

Dielectric screening effects on the photoabsorption cross section of embedded metallic clusters

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The surface plasmon resonance of alkali-metal (potassium) and noble-metal (silver) clusters embedded in different dielectric matrices is studied within the time-dependent density-functional formalism and the jellium model, including dielectric screening for the electron-electron interaction. The calculated redshift of the plasma frequency as the dielectric constant (ϵ) of the matrix increases is in good agreement with the available experimental data for both potassium and silver clusters. In the case of potassium, the shifts induced by rare-gas matrices are predicted. A tendency to saturation in the polarizability and surface plasmon resonance when ϵ increases is obtained and is due to the screening of the Coulomb interaction by the dielectric surrounding the cluster. We conclude that the basic effect of the dielectric matrix comes from the direct screening of the electron-electron interaction and not from the modification of the cluster ground state.

I. INTRODUCTION

Among the electronic properties of free metallic clusters, the collective excitation or surface plasmon has received much attention both experimentally, since the work of de Heer *et al.*,^{1,2} who used molecular-beam photodepletion spectroscopy to study the photoabsorption cross section of small alkali-metal clusters, and theoretically, using simple models including the electronic and geometrical degrees of freedom.³⁻⁸ Classically such a collective excitation is equivalent to the first excitation mode in the Mie theory. Within a simple picture, it can be understood as the result of the coherent motion of the delocalized electrons of the cluster with respect to the fixed ionic background.

The optical spectra of free, neutral, and charged alkali-metal clusters show that only a few atoms are needed to establish this surface plasmon excitation.^{1,2,9-11} Within this scenario, the optical properties of alkali-metal clusters are well understood in terms of the *s*-delocalized conduction electrons that dominate the response function in the optical region. The use of a simple jellium model allows us to appropriately describe the evolution with size of the collective resonance of most alkali-metal clusters¹²⁻¹⁴ as well as the linewidth of the resonance by the inclusion of the shape fluctuations of the cluster.¹⁵⁻¹⁷ On the other hand, the optical properties of noble-metal clusters are more difficult to interpret since probably the effect of interband transitions due to the *d* electrons of the ionic cores must be considered. This seems to be the case for the description of the surface plasmon dispersion in silver metallic surfaces^{18,19} but it is not clear for small silver clusters.^{11,20,21}

Understanding how the optical properties of metal

clusters vary when they are embedded in another material, such as a dielectric matrix, is of high importance. Recently, the laser desorption technique has been applied to successfully manipulate the size of clusters supported on surfaces as well as for having free mass selected clusters.²² The physical mechanism is the fragmentation of the cluster through the excitation of its surface plasmon, the size dependence of this excitation allows for the size manipulation. Also, a mass selected sputtering technique has been recently applied by the experimental group in Lausanna to do a size-controlled deposition of clusters on inert rare-gas matrices.²¹ This technique could have some importance in technological processes involving supported clusters.²² As a difference to free clusters, the matrix influence on the optical response of the embedded ones must be taken into account. This will be the main goal of the present work.

We have developed a model to include the dielectric screening effects into the optical response calculations within the time-dependent density functional formalism.^{23,24} We will apply this theoretical model to the study of two types of embedded clusters. One, alkali-metal potassium, for which we know that the *s*-delocalized valence model works quite well for free clusters^{12,13,24} and, consequently, we will apply it to the supported clusters in order to discern the different matrix effects on the photoabsorption cross section. Partial results concerning K_{92} embedded in different matrices were presented in Ref. 24. Second, we will study silver clusters, where the *d* electrons are, in principle, expected to play some role. The optical properties of embedded silver clusters have been reviewed²⁵ showing the controversy about the position of the resonance as a function of cluster size. This question is now settled from the experiments of Ref. 26 where a redshift as the size increases

is found for large clusters. The matrix effects for small size clusters have been studied experimentally in detail in Ref. 21. The comparison of these results with previous ones for larger supported clusters²⁶ shows a crossover in the evolution of the plasma frequency with size. To be more specific, for small sizes an increase in the resonance energy with size is observed, but this tendency is inverted for larger sizes.²⁶ These results are used in Ref. 21 to conclude that for small Ag clusters the influence of the d electrons is not very relevant.²⁷ This conclusion is also supported by the measurements of the plasmon resonance in free, positive, and negative small Ag clusters,^{11,20} where a reasonable agreement is found with a jellium model for the s -valence electrons in small cluster sizes. Relying on these results, we will theoretically estimate the matrix effects for these small Ag clusters using the jellium model and treating only the s electrons within the time-dependent local density approximation (TDLDA).²⁸ Due to these simplifications, our calculation of small Ag clusters does not pretend to provide a very accurate description of their optical properties, but only to point out the correct size of the matrix influence on their optical response.

The paper is organized as follows. In Sec. I we present the theoretical model for the ground state calculation within the density-functional formalism including the dielectric screening. In Sec. II we give some details about the response theory (TDLDA) that we have used to obtain the photoabsorption cross sections and surface plasma resonances. Section III gives the results of the present work for both potassium and silver clusters. The conclusions are given in Sec. IV.

