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Theoretical study of the photoabsorption spectrum of Na_8, Na_{20}, Cs_8, and $Cs_{10}O$ clusters

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We have used the spherically-averaged-pseudopotential model to study, within the time-dependent density-functional theory, the response to light of Na_8, Na_{20}, Cs_8, and $Cs_{10}O$ clusters. The influence of electronic and geometrical effects has been analyzed by comparing our results to experiment and with other available calculations. From this analysis we conclude (1) the position of the surface plasmon in the photoabsorption spectrum depends mainly on the cluster size; (2) the two-peak structure of the photoabsorption spectrum of Na_{20}, Cs_8, and $Cs_{10}O$ originates from the coupling of the collective mode (surface plasmon) with a particle-hole transition; (3) in the cases of Cs_8 and $Cs_{10}O$ the geometries which lead to agreement with experiment are such that Cs atoms are absent from the cluster center; and (4) the particle-hole transition responsible for the plasmon fragmentation in $Cs_{10}O$ involves a p-type electronic level with partial oxygen character, contrary to the picture of treating $Cs_{10}O$ as a system with only eight active electrons.

I. INTRODUCTION

Recent photodepletion spectroscopy experiments provide useful information on the response to light of Na_N ($N \leq 40$) clusters[1,2] and of Cs_8 and $Cs_{10}O$ clusters.[3] In these experiments the photoabsorption spectrum of a beam of clusters is obtained based on the fact that the clusters suffer fragmentation upon absorption of light and this leads to a deviation from the original direction of the molecular beam. Then the ratio between the number of clusters (of a given size) arriving at the detector with and without laser light excitation is proportional to the value of the absorption cross section. The physical process involved in the experiment is the excitation of a collective mode (surface plasmon) which for the case of sodium clusters, for instance, corresponds to an energy of about 3 eV. Since this energy is larger than the binding energy of an atom in the cluster (~ 1 eV), then the clusters cool down by evaporating neutral atoms. This evaporation occurs within the time of flight of the aggregate in the mass spectrometer.

A comparison with the theoretical calculations of the photoabsorption spectrum of these clusters sheds some light on their electronic and ionic distributions. *Ab initio* calculations are only possible for very small clusters.[4] For medium size or larger metal clusters, one of the traditional approaches to study the collective excitations of the valence electrons[5–8] is to use the spherical-jellium-background model and the time-dependent density-functional theory[9] with a local-density approximation of exchange and correlation effects (TDLDA). Another approach, also based on the spherical jellium model, employs the random-phase approximation[10–12] (RPA) and gives similar results. Considering as a typical example the cases of Na_8 and Na_{20}, photoabsorption experiments[2] give the energy of the Mie resonance[13] (or surface plasmon) of these closed shell clusters at ≈ 2.5 eV, which is substantially smaller than the classical value of 3.4 eV. On the other hand, the TDLDA photoabsorption cross sections of these two clusters, calculated within the spherical-jellium-background model, show Mie plasmon peaks around 2.8–2.9 eV. While this result shifts the classical value in the correct direction, these energies are still larger than the observed values. Also, due to their finite size, the clusters can exhibit an interplay between collective and single particle-hole excitations, giving rise to a fragmentation of the strength of the collective mode. This is the so-called Landau damping and it has been observed experimentaly in clusters such as Na_{20}, Cs_8, and $Cs_{10}O$, which show an additional peak near the plasmon resonance. In other clusters such as Na_{40},[11] the fragmentation is so strong that it is no longer possible to identify a clear collective mode. Those fragmentation processes are beyond classical (or semiclassical) methods that predict only the collective mode, and need a full quantum-mechanical description of the electrons. Let us also say that jellium model calculations are not able to reproduce the fragmentation pattern of Cs_8 and $Cs_{10}O$.[12]

The discrepancies between theory and experiment for these and other more complicated clusters can be ascribed to two different sources. One of them is the use of the local-density description of exchange and correlation effects. Steps to improve the LDA description have already been undertaken. Time-dependent density-functional theory with self-interaction corrections has been used by Saito, Bertsch, and Tománek[8] and by Pacheco and Ekardt.[14] The nonlocal weighted-density approximation has been used by us in a previous paper.[15] Finally, Guet and Johnson[16] have used an RPA description based on an exact treatment of exchange effects, although neglecting correlation. All these works give results which are an improvement with respect to the LDA. However, the ionic background was still described by the spherical jellium model.

