

Effect of molecular adsorbates on the plasmon resonance of metallic nanoparticles

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ABSTRACT

From a simple time-dependent tight-binding model we calculate the influence of molecular adsorbates on absorption spectra of spherical metallic nanoparticles. The model allows arbitrary coupling to the surface as well as changing the molecular excitation characteristics through its HOMO–LUMO gap. Adsorbates cause shifting and widening of the plasmon resonance peak for small coupling and even splitting of the resonance in two different excitations located on the particle surface and the adsorbate layer, respectively, for strong couplings.

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1. Introduction

The particular optical properties of metal nanoparticles have been known since the middle ages [1,2]. Their special light absorption and dispersion characteristics are determined by light stimulated collective oscillation of their conduction electrons giving rise to confined plasmon excitations [3]. Confined nanoparticle plasmons have energies much lower than their bulk counterparts, well within the visible spectrum and these can be modified at through control of particle shape and size [4] making these materials very prone to a multitude of applications.

In order to form colloidal suspensions of these particles in solution some kind of stabilizing agent must be used to prevent aggregation and precipitation [5,6]. Stabilization of nanoparticle colloidal suspensions can be achieved through three different mechanisms: a chemical one, on which stabilizers are linked to the particle through strong covalent bonds via end groups such as –SH, –SeH or –COOH, an electrostatic one which works by controlling the width of the electrical double layer surrounding the particles in order to avoid their coalescence and steric stabilization employing polymers to avoid particle aggregation [7]. Adsorbates can also be used as a means to recognize specific molecular targets, releasing therapeutic drugs be attached to an electronic circuit [8,9]. Adsorbates that have acid–base character can render the plasmon resonance sensitive to the pH of the solvent [10].

It has long been recognized that the surrounding medium has influence on the optical properties of nanoparticles [4]. In the simplest theoretical description, the surroundings act as a mere dielectric, lowering the energy of the plasmonic excitation by stabilizing oscillating charges on the particle surface [3]. Effects on the excitation lifetime, however, are more difficult to describe using simple

electrostatic models, which cannot capture the effects of adsorbates on the underlying electron dynamics [11]. Mie theory permits to calculate the particle plasmon resonance by modeling the adsorbates as a dielectric surrounding shell (see for example [12]), however, influence of surrounding adsorbates are also important even at low coverages adsorption scheme where a dielectric function and layer thickness is difficult to associate to the adsorbate layer. An atomistic description that takes into account the electronic structure of particle and adsorbates on the same footing might prove useful towards a full description of the problem. Some of the effects of adsorbates on the width of the plasmon resonance can be qualitatively described through the simple picture of *chemical interface damping* [13,14]. According to this model, hot plasmonic electrons can tunnel in and out of adsorbate states close to the Fermi level losing coherence in the process and therefore decreasing the lifetime of the plasmonic excitation, this image has been helpful to qualitatively describe the effects that the surroundings have on the homogeneous width of the plasmonic excitation [15,16,13]. Adsorbates can also transfer charge to the particle thus altering the plasmonic resonance energy and width [14,17]. Although this simple pictures are physically appealing and can (via modifications of the classical electromagnetic theory) successfully describe some of the effects that surface modification creates [17], they cannot fully describe the complex interplay between molecular and particle excitations which can give rise to strong shifts of the plasmonic excitation whenever molecular excitations of the adsorbates are in resonance with it [18], splitting of the plasmonic peak in two distinct excitations [19] or describe the relation between damping and chemical nature of adsorbates [20].

We have previously shown that simple adsorbates such as metallic atoms of the same chemical nature as those forming the cluster have strong effects on both resonance energy and width [21] which are linear with surface concentration. In this work we extend the model to describe the adsorption of diatomic molecules

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as simple molecular adsorbates and describe the effect of these adsorbates on the energy and width of the plasmonic excitation in relation to the HOMO–LUMO gap of the adsorbate and the strength of the coupling to the particle surface.