II. GROUND STATE

Within the density-functional theory (DFT) formalism (Refs. 29 and 30) the total energy of a cluster embedded

in a dielectric matrix can be written as a functional of the electronic density $n(\mathbf{r})$ of the form

$$E = T[n(\mathbf{r})] + \frac{1}{2} \int n(\mathbf{r}) V_{\text{ion}}(\mathbf{r}) d^3r + \int n(\mathbf{r}) V_H(\mathbf{r}) d^3r + E_{\text{xc}}[n(\mathbf{r})], \quad (1)$$

where the first term gives the single-particle kinetic energy, the second is the electron-ion interaction, the third is the classical general electrostatic interaction between electrons including the dielectric media, and the fourth one is the energy due to exchange and correlation effects. The ionic background has been described within the spherical jellium model. V_{ion} is thus the electrostatic potential created by a homogeneous spherical distribution of positive charge of radius R ,³¹ surrounded by an infinite medium of dielectric constant ϵ . Analogously, the Hartree potential V_H is given by

$$V_H(\mathbf{r}_1) = \int d^3r_2 V(\mathbf{r}_1, \mathbf{r}_2) n(\mathbf{r}_2), \quad (2)$$

where $V(\mathbf{r}_1, \mathbf{r}_2)$ is the general Coulomb interaction between electrons in the presence of the dielectrics. Its expression can be obtained by imposing the appropriate boundary conditions at the jellium edge to the solutions of the Poisson equation for a point charge.²³ For the sake of completeness we reproduce here its general expression for a sphere of dielectric constant ϵ_1 embedded in a medium of dielectric constant ϵ_2 ,

$$V(\mathbf{r}_1, \mathbf{r}_2) = \begin{cases} \frac{4\pi}{\epsilon_2} \sum_{\ell m} \frac{1}{2\ell+1} \left[\frac{r_1^\ell}{r_2^{\ell+1}} + \frac{R^{2\ell+1}}{r_1^{\ell+1} r_2^{\ell+1}} \frac{\ell(\epsilon_2 - \epsilon_1)}{\epsilon_1 \ell + \epsilon_2 (\ell + 1)} \right] Y_{\ell m}^*(\Omega_1) Y_{\ell m}(\Omega_2) & \text{if } r_1, r_2 > R, \\ 4\pi \sum_{\ell m} \frac{r_2^\ell}{r_1^{\ell+1}} \frac{Y_{\ell m}^*(\Omega_1) Y_{\ell m}(\Omega_2)}{\epsilon_1 \ell + \epsilon_2 (\ell + 1)} & \text{if } r_1 > R, r_2 < R, \\ 4\pi \sum_{\ell m} \frac{r_1^\ell}{r_2^{\ell+1}} \frac{Y_{\ell m}^*(\Omega_1) Y_{\ell m}(\Omega_2)}{\epsilon_1 \ell + \epsilon_2 (\ell + 1)} & \text{if } r_1 < R, r_2 > R, \\ \frac{4\pi}{\epsilon_1} \sum_{\ell m} \frac{1}{2\ell+1} \left[\frac{r_1^\ell}{r_2^{\ell+1}} + \frac{r_1^\ell r_2^\ell}{R^{2\ell+1}} \frac{(\ell+1)(\epsilon_1 - \epsilon_2)}{\epsilon_1 \ell + \epsilon_2 (\ell + 1)} \right] Y_{\ell m}^*(\Omega_1) Y_{\ell m}(\Omega_2) & \text{if } r_1, r_2 < R. \end{cases} \quad (3)$$

As a particular case, the interaction in vacuum corresponds to the well known Coulomb term $V = 1/r_{12}$. In our calculations we will assume $\epsilon_1 = 1$ and $\epsilon_2 = \epsilon$ of the embedding matrix.

Based upon the variational principle of the density-functional theory, the electronic density is obtained by a self-consistent solution of the Kohn-Sham (KS) equations^{29,30} for the valence electrons moving in an effective potential given by

$$V_{\text{eff}}(\mathbf{r}) = V_H(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) + V_{\text{ion}}(\mathbf{r}), \quad (4)$$

where V_{xc} is the exchange-correlation potential that in all the calculations of the present work has been evaluated in the local density approximation (LDA) using the Gunnarsson-Lundqvist functional.³² Hartree atomic units will be used throughout the paper unless explicitly stated otherwise.

III. TIME-DEPENDENT LOCAL-DENSITY APPROXIMATION (TDLDA)

The TDLDA theory has proved to yield a good description of the collective plasmon states in small alkali-

metal clusters.^{3–8} Within this theory, the collective states arise from the coherent excitation of particle-hole (ph) electronic transitions, in the independent particle scheme (KS) of the ground state, with a residual ph interaction which in DFT is given by the variation of the ground state mean-field induced by the applied external field. Technically, the solutions can be worked out in two different ways: in coordinate space, by building the different single-particle Green's functions;³ equivalently, the solutions can be worked out in the discrete space given by a basis of single-particle wave functions, discretizing in some way the continuum part of the spectrum, and building the matrix representation of the TDLDA equations in this space.⁶ In the present work we are going to apply the first *continuum* approach. We will describe now the main points of the TDLDA formulation; for further details we refer the reader to Refs. 3 and 28.