The second source of discrepancy between theory and experiment is the spherical jellium description of the ionic background. Global shape deformations with respect to the spherical shape have been taken into account by an spheroidal jellium model.[17] In their RPA study of the optical absorption spectra of Na_8, Cs_8, and $Cs_{10}O$, Yannouleas and Broglia[12] have found that an *ad hoc* modification of the jellium potential (while still maintaining the spherical symmetry) was required to obtain agreement between the calculated and experimental positions of the surface plasmon and fragmentation peaks. The essence of this modification was that the potential is made less attractive in the inner region of the cluster. The motivation for this change of the potential was that calculations for the structure of Na_8, taking into account the granularity of the ionic background, indicate a depletion of the atom population on the cluster center.[4,18] The work of Yannouleas and Broglia demonstrates that a description of the cluster background beyond the jellium model is required for an accurate calculation of the photoabsorption spectrum. Since *ab initio* methods are only practical for small clusters, other intermediate methods specially devised to take into account the geometry in larger clusters are of upmost interest in this context.

In this paper we use the spherical-average-pseudopotential (SAPS) model and the TDLDA to investigate the photoabsorption spectra of Na_8, Na_{20}, Cs_8, and $Cs_{10}O$. Although the SAPS model is not an *ab initio* method it takes into account, to some extent, the granular character of the ionic background. This allows us to investigate the influence of the geometry of the cluster on the photoabsorption spectrum. The layout of the paper is as follows. In Sec. II we present a brief account of the SAPS model and of the geometries obtained for the clusters of interest here. Results obtained for the photoabsorption spectrum using the TDLDA method are presented in Sec. III, and a summary of our conclusions is offered in Sec. IV.

II. SAPS MODEL AND CLUSTER GEOMETRIES

In the SAPS model[18] the geometrical structure (and, of course, also the ground-state electronic structure) of a cluster is obtained by minimizing the total energy E_T with respect to the positions of all the ions. E_T can be written

$$E_T = E[\rho] + E_{\text{ion-ion}}, \tag{1}$$

where $E[\rho]$ is the energy of the valence electrons in the field created by the ionic background, and the second term gives the ion-ion interaction energy. The electronic energy $E[\rho]$ for a given configuration $(\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N)$ of the ions is obtained in the standard way[19,20] from the electron density $\rho(\mathbf{r})$

$$\rho(\mathbf{r}) = \sum_{i=1}^{\text{occ}} |\psi_i(\mathbf{r})|^2, \tag{2}$$

calculated by self-consistently solving the Kohn-Sham equations of the density-functional formalism[19,20] (Hartree atomic units are used unless explicitly stated)

$$\{-\tfrac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r})\}\psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}). \tag{3}$$

$V_{\text{eff}}(\mathbf{r})$ is the effective potential felt by the valence electrons. In the SAPS model this effective potential is expressed

$$V_{\text{eff}}(\mathbf{r}) = V_H(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) + V_{\text{ion}}^{\text{SAPS}}(r). \tag{4}$$

Here V_H is the electrostatic Hartree potential, V_{xc} is the exchange-correlation potential (in the local-density approximation), and $V_{\text{ion}}^{\text{SAPS}}$ is constructed by first forming the total ionic potential

$$V_{\text{ion}}(\mathbf{r}) = \sum_{j}^{N} V_{ps}(\mathbf{r} - \mathbf{R}_j), \tag{5}$$

and then calculating the spherical average $V_{\text{ion}}^{\text{SAPS}}(r)$ of $V_{\text{ion}}(\mathbf{r})$ around the center of mass of the cluster. On the other hand, the ion-ion interaction energy is evaluated as a pointlike interaction between the ions and consequently it takes precise account of the geometry. For the electron-ion pseudopotential V_{ps}, we have taken a pseudopotential used before by Manninen.[21] This is the electrostatic potential of a homogeneously charged sphere of radius r_c. Our criterion for choosing r_c has been to reproduce the eigenvalue of the valence electron of the free atom obtained in an all-electron LDA calculation. In this way we have obtained r_c=4 a.u. for Na and r_c=5.1 a.u. for Cs. The reader can consult Ref. 18 for further details of the SAPS model.

