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Optical properties of Al nanostructures from time dependent density functional theory

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The optical properties of Al nanostructures are investigated by means of time dependent density functional theory, considering chains of varying length and ladders/stripes of varying aspect ratio. The absorption spectra show redshifting for increasing length and aspect ratio. For the chains the absorption is dominated by HOMO $\rightarrow$ LUMO transitions, whereas ladders and stripes reveal more complex spectra of plasmonic nature above a specific aspect ratio. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4945338>]

I. INTRODUCTION

The application of nanoparticles in the field of photonics has seen important advances in recent years, for example, in plasmon-enhanced light harvesting,^{1,2} photocatalysis,^{3,4} surface-enhanced spectroscopy,^{5,6} and ultraviolet-visible fluorescence.⁷ Widely used nanostructures for plasmonic applications are based on Ag and Au, since one can tune the optical response from the visible to the infrared spectral region by varying the size and shape. However, extending the optical response into the ultraviolet region is highly challenging due to inherent limitations. In the Au case interband transitions cause a dissipative channel for plasmons at wavelengths shorter than 550 nm. On the other hand, Ag supports plasmons down to 350 nm but suffers from oxidation.⁸ Only recently Al has emerged as a serious contender for plasmonics because its empty d bands enable plasmons in the ultraviolet. In addition, Al shows strongly enhanced local electric fields due to lower screening ($\epsilon_K \approx 1$) as compared to Ag ($\epsilon_K \approx 4$) and Au ($\epsilon_K \approx 9$). The electron density (3 electrons/atom) is higher than in Ag and Au (both 1 electron/atom). Moreover, oxidation of Al self-terminates after a durable and protective oxide layer of 2–3 nm thickness has been formed, which fortunately preserves the optical properties.⁹

Experimental investigations on Al plasmonics have addressed different structures. Nanodisks with diameters ranging from 50 to 550 nm showed strongly localized plasmon resonances, tunable from the ultraviolet to the near-infrared spectral regime.¹⁰ Employing Mie theory,¹¹ Al spheres with diameters from 40 to 200 nm have been studied.¹² Nanostructures of sizes below ~ 5 nm cannot be addressed by this approach because the discrete atomic structure and quantum size effects become important. The properties of structures from sub-nanometer to ~ 2 nm size, on the other hand, can be simulated by time dependent density functional theory. For example, the plasmon evolution has been studied in Ref. 13 for a series of Au clusters with increasing size up to 146 atoms. Effects of the geometry, solvent, and ligand on

the optical absorption of Au₁₄₄ clusters protected by thiolates have been analyzed in Ref. 14.

Lian and co-workers were the first to study the evolution of the absorption spectra of Au chains (2–20 atoms) by time dependent density functional theory.¹⁵ Other investigations have addressed Ag and Au nanostructures^{16–19} and the effect of transition metal doping.^{20,21} Piccini and co-workers have demonstrated that it is possible to distinguish between single-particle excitations and plasmons in Au chains and nanowires.²² A plasmonic nature can be ascribed to an absorption peak to that many intraband transitions contribute and that reveals a high oscillator strength due to constructive interference. A similar analysis will be conducted in the present study. Since for Al sub-nanometer structures so far no theoretical investigation exists, it is the aim of the present work to provide knowledge about the plasmonic properties of prototypical Al structures. We address chain, ladder, and stripe configurations for varying size and aspect ratio.

II. COMPUTATIONAL ASPECTS

All calculations are performed using version 6.6 of the Turbomole software.^{23–25} We employ the local density

FIG. 1. Absorption spectra of chains consisting of 10, 20, 30, and 40 Al atoms. The spectra are convoluted with a Gaussian function of 0.2 eV width.

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TABLE I. HOMO-LUMO gap, position of the dominant absorption peak, and main transitions of the dominant absorption peak for Al chains of different length.

Atoms	HOMO-LUMO gap (eV)	Dominant peak position (eV)	Main transitions
10	0.8	5.3	86% HOMO → LUMO
20	0.5	3.9	88% HOMO → LUMO
30	0.3	2.8	90% HOMO → LUMO
40	0.2	2.4	92% HOMO → LUMO

approximation to the exchange correlation functional together with an all-electron triple-zeta plus polarization basis set. The multipole accelerated resolution of identity method is used for the Coulomb term and quadrature grids of m3 quality are employed. All structures are based on the experimental Al–Al bulk distance of 2.863 Å. The optical spectra are calculated within time-dependent density functional theory,²⁶ using the same basis set and exchange correlation functional as in the static calculations. The number of roots to be extracted is critical for the required computation time but must be chosen sufficiently high as it controls the upper limit of the spectrum. The following results are based on 150 roots.

