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Theoretical study of the photoabsorption spectrum of small chromium clusters

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The photoabsorption spectra of Cr_N ($N=2-11$) clusters have been calculated using the time-dependent density functional theory. Different approximations for exchange and correlation lead to a similar picture for the spectra. Small chromium clusters show a dimerization effect that controls the initial growth of the clusters up to $N=11$. This effect consists in the formation of robust Cr_2 dimers with a strong bond and an unusually short bond length. The dimerization effect becomes reflected in the high-energy part of the absorption spectra: An excitation peak appears at energies near 20 eV, and its intensity increases each time a new Cr dimer forms in the structure as the cluster grows. However, experimental detection of this effect will be hard because of the competition from ionization.

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I. INTRODUCTION

Transition metal clusters exhibit unusual physical and chemical behavior,[1–4] for instance, unexpected magnetic properties and catalytic activity, two important features from both the scientific and the technological points of view. In particular, the small-sized aggregates of chromium show features that make them special compared to other 3*d* transition metal clusters.

A free chromium atom has a $3d^5 4s^1$ electronic structure with six unpaired valence electrons. This electronic configuration with half-filled 3*d* and 4*s* shells leads to a strong sextuple bond in Cr_2, arising from the filling up of the 3*d*-bonding molecular orbitals: $\sigma_{3d}^2\pi_{3d}^4\delta_{3d}^4\sigma_{4s}^2$. The dimer has an unusually short bond length of 1.68 Å,[5–7] compared to 2.50 Å in the body-centered-cubic (bcc) structure of the metal.[8] This short bond length was first measured in a flash photolysis experiment[5] and was confirmed later by other experiments[6] and by *ab initio*[7] and density functional calculations.[9] The electronic structure of the dimer is extremely robust and controls the growth of small Cr_N clusters up to $N=11$: all those clusters are formed by Cr_2 dimers with a short bond length and one isolated Cr atom (in Cr_3, Cr_5, Cr_7, and Cr_9), two (in Cr_{10}) or three isolated Cr atoms (in Cr_{11}) bonded to adjacent dimers. The intradimer bonds are strong, and the interdimer bonding is weak.[9] This growth pattern stops at Cr_{12}, where the Cr-Cr distances suddenly become larger and the dimerization effect vanishes, leading to a transition from dimer growth to bcc-like structures. It is expected that this kind of growth pattern becomes reflected as an odd-even effect in the properties of Cr_N clusters while the dimerization channel is active, up to $N=11$. Indeed, even-odd oscillations have been observed in the calculated magnetic moments per atom,[9] in the measured dissociation energies,[10] in the features of the photoelectron spectra measured for Cr_N^- anionic clusters,[11] and in the bonding of deuterium atoms to cationic Cr_N^+ clusters.[12]

To our knowledge, spectroscopic information is available for the dimer,[7] but not for larger Cr clusters. In this paper, we present a theoretical study of the photoabsorption spectrum of Cr_N clusters, from Cr_2 up to Cr_{11}, using the time-dependent density functional theory[13–15] (TDDFT) to treat the electronic excitations. The lack of information for those clusters is the main motivation for this work. In addition, we would like to investigate if the dimerization effect has measurable consequences on the shape of the photoabsorption spectra.

II. METHOD

Prior to the calculation of the photoabsorption spectrum, we need to determine the lowest-energy geometrical structure of each cluster. For this purpose, we use the density functional theory.[16] The ion-electron interaction is modeled by replacing the ionic cores ($1s^2 2s^2 2p^6 3s^2 3p^6$ argon-like core) by pseudopotentials within the scheme of Hartwigsen *et al.*,[17] previously validated for transition elements in pure and organometallic clusters.[18,19] This pseudopotential is built in such a way that is separable by construction, is highly accurate, and has an analytical form that can be specified by a small number of parameters. For exchange and correlation (xc) effects, we have used the local spin-density approximation (LSDA).[20]

We took, as initial geometries for the structural optimization of the Cr_N clusters, the structures previously obtained by Cheng and Wang.[9] Starting from those geometries, we performed structural relaxations by making use of the Broyden algorithm[21] with a convergence criterion of 10^{-4} hartree/bohr in the forces on every atom. The structural relaxations, performed with the ABINIT package,[22] did not produce significant variations with respect to the original structures. The geometries obtained, which are then used in the calculations of the photoabsorption spectra, are shown in Fig. 1. Several tests performed with generalized gradient (GGA) functionals for exchange and correlation led to practically identical optimized geometries.

Once the ground-state structures of the different clusters were established, we performed the calculation of the excitation spectra. For this purpose, we have used TDDFT, implemented in the real space code OCTOPUS.[23] The theoretical foundations underlying the TDDFT calculations, as well as the computational scheme, have been presented

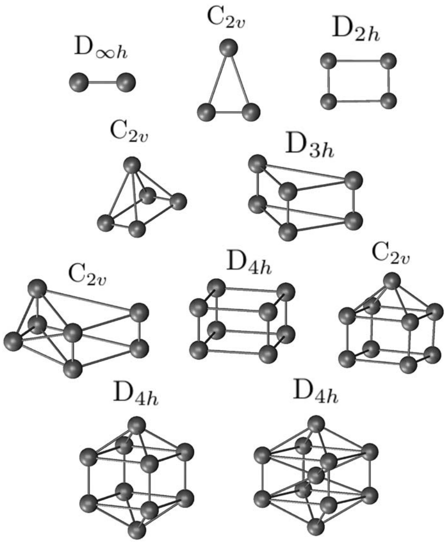

FIG. 1. Optimized structures of Cr_N clusters up to $N=11$. The symmetry group is indicated in each case. All clusters are formed by Cr_2 dimers with a short bond length of 1.7 Å, and one (in Cr_3, Cr_5, Cr_7, and Cr_9), two (in Cr_{10}), or three (in Cr_{11}) isolated atoms bonded to adjacent dimers.

elsewhere,[23–26] and here we only summarize the main points. The photoabsorption spectrum is calculated by using the formalism developed by Casida.[24,27] Application of this technique to obtain the oscillator strengths requires a previous calculation of the ground-state electronic structure, that is, the occupied electronic states, and also the unoccupied states. Thirty unoccupied states for each spin channel have been necessary to reach convergence of the excitation spectra. After that, each excitation peak is broadened by a Lorentzian profile to give the photoabsorption cross section

$$\sigma_{\text{abs}}(\epsilon) = \sum_{\epsilon_i} \frac{A^2}{(\epsilon - \epsilon_i)^2 + A^2}. \tag{1}$$

In this equation, ϵ is the energy, ϵ_i are the discrete excitation energies obtained by the Casida method, and the value of the parameter A determines the full width at half maximum. The values of A will be indicated below.

We have performed the calculations of the photoabsorption spectrum with the adiabatic LSDA using the Perdew-Wang parametrization[20] of electronic correlation. The adiabatic LSDA has been used successfully in the calculation of the optical spectrum of atoms and clusters.[18,19,28–34] In the case of free atoms, the energies for one-particle low-energy excitations agree with experiment to within 5%–10%.[30] For clusters of *s*-*p* metals, the errors in the position of the absorption peaks are usually in the 0.1–0.2 eV range,[30–32] and the results are also very reasonable for carbon and BN clusters,[33,34] transition metal clusters,[19] and organometallic clusters,[18] even in the high-energy range. From a comparison between the photoabsorption spectrum of fullerenelike boron nitride clusters obtained with local-density approximation (LDA) and generalized gradient functionals (the GGA functional of Perdew *et al.*[35]), Koponen *et al.*[34] concluded that the LDA performs much better in the TDDFT, compared to static DFT.

The calculation of excitations in finite systems using the LDA has been sometimes criticized because the exchange-correlation potential of the LDA does not show the correct asymptotic behavior[25] (the same occurs for the usual GGAs). However, the good results mentioned above and the arguments given by Vasiliev *et al.*[30] indicate that the wrong asymptotic behavior of the LDA potential is not as important for the excited-state properties as previously thought. A study of the electronic excitations in free atoms by Wasserman *et al.*[36] confirms this point: Some high lying excitations may be shifted to the continuum, but their frequency and oscillator strength remain quite accurate. We have additionally checked the LDA by comparison with two functionals giving potentials with improved asymptotic behavior: The LSDA with the self-interaction correction (SIC) of Perdew-Zunger[37] and the van Leeuwen–Baerends (LB94) GGA functional.[38]

The SIC-LDA exchange functional belongs to the class of orbital-dependent functionals $E_{xc}[\varphi_1(\mathbf{r}), \ldots, \varphi_N(\mathbf{r})]$. These lie outside the usual Kohn-Sham scheme, because they lead to orbital-dependent potentials. However, the orbital-dependent functionals can be recast into a Kohn-Sham scheme by using the optimized effective potential (OEP) method,[39] in which a common local, multiplicative potential $v_{xc}^{OEP}(\mathbf{r})$ is obtained by solving an integral equation. The solution of this integral equation is very involved, and the usual alternative is to perform the approximation of Krieger-Li-Iafrate[40] (KLI), which transforms the hard task of solving the integral equation into the simpler one of solving a small set of linear equations. This KLI method is the one we have used to calculate the ground-state electronic structure. In a second step, the corresponding occupied and unoccupied single-particle states are used in the Casida method with the adiabatic LDA exchange-correlation kernel. Although not entirely consistent, this is common practice, because the use of a better kernel does not affect much the results as long as the single-particle orbitals have been calculated with a good static $v_{xc}(\mathbf{r})$ potential, like the OEP potential. In a similar way, in the calculations with the LB94 functional, this GGA functional is used to obtain the single-particle orbitals and energies of the ground state, and the LDA kernel is used in the calculation of the excitations.

III. RESULTS AND DISCUSSION

Figure 1 shows the calculated lowest-energy structures of small Cr_N clusters with $N=2-11$. A dimer-growth pattern is clearly seen for these structures up to Cr_{11}. Clusters with even number of atoms up to Cr_8 are simply made of dimers stacked together, while the odd clusters up to Cr_9 consist of dimers and an isolated atom bonded to the adjacent dimers. The first deviation with respect to pure dimer growth occurs for Cr_{10}, which possesses four dimer bonds and two isolated atoms. The structure can be justified by its high symmetry. Cr_{11} further deviates from the dimer growth by the insertion of an atom at the cluster center and leads to a natural transition from the dimer stacking to a bcc-like structure. It possesses four dimerlike bonds and, at the same time, this is the

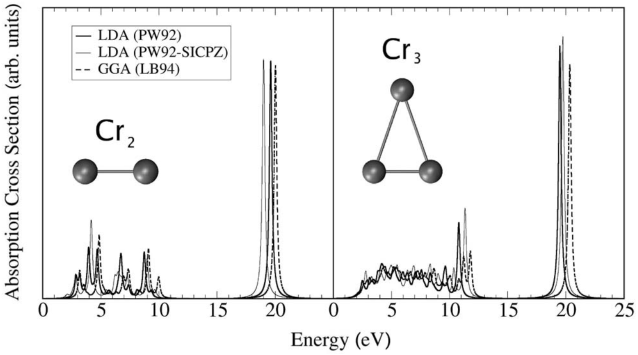

FIG. 2. Calculated photoabsorption cross sections of Cr_2 and Cr_3 using the LSDA functional (Ref. 20), the SIC-LSDA functional (Ref. 37), and the GGA functional LB94 (Ref. 38).

smallest cluster where a distorted bcc-like structure is energetically favorable. The lengths of the dimerlike bonds in clusters up to Cr_{11} do not exceed the value of 1.8 Å, and the dimer-dimer distances for even-N structures are between 2.7 and 3.2 Å. Beyond $N=11$, bulklike bcc structures dominate the cluster growth[9] and dimerization cannot be identified any further.