2. Model and simulation method

The electronic structure of the metallic aggregate is represented through a self-consistent single-orbital orthogonal tight-binding Hamiltonian. This Hamiltonian includes electron–electron interaction within a mean field DFT like approximation through the inclusion of electrostatic interaction between atomic charges and a local Hubbard U parameter:

$$\hat{H} = \sum_{i \neq j} |i\rangle H_{ij} \langle j| + \sum_i |i\rangle \left(U \Delta q_i + \sum_{j \neq i} f_{ij} \Delta q_j \right) \langle i| \quad (1)$$

where $\Delta q_i = 2(\rho_{ii} - 1/2)$ and ρ_{ii} is the charge on atom i given by the corresponding diagonal element of the single-particle reduced density matrix. The function $f_{ij} = K / \sqrt{R_{ij}^2 + K^2/U^2}$, with $K = e^2/4\pi\epsilon_0$, smoothly interpolates between the local Hubbard U and the bare Coulomb interaction at large separation. This model, despite its extreme simplicity, includes all essential details of the electronic structure of simple metals such as Au and can be viewed as a jellium model including atomistic structure. In its time-dependent incarnation the Hamiltonian in Eq. (1) represents the simplest form of adiabatic time-dependent density functional theory in a localized basis [22–24]. Hamiltonian matrix elements are calculated according to the model for bulk Au described in [25]. In order to reproduce the experimental plasmon adsorption of spherical Au particles the relative dielectric constant embedded in the constant K has been modified from its vacuum value in order to account for the screening effect of d electrons as we have described in detail in [21].

The electronic structure of adsorbates is represented through a simple two level system (TLS) Hamiltonian characterized by two parameters, the coupling to the surface atoms (NP), given by a hopping integral γ and the coupling between the two sites of the two level system characterized by the hopping matrix element δ (Fig. 1). The atom of the adsorbed molecule closest to the metallic surface (atom A) corresponds to an fcc site of the nanoparticle lattice, chosen at random, and the second atom (atom B) is located radially outwards from the particle center. The Hubbard U parameter for adsorbate atoms is of 10 eV.

Initially, the ground state single-particle density matrix of the system is found in the presence of a static electric field. At $t > t_0$ the external field is removed abruptly and the particle, which is no longer in a stationary state, evolves in time according to the following equation of motion:

$$\frac{\partial \hat{\rho}}{\partial t} = \frac{1}{i\hbar} [\hat{H}[\hat{\rho}], \hat{\rho}] \quad (2)$$

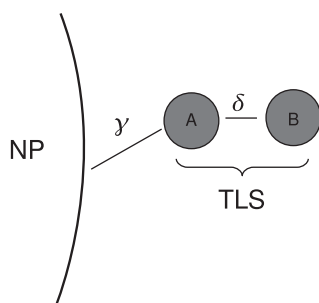


Fig. 1. Schematic representation of the system Hamiltonian: $\delta = H_{ij}$ (atom–atom) and $\gamma = H_{ij}$ (atom–metal).

which is integrated numerically by the following algorithm

$$\rho(t + \Delta t) = \rho(t - \Delta t) + 2\Delta t \frac{\partial \rho}{\partial t} \Big|_t \quad (3)$$

For small initial applied field, the response is assumed to be within the linear regime and the absorption spectra are calculated from Fourier transforming the time-dependent dipole moment as described in [21].

3. Results and discussion

All calculations shown below were performed using a spherical fcc 1985 atom gold nanoparticle with a radius of approximately 20 Å. Four hundred and eighty (24%) of the nanoparticle atoms are located on the surface. Seventy five diatomic molecules were adsorbed at random covering approximately an 17% of the cluster surface (Fig. 2). Calculations were repeated for a coverage of 36% and results for this calculations are quoted whenever significant differences are observed respect to the lower coverage data. This cluster has a plasmonic resonance at 370 nm with a full width at half maximum (fwhm) of 27.62 nm when no adsorbates are present on its surface. Figs. 3 and 4 show contour plots of the plasmon resonance fwhm and its resonance energy for a range of values of the two parameters γ and δ related to the strength of the interaction with the surface and the HOMO–LUMO gap in the diatomic molecule, respectively, as shown in Fig. 1. Please note that, unless made explicitly, the negative sign in γ and δ will be ignored in the following discussion of their effects. The plasmon resonance is influenced by the presence of the adsorbate molecules, which cause shifting of the resonance frequency, widening of the peak (reflecting changes in the plasmon lifetime) as well as splitting of the resonance in two different excitations depending on the values of the parameters.

For the weak adsorption regime, corresponding to values of γ less than about 1 eV, the effect of adsorbates on the plasmon resonance characteristics influences mainly the resonance width which can even be doubled with respect to the bare particle value, the resonance energy, however, is only slightly shifted to a higher value by less than 10 nm. The effect on the resonance width can be understood from the fact that adsorbates act as electron scatterers on the surface, decreasing their coherence time and increasing Landau damping [21] which is still present at low coupling parameter γ . The scattering effect originates both from charge transfer to and from the molecular adsorbate and changes to the local electronic structure of surface atoms due to changes in the bond order and

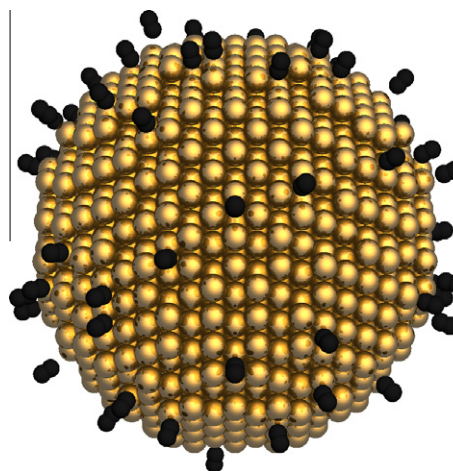


Fig. 2. 1985 Atom gold nanoparticle partially covered with 75 diatomic adsorbates.

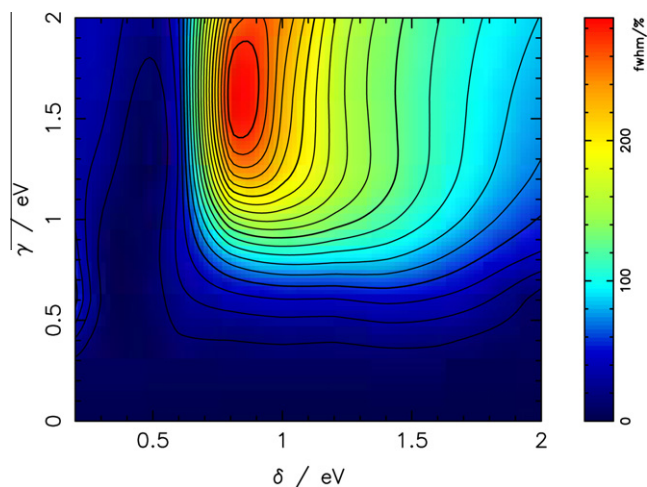


Fig. 3. Dependence on the nanoparticle plasmon peak full width at half maximum on Hamiltonian parameters describing the coupling to the surface atoms (γ) and coupling between the atoms in the diatomic adsorbate (δ). Changes are expressed as percentage with respect to the fwhm of the bare sphere plasmon resonance. For cases in which the resonance splits in two different excitations the value in the plot corresponds to the plasmon excitation.

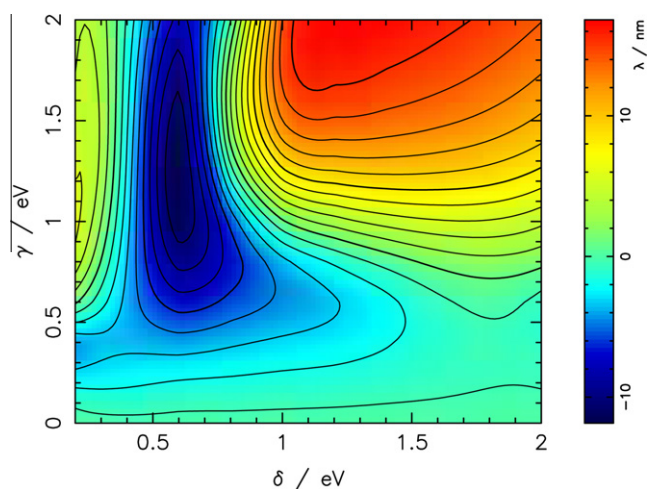


Fig. 4. Dependence of the nanoparticle plasmon resonance energy on Hamiltonian parameters describing the coupling to the surface atoms (γ) and coupling between the atoms in the diatomic adsorbate (δ). Contours correspond to the difference between the plasmon resonance wavelength of the adsