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Microscopic structure of the plasma resonance in charged potassium microclusters

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The dipole strength function of K_9^+, K_{21}^+, and K_{22}^{2+} charged microclusters is calculated within the framework of the random-phase approximation. Contrary to the case of neutral clusters, essentially no Landau damping is found in the systems under study here, the spectrum being dominated by a single peak carrying most of the oscillator strength. The coupling of the plasmon to thermal fluctuations of the surface can account for about 60% of the observed spreading width.

A microcluster is an aggregate of a small number of atoms. A variety of properties of this system exhibit a distinct shell structure, first observed in potassium and sodium clusters.[1-4] They can be described in terms of delocalized valence electrons subject to an effective smooth potential generated by replacing the structure of the lattice by a uniform positively charged background.

When one shines metal microclusters with a source of photons of variable frequency, one observes that, for a given range of frequencies within the visible part of the spectrum, the amount of quanta intercepted by the system increases markedly. The integrated photoabsorption cross section is found to be proportional to the total number of electrons, implying the collective response of the system as a whole. The ratio of the centroid energy to the width of these giant resonances is of the order of 10 (cf., for example, Ref. 5), consistent with the fact that the electrons oscillate against the positive background a few times before losing their coherence.

In this context, it is useful to view the surface plasmon as a correlated state of a particle above the Fermi surface and of a hole inside the Fermi sea. The dipole vibration is built mainly out of excitations that change the principal quantum number [i.e., $N=2(n-1)+l$] by one, this being the most economic way of changing parity as required by the quantum number of the giant vibration ($L^\pi=1^-$). Excitations where the principal quantum number changes by three also play a role, mainly in the details of the fragmentation of the main peak. They are, in any case, essential to account for the Thomas-Reiche-Kuhn sum rule, together with excitations of $\Delta N=5$ and $\Delta N=7$ character.

The correlation between the particle and the hole can be lost through a variety of mechanisms, among which one can list the following: (i) scattering of the particle or the hole with the phonons of the lattice (resistivity), (ii) decay of the vibration into incoherent single-particle states (Landau damping), (iii) breaking of the dipole strength due to the static deformation of the cluster, (iv) coupling of the plasmon to thermal fluctuations of the surface.

Although these phenomena reflect very different physics, they all contribute to the broadening of the resonance, and it is not simple to isolate their separate contributions. Recently, detailed experimental information on the dipole oscillation of the electrons in the charged clusters K_9^+ and K_{21}^+ has been provided.[6] In both cases, unlike the corresponding neutral sodium clusters,[5] a single, narrow peak exhausting most of the oscillator strength has been observed. The associated damping mechanisms are expected to be particularly simple in this case, since both clusters are closed-shell systems, having 8 and 20 electrons, respectively, and thus are expected to be spherical. Furthermore, the potentials of the charged clusters in this

mass region are much deeper than the potentials for the corresponding neutral clusters. As a result, the influence of the $\Delta N=3$ unperturbed particle-hole excitations is different depending on whether the cluster is neutral or charged. Specifically, for neutral clusters these excitations lie within the immediate neighborhood of the dipole plasmon and couple strongly to it producing considerable fragmentation (cf., Refs. 7–9, and references therein). On the other hand, the $\Delta N=3$ excitations of charged clusters in the mass region 8–20 are much higher in energy and thus almost decoupled from the dipole plasmon. Therefore, unlike the case of neutral clusters, Landau damping is almost absent in the case of charged clusters in this mass region. Landau damping is expected to be even more marginal as a decay mode of the giant resonance in the case of doubly charged clusters.

In keeping with the above discussion, we expect both mechanisms (ii) and (iii) to be, in the cases under consideration here, essentially nonoperative, allowing for a detailed study of the quantal size effect listed as (iv).

In the present paper, following Ref. 9, the surface plasmons of both K_9^+ and K_{21}^+ are calculated within the framework of the random-phase approximation (RPA). Quantal size effects are then included making use of potential-energy surfaces provided by the spheroidal shell model[10] and treating the coupling between the dipole vibration to the thermal fluctuations in the adiabatic approximation. It will be concluded that this mechanism plays an essential role in the relaxation process, accounting for about 60% of the plasmon broadening experimentally observed.

We also present a calculation of the plasmon resonance for the case of the doubly charged K_{22}^{2+} cluster. This doubly charged potassium cluster has been observed experimentally,[11] although its photoabsorption response has not as yet been measured. The theoretical calculation exhibits a trend towards a stronger single-peak plasmon with increasing positive charge, making this doubly charged spherical cluster an even more promising candidate for the investigation of relaxation mechanisms in the absence of Landau damping.