Within linear response theory, the variation in the ground state density $\delta n(\mathbf{r}; \omega)$ induced by a weak external field $Q(\mathbf{r})$ with a time variation frequency ω is expressed in terms of the external field by means of the density-density correlation function $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ as

$$\delta n(\mathbf{r}; \omega) = \int d^3 r' \chi(\mathbf{r}, \mathbf{r}'; \omega) Q(\mathbf{r}'). \quad (5)$$

In the case of independent particles, the corresponding density-density correlation function $\chi^0(\mathbf{r}, \mathbf{r}'; \omega)$ can be exactly expressed in terms of the single-particle Green's functions $G(\mathbf{r}, \mathbf{r}'; \omega)$ as

$$\begin{aligned} \chi_0(\mathbf{r}, \mathbf{r}'; \omega) = & \sum_h \phi_h^*(\mathbf{r}) \phi_h(\mathbf{r}') G(\mathbf{r}, \mathbf{r}'; \varepsilon_h + \omega) \\ & + \phi_h(\mathbf{r}) \phi_h^*(\mathbf{r}') G^*(\mathbf{r}, \mathbf{r}'; \varepsilon_h - \omega), \end{aligned} \quad (6)$$

where the ϕ 's and ε 's are the single-particle wave functions and energies, respectively, and the label h refers to occupied states. The Green's function is defined as

$$G(\mathbf{r}, \mathbf{r}'; \omega) = \langle \mathbf{r} | \frac{1}{H - \omega - i\eta} | \mathbf{r}' \rangle, \quad (7)$$

where H is the single-particle Hamiltonian and η is an infinitesimal positive.

The TDLDA theory assumes that the electrons respond as free particles to the self-consistent induced field, which consists of the external one plus the induced variation of the ground state mean-field potential. This condition defines a new equation for the density-density correlation function χ in terms of the noninteracting one by means of the Dyson-type integral equation,

$$\begin{aligned} \chi(\mathbf{r}, \mathbf{r}'; \omega) = & \chi_0(\mathbf{r}, \mathbf{r}'; \omega) + \int d^3 r_1 d^3 r_2 \chi_0(\mathbf{r}, \mathbf{r}_1; \omega) \\ & \times K(\mathbf{r}_1, \mathbf{r}_2) \chi(\mathbf{r}_2, \mathbf{r}'; \omega). \end{aligned} \quad (8)$$

K is the residual ph interaction, and in the LDA is given by

$$K(\mathbf{r}, \mathbf{r}') = V(\mathbf{r}, \mathbf{r}') + \frac{dv_{xc}}{dn} \delta(\mathbf{r} - \mathbf{r}'), \quad (9)$$

where the first term corresponds to the general electron-electron interaction in the presence of dielectrics that we have described for the ground state calculations, and v_{xc} is the exchange-correlation contribution to the KS mean-field. The vertex correction is included in the LDA approximation as a contact interaction in the residual ph interaction.

After performing a multipole decomposition, Eq. (8) is solved as a matrix equation in coordinate space, and then the induced density is obtained from Eq. (5). Once this is known, the response function (or dynamical polarizability) α can be easily computed from

$$\alpha(\omega) = \int d^3 r \delta n(\mathbf{r}; \omega) Q(\mathbf{r}). \quad (10)$$

The strength function $S(\omega)$, which contains the information about the complete response of the system to the external field Q , is given by the imaginary part of $\alpha(\omega)$,

$$\begin{aligned} S(\omega) \equiv & \sum_n |\langle \Phi_n | Q | \Phi_0 \rangle|^2 \delta[\omega - (E_n - E_0)] \\ = & -\frac{1}{\pi} \text{Im}(\alpha(\omega)), \end{aligned} \quad (11)$$

where $|\Phi_n\rangle$ and $|\Phi_0\rangle$ are the excited and ground states of the system, respectively, while $(E_n - E_0)$ are the excitation energies. The value of $\alpha(\omega)$ for $\omega = 0$ gives the static polarizability. Finally the photoabsorption cross section $\sigma(\omega)$ that we can compare with available experimental data can be obtained from the strength function using Fermi's golden rule as follows:

$$\sigma(\omega) = \frac{4\pi^2 \omega}{c} S(\omega). \quad (12)$$

Since we are interested in dipole surface excitations, we will consider the dipole external field $rY_{10}(\theta, \phi)$ to calculate the response function that afterwards can be compared with photoabsorption experiments or electron-energy-loss experiments in the limit of small momentum transfer. In the numerical calculations we have added a small and positive imaginary part $\Gamma=5$ meV to the energies in (6). This amounts to transforming the δ functions of the response below the continuum threshold in Lorentzians of width 2Γ , and thus simplifies the analysis of the strength function. We note that in our approximation, the embedding insulating medium has been described by means of a classical macroscopic dielectric constant, that is, we made an approximation by neglecting contributions from the matrix electronic transitions to the response function. This is generally a quite justified assumption, since for most common matrices the electronic transitions are at much higher energies than those corresponding to the valence electron gas of the metal.

IV. RESULTS

In previous calculations of embedded clusters, the dielectric matrix was already incorporated in the descrip-

tion of the electronic ground state via the solution of the corresponding Poisson equation. As obtained in Ref. 5, we find that the main change stemming from the dielectric matrix on the electronic ground state is a rather rigid shift of the total effective potential and energy eigenvalues. Consequently, the independent-particle density-density response function has nearly the same structure for different dielectric constants.²⁴ This explains that if we keep the residual ph interaction unchanged and equal to the vacuum potential $1/r_{12}$, the matrix effect on the resonance frequencies and polarizabilities would be small.^{5,24}

As ϵ increases, screening of the electron-electron interaction is more effective and the electronic density penetrates the matrix more and more, leading to a higher spill-out. As a consequence, a higher static polarizability and smaller surface plasma frequency is expected when ϵ increases, due to the change of the ground state. To this indirect effect of the dielectric on the optical properties, by means of the modification of the ground state, one has to add the effect of the direct screening of the residual ph interaction. It will be shown in the following that the influence of the dielectric on the optical properties comes basically from this direct screening of the residual interaction.

In this section we are going to present results corresponding to two types of clusters for which the model of delocalized s electrons in jellium is known to work reasonably well, and consequently we can use it to estimate the matrix effects on the optical response. We will first study potassium clusters, for which the previous model is particularly adequate,¹² and second we will study small silver clusters, for which, as explained in Sec. I, the effects of the d electrons are not expected to be very important.

A. Potassium clusters

First we want to analyze which are the matrix effects on the optical dipole response of metallic potassium clusters. We have taken K_{92} as a test case because we have experimental electron-energy-loss-spectroscopy (EELS) data of potassium embedded in an insulating MgO matrix³³ to compare with. The experimental results at very low impact electron momentum transfer ($q \approx 0$) are dominated by the dipole component of the external field; thus with that technique we are probing the dipole response of the embedded cluster, which generally is dominated by a peaked collective excitation (surface plasmon). We can directly compare the experimental resonance frequency at low q with our theoretical dipole resonance frequency.

Figure 1 shows calculations following two ways of evaluating the kernel of Eq. (3). The results, plotted as open circles, are obtained considering the dielectric only in solving, the Poisson equation for the ground state, and the ϵ -independent Coulomb interaction $V = 1/r_{12}$ is used for the residual interaction. This procedure implies a non-consistent treatment of the excited and ground states, since the electron-electron interaction is treated in a different way for each case. Filled circles corre-

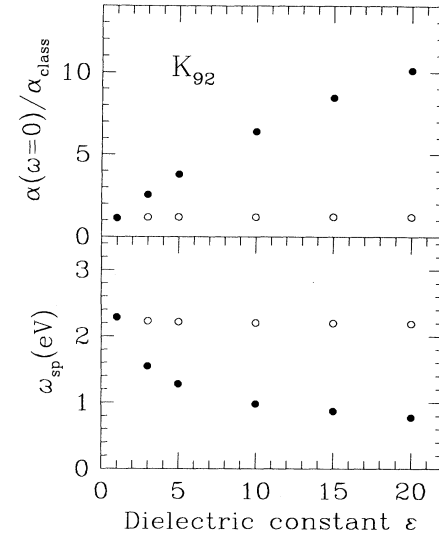


FIG. 1. Static dipole polarizability in units of the classical value (R^3) and surface plasmon resonance for K_{92} potassium cluster as a function of the dielectric constant ϵ of the surrounding medium. Open circles correspond to the calculation of the response function including only the dielectric screening in the ground state and filled circles correspond to the full calculation of the present work.

spond to the calculation of the present work including the dielectric screening in the ground-state and residual ph interactions. We note that when the screening of the residual interaction is not considered, the plasmon energy and polarizability are almost insensitive to the dielectric matrix. In both calculations a tendency to saturation is observed in the surface plasma resonance and static polarizability, but the convergence values are very different. The saturation comes about as the Coulomb potential approaches zero outside the jellium sphere, due to the electronic-matrix screening, whereas the difference in the convergence values is due to the different way of treating the excited and ground states. Our theoretical result for the surface plasmon resonance of K_{92} surrounded by a dielectric matrix of $\epsilon = 3$ (Ref. 34) is 1.55 eV, which is in quite good agreement with the experimental results in the limit $q \rightarrow 0$ of ≈ 1.7 eV for a cluster distribution size around the one we have used in our calculations.³³ It is important to remark here that if we do not include the dielectric matrix in the calculation of the residual ph interaction, a value of 2.17 eV is obtained for the surface plasmon resonance. We can quantify the matrix effect on the ground state to be of 7% and of 30% for the residual ph interaction of the total matrix energy shift. The photoabsorption cross sections corresponding to these calculations are shown in Fig. 2. We see a small change in the shape of the photoabsorption cross section when the dielectric is included only in the ground state calculation as compared to the free cluster cross section, where the change is much more remarkable for the complete results of the present calculation. The full effect of the dielectric causes a stronger redshift of the energy and also a big increase in the collectivity of the state. The Landau

damping, which is very important in free clusters, almost completely disappears as a result of the dielectric.

From the previous discussion we can conclude that the basic physical effect for the collective excitations of embedded clusters is the direct screening of the residual ph interaction. The effect coming from the modification of the ground state spill-out and single-particle quantities (wave functions and eigenvalues) is much less important. It is also interesting to note that the enhancement of the polarizability by the embedding insulating medium is a quantum-mechanical effect, in the sense that classical electrostatics predicts no change in the induced dipole moment when a conducting sphere is placed in a dielectric.