The immediate consequence of the dimer-growth pattern is that there should be noticeable differences in the cluster properties between even-N and odd-N clusters. Indeed, as reviewed in the Introduction, the odd-even effect becomes reflected in different electronic properties of small Cr clusters. Our calculated ground-state results are consistent with the odd-even effect. The cohesive energies, which range from 1.3 eV per atom for Cr_2 up to 2.2 eV per atom for Cr_{11}, show an odd-even effect, with smaller values for odd-N clusters, compared to even N. Similar results have been obtained in previous calculations[9] and in the experiments.[10] Odd-even alternation is also observed in the calculated magnetic moments. With the exception of Cr_3, with a total magnetic moment of 1.5 μ_B per atom, the other Cr_N clusters up to $N=11$ show magnetic moments per atom below 1 μ_B, with negligible values for even-N clusters and moments between 0.3 and 0.8 μ_B per atom for odd N. Similar results were obtained in previous studies.[9]

However, our main objective is the study of the photoabsorption spectra. A comparison of the photoabsorption spectra of Cr_2 and Cr_3 calculated by the LSDA functional, the SIC-LSDA functional, and the GGA functional of van Leeuwen–Baerends[38] (LB94) is shown in Fig. 2. The finite width of the experimental absorption peaks, linked to the accessible resolution, is mostly determined by the temperature. We have broadened the absorption peaks by setting the parameter A of Eq. (1) equal to 0.05 eV, which is the value commonly used in order to mimic the available resolution in experiments of photoabsorption and photodissociative spectroscopy.[19]

The shapes of the spectra corresponding to the three functionals are very similar, presenting only small differences of detail. The low-energy part of the LDA spectrum of Cr_2 presents a structure formed by two peaks with the same intensity, at 2.8 and 3.2 eV, and other two pronounced excitation peaks at 3.9 and 4.7 eV (the spectrum can be seen more clearly in Fig. 3). The first two peaks may correspond to transitions observed at 1.8 eV by Casey and Leopold[41] and at 2.7 eV by Bondybey and English[42] and Michalopoulos.[6] The two lowest-energy peaks of the SIC spectrum of Cr_2, located at 2.1 and 2.8 eV, are in better agreement with the experimental observations than the LSDA spectrum. On the other hand, the functional of van Leeuwen–Baerends leads to less accurate positions for those two peaks compared to the LSDA. The whole GGA spectrum is shifted to higher energies with respect to the other two. A high-energy excitation appears in the three spectra near 20 eV; the LSDA peak is blueshifted by 1 eV with respect to SIC-LDA, but not the portion of the spectrum below 10 eV. This high-energy excitation has a collective character. It is built from one-particle excitations from the three deepest (that is, highest bound) electronic states of the Cr_2 molecule ($\sigma_{3d}^2\pi_{3d}^4$) to the three lowest-energy unoccupied states, mixed and shifted by strong electronic correlations. The excitation can be visual-