A discrete particle-hole basis of dimension $\mathcal{N}$ is constructed and the Hamiltonian

$$H=H_0+V,$$

sum of the Hartree-Fock Hamiltonian, H_0, and the residual interaction V, is diagonalized in the RPA. The single-particle potentials (cf. Fig. 1) were calculated self-consistently in the jellium background model using the density-variational formalism in a semiclassical approximation.[12,13]

The associated unperturbed particle-hole excitations exhaust the Thomas-Reiche-Kuhn (TRK) sum rule $S(E1)=N\hbar^2e^2/2m$, that is

$$\tfrac{2}{3}\sum_{ph}(\varepsilon_{n_p,l_p}-\varepsilon_{n_h,l_h})\,|\langle p||\mathcal{M}(E1)||h\rangle|^2=S(E1),$$

where ε_{n_i,l_i} are the single-particle energies and the dipole operator is given by $\mathcal{M}(E1;\mu)=\sqrt{4\pi/3}er\mathcal{Y}_{1\mu}(\hat{\mathbf{r}})$. This result is also valid for the RPA correlated eigenstates and associated eigenvalues E_n, since for all multipolarities the RPA preserves the energy-weighted sum rule, of which the TRK sum rule is a specific example for the case of dipole. For details on this RPA method cf. Ref. 9.

The most striking feature of the RPA results is that essentially all the dipole strength is concentrated in a single line which carries most of the oscillator strength; specifically, 96% for K_9^+ and 89% for K_{21}^+ (cf. Fig. 1). In the case of the doubly charged K_{22}^{2+}, a single line at 2.38 eV carries 95% of the oscillator strength. Landau damping is thus negligible for these systems. The wave functions associated with these states show typical collective properties, as testified by the fact that the correlated state is distributed over several configurations. Moreover, for K_{21}^+, the ground-state correlations, as measured by the sum, $\sum_{ph}[Y(ph)]^2$, of the square of the backwards-going amplitudes are of the order of 0.20 and quench the dipole by 33%. These results are in contrast with those associated with the weak states, that is, states which carry a small fraction of the oscillator strength, which are dominated by a couple of configurations and for which ground-state correlations play no role.

The energies of the main peaks are 2.34 and 2.30 eV for K_9^+ and K_{21}^+ clusters, as compared to the observed values of 1.93 and 1.98 eV, respectively. This discrepancy between theory and experiment is likely to be correlated with the poor treatment of the outer part of the potential and reflects the limitations of the local-density approximation.

Quantal size effects are taken into account through a macroscopic model[14] which has been used extensively in studies of giant resonances in nuclei.[15–17] The coupling of the plasma resonance to the quadrupole shape fluctua-

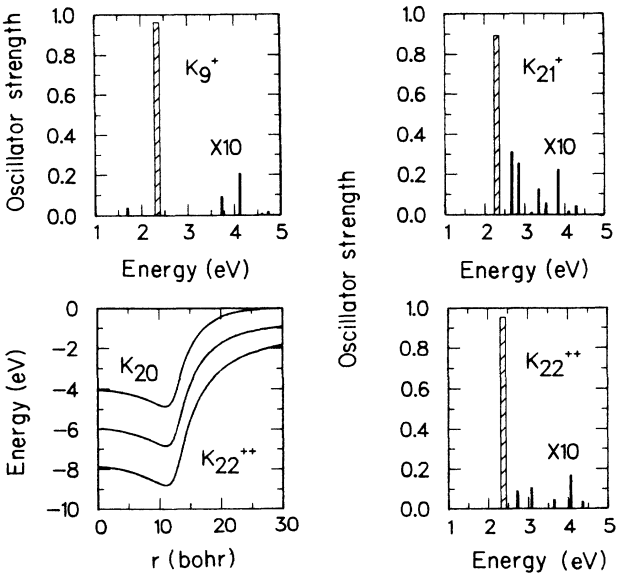

FIG. 1. Dipole oscillator strength for the charged potassium clusters K_9^+, K_{21}^+, and K_{22}^{2+}. Solid bars indicate values multiplied by ten. For the same number of delocalized electrons, the reduction of fragmentation with increasing positive charge is apparent. In the lower-left corner, the average potentials corresponding to K_{20}, K_{21}^+, and K_{22}^{2+} clusters are plotted. The depth of the potentials increases by ≈ 2 eV per extra charge.