Using a steepest-descent method, the equilibrium geometries obtained for Na_8 and Cs_8 are both of the D_{4d} symmetry (square antiprism; see Fig. 1) as in the three-dimensional calculations of Manninen.[21] For Na_{20} the calculated geometry is the same as that reported by Mañanes *et al.*,[22] namely, a surface shell of 18 atoms enclosing two inner atoms (see Fig. 2). Finally, for $Cs_{10}O$, instead of calculating the ground-state geometry by an energy optimization, we assume the geometry reported previously by Mañanes *et al.* using an empty-core pseudopotential.[23] This geometry, shown in Fig. 3, is a square pyramid formed by five Cs atoms, with each of their five faces capped by one Cs atom. The oxygen atom is at the center of the pyramid. The spherical average of the potential is not a drastic approximation for the clus-

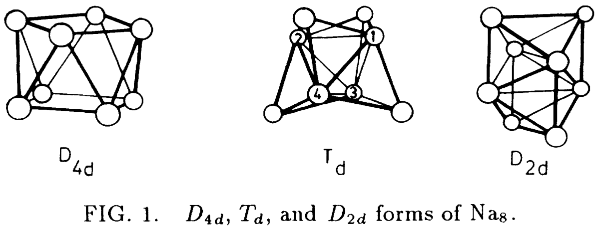

FIG. 1. D_{4d}, T_d, and D_{2d} forms of Na_8.

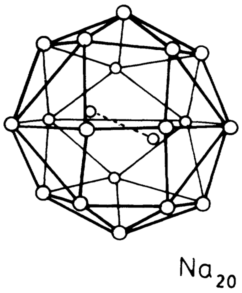

FIG. 2. SAPS geometry for Na_{20}.

ters under study (Na_8, Na_{20}, Cs_8, $Cs_{10}O$) because these clusters have closed electronic shells.

Let us first comment on the SAPS geometries by comparing those with the results of other available calculations. The ground-state geometry of Na_8 obtained by *ab initio* configuration interaction (CI) methods[4] is of T_d symmetry (tetracapped tetrahedron; see Fig. 1), and can be viewed as formed by two atomic shells, each shell containing four atoms: the first shell is formed by the atoms labeled 1–4 in Fig. 1, and the second shell is formed by the remaining four atoms. An atomic arrangement of two shells, corresponding, however, to a D_{2d} symmetry (dodecahedron; see Fig. 1), has been obtained by Röthlisberger and Andreoni[24] as the ground state of Na_8 using the Car-Parrinello (CP) method.[25] In this CP calculation the T_d structure is a low-lying local energy minimum, and the D_{4d} structure is another local minimum with energy in between D_{2d} and T_d. The energy differences between the CP local minima are so small that the question of what is the ground-state geometry of Na_8 is still open, and in practice one can expect the clusters to fluctuate easily between those structures. A CI calculation[4] for the D_{4d} structure (in which the atoms are arranged forming one shell, leaving the cluster center empty) leads to an equilibrium shell radius of about 5.71 a.u. This indicates that the interatomic distances are reduced by about 15% with respect to the first-neighbor distances in bulk sodium (a similar contraction was observed for the T_d form). The SAPS calculation gives an equilibrium shell radius of 5.24 a.u. for the D_{4d} cluster which is ~ 10% lower than the CI shell radius. The further reduction of interatomic distances obtained in the SAPS method with respect to CI may be due to the LDA description of the exchange-correlation potential, which, being of shorter range than the correct one, tends to compress the electronic density and the corresponding distribution of ions. This conclusion is supported by the observation that the interatomic distances in neutral sodium clusters obtained by CI calculations[26] are systematically larger than the corresponding distances obtained by the LDA calculations of Martins, Buttet, and Car[27] and Röthlisberger and Andreoni.[24] Consequently, we expect similar contracted interatomic distances in our SAPS calculations for Cs_8, Na_{20}, and $Cs_{10}O$.

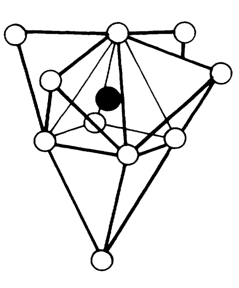

FIG. 3. SAPS geometry for $Cs_{10}O$ (Ref. 23).

The ground-state geometry of Na_{20} obtained by the CP method[24] is rather compact, and can be viewed as formed by four parallel planes containing one, six, eight, and five atoms, respectively. The SAPS geometry (see Fig. 2) is formed by five parallel planes containing one, five, eight, five, and one atoms, respectively. This geometry is very similar to that of a CP local minimum essentially degenerate with the CP ground state and also structurally rather similar to the CP ground state.[24] Furthermore, the CP energy hypersurface of this cluster is rather flat around the absolute energy minimum.[28] Finally, we are not aware of calculations for Cs_8 and $Cs_{10}O$ to which our SAPS geometries could be compared.