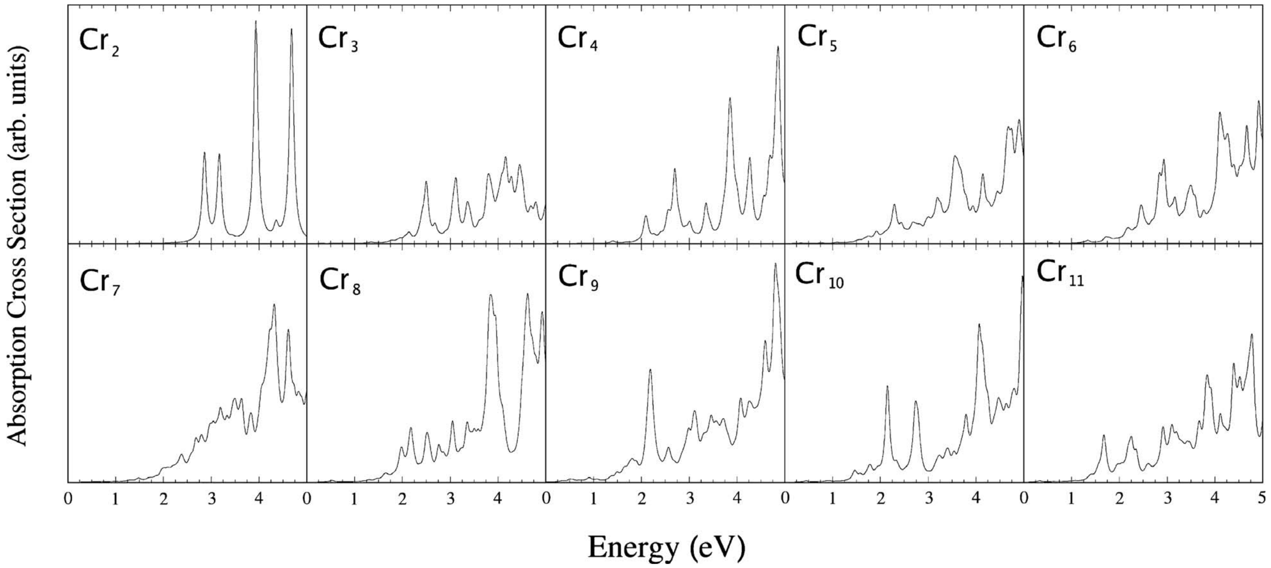

FIG. 3. Calculated (LSDA) photoabsorption cross sections (in arbitrary units) of Cr_N clusters for energies up to 5 eV.

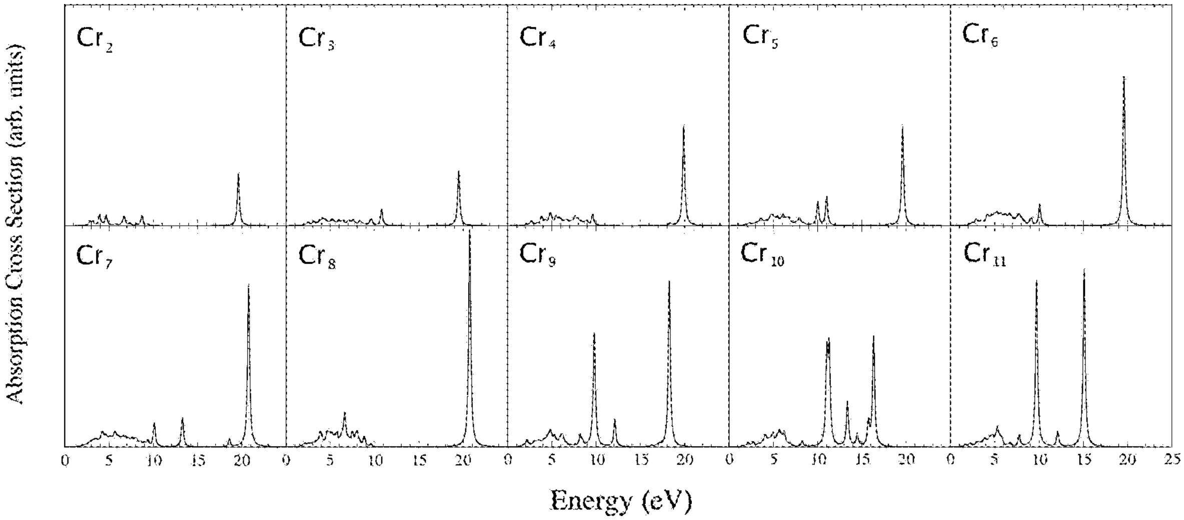

FIG. 4. Calculated (LSDA) photoabsorption cross sections of Cr_N clusters for energies up to 25 eV.

ized as a collective oscillation of those electrons against the ion cores along the direction of the molecular axis. The comparison of the three spectra of Cr_3 leads to similar conclusions, and a small shift of the GGA spectrum with respect to the other two can be appreciated.

