuum chamber just upstream of the collimating slit, with use of calibrated photodiodes.

For a given mass, the detected counts are recorded as a function of time following the laser pulse. The counting rate decreases for about 2 ms before it recovers to its original value. This time interval corresponds to the cluster time of flight (TOF) from source to detector. The ratio of the reduced to the original counting rate is called the on/off ratio r. The laser intensity is adjusted so that r lies between 0.2 and 0.9. As we will show below, the depletion is caused by photodissociation of neutral clusters which absorb a photon *en route* to the detector. The transverse momentum imparted to the daughter clusters is sufficient to remove them from the cluster beam. The photoabsorption cross section σ is related to r as follows:

$$r=\exp\{-\sigma\phi\}, \tag{1}$$

where ϕ is the number of photons per square centimeter per pulse. The observed effect results from single-photon absorptions, and the dependence of r on ϕ given by Eq. (1) has been confirmed experimentally.

In a typical experiment, the mass analyzer is set to detect a specific mass and counts are accumulated alternately in light-on and light-off channels of multichannel scalar whose channel address is synchronized with the laser pulse. This is repeated for successive masses over predetermined ranges covering $N=2-20$ and $N=20-40$. Light-on counts are sampled during times less than the TOF of 2 ms after the laser pulse, in order to avoid counting clusters formed during the irradiation.

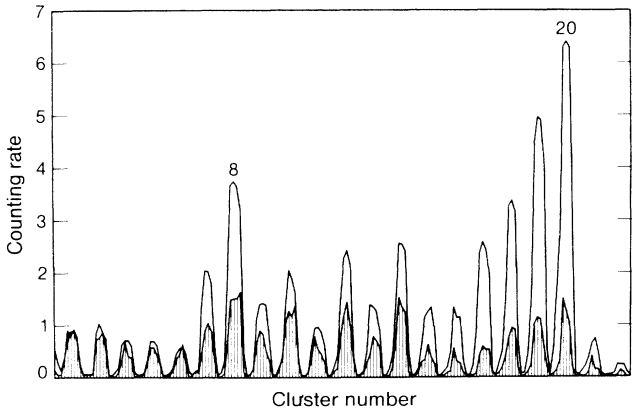

FIG. 1. Undepleted, i.e., light off, and depleted (shaded) sodium-cluster mass spectra. The depletion is caused by illumination of the neutral-cluster beam with laser light at 505 nm.

The result for 25 such sequences is shown in Fig. 1, in which the light-off mass spectrum shows the spherical-shell closings at $N=8$ and 20. The light-on spectrum shows the size-dependent depletion of different clusters caused by the laser light. The photoabsorption cross sections are determined from these data with use of Eq. (1) for sodium clusters with 2 to 40 atoms. Our data were acquired at five wavelengths between 584 and 604 nm, at four wavelengths between 498 and 513 nm, and at 458 nm. The bandwidth of the laser is about 0.2 nm.

Figure 2 shows measured and calculated cross sections for Na clusters with $N=2,3,\ldots,40$ at 505 and 604 nm. At 505 nm [Fig. 2(a)], a general increase of the cross section with cluster size ($d\sigma/dN=0.85$ Å^2) is observed. The cross section drops following maxima near the shell-closing numbers 8 and 20. In contrast, the cross sections for 8 and 20 at 604 nm [Fig. 2(b)] are local minima. The experimental accuracy is about 15% of the measured value. With the exception of $N=2$, 3, 4, and 21, experiment and theory (see below) agree within experimental uncertainties.

Beam depletion results from absorption of a photon of energy E, which rapidly appears as heat with a temperature rise depending on cluster heat capacity C. The transverse momentum components of the evaporating atoms cause recoil of the daughter cluster and its removal from the collimated beam. The Dulong-Petit law gives a reasonable approximation for C. For clusters $N\approx 20$, the temperature rise is $\simeq 430$ K for $E\simeq 2$ eV. Assuming initial temperatures larger than 100 K and solid-surface evaporation rates, we estimate that an atom will evaporate in a time of $\simeq 30$ μs, which is smaller than the beam TOF. On the assumption of desorption at the above temperature, the transverse momentum deflects the daughter by an average angle of $\simeq 20$ mrad, which is much larger than the collimation angle. It is reasonable therefore to expect that the absorption of a