III. TDLDA CALCULATION OF THE PHOTOABSORPTION SPECTRUM

The dynamical screening properties of the metallic clusters can be studied using the time-dependent density-functional theory in the local-density approximation (TDLDA),[6,9] in which the time-independent one-particle susceptibility χ_0 is constructed via the eigenvalues ϵ_i, the wave functions ψ_i, and the retarded one-electron Green's function G, of the self-consistent effective potential of the ground-state Kohn-Sham calculation. This susceptibility reads as follows:[6,9]

$$\chi_0(\mathbf{r}_1,\mathbf{r}_2,\omega)=\sum_{i=1}^{\mathrm{occ}}\{\,\psi_i^*(\mathbf{r}_1)\psi_i(\mathbf{r}_2)G(\mathbf{r}_1,\mathbf{r}_2,\epsilon_i+\omega)+\psi_i(\mathbf{r}_1)\psi_i^*(\mathbf{r}_2)G^*(\mathbf{r}_1,\mathbf{r}_2,\epsilon_i-\omega)\}. \tag{6}$$

The susceptibility for the interacting electrons, χ, is obtained from χ_0 and the functional derivative of the effective potential, $K(\mathbf{r}_1,\mathbf{r}_2)=\delta V_{\mathrm{eff}}(\mathbf{r}_1)/\delta\rho(\mathbf{r}_2)$,[29] by solving the Dyson-type integral equation,

$$\chi(\mathbf{r}_1,\mathbf{r}_2,\omega)=\chi_0(\mathbf{r}_1,\mathbf{r}_2,\omega)+\int\chi_0(\mathbf{r}_1,\mathbf{r}_3,\omega)K(\mathbf{r}_3,\mathbf{r}_4)\times\chi(\mathbf{r}_4,\mathbf{r}_2,\omega)d\mathbf{r}_3d\mathbf{r}_4. \tag{7}$$

Due to the spherical symmetry of the electron density of our systems these equations can be reduced using an angular momentum representation of the electronic susceptibility χ. In that way, for the dipolar photoabsorption cross section we need only to calculate the $\chi_{l=1}$ component.[6]

We have obtained the photoabsorption spectrum of Na_8, Na_{20}, Cs_8, and $Cs_{10}O$ using the TDLDA and the SAPS approximation for the effective potential acting on the valence electrons. The influence of the geometry and of the ionic pseudopotential (namely, the value of the parameter r_c) has been investigated. Some preliminary results for Na_8 and Cs_8 have been presented in Ref. 30. In addition, we would like to stress that, in the case of $Cs_{10}O$, the core electrons of the oxygen atom are also explicitly included in the calculations.

Photodepletion experiments[1,2] for Na_8 show a resonance peak at 2.53 eV (with a width Γ=0.19 eV), which has been attributed[1,4] to vibrational sampling of the positions and oscillator strengths of optically allowed transitions from the T_d, D_{2d}, and D_{4d} isomers (see Fig. 1). Using the spherical jellium model within the TDLDA approach, we have obtained a surface plasmon peak at 2.92 eV, whereas the recent RPA calculation of Yannouleas and Broglia[12], based on an *ad hoc* modification of the jellium potential, yields a plasmon peak near the observed position. The argument used in Ref. 12 to modify the jellium potential was that the distribution of atoms in Na_8 obtained from both CI (Ref. 4) and SAPS (Ref. 18) calculations exhibits a depletion of the atom population in the inner region of the cluster, leading to a less attractive potential than that of the jellium model in that region. Assuming first the T_d and D_{4d} geometries for Na_8 with the interatomic distances given by the CI calculations, we have constructed for each isomer the associated spherical average of the total ionic potential (using the pseudopotential of Manninen with r_c=4 a.u.) and we have calculated the corresponding ground-state electronic structures. Then we have obtained the TDLDA photoabsorption cross sections shown in Fig. 4. For each geometry there is one plasmon peak, located at 2.52 eV (T_d) and 2.54 eV (D_{4d}), respectively (the experimental peak is at 2.53 eV). The lines are not δ functions because we have used, for numerical convenience, a complex photon frequency $\omega + i\epsilon$ with ϵ = 0.01 eV. The positions of these peaks are in good agreement with the energy of optically allowed transitions of the CI calculations.[4] For the D_{4d} form with interatomic distances given by the SAPS calculation (i.e., one shell of atoms with radius 5.24 a.u.) we obtain a surface plasmon at 2.75 eV. We then conclude that for each geometry the position of the surface plasmon line is determined by the size of the cluster.

