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Size Dependence of the Optical Response of Spherical Sodium Clusters

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The optical response of spherical Na_j^+ clusters ($9 \le j \le 93$) shows one large maximum at about 2.7 eV. As a function of the inverse cluster radius its peak position and root mean square energy extrapolate linearly, but with different slopes, to the bulk Mie plasmon. The slopes are compared to two theoretical predictions: the static spill-out equation of cluster science and the dynamic screening theory of surface science as generalized to clusters. Good agreement is obtained. The similarity of collective excitations of surfaces and clusters is emphasized.

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Metals are called *simple* if they can be treated in the nearly free electron gas approximation or jellium model, where the strongly interacting electrons are confined by a homogeneous, rigid, positively charged background. The best examples are sodium and potassium. The dominant electronic excitation of these metals can be described by collective charge density oscillations or plasmon waves, whose energy $\hbar\omega_P$ can be derived in the long wavelength limit already by classical electrodynamics as [1]

$$\hbar\omega_P = (ne^2/\epsilon_0 m)^{1/2} . \qquad (1)$$

Here ω_P is the plasma frequency, n the electronic density, m the free electron mass, and SI units are used. Equation (1) agrees within 4% with the experimental value for sodium [2]. Similarly, a flat metal surface can support a surface plasmon, which is a surface charge density oscillation [1,3–6]. For simple metals its energy is given by $\hbar\omega_S = \hbar\omega_P/\sqrt{2}$. Applying the same calculation to a metallic sphere, one obtains the well known dipolar Mie plasmon which has a frequency of $\omega_{\mathrm{Mie}} = \omega_P/\sqrt{3}$. Also the equations for ω_S and ω_{Mie} agree within a few percent with experiment, showing that the jellium model is indeed a good first approximation for real sodium, be it in bulk form, as a planar surface, or a (not too small) cluster.

When the same type of process is studied for either a flat or a spherical surface, one should expect some similarities between the collective excitations for surfaces and clusters. Electronic excitations at flat surfaces of these model metals have been studied for more than 30 years, and the understanding has improved dramatically in recent times [3–6]. Much less is known on the electronic excitations of clusters composed of simple metals. The first absorption spectra of free sodium clusters were published by Knight and coworkers [7] in 1987. Much progress has been made since [8–16].

Already in 1982 Apell and Ljungbert pointed out that the size dependence of the small particle plasmon resonance should be similar to wave vector dispersion of the flat surface plasmon [17]. The latter was measured for Na and K in 1989 by Tsuei, Plummer, and Feibelman [3]. We present here new data for spherically symmetric Na_j^+ clusters, which show for the first time that this similarity is indeed observed for clusters of simple metals. Moreover, it is found that the theory developed for the plane surface gives a good fit to the observed cluster size dependence of the Mie plasmon. Surprisingly, the agreement is better with the cluster than with the surface experiments.

The standard method of depletion spectroscopy was used to measure absolute photoabsorption cross sections for Na_j^+ clusters, with $j = 9$, 21, 41, 59, and 93 [8,10,11]. These clusters have closed electronic shells of $j - 1$ valence electrons and are spherically symmetric in the jellium approximation [8–13]. The data, shown in Fig. 1, display one large peak. The resonance energies decrease for decreasing cluster size until $j = 41$, while for smaller j they increase again, a change in slope which to our knowledge has not been observed before. All absorption curves show a shoulder on the high energy side, which could be due to fragmentation of the oscillator strength [9,12,13] or, alternatively, to the first appearance of the bulk interband transition [1], which should occur in this energy range. The oscillator strength in the energy range covered (1.6 to 3.7 eV) is 0.81 to 0.92 per $3s$ electron. Proceeding as in Ref. [18], one obtains temperatures of 560, 340, 310, 295, and 290 K for $j = 9$ to 93, respectively. In Fig. 2 and the discussion below, the data are normalized to the classical Mie resonance of a small sphere (3.27 eV for Na), as calculated [19] from the room temperature dielectric function [20]. Thus the $j = 41$, 59, and 93 cluster data and the Mie resonance have been obtained at nearly the same temperature. The small difference of 10 to 20 K can be expected to have a negligible effect, as judged from the temperature dependence of the optical spectrum for $j = 9$ to 41 reported earlier [21].

The data agree within experimental error with earlier results for $j = 9$ and 21 of the Orsay group [22] and for $j = 21$ and 41 of the Copenhagen group [23]. The peak maxima agree with the calculations of Refs. [12,13] to better than 8%. The agreement is better than 3% if the theoretical and experimental results are normalized by their different asymptotic values, which are 3.41 eV for the jellium model versus 3.27 eV for real sodium. The

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different scaling of experimental and theoretical results is suggested by Eqs. (4) and (5) below. This 4% difference is mainly due to the effective mass of the Na valence electrons, and to the influence the core electrons exert on the valence electrons (core polarization) [2].

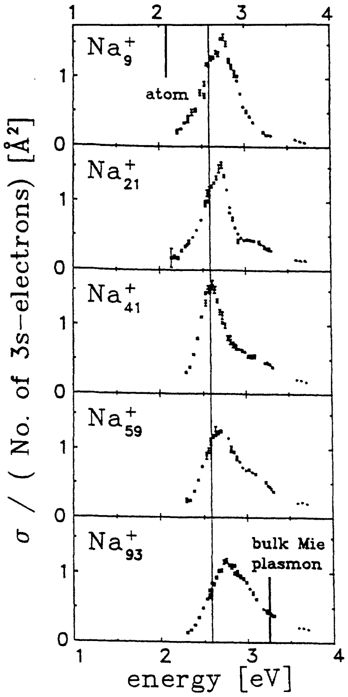

FIG. 1. Optical response of spherical sodium cluster ions. One large maximum is observed, accompanied by a shoulder on the high energy side. The vertical line gives the peak position for $j = 41$, indicating the blueshift for smaller and larger clusters. The positions of the atomic and the Mie resonance are also indicated.

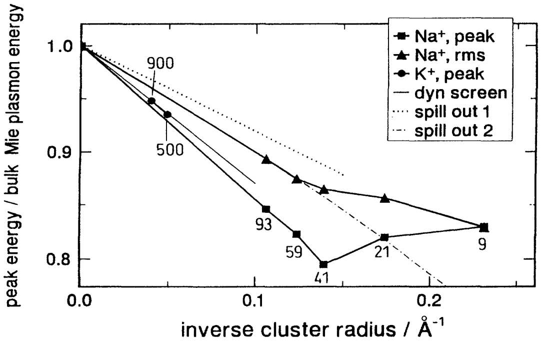

FIG. 2. Normalized peak positions for spherical Na_j^+ and large K_j^+, as well as the root mean square [rms, see Eq. (2)] excitation energies of Na_j^+ are plotted against the inverse cluster radius. For $j \geq 41$ the peak and the rms energies extrapolate linearly to the Mie plasmon. The experimental slopes are in agreement with the predictions of the dynamic screening theory of surface science [Eq. (5)] and the spill-out equation of cluster science [Eq. (4)].

The mean square frequency is defined as

$$\langle \omega^2 \rangle = \int_0^\infty \omega^2 \sigma(\omega)\, d\omega \Big/ \int_0^\infty \sigma(\omega)\, d\omega\,. \tag{2}$$

The peak maxima and the root mean square (rms) energies, $\langle \omega^2 \rangle^{1/2}$, are plotted in Fig. 2 as a function of the inverse cluster radius R, which has been calculated as $R = j^{1/3} r_s$, with $r_s = 2.08$ Å [1]. Both energies have been normalized by 3.27 eV as discussed above. The peak position and the rms energy show a linear behavior above $j = 41$. The two straight lines have very nearly the same asymptote at $R^{-1} = 0$, as the rms of the Mie resonance coincides within 0.01 eV with the peak position. The difference between the peak and the rms energies for finite R is mainly due to the high energy shoulder in the cross sections.

We will discuss now two seemingly different theoretical interpretations of the observed linear behavior. It is commonly accepted in cluster physics that the redshift of the plasmon energy with decreasing cluster size is due to the quantum-mechanical spill out δ of the electrons over the jellium edge [8,9]. Starting from Eq. (2), one can derive [25] for a hard jellium sphere

$$\langle \omega^2 \rangle / \omega_{\mathrm{Mie}}^2 = 1 - \Delta n / n\,, \tag{3}$$

where n is the number of electrons, and Δn their number outside the jellium edge. This gives in the large R limit

$$\langle \omega^2(R) \rangle^{1/2} / \omega_{\mathrm{Mie}} = 1 - 3(\delta/R)/2 - 21(\delta/R)^2/8 - \cdots. \tag{4}$$

The experimental spectrum $\sigma(\omega)$ was measured between 1.6 and 3.7 eV, only. Integrating Eq. (2) between these values, one obtains a lower limit for the rms energy which gives an upper limit of 0.60 Å for δ (dot-dashed line, marked spill out 2, in Fig. 2). The theoretical value of 0.54 Å [26] is given by the dotted line (spill out 1).