Up to now we have only discussed the effect of the matrix screening in the residual interaction. For the sake of completeness it will be interesting to study the contribution of the exchange-correlation local-field correction to the response properties of this cluster. In the calculations presented here we assume that the matrix screening does not change the exchange-correlation energy functional. Then as we increase the dielectric constant of the matrix, and due to the screening of the Coulomb potential, exchange and correlation effects are expected to play a more important role. To quantify this effect, we have performed two calculations, one with local-field corrections (exchange-correlation part of the residual ph interaction) included and the other without (that is, only the

Coulomb part is included in the residual interaction) for the K_{92} cluster in vacuum and embedded in a matrix of $\epsilon = 15$. We have obtained that the local field shifts to the red the collective resonance.^{7,35} The shift is 0.15 eV for $\epsilon = 1$ and 0.29 eV for $\epsilon = 15$. This confirms our expectations that the exchange-correlation contribution will be relatively more important the higher the dielectric constant of the surrounding matrix is.

Once we have studied the matrix influence for a fixed cluster size, it will be very relevant to observe the size evolution of these properties. In Fig. 3 we show the surface plasma frequency as a function of size for closed shell potassium clusters in vacuum ($\epsilon = 1$) and for different values of the external matrix: the rare gases Ar ($\epsilon = 1.7$), Kr ($\epsilon = 1.95$), and Xe ($\epsilon = 2.31$),²¹ and MgO matrix ($\epsilon = 3$).³³ We notice that as the dielectric constant increases, the size effects in the evolution of the plasmon energy are less and less important, the energy being almost independent of size already at $\epsilon = 3$. The distance to the classical Mie limit

$$\omega_M = \omega_p \frac{1}{\sqrt{2\epsilon + 1}} \quad (13)$$

also decreases with increasing ϵ . The classical Mie value for pure potassium is 2.54 eV, whereas for an embedded potassium cluster in a matrix of $\epsilon = 3$ it is 1.66 eV. That

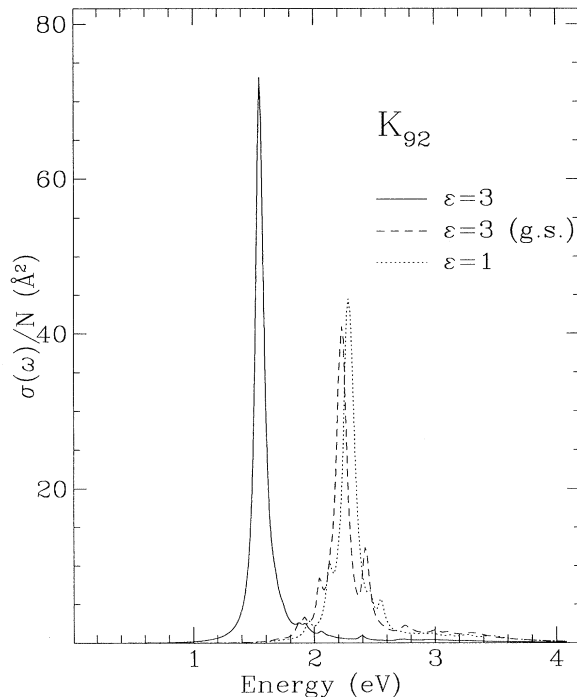


FIG. 2. Photoabsorption cross section per electron of the potassium cluster K_{92} in vacuum (dotted line) and embedded in a MgO matrix (continuous line). Dashed line shows the result of a calculation neglecting the matrix screening effects on the residual ph interaction and included only in the ground state (gs) (see text).

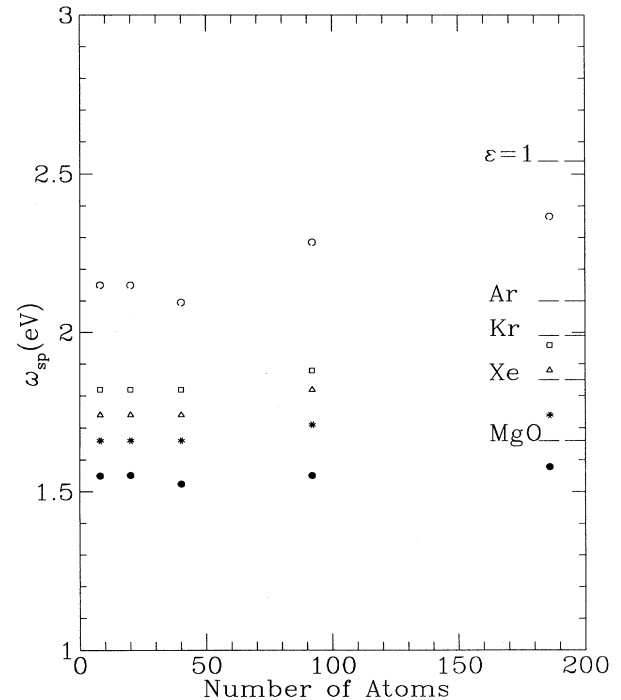


FIG. 3. Size dependence of the surface plasmon energy in eV for potassium clusters in vacuum (open circles) and embedded in different dielectric matrices: the rare gases Ar ($\epsilon = 1.7$, squares), Kr ($\epsilon = 1.95$, triangles), and Xe ($\epsilon = 2.31$, stars), and the insulating MgO matrix ($\epsilon = 3$, filled circles). The corresponding classical Mie limit is indicated by a dashed line on the right.