This conclusion is also valid for the other clusters studied in this paper. For Na_{20}, for example, by increasing by 10% the radius of our SAPS geometry (to correct for the LDA error), we obtain two resonance frecuencies at 2.42 and 2.72 eV, in very good agreement with the experimental peaks (2.42 eV, Γ=0.2 eV and 2.78 eV, Γ=0.4 eV, respectively).[1] These results are given in Fig. 5 where we show the TDLDA photoabsorption cross sections for Na_{20} for three different ionic-background models: jellium (curve *A*), the original SAPS geometry (curve *B*), and the SAPS geometry with expanded interatomic distances (curve *C*). The positions of the experimental resonances are indicated by vertical lines. Previous TDLDA (Ref. 6) and RPA (Refs. 10 and 11) calculations using the jellium model attribute the two-peak structure to the fragmentation of the oscillator strength of the surface plasmon due to the proximity of a particle-hole (*p-h*) transition ($2s \rightarrow 3p$).[31] The fragmentation that we have obtained is due precisely to this reason.

We have seen above for Na_8 that different geometries with a similar overall size (like the T_d and D_{4d} forms with interatomic distances from *ab initio* CI calculations) lead to similar results for the position of the plasmon line. However, the one-particle transition energies can be instead very different. These facts are important in the case of Cs_8 because the fragmentation peak (1.48 eV, Γ=0.04 eV) observed near the surface plasmon line (1.55 eV, Γ=0.04 eV) has been proposed to be related to the $1p \rightarrow 2s$ one-particle transition.[3,12] For jelliumlike Cs_8 we have obtained, within the TDLDA approach, a surface plasmon peak at 1.79 eV, but not the fragmentation feature, whereas the RPA calculation of Yannouleas and Broglia[12] using a modified jellium potential yields two peaks at 1.39 and 1.32 eV, respectively (i.e., shifted by 0.16 eV with respect to the experimental ones). The

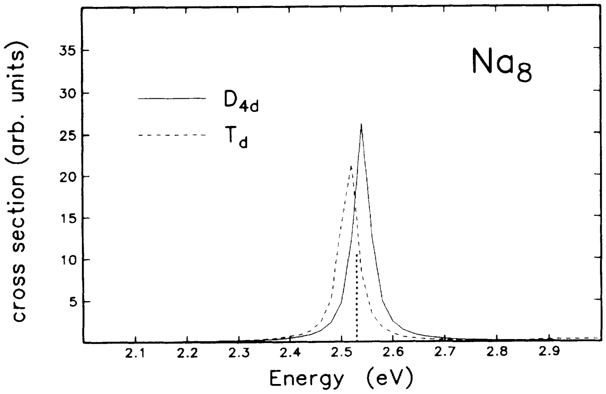

FIG. 4. Calculated photoabsorption cross sections for the D_{4d} and T_d forms of Na_8. The position of the experimental peak (Refs. 1 and 2) is indicated by the vertical dotted line.

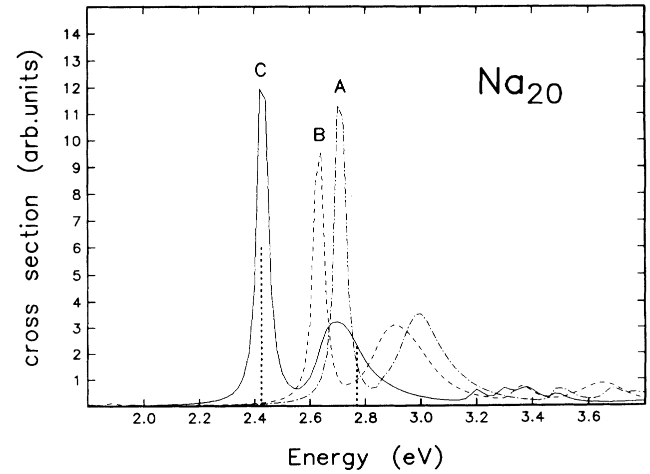

FIG. 5. Na_{20} photoabsorption cross section calculated from different models: jellium (curve *A*); SAPS ground-state geometry (curve *B*); same as *B* but with a cluster radius increased by 10% (curve *C*). The experimental resonance positions (Ref. 1) are indicated by the two vertical dotted lines.