The results for Cr_2 and Cr_3 confirm the good performance of the adiabatic LDA in the description of the excitation spectrum of clusters and guarantee its adequacy for Cr clusters. Consequently, in the rest of the paper, we present the results of adiabatic LSDA calculations with the Perdew-Wang parametrization[20] of correlation. Figure 3 shows the photoabsorption cross sections of Cr_2 to Cr_{11} in the energy range up to 5 eV. All clusters show a rich spectrum in this energy range. The absorption threshold energy decreases as the number of Cr atoms increases. The first important absorption peak occurs at 2.8 eV of Cr_2, near 1.8 eV for Cr_9 (with a tail corresponding to transitions with weak strength), and near 1.6 eV for Cr_{11} (again with a low-energy tail). The clusters with even N show less and sharper features than those with odd N due to the higher symmetry of the geometrical structures for even N. Two sharp absorption peaks near 4 and 5 eV, respectively, are a common characteristic of the even-N clusters. The spectra of the odd-N clusters do not present such distinct absorption peaks. The absorption peaks cannot be easily identified with one-particle transitions between Kohn-Sham single-particle states. Due to strong electronic correlations, present through the Hartree–exchange-correlation kernel $f_{HXC}=1/|\mathbf{r}-\mathbf{r}'|+f_{xc}(\mathbf{r},\mathbf{r}',\omega)$ appearing in the self-consistent formulation of the TDDFT, the actual excitations differ markedly from the simple Kohn-Sham energy differences.[43]

The calculation of the photoabsorption cross sections has been extended to the high-energy regime, and the results are given in Fig. 4. Experimentally, the region of high-energy excitations is difficult to access because of the competition of the ionization channel. Two regions can be distinguished in the spectra of all clusters up to Cr_9: a region of energies up to about 14 eV, followed by an intense peak near 20 eV. This intense peak keeps its energy location for $N<9$, but not its strength. It can be noticed that the strength increases with every new Cr_2 unit added along the growth pattern of the Cr_N clusters. That is, the strength is equal for Cr_2 and Cr_3, for Cr_4 and Cr_5, and for Cr_6 and Cr_7, and it increases between Cr_3 and Cr_4, between Cr_5 and Cr_6, and between Cr_7 and Cr_8. The evolution of the strength of the peak is shown in Fig. 5. The high-energy peak can be interpreted as a direct consequence of the dimerization effect. In fact, the calculated photoabsorption spectrum of an isolated Cr atom does not show an excitation peak near that energy, which means that the peak is characteristic of the robust bonds of the Cr_2 dimers. This justifies the fact that the strength of the peak does not increase by adding a Cr atom to the even-N clusters. As mentioned above, this excitation can be interpreted as a collective excitation involving the electrons in the $\sigma_{3d}^2\pi_{3d}^4$ molecular orbitals of each dimer. As more Cr_2 dimers form, the strength of the excitation progressively grows, but the excitation energy changes little. The trend changes after Cr_9 when the clusters begin deviating from the dimer-growth pattern.

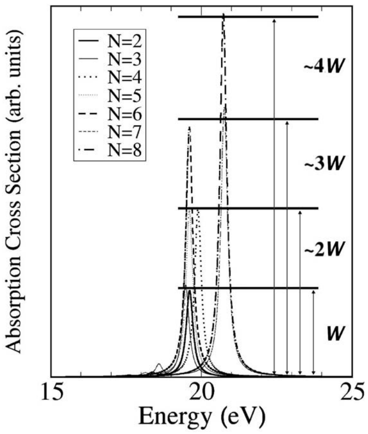

FIG. 5. Comparison of the high-energy region of the photoabsorption spectra of Cr_N for $N=2-8$. The intensity of the absorption peak of Cr_2 and Cr_3 is labeled as W. Then, the absorption strength for Cr_4 and Cr_5 has magnitudes of 2 W and 3 W for Cr_6 and Cr_7 and 4 W for Cr_8.

IV. SUMMARY AND CONCLUSIONS

The photoabsorption spectra of Cr_N clusters have been calculated using the time-dependent density functional theory. A strong dimerization effect, due to the formation of robust Cr_2 dimers, controls the growth of the clusters up to $N=11$. Ground-state magnitudes, such as cohesive energies and magnetic moments per atom, show even-odd alternation induced by the dimerization. In addition, the dimerization also affects the absorption spectrum, in particular, the high-energy part: An excitation peak appears at 20 eV, and its intensity shows even-odd alternation, increasing each time a new Cr dimer forms as the cluster grows. This peak is interpreted as a collective excitation of the electrons in the $\sigma_{3d}^2\pi_{3d}^4$ molecular orbitals of each dimer. Different exchange-correlation functionals lead to the same conclusions. However, experimental detection of this high-energy peak will be hard because of the competition from ionization.

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