tions of the cluster is expected to be the dominant quantal size effect. This is because this coupling is the only one that fulfills, in lowest order in the coupling, both angular momentum and parity selection rules. Such a coupling breaks the dipole strength in 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, in the body-fixed frame of reference, the size of the quadrupole moment of the cluster, and its departure from axial symmetry. The values of the three frequencies can then be expressed in terms of the directional polarizabilities a_κ of the ellipsoid,

$$\omega_\kappa^2 = Ne^2/ma_\kappa \quad (\kappa = 1,2,3),$$

where the quantities a_κ are related to the average polarizability a_0 via the depolarization factors of the ellipsoid through

$$a_\kappa/a_0 = 3D_\kappa^{-1} \Big/ \sum_\kappa D_\kappa^{-1}.$$

For a given ellipsoidal deformation (β,γ), the photoabsorption cross section for a strong peak carrying a fraction f of the oscillator strength can be written as

$$\sigma_\kappa(\omega;\beta,\gamma) = \frac{(4\pi f Ne^2/m_e c)\omega^2\Gamma}{[\omega^2 - \omega_\kappa^2(\beta,\gamma)]^2 + \omega^2\Gamma^2}, \tag{1}$$

where N here is the number of delocalized electrons in the cluster and Γ the intrinsic width of the giant resonance arising from relaxation processes different from that associated with the thermal fluctuations of the surface of the cluster. In the present case, Γ can be identified with the collision damping width mentioned above under point (i).

At finite temperatures, the system will explore the potential-energy surface $\Phi(\beta,\gamma)$ with a probability

$$P(\beta,\gamma) = Z^{-1}\exp[-\Phi(\beta,\gamma)/T], \tag{2}$$

the quantity Z being the partition function,

$$Z = \int d\tau \exp[-\Phi(\beta,\gamma)/T], \tag{3}$$

and $d\tau$ the volume element.

The average cross section can then be written as

$$\langle\sigma(\omega)\rangle = \sum_\kappa \int d\tau\, \sigma_\kappa(\omega;\beta,\gamma)P(\beta,\gamma). \tag{4}$$

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. The single lines predicted within the framework of the RPA become broadened and the associated full width at half maximum (FWHM) can be parametrized according to

$$\Gamma_T = a\sqrt{T_{eV}},$$

where $a = 1.02$ and 0.65 eV for K_9^+ and K_{21}^+, respectively. A simple estimate of this result can be obtained assuming a harmonic behavior for the potential-energy surface of the systems under study, that is

$$\Phi(\beta,\gamma) \approx \tfrac{1}{2}C\beta^2.$$

Comparison to the detailed numerical calculations leads to restoring force coefficients $C = 11$ and 29 eV for K_9^+ and K_{21}^+, respectively. The dispersion in the frequencies of the plasmon induced by thermal fluctuations can now be calculated analytically,[18,19] leading to

$$\Gamma_T = 0.83(2T/C)^{1/2}\hbar\omega_0,$$

where $\hbar\omega_0$ is the centroid energy of the plasmon.

From the results displayed in Fig. 2, it is seen that the coupling of the plasmon to the fluctuations of the surface accounts for about 60% of the observed widths (dashed line). Making the ansatz that the intrinsic width Γ can be associated with the plasmon damping in bulk,[20,21]

$$\Gamma \sim \gamma T, \tag{5}$$

where γ is a constant of the order of 1–3, one obtains from Eqs. (1)–(4) the results also displayed in Fig. 2 (solid line).

The validity of using bulk estimates for a cluster as small as K_{21}^+ is not obvious. In any case, by studying the temperature dependence of the FWHM of the plasmon strength function in singly or eventually doubly charged clusters, the two contributions discussed in this paper can eventually be disentangled.