III. CHAINS

Chains of noble metal atoms have been studied experimentally both for their fundamental properties²⁷ and as conducting wires for technological applications.²⁸ Supported chains are typically formed by manipulation of adsorbed atoms on surfaces²⁹ and suspended chains by the break junction technique.³⁰ Experimentally, the formation of a one-dimensional band structure out of the atomic states as the chain length increases has been demonstrated in Ref. 29. Its energy dispersion is characteristic for plasmons in a one-dimensional electron gas.³¹ Our aim is to elucidate, on a conceptual basis, how collective electronic excitations emerge and how they relate to surface plasmons.

We consider chains consisting of 10, 20, 30, and 40 Al atoms with lengths of 2.6, 5.4, 8.3, and 11.2 nm, respec-

FIG. 2. Absorption spectra of ladders consisting of 10, 20, and 40 Al atoms. The spectra are convoluted with a Gaussian function of 0.2 eV width.

TABLE II. HOMO-LUMO gap, position of the dominant absorption peak, and main transitions of the dominant absorption peak for Al ladders of different length.

Atoms	HOMO-LUMO gap (eV)	Dominant peak position (eV)	Main transitions
10	0.20	6.3	80% HOMO → LUMO
20	0.03	5.2	26% HOMO → LUMO 24% HOMO-1 → LUMO 20% HOMO-2 → LUMO+1
40	0.02	3.9	20% HOMO → LUMO 16% HOMO-1 → LUMO+2 15% HOMO-2 → LUMO+4

tively. From previous results on Au chains,^{15,16,18,20-22} lengths exceeding 2 nm can be expected to result in collective excitations. For the interpretation of the absorption spectra shown in Fig. 1 the basic question is whether the observed features are due to plasmon resonances or one-electron transitions. Transversal modulations of the electron density in an atomic chain in general are weaker than longitudinal modulations. Both types can be observed for the simple metals Na and K and the noble metals Ag and Au.^{15-18,20} The same applies to our Al chains, but the transversal modulations are not covered by the energy range of Fig. 1.

For each chain length we find a pronounced absorption peak in Fig. 1, which is redshifted (5.3, 3.9, 2.8, and 2.4 eV) for increasing length. This behavior is typical of a plasmon. The intensity also increases almost linearly as a function of the length (more electrons are available). The same feature previously has been found in Na, K, Ag, and Au chains.^{15-18,20} We present in Table I the largest contributions of electronic transitions to the dominant absorption peaks. In each case there is mainly one strong transition from the highest occupied to the lowest unoccupied molecular orbital (HOMO → LUMO).

FIG. 3. Orbitals involved in the dominant absorption peak of the 20 atom ladder (0.03 electrons/Å³ contour plot).

FIG. 4. Orbitals involved in the dominant absorption peak of the 40 atom ladder (0.03 electrons/Å³ contour plot).

FIG. 5. Absorption spectra of stripes consisting of 10, 20, and 40 Al atoms. The spectra are convoluted with a Gaussian function of 0.2 eV width.

TABLE III. HOMO-LUMO gap, position of the dominant absorption peak, and main transitions of the dominant absorption peak for Al stripes of different length.

Atoms	HOMO-LUMO gap (eV)	Dominant peak position (eV)	Main transitions
10	0.20	5.5	76% HOMO → LUMO 24% HOMO-1 → LUMO+2
20	0.02	4.8	24% HOMO → LUMO 23% HOMO-2 → LUMO 20% HOMO-4 → LUMO+1
40	0.01	3.6	18% HOMO → LUMO 20% HOMO-1 → LUMO+2 17% HOMO-2 → LUMO+3

For increasing length this contribution becomes even more dominant (86%, 88%, 90%, and 92%). The redshift seen in Fig. 1 thus is not connected to a plasmonic resonance but is purely a consequence of a reduced HOMO-LUMO gap, see

Table I. We find that Al chains of lengths up to 11.2 nm do not display plasmonic behavior. We have confirmed this conclusion by the transition density analysis of Bernadotte and co-workers³² for the chain with 20 Al atoms.

IV. LADDERS

We next connect two atomic chains to obtain ladders, for which we report in Fig. 2 absorption spectra for cases of 10, 20, and 40 Al atoms. For the shortest ladder the dominant peak at 6.3 eV is governed by the HOMO → LUMO transition (80%), see Table II. Doubling of the length shifts the dominant peak to 5.2 eV and its nature becomes strongly mixed with different transitions contributing, see Table II, none more

FIG. 6. Orbitals involved in the dominant absorption peak of the 20 Al stripe (0.03 electrons/Å³ contour plot).

FIG. 7. Orbitals involved in the dominant absorption peak of the 40 Al stripe (0.03 electrons/ $\text{\AA}^3$ contour plot).

than 26%. The orbitals involved in these transitions are shown in Fig. 3. Further doubling of the length shifts the dominant peak to 3.9 eV and enhances the mixed nature. No transition contributes more than 20% and there are many transitions involved with very small contributions. Only the largest contributions are given in Table II and the involved orbitals are shown in Fig. 4.

Since the HOMO-LUMO gap is close to zero for ladders of 20 and 40 atoms, the redshifts seen in Fig. 2 must have a fundamentally different origin than in the case of the linear chains. Indeed, they reflect a plasmonic nature of the dominant absorption peak. In terms of the one-dimensional electron gas model (the aspect ratio is large), the wavelength of the standing wave associated with the plasmon must fit to the length of the ladder. For longer ladders the wavelength thus increases and the plasmon energy accordingly decreases. While an inverse proportionality is expected, Table II shows that the plasmon peak shifts from 5.2 eV to 3.9 eV when going from 20 to 40 atoms. This deviation can be explained by the atomic structure details of the Al ladders and their finite width of two atoms. From the ladder with 20 atoms to that with 40 atoms the plasmon peak intensity increases by almost a factor of 4, see Fig. 2, showing that more electrons are contributing. We can conclude that Al ladders consisting of 20 and more atoms are subject to collective excitations. The effect of passivation on the absorption spectrum is studied by adding two O atoms to both sides of the ladder with 40 atoms. Figure 2 shows that this modification results in a distinct reduction of the oscillator strength (due to the ionic character of the Al–O bond), similar to previous reports on Au clusters passivated by thiolates.³³

V. STRIPES

Shifting the two atomic chains of a ladder by half an interatomic distance with respect to each other results in a stripe configuration. In Fig. 5 we show results for stripes consisting of 10, 20, and 40 Al atoms. The absorption spectra

reveal close similarity to those of the ladders but the dominant peak is always redshifted about 0.3 eV and the intensity is slightly reduced. For the shortest stripe the dominant peak is mainly due to the HOMO $\rightarrow$ LUMO transition, see Table III, and a plasmonic resonance can be ruled out. On the other hand, we obtain for the longer stripes a strongly mixed nature of the dominant absorption peak and enhancement of the intensity with increasing aspect ratio, reflecting a plasmonic nature, since the HOMO-LUMO gap does hardly change. The involved orbitals in the cases of 20 and 40 atoms are shown in Figs. 6 and 7, respectively. The redshift of the dominant absorption peak between stripes of 20 and 40 atoms is again qualitatively described by the one-dimensional electron gas model. The quantitative deviations (plasmon peak positions of 4.8 eV and 3.6 eV for 20–40 atoms, respectively) are of similar size as discussed earlier for the ladders. Finally, for increasing length of the stripes more electrons are contributing to the plasmon so that the peak intensity in Fig. 5 increases.

VI. CONCLUSION

In conclusion, we have investigated the nature of the absorption spectra in three classes of Al nanostructures by means of time dependent density functional theory: chains, ladders, and stripes. For each class the possibility of plasmonic behavior and its dependence on the size of the nanostructure have been analyzed. The absorption spectra show redshifting for increasing length of the chains and aspect ratio of the ladders/stripes. In the case of the chains the absorption is dominated by HOMO $\rightarrow$ LUMO transitions, whereas ladders and stripes reveal more complex spectra of plasmonic nature above a specific aspect ratio. There is no indication of collective excitations in chains up to 40 atoms length, in contrast to ladders and stripes with 20 or more atoms incorporated. Our results can guide the design of Al-based plasmonic nanodevices.

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