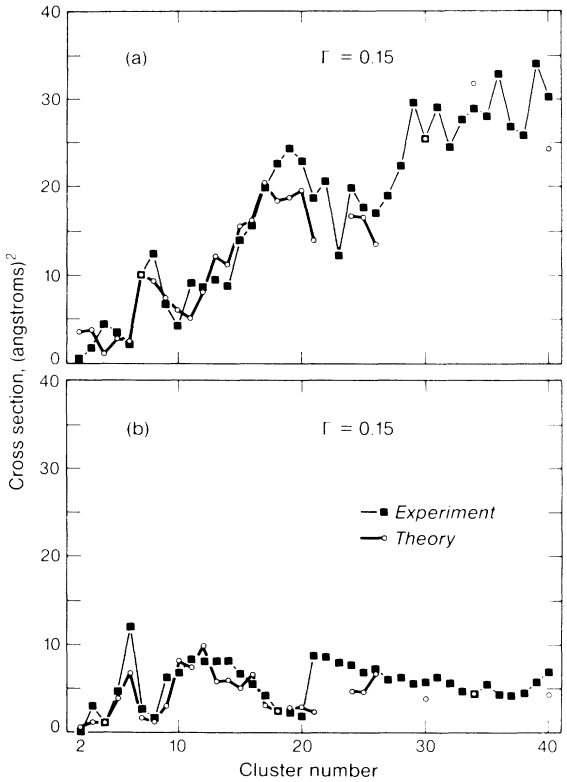

FIG. 2. Experimental (squares) and theoretical (circles) photoabsorption cross sections for sodium clusters with 2–40 atoms at (a) 505 nm and (b) 604 nm. Cross sections near $N=8$ and 20 correspond to minima at 604 nm and to local maxima at 505 nm.

2-eV photon severely reduces the probability of detection. With laser intensity increased tenfold, all clusters (except dimers) show $r\simeq 0$, verifying that daughters of clusters absorbing a photon are not detected.

The absorption of light by small metal spheres has been investigated theoretically by Mie.[5] For particles which are much smaller than the wavelength, the absorption cross section based on the Drude dielectric function is

$$\sigma(\omega)=4\pi\frac{Ne^2}{m_e c}\frac{\omega^2\Gamma}{(\omega_0^2-\omega^2)^2+\omega^2\Gamma^2}. \quad (2)$$

Here ω_0 is the classical Mie frequency which is also known as the surface-plasma frequency of a sphere with N free electrons. The resonance is the collective dipole oscillation of the spherical valence-electron cloud against the spherical positive background of the cores. Equation (2) can be generalized by setting[6]

$$\omega_0^2=Ne^2/m_e\alpha, \quad (3)$$

where α is the static polarizability of the cluster which, in the bulk limit, is the particle radius cubed. Equation (2) is derived by the assumption that all of the dipole oscillator strength is represented by the resonance at ω_0.[7]

Then the collective dipole resonance of a spherical cluster can be calculated once the polarizability is known. For a metal ellipsoid, the polarizabilities along the three axes are uniquely determined by the classical depolarization factors and the average polarizability.[2] For sodium clusters in a molecular beam, the average polarizabilities have been measured[4] and the ellipsoidal shapes have been determined with use of the extended Clemenger model as shown below.

The Clemenger[8] model, which is based on the Nilsson model for nuclei,[9] determines the equilibrium shapes of the clusters. It assumes that the one-electron potential can be approximated by that of an anisotropic harmonic oscillator with a small angular-momentum-dependent perturbation. The cluster shape is determined by the minimization of the sum of the one-electron energies. Clemenger further constrained the shapes to spheroids, as was previously done for nuclei. Recent self-consistent spheroidal-jellium calculations by Ekardt[10] agree with Clemenger's shapes. We have extended Clemenger's calculations to ellipsoids and have ignored the perturbation term mentioned above, which is nonessential for clusters with fewer than 21 atoms. The shapes (i.e., the axial ratios) of the clusters can then be calculated analytically. These determine the depolarization factors and the three resonance frequencies [Eq. (3)]. The photoabsorption cross sections are determined by Eq. (2) by summing of the contributions of the three resonances with equal weight. The damping constant Γ is the only free parameter.

We find a best fit of the measured cross sections by setting $\Gamma/\omega_0=0.15$, independent of cluster size (cf. Fig. 2). In Fig. 3, theoretical photoabsorption cross sections for $N=12$, 16, and 20 are plotted as functions of wavelength and are compared with the experimental values. Note that the multipeaked structures for $N=12$ and 16 are caused by Clemenger distortions which enhance the cross sections at 600 nm and reduce them at 500 nm as compared with $N=20$. This is generally true for the open-shell clusters and is experimentally observed (Fig. 2) as noted above. From Fig. 3 it is clear that an error of only 50 nm in the predicted resonance wavelengths would cause significant discrepancies with the experiment. This makes the agreement even more remarkable. The agreement is poor for $N=2$, 3, and 4. An absorbed phonon generally does not cause the dissociation of the dimer, but most of the energy is reradiated. The sodium trimer, on the other hand, does dissociate. In a depletion experiment,[1] the spectra for the trimer show fine structure which is caused by resolved vibrational states.