A related, but conceptually very different explanation has its origin in surface science. Apell and Ljungbert [17] have derived

$$\omega(R)/\omega_{\mathrm{Mie}} = 1 - \mathrm{Re}(d)/R \cdots, \tag{5}$$

where $\omega(R)$ is the peak maximum of the collective resonance, and $\mathrm{Re}(d)$ is the real part of Feibelman's d parameter as discussed below. Using Eq. (5) for the peak maxima of Fig. 2, one obtains 1.45 Å, while the theoretical value is 1.3 Å [5], calculated in the TDLDA (time dependent local density approximation) for a flat jellium surface near ω_{Mie}. The agreement is surprisingly good, better than in surface science, for which the theory was originally formulated [4–6].

There exists another piece of evidence supporting the use of Eq. (5) in cluster science. One can calculate the static polarizability α from the optical spectrum [9,24].

Applying this to the data of Fig. 1, one obtains a linear behavior of $\alpha(R)$ for $j \geq 41$. Using the plasmon pole approximation [26] together with Eq. (5), one derives $\mathrm{Re}(d) \approx 1.50$ Å, while a value of 1.45 Å was obtained above. Thus Eq. (5) gives a good fit to both the asymptotic behavior of the plasmon peak positions and of the static polarizabilities. More details will be given elsewhere [27].

Equation (5) was derived in analogy [17] to a similar result for plane surfaces [Eq. (6) below]. In order to better appreciate the close connection between the collective excitations at plane or spherical surfaces, we sketch briefly the dynamic screening theory of surface science. An external electric field $E_{\mathrm{ext}}(\mathbf{r}, \omega)$ interacting with a metal surface induces a surface charge density $\rho(\mathbf{r}, \omega)$. Classically, this charge is given by a δ function located in the surface. Quantum mechanically the charge density shifts and broadens and displays oscillations and "spill out" into the vacuum [3–6]. The surface charge induces an electric field $E_{\mathrm{ind}}(\mathbf{r}, \omega)$, which counteracts the external field, i.e., the induced surface charge "screens" the external field. In this experiment, the external field and thus also the electrons are oscillating with the frequency ω of the photon field. The photon energies employed (1.6 to 3.7 eV) are not too far from the eigenfrequency of the bulk collective electronic motion [$\hbar\omega_P = 5.9$ eV for Na, see Eq. (1)], so that screening must be considered not as a static but a dynamic process at optical frequencies. The theory of dynamic screening can describe a wide variety of electronic surface properties, such as light reflection, photoemission, surface plasmon dispersion, second harmonic generation, etc. [3–6].

An important parameter in this theory is the centroid $d(\omega)$ of the position of the induced charge density $\rho(z, \omega)$ relative to the jellium edge. The d parameter was introduced by Feibelman [4] in 1973, and its frequency and density dependence has been calculated by several authors [4,5]. The centroid of the induced charge density is outside the jellium edge for simple metals, so that the real part of $d(\omega)$ is positive. For a simple and physically appealing interpretation of the d parameter see Refs. [3,4]. Using these concepts, the dispersion relation of the plain surface plasmon can be calculated for small wave vectors q, or long wavelengths $l_S = 2\pi/q$ [3–5]:

$$\omega(q)/\omega_S = 1 - \mathrm{Re}(d)q/2 + \cdots . \tag{6}$$

The experimental value of $\mathrm{Re}(d)$ for Na near ω_S is $+0.78$ Å [3], while theory gives $+1.0$ Å [4] or $+1.58$ Å [5] for the RPA (random phase approximation) or TDLDA, respectively. A deviation from linearity is observed experimentally for $q \geq 0.15$ Å^{-1}.

What is the physical idea behind the surprisingly similar equations and slopes for the surface [Eq. (6)] and cluster [Eq. (5)]? As pointed out already by Apell and Ljungbert [17] and elaborated by Ekardt [28], the induced charge density of a spherical cluster has a periodicity of length $l_C \approx 2\pi R$, as the induced charge density is localized mainly in the surface region. For a plane surface one has correspondingly $l_S = 2\pi/q$. This suggests a correspondence between q and R^{-1}.