TABLE I. Theoretical energy shifts in eV of the average plasmon resonance for potassium clusters embedded in Ar, Kr, Xe, and MgO matrices as a function of size. The classical Mie shifts are also given for comparison.

| | MgO \rightarrow Xe | Xe \rightarrow Kr | Xe \rightarrow Ar | Ar \rightarrow vacuum |
|-----------|----------------------|---------------------|---------------------|-------------------------|
| K_8 | 0.11 | 0.08 | 0.16 | 0.30 |
| K_{20} | 0.11 | 0.08 | 0.16 | 0.30 |
| K_{40} | 0.08 | 0.08 | 0.16 | 0.28 |
| K_{92} | 0.16 | 0.11 | 0.17 | 0.31 |
| K_{186} | 0.16 | 0.14 | 0.22 | 0.41 |
| Mie limit | 0.19 | 0.14 | 0.24 | 0.44 |

is, we are 7% away from the classical value for free potassium clusters and 5% for embedded ones at the largest cluster studied here. This slow convergence has also been observed in free potassium clusters.^{12,13} In Table I we list the energy shifts predicted when going to different dielectric matrices and compared to the shifts given by the Mie limit. The evolution to this limit is not always smooth due to the different relative importance of the finite size effects for different matrices.

Another interesting aspect of the theoretical calculation is that the plasma frequency is close to the continuum threshold (which in the calculation coincides with minus the highest occupied molecular orbital, ϵ_{HOMO}) for this small size. This causes the high energy shoulder in the spectrum of the free cluster. This effect is more important for free clusters than for embedded ones, because the shift in the plasma resonance as a function of the dielectric constant is larger than the shift in the continuum threshold. To be quantitative, in the case of K_{20} the plasma frequency shifts to lower energies by 0.6 eV,

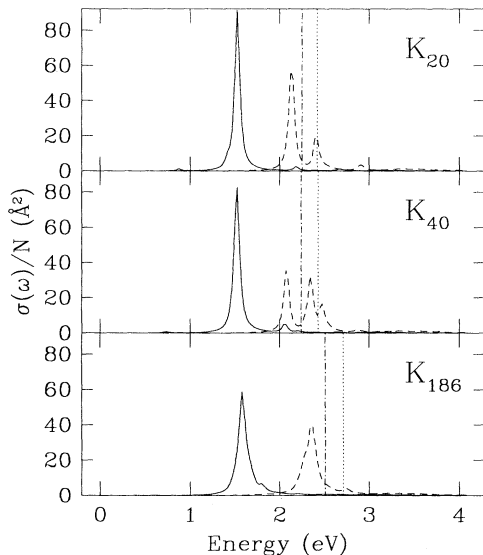


FIG. 4. Photoabsorption cross section for potassium clusters (K_{20} , K_{40} , and K_{186}) in vacuum (dashed line) and embedded in a MgO matrix (continuous line). The vertical lines correspond to the position of the theoretical ionization threshold (ϵ_{HOMO}). Dotted line is for vacuum and dash-dotted line for the embedded cluster.

whereas the ϵ_{HOMO} it shifts by 0.17 eV. In Fig. 4 the photoabsorption cross section for free (dashed line) and embedded (continuous line) clusters with sizes of 20, 40, and 186 potassium atoms is shown. The ϵ_{HOMO} is also shown by vertical lines, dotted for $\epsilon = 1$, and dash-dotted for $\epsilon = 3$. From the data in Fig. 4 the effects discussed before are clearly seen, that is, a redshift of the plasma resonance and a big reduction in the fragmentation of the peak.

A comment has to be made with respect to the previous calculations. We have compared the results for our perfectly embedded cluster with experiments done on supported clusters in matrices. In the experiments, the matrix screening will be less efficient than if the cluster were perfectly embedded. This qualitative argument is in agreement with the fact that our calculated values are a little below the experimental ones (the less efficient screening is, the higher the resonance frequency). This comment also holds for the calculations we will present in the next section on silver clusters.

B. Small silver clusters

We have performed a similar study for small silver clusters as for potassium, treating in the same way the modification induced by the dielectric on the electron-electron interaction. Since all of the conclusions reached in the previous section hold here, they will not be repeated. The interest in this silver cluster stems from the fact that very careful measurements of the optical absorption spectra for small mass selected silver clusters (up to 21 atoms) embedded in different matrices (argon, krypton, and xenon) exist.²¹ Using these data we can test our dielectric model looking at the change in the resonance frequency when we change the embedding matrix. Besides, for these small sizes the influence of the d electrons of the Ag ion cores is not expected to be very important and a good estimate of the dielectric effect will be given by the same model that we have been using for the K clusters, i.e., the jellium+LDA model.³⁶ Further evidence in this direction is provided by the fact that the shell structure observed in field emission spectra of gold clusters³⁷ supports somehow the applicability of a jellium model to describe the electronic states of noble-metal clusters.

In Table II we have compared the results of the present

TABLE II. Energy shifts in eV of the average plasmon resonance for silver cluster embedded in Ar, Kr, and Xe matrices as a function of size. The experimental data have been extracted from a linear fit of the experimental energy shifts. The data in parentheses correspond to the calculation of the resonance frequency without including the dielectric in the residual ph interaction (see text).

| | Xe \rightarrow Kr | | Xe \rightarrow Ar | |
|-----------|---------------------|-------|---------------------|-------|
| | Theory | Expt. | Theory | Expt. |
| Ag_8 | 0.14 | 0.14 | 0.25 | 0.23 |
| Ag_{20} | 0.11 (0.06) | 0.13 | 0.19 (0.11) | 0.22 |
| Ag_{40} | 0.13 | | 0.24 | |

calculation for the shift in the average plasma resonance frequency for three closed shell clusters embedded in three different rare-gas matrices, argon ($\epsilon = 1.7$), krypton ($\epsilon = 1.95$), and xenon ($\epsilon = 2.31$), with the experimental data of Ref. 21. Because experimentalists have measured different sizes (Ag_7 , Ag_{11} , Ag_{15} , and Ag_{21}) from the ones calculated here, we have used their linear fit to extract the values presented in Table II. It is important to remark that in the experiments a nearly size-independent energy shift (for the sizes studied there) is observed by changing the matrix gas, that is, ~ 0.13 eV in changing from xenon to krypton and ~ 0.22 eV from xenon to argon. From Table II we observe a very good agreement between the present theoretical estimates and the experimental values. To get more insight into the matrix screening, we have performed a calculation for Ag_{20} neglecting the contribution of the matrix to the residual ph interaction. These results are shown in Table II in parentheses. As we found for the general shift of the resonance frequency in embedded potassium clusters, the contribution of the matrix screening in the residual ph interaction is very important. In this case half of the total energy shift caused by the change in the embedding matrix comes from this contribution.

In spite of the previous good agreement in the energy shifts of small silver clusters, when looking at the absolute values of the resonance energy the agreement is less good. The predicted values generally lie 20% below the measured ones, a difference that is even bigger than that obtained when comparing the calculation for free clusters (using the same model) with the experimental values for free (in gas phase) clusters.¹¹ A possible explanation for this fact could be that an effect of the matrix, besides the screening of the electron-electron interaction that we have been discussing, is to induce a contraction in the cluster volume, and this in turn induces an increase in the resonance energy compared to what one would expect from the data of free clusters. However, this effect is still present when changing the matrix, and the result is that the relative shift is mainly given by the difference in the screening effect of the residual interaction, as we have obtained in our simplified model. Due to the nearly rigid shift produced by the inert gas matrix in the opti-

cal spectra of clusters, we can conclude that the relative position and shape of the photoabsorption cross section corresponding to different sizes is an intrinsic feature of the clusters and not of the embedding matrix.²¹

V. CONCLUSIONS

We have studied the effect of dielectric matrices on the optical properties of embedded clusters. The dielectric matrix induces a modification of the cluster ground state, changing its electronic density and also the corresponding effective potential. However, for the optical properties, we have shown that the most important effect of the matrix is the direct screening of the electron-electron residual interaction; the modification coming from the previous changes in the cluster ground state is much less important. This screened interaction has been obtained by means of a solution to the Poisson equation for point charges, in the presence of the surrounding dielectric.

An analysis of two types of clusters has been presented. For potassium aggregates, once the effect of the dielectric has been taken into account, we obtain good agreement with the experimental values from EELS measurements with K clusters embedded in a matrix of MgO. The shifts induced by matrices of the rare gases Ar, Kr, and Xe on K clusters have also been calculated. As the dielectric constant of the matrix increases, the quantum size effects are less and less important, since the plasmon is almost independent of size already at $\epsilon = 3$. For small silver clusters, we have shown that the recently measured shifts induced by the previous rare-gas matrices are also well explained within our simple model.

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¹ W.A. de Heer, K. Selby, V. Kresin, J. Masui, M. Vollmer, A. Châtelain, and W.D. Knight, *Phys. Rev. Lett.* **59**, 1805 (1987); W.A. de Heer, W.D. Knight, M.Y. Chou, and M.L. Cohen, in *Solid State Physics: Advances in Research and Applications*, edited by H. Ehrenreich and D. Turnbull (Academic, Orlando, 1987), Vol. 40, p. 93.

² K. Selby, V. Kresin, J. Masui, M. Vollmer, A. Scheidemann, and W.D. Knight, *Z. Phys. D* **19**, 43 (1991), and references therein.

³ W. Ekardt, *Phys. Rev. Lett.* **52**, 1925 (1984); *Phys. Rev. B* **35**, 7325 (1987).

⁴ D. E. Beck, *Phys. Rev. B* **35**, 7325 (1987).

⁵ M.J. Puska, R.M. Nieminen, and M. Manninen, *Phys. Rev. B* **31**, 3486 (1985).

⁶ C. Yannouleas, R.A. Broglia, M. Brack, and P.F. Bortignon, *Phys. Rev. Lett.* **63**, 255 (1989).

⁷ A. Rubio, L.C. Balbás, and J.A. Alonso, *Phys. Rev. B* **45**, 13 657 (1992); **46**, 4891 (1992).

⁸ Ll. Serra, G.B. Bachelet, N. Van Giai, and E. Lipparini, *Phys. Rev. B* (to be published).

⁹ C. Bréchnignac, Ph. Cahuzac, F. Carlier, M. de Frutos, and J. Leygnier, *Z. Phys. D* **19**, 1 (1991), and references therein.

¹⁰ H. Fallgren and T.P. Martin, *Chem. Phys. Lett.* **168**, 233 (1989).

¹¹ J. Tiggesbäumker, L. Köller, H.O. Lutz, and K.H. Meiwes-Broer, *Chem. Phys. Lett.* **190**, 42 (1992); (unpublished).