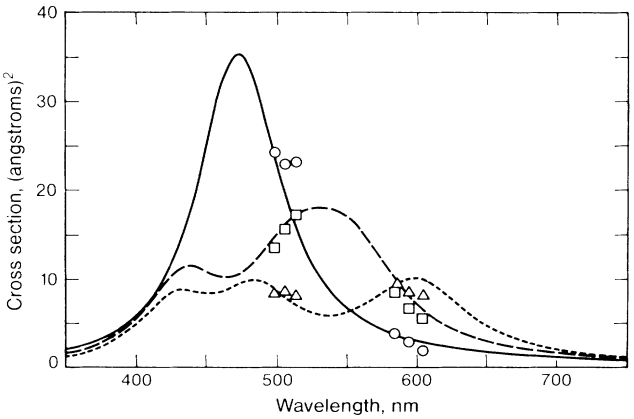

FIG. 3. Comparison of theoretical and experimental photoabsorption cross sections of sodium clusters. $N=12$: theory, short-dashed curve; experiment, triangles. $N=16$: theory, long-dashed curve; experiment, squares. $N=20$: theory, solid curve; experiment, circles. The multiple peaks of 12 and 16 are caused by ellipsoidal distortions. The damping constant is assumed to be $0.15\omega_0$ for all clusters.

Collective resonances in larger clusters have been observed by a number of investigators.[11-13] Sodium clusters ranging from $N=10^3$ to 10^7 in the gas phase exhibit plasma-resonance scattering of violet light (between 300 and 450 nm).[11] Recent experiments with Na clusters on LiF surfaces show resonant photodesorption at $\simeq 500$ nm,[12] which is attributed to plasma resonances. Most related optical-absorption experiments of clusters ($N > 10^3$) have been done in matrices.[13] These give spectra which have line shapes given by Eq. (2). Theoretical treatments[13] which include the coupling of single-particle states to the collective electronic motion predict a linear dependence of the damping on the inverse of the particle radius. In order to obtain a damping constant, these theories assume that the single-particle spectrum is dense. While these theories seem to be adequate for large clusters, they are not consistent with the present observations.

Ekardt[6] calculated the photoabsorption spectra of sodium microclusters self-consistently within the jellium model, and he found that the spectra should consist of several narrow lines corresponding to single-particle transitions as well as collective resonances. Similar results were recently obtained by Beck.[14] We have not yet observed these single-particle lines. It should be noted that Ekardt arbitrarily broadens the single-particle transitions by 10 meV. In reality, the observed widths are much larger because of strong couplings to vibrational modes of the cluster. More accurate theories should also include the coupling of the collective electronic modes to the cluster-shape oscillations.

There are striking similarities between our experiments and the observations of giant dipole resonances in nuclei. The giant dipole resonance is the collective motion of the protons against the neutrons and may be observed in photoneutron spectroscopy where low-energy neutrons are emitted from nuclei after absorption of a photon.[15] Moreover, the predictions of the resonance frequencies and the photoabsorption cross sections[15] parallel our discussion.

To summarize, the photoabsorption proceeds by the

damped collective resonances of the valence electrons. The resonance frequencies depend directly on cluster shape, and three resonances occur for ellipsoidal clusters with unequal axes. The resonances and cross sections obtained from the ellipsoidal–harmonic-oscillator model agree well with experiment at several wavelengths. The cross sections depend linearly on N, the number of electrons contributing to the oscillator strength. The experimental damping constant appears not to vary significantly with cluster size.

Although a complete resonance curve has not yet been traced for any cluster experimentally, the agreement of the cross sections for clusters $N > 4$ for all wavelengths investigated is sufficient to justify the use of the simple model. Preliminary results at 458 nm indicate satisfactory agreement of experimental and theoretical cross sections. Also, preliminary experiments on potassium give results consistent with the foregoing analysis. Further experiments on the size and wavelength dependence of the photoabsorption cross section for sodium, potassium, and for mixed NaK clusters are in progress.

The absence of conspicuous single-particle features in the spectra indicates that the collective resonances dominate the optical spectrum. Further experiments may reveal any small size dependence of the damping constant which might exist and whether single-particle features can be observed as a fine structure. The effects found in neutral alkali-metal clusters should also appear in cluster ions and in other metal clusters. The development of conductivity can be explored for large particles, and the onset of conductivity in metal-insulator transitions may be studied.

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