peaks in the spectrum of Cs_8 were interpreted by Yannouleas and Broglia[12] as a surface plasmon and a fragmentation of the plasmon due to the coupling to single-particle transitions (mainly $1p \rightarrow 2s$). The TDLDA photoabsorption spectrum of Cs_8 with the D_{4d} geometry (see Fig. 1) and interatomic distances obtained in the SAPS calculation (that is, a cluster radius of 7.06 a.u.) shows a surface plasmon at 1.93 eV but fragmentation does not occur. If we increase the interatomic distances (preserving the D_{4d} geometry) up to a value close to the first-neighbor distances in bulk cesium, the surface-plasmon line moves towards the experimental position and we obtain the expected fragmentation peak. Nevertheless, we cannot obtain simultaneously both peaks at their experimental positions by simply changing the cluster radius. In Fig. 6 we show the TDLDA photoabsorption cross sections of Cs_8 obtained for the D_{4d} geometry with different values of the interatomic distances and different values of the pseudopotential parameter r_c. Curve A corresponds to a cluster radius of 9.76 a.u. and r_c=5.1 a.u. The results of curve A are similar to those obtained in Ref. 12. By increasing the cluster radius to 10.39 a.u. (curve B) the plasmon line moves to the red as expected, but the fragmentation peak remains around the same value as in curve A. However, in order to obtain both the plasmon line and the fragmentation peak close enough to the experimental positions we need to use a cluster radius of 9.09 a.u. and to decrease the pseudopotential parameter r_c up to a value 4.6 a.u. In this way we obtain curve C of Fig. 6 in very good agreement with experiment.[3] The interatomic distances for this cluster radius are about 10% smaller than the first-neighbor distances in bulk cesium. For a given cluster size, the effect of reducing the value of r_c (more attractive pseudopotential) is that the one-particle transition energies become higher. Although, the value r_c=4.6 a.u. remains as an empirical value for Cs, we stress that the same value of r_c is appropriate to explain the photodepletion experiments[3] for $Cs_{10}O$ (see below).

For the T_d geometry (i.e., a configuration with two atomic shells), it was not possible to obtain the surface plasmon and the associated fragmentation peak of Cs_8 simultaneously at the experimental positions. For example, taking radii of 9 and 12.8 a.u. for the two shells, respectively, we obtain the plasmon at 1.12 eV and the fragmentation peak at 1.08 eV. By increasing both radii the positions of the peaks move to lower energies as expected. Finally, as the shell radii decreases the fragmentation disappears because the $1p \rightarrow 2s$ and $1p \rightarrow 1d$ transition energies move far away from the plasmon line. These results suggest a geometry for Cs_8 with only one atomic shell, such that the inner region of the cluster is empty, in agreement with the conclusions of Ref. 12. The position of the surface-plasmon line depends primarily on the size of the cluster, as in the cases of Na_8 and Na_{20} discussed above.

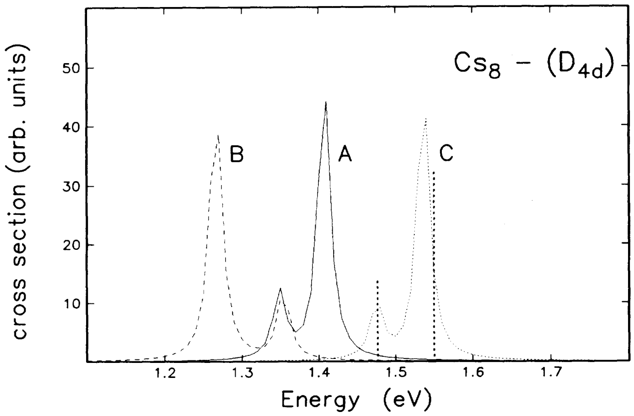

FIG. 6. Calculated photoabsorption spectrum of Cs_8 with D_{4d} geometry. Curves A, B, and C correspond to different values of the cluster radius and pseudopotential parameter (see text). Experimental resonance positions (Ref. 3) are indicated by vertical dotted lines.

In Fig. 7 we show the total effective potential corresponding to curve C of Fig. 6. The effective potential of the spherical jellium model has also been drawn for comparison. The SAPS potential for the D_{4d} structure is substantially less atractive than the jellium potential in the inner region of the cluster. This result, and the fact that the D_{4d} structure is the one that leads to agreement with the experimental photoabsorption cross section, serves to justify the *ad hoc* modification of the jellium potential by Yannouleas and Broglia[12] as qualitatively correct.