¹² C. Bréchnignac, Ph. Cahuzac, N. Kebaïli, J. Leygnier, and A. Sarfati, *Phys. Rev. Lett.* **68**, 3916 (1992).

- ¹³ A. Rubio and Ll. Serra, *Z. Phys. D* **26**, 5118 (1993).
- ¹⁴ In the case of Li clusters the jellium approximation fails to describe the plasmon resonances, since their energies are overestimated by more than 30%. A pseudojellium model, which includes the effects of core electrons on the valence electrons, has recently proved to correctly explain the optical properties of these clusters (Ref. 8).
- ¹⁵ J.M. Pacheco and R.A. Broglia, *Phys. Rev. Lett.* **62**, 1400 (1989).
- ¹⁶ G.F. Bertsch and D. Tománek, *Phys. Rev. B* **40**, 2749 (1989).
- ¹⁷ Z. Penzar, W. Ekardt, and A. Rubio, *Phys. Rev. B* **42**, 5040 (1990).
- ¹⁸ S. Suto, K.D. Tsuei, E.W. Plummer, and E. Burstein, *Phys. Rev. Lett.* **63**, 2590 (1989); M. Rocca, M. Lazzarino, and U. Valbusa, *ibid.* **67**, 3197 (1991); **69**, 2122 (1992); G. Lee, P.T. Sprunger, E.W. Plummer, and S. Suto, *ibid.* **67**, 3198 (1991).
- ¹⁹ A. Liebsch, *Phys. Rev. Lett.* **71**, 145 (1993).
- ²⁰ J. Tiggesbäumker, L. Köller, K.H. Meiwes-Broer, and A. Liebsch, *Phys. Rev. A* **48**, 1749 (1993).
- ²¹ W. Harbich, S. Fredigo, and J. Buttet, *Chem. Phys. Lett.* **195**, 613 (1992); *Z. Phys. D* **26**, 138 (1993); S. Fredigo, W. Harbich, and J. Buttet, *Phys. Rev. B* **47**, 10706 (1993).
- ²² M. Vollmer, R. Weidenauer, W. Hoheisel, U. Schulte, and F. Träger, *Phys. Rev. B* **40**, 12509 (1989), and references therein.
- ²³ This interaction was obtained in a study of the electronic excitations of bubbles in metals by Ll. Serra, F. Garcias, J. Navarro, N. Barberan, M. Barranco, and M. Pi, *Phys. Rev. B* **46**, 9369 (1992). See Appendix A for the general expression of the Coulomb interaction in the presence of dielectrics.
- ²⁴ Ll. Serra and A. Rubio, *Z. Phys. D* **26**, 5122 (1993).
- ²⁵ U. Kreibig and L. Genzel, *Surf. Sci.* **156**, 678 (1985).
- ²⁶ K.P. Charlè, W. Schulze, and B. Winter, *Z. Phys. D* **12**, 471 (1989).
- ²⁷ A small contribution of the *d* electrons of silver to the main optical transition was obtained through a pseudopotential calculation that includes all the *d* electrons for the silver heptamer in Ref. 21. This preliminary calculation indicates that the observed transitions in the small cluster are dominated by *s-p* contributions, which explains the similar behavior of this small silver cluster to alkaline ones.
- ²⁸ M.J. Stott and E. Zaremba, *Phys. Rev. A* **21**, 12 (1980); A. Zangwill and P. Soven, *ibid.* **21**, 1561 (1980).
- ²⁹ W. Kohn and L.J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- ³⁰ *Theory of the Inhomogeneous Electron Gas*, edited by N.H. March and S. Lundqvist (Plenum Press, New York, 1983).
- ³¹ The constant density and radius are related to the Wigner-Seitz radius r_s , the number of atoms in the cluster Z , and of the valence electrons of each atom z_v by $n_0 = 4/4\pi r_s^3$ and $R = r_s(z_v Z)^{1/3}$. The electron-ion interaction inside the jellium sphere will be considered as in vacuum but a general dielectric interaction could be incorporated in the same way as for the surrounding matrix.
- ³² O. Gunnarsson and B.I. Lundqvist, *Phys. Rev. B* **13**, 4274 (1976).
- ³³ A. vom Felde, J. Fink, and W. Ekardt, *Phys. Rev. Lett.* **61**, 2249 (1988).
- ³⁴ MgO is an insulator with an energy band gap of ≈ 8 eV, thus for the energy involved in the study of the collective excitation the approximation of a constant macroscopic dielectric constant will be quite good. The approximate value for this dielectric constant is $\epsilon = 3$ (Ref. 33).
- ³⁵ A. Rubio, L.C. Balbás, Ll. Serra, and M. Barranco, *Phys. Rev. B* **40**, 10950 (1990).
- ³⁶ For small clusters the ratio of volume to surface is small and the response will be mainly dominated by the unscreened valence electrons. When the size increases, the inner part of the cluster will have a more bulklike behavior where the core *d* electrons will act as a polarizable dielectric medium, thus the surface plasmon resonance changes from the classical value to the *d*-screened value.
- ³⁷ M.E. Lin, R. Reinferberger, and R.P. Andres, *Phys. Rev. B* **46**, 15490 (1992); *Phys. Rev. Lett.* **67**, 477 (1991).