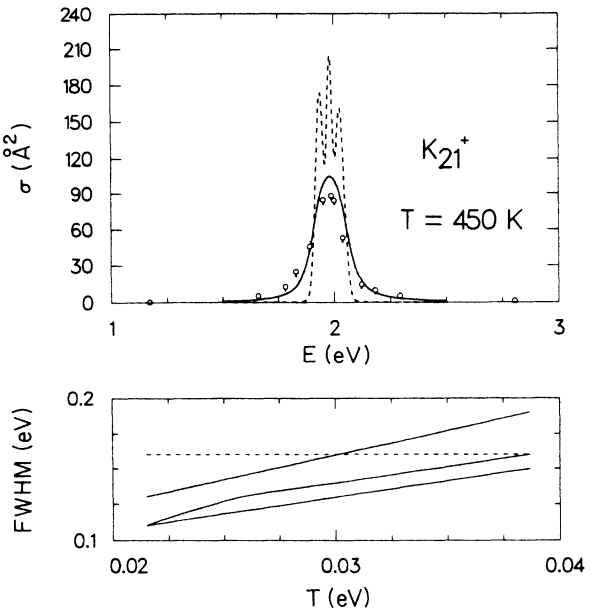

FIG. 2. Quantal size effects for K_{21}^+: Lower part: Results for the FWHM obtained using Eqs. (1)–(4), and taking for Γ in Eq. (1) the parametrization of Eq. (5) with $\gamma = 1$ (lower curve), $\gamma = 2$ (middle curve), and $\gamma = 3$ (upper curve). The horizontal dashed line corresponds to the experimentally determined FWHM for the range of possible temperatures of the cluster (Ref. 22). Upper part: Photoabsorption cross section. The experimental data (Ref. 6) are plotted with open circles; the dashed line displays the resulting broadening due solely to thermal fluctuations (zero intrinsic width). The full drawn curve includes the relaxation process (i) (cf. text), using the parametrization in Eq. (5) with $\gamma = 2$. The temperature selected corresponds to the crossing point between the middle solid and the horizontal dashed curves in the lower part of this figure.

In conclusion, the plasmon strength function of positively charged, spherical potassium microclusters in the mass region 8–20 seems to be controlled by a single line carrying most of the oscillator strength. The coupling to the quadrupole fluctuations of the cluster accounts for about 60% of the observed widths. This damping mechanism displays a weak (square-root) dependence with temperature. An overall account of the observations may be obtained including the resistivity contribution to the relaxation process. Although the actual size of this contribution is rather uncertain, this mechanism should behave linearly with temperature. Measurements of a variety of temperatures may disentangle this contribution from the quantal size effect discussed above.

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[1]W. D. Knight *et al.*, Phys. Rev. Lett. **52**, 2141 (1984).
[2]W. D. Knight, W. A. de Heer, K. Clemenger, and W. A. Saunders, Solid State Commun. **53**, 445 (1985).
[3]W. D. Knight, K. Clemenger, W. A. de Heer, and W. A. Saunders, Phys. Rev. B **31**, 2539 (1985).
[4]W. A. Saunders, K. Clemenger, W. A. de Heer, and W. D. Knight, Phys. Rev. B **32**, 1366 (1985).
[5]K. Selby *et al.*, Phys. Rev. B **40**, 5417 (1989).
[6]C. Bréchignac, Ph. Cahuzac, F. Carlier, and J. Leygnier, Chem. Phys. Lett. **164**, 433 (1989).
[7]W. Ekardt, Phys. Rev. B **31**, 6360 (1985).
[8]D. E. Beck, Phys. Rev. B **35**, 7325 (1987).
[9]C. Yannouleas, R. A. Broglia, M. Brack, and P. F. Bortignon, Phys. Rev. Lett. **63**, 255 (1989).
[10]S. G. Nilsson, K. Dan. Vidensk. Selsk. Mat. Fys. Medd. **29** (16) (1955); K. Clemenger, Ph.D. thesis, University of California, Berkeley, 1986; K. Clemenger, Phys. Rev. B **32**, 1359 (1985).
[11]C. Bréchignac, Ph. Cahuzac, F. Carlier, and J. Leygnier, Phys. Rev. Lett. **63**, 1368 (1989).
[12]M. Brack, Phys. Rev. B **39**, 3533 (1989).
[13]H. Nishioka (private communication).
[14]J. M. Pacheco and R. A. Broglia, Phys. Rev. Lett. **62**, 1400 (1989).
[15]M. Gallardo, M. Diebel, T. Døssing, and R. A. Broglia, Nucl. Phys. **A443**, 415 (1985).
[16]J. M. Pacheco, C. Yannouleas, and R. A. Broglia, Phys. Rev. Lett. **61**, 294 (1988).
[17]Y. Alhassid, B. Bush, and S. Levit, Phys. Rev. Lett. **61**, 1926 (1988).
[18]J. Le Tourneux, K. Dan. Vidensk. Selsk. Mat. Fys. Medd. **34** (11) (1965).
[19]R. A. Broglia, W. E. Ormand, and M. Borromeo, Nucl. Phys. **A482**, 141c (1988).
[20]N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt Saunders, New York, 1976).
[21]D. M. Wood and N. W. Ashcroft, Phys. Rev. B **25**, 6255 (1982).
[22]C. Bréchignac (private communication).