The physical concepts leading to Eqs. (4) and (5) seem to be very different. The spill-out argument is essentially a static one. An electronic property at frequency zero determines the shift with cluster size of a resonance at optical frequencies, while the dynamic screening theory seems to describe the dynamics of the electronic motion more adequately. The solution of this problem lies in the existence of sum rules, which relate the moments of the optical response to ground state properties [9,25]. Surely, the electrons react dynamically to the photon field, but a sum rule relates the second moment of the dynamical response to the static spill out [Eqs. (2) and (3)] making both the static and the dynamic descriptions valid.

According to the calculation of Liebsch [5], $\mathrm{Re}(d)$ should be similar for Na and K near $\omega_P/\sqrt{3}$. Indeed, the data of the Orsay group [29] for large K_j^+ clusters (full circles in Fig. 2, the temperature corrected values of Ref. [29] have been used) fall on the calculated line, provided the peak positions are normalized by $\hbar\omega_{\mathrm{Mie}}(K)$ as obtained from the potassium bulk dielectric constant.

Equation (5) had originally been used to discuss the absorption of silver clusters in a dielectric matrix [17]. The experiment and its analysis have recently been repeated for embedded [30] and free [31] silver clusters. The experimental d parameter is negative for silver surfaces [32] and clusters [17,31,32], while it is positive for the simple metals. Qualitatively this behavior is well understood: The change in sign is due to the interaction of the s electrons with the low lying d electrons [17,31,32]. The collective excitation of mercury clusters (Hg_j^{+} and Hg_j^{++}) [19] exhibits nearly no shift of the plasmon peak positions, i.e., from Eq. (5) one obtains $\mathrm{Re}(d_{\mathrm{Hg}}) \approx 0$. A similar result was very recently observed for the Hg surface [33].

The main emphasis of this Letter was to stress the similarities between surface and cluster results, so that many problems could not be discussed. Among them are as follows: (1) The spill-out parameter has not reached its asymptotic value in the cluster size range considered here, but depends somewhat on the size and charge of the cluster [9,34]. (2) The problem of the width of the resonance has not been discussed at all. (3) In reality, the alkali are not that simple metals [35].

The cluster results can be summarized as follows: (1) The optical spectra for spherical Na_j^+ clusters $9 \leq j \leq 93$ show one large maximum and for $j \geq 21$ a shoulder on the high energy side. (2) Peak and root mean square (rms) energies differ because of this shoulder. (3) As a function of the inverse cluster radius, both energies extrapolate linearly to nearly the same asymptote. (4) The linear behavior is observed down to $R^{-1} = 0.15$ Å^{-1}, or equivalently (for Na) $j = 41$. For smaller clusters the peak and rms energies increase again. (5) Experimentally, the static spill-out equation [Eq. (4)] gives a somewhat better agreement with the data if the rms energy, Eq. (2), is used, while the peak maxima are also somewhat better reproduced by the dynamic screening equation, Eq. (5). (6) The static polarizabilities calculated from the experimental data agree also with Eq. (5) within experimental error. (7) The normalized peak positions of large potassium clusters (K_j^+, $j =$ 500 and 900) agree beautifully with the normalized sodium data and the dynamic screening theory. (8) The experimental peak positions agree with the theoretical results of Refs. [12,13] to better than 3% if (jellium) theory and experiment are normalized to their different asymptotes.

The most important result of this Letter is that the collective excitations of clusters and surfaces composed of simple metals have a similar behavior. A linear decrease of the plasmon frequency is observed in both cases as a function of R^{-1} or q in the long wavelength limit. For clusters and surfaces of silver and mercury a similar asymptotic behavior is observed. The slopes are different, positive for Ag, near zero for Hg, while they are negative for simple metals.