Two resonance frequencies, at 1.39 eV (Γ=0.09 eV) and 1.54 eV (Γ=0.07 eV), respectively, have been observed[3] for $Cs_{10}O$. In Fig. 8 we present the results of a TDLDA calculation of the photoabsorption cross section of this cluster with the geometry predicted by a SAPS calculation.[23] This geometry, given in Fig. 3, is a square pyramid capped in all its five faces, and with the oxygen atom at the cluster center. It can be considered as two Cs shells, each formed by five atoms, surrounding the central atom. The radii of these two shells are 5.5 and 10 a.u., respectively.[32] The TDLDA calculation uses again Manninen's pseudopotential for Cs with r_c=4.6 a.u.; on the other hand, all eight electrons of the oxygen atom are included in the calculation. Panel a of Fig. 8 is obtained for the interatomic distances (or shell radii) of the SAPS calculation of Ref. 23. In panels b and c the cluster

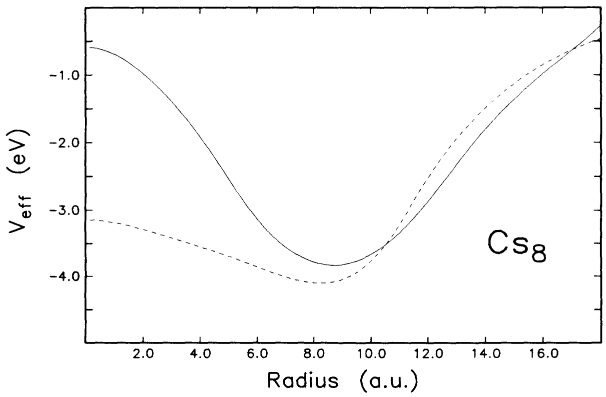

FIG. 7. Effective potential for Cs_8. Dashed line: jellium model. Continuous line: SAPS model for D_{4d} geometry.

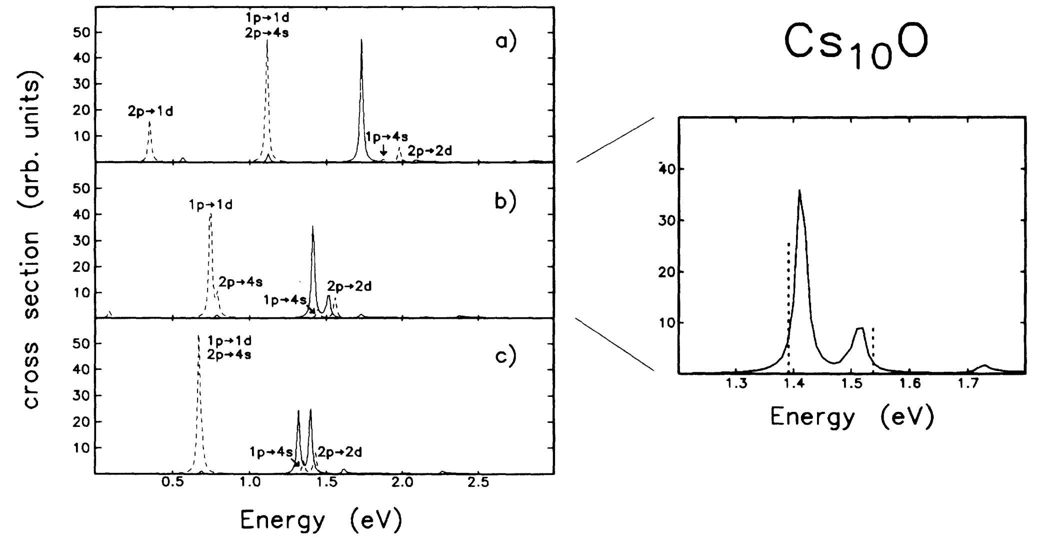

FIG. 8. Calculated photoabsorption spectrum (continuous lines) of $Cs_{10}O$. (a), (b), and (c) correspond to different interatomic distances (see text), although the cluster geometry is the same in the three cases (that of Fig. 3). The most probable particle-hole transitions are indicated by broken lines. The expanded inset gives a comparison of the results of (b) and the positions of the experimental resonances (Ref. 3) (vertical dotted lines).

size (or shell radius) has been enlarged by 15% and 20%, respectively. We have also indicated in the figure the most probable one-electron transitions between the occupied ($1s^2\ 2s^2\ 1p^6\ 3s^2\ 2p^6$) and unoccupied levels. The $1s$ and $2s$ are oxygen core levels, which are unaffected by an increase of the cluster radius; their eigenvalues remain around −501 eV ($1s$) and −16 eV ($2s$). Electrons in these levels are inert for the energy range of excitations considered here (up to 3 eV). The $1p^6$ and $3s^2$ levels are practically degenerate, forming a kind of mixed oxygen-cesium band at ≈ -3 eV. These electrons can actively contribute to the photoabsorption spectrum; finally, the external $2p^6$ electrons are bound at −2 eV. From the results plotted in the figure we can observe the following.

(1) The energies of the particle-hole transitions from the mixed $1p^6 3s^2$ band depend sensitively on the cluster size. For example, the energy of the $1p \rightarrow 4s$ transition, which is the most important one to explain the plasmon fragmentation, changes with cluster size due to the change in the energy of the $1p$ level: this energy is −2.84, −2.34, and −2.29 eV for cases (a), (b), and (c), respectively of Fig. 8. The change of energy of this electronic level can be understood from the spatial location of its wave function, which is influenced by the position of the inner shell of Cs atoms surrounding the oxygen impurity. Notice that in case (a), for which the $1p$ binding energy is largest, the interatomic distances minimize the cluster energy in the original SAPS calculation. The energy of the unoccupied $4s$ level, on the other hand, changes very little because the $4s$ electrons are located in the outermost part of the cluster and these are less sensitive to internal atomic rearrangements.

(2) Although, in both Cs_8 and $Cs_{10}O$ the most important p-h transition involves an initial state of p character and a final state of s character, a crucial difference is that in Cs_8 this p level is the most externally occupied p level of the cluster (actually, the only occupied p level), whereas in $Cs_{10}O$ this active p level is not the most external one ($2p$) but the internal $1p$ level with mixed oxygen-cesium character. In other words, it is not enough to consider $Cs_{10}O$ as a cluster with eight active valence electrons. The modified jellium calculation of Yannouleas and Broglia[12] accounted for the different effective potential seen by the eight valence electrons in Cs_8 and $Cs_{10}O$ but did not consider the p electrons of the oxygen atom as active ones. Yannouleas and Broglia obtained the fragmentation of the surface plasmon, which they attributed to a p-h transition involving the valence p levels, but a difference of 0.18 eV remained between the position of the theoretical and experimental peaks. This difference does not occur in our calculation due to the different active p level involved in the particle-hole transition responsible for the fragmentation.

(3) The position of the surface-plasmon line moves towards lower energies by increasing the cluster radius, as in the cases of Na_8, Na_{20}, and Cs_8 studied above. This conclusion supports the qualitative expectation from the classical Mie theory[13] for the resonance frequency of a metallic sphere.

(4) The best agreement with experiment is obtained in Fig. 8(b) (see inset). The energy separation between the peaks fits in the experimental error bars. By including the thermal effects that contribute to the width of the resonances,[33,34] our calculated spectrum should become smooth and closer to the experimental shape.

IV. CONCLUSIONS

To summarize, we have studied the TDLDA photoabsorption spectrum of Na_8, Na_{20}, Cs_8, and $Cs_{10}O$ clusters using a SAPS description of the effective potential. The fragmentation of the spectrum in Na_{20}, Cs_8, and $Cs_{10}O$ is mainly due to the interaction of the plasmon resonance with a particle-hole transition. Geometrical effects are important for the correct position of this *p-h* line: Cs atoms are absent from the cluster center in both Cs_8 and $Cs_{10}O$ cases. Also important is that, in $Cs_{10}O$, the *p-h* transition responsible for the fragmentation peak involves an internal *p* level with mixed oxygen-cesium character. This result is contrary to the picture which treats $Cs_{10}O$ as an effective eight-electron system. It should be stressed that, in order to achieve quantitative agreement with the experiments, we had to increase the interatomic distances (or the cluster radii) a little with respect to the distances obtained in the original SAPS calculation (although in all the cases the optimized interatomic distances are lower than the first-neighbor distances in the corresponding bulk metal). This increase of interatomic distances is, in a sense, an effective way to correct for the well-known deficiency of the LDA, which underestimates interatomic separations. The value r_c=4.6 a.u. used for the Cs pseudopotential parameter remains empirical, but this value is consistent in the sense that the same value works for both Cs_8 and $Cs_{10}O$ clusters.

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