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[1] N.W. Ashcroft and N.D. Mermin, *Solid State Physics* (Saunders College, Philadelphia, 1976), Chaps. 1 and 15.
[2] A. vom Felde, J. Sprösser-Prou, and J. Fink, Phys. Rev. B **40**, 10 181 (1989).
[3] K.-D. Tsuei, E.W. Plummer, and P.J. Feibelman, Phys. Rev. Lett. **63**, 2256 (1989).
[4] P.J. Feibelman, Phys. Rev. B **40**, 2752 (1989), and references therein.
[5] A. Liebsch, Phys. Rev. B **36**, 7378 (1987).
[6] F. Forstmann and R.R. Gerhardts, *Metal Optics Near the Plasma Frequency* (Springer, Berlin, 1986).
[7] W.A. de Heer, K. Selby, V. Kresin, J. Masui, M. Vollmer, A. Châtelain, and W.D. Knight, Phys. Rev. Lett. **59**, 1805 (1987).
[8] W.A. de Heer, Rev. Mod. Phys. **65**, 611 (1993).
[9] M. Brack, Rev. Mod. Phys. **65**, 677 (1993).
[10] C. Bréchignac, Chap. 4.1 in Ref. [11].
[11] *Clusters of Atoms and Molecules*, edited by H. Haberland, Springer Series in Chemical Physics Vol. 52 (Springer, Berlin, 1994).
[12] J.M. Pacheco and W. Ekhardt, Ann. Phys. **1**, 235 (1992).
[13] C. Guet and W.R. Johnson, Phys. Rev. B **45**, 11 283 (1992).
[14] V. Bonačić-Koutecký, P. Fantucci, and J. Koutecký, Chem. Rev. **91**, 1093 (1991).
[15] S. Pollack, C.R.C. Wang, and M.M. Kappes, J. Chem. Phys. **94**, 2496 (1991).
[16] T. Baumert, R. Thalweiser, V. Weiß, and G. Gerber, Z. Phys. D **26**, 130 (1993).
[17] P. Apell and Å. Ljungbert, Solid State Commun. **44**, 1367 (1982).
[18] H. Haberland, H. Kornmeier, C. Ludewigt, and A. Risch, Rev. Sci. Instrum. **62**, 2621 (1991). For $j \geq 41$ the data have been measured on the so-called "metastable" peak of the mass spectrum, which corresponds to clusters having lost an atom in the field free region of the mass spectrometer. This explains the relatively low temperatures for $j \geq 41$. The resolution of the mass spectrometer has been increased to $m/\Delta m \approx 3500$, so that the peaks due to the metastable decay could be easily separated.
[19] H. Haberland, B.v. Issendorff, Ji Yufeng, and Th. Kolar, Phys. Rev. Lett. **69**, 3212 (1992).
[20] N.V. Smith, Phys. Rev. **183**, 634 (1969).
[21] Th. Reiners, W. Orlik, Ch. Ellert, M. Schmidt, and H. Haberland, Chem. Phys. Lett. **215**, 357 (1993).
[22] C. Bréchignac, P. Cahuzac, F. Carlier, M. de Frutos, and J. Leygnier, Z. Phys. D **19**, 1 (1991).
[23] J. Pedersen, J. Borggreen, P. Chowdhury, N. Kebaïli, L. Lundsberg-Nielsen, K. Lützenkirchen, M.B. Nielsen, and D. Rasmussen, Z. Phys. D **26**, 281 (1993); Phys. Rev. B **48**, 17 507 (1993).
[24] C. Guet, Comments At. Mol. Phys. (to be published).
[25] E. Engel and J.P. Perdew, Phys. Rev. B **43**, 1331 (1991).
[26] W. Ekardt and G. Penzar, Phys. Rev. B **43**, 1322 (1911), Eq. 28.
[27] Ch. Ellert, H. Haberland, Th. Reiners, and M. Schmidt (to be published).
[28] W. Ekardt, Phys. Rev. B **32**, 1961 (1985).
[29] C. Bréchignac, P. Cahuzac, N. Kebaïli, J. Leygnier, and A. Sarfati, Phys. Rev. Lett. **68**, 3916 (1992).
[30] S. Frederigo, W. Harbich, and J. Buttet, Phys. Rev. B **47**, 10 706 (1993).
[31] A. Liebsch, Phys. Rev. Lett. **71**, 145 (1993); A. Liebsch, Phys. Rev. B **48**, 11 317 (1993); J. Tiggesbäumker, L. Köller, K.-H. Meiwes-Broer, and A. Liebsch, Phys. Rev. A **48**, 1749 (1993).
[32] M. Rocca and U. Valbusa, Phys. Rev. Lett. **64**, 2398 (1990); P.J. Feibelman, Phys. Rev. Lett. **72**, 788 (1994); A. Liebsch, Phys. Rev. Lett. **72**, 789 (1994).
[33] E.W. Plummer (private communication).
[34] D.E. Beck, Phys. Rev. B **30**, 6935 (1984).
[35] E. Jensen and E.W. Plummer, Phys. Rev. Lett. **55**, 1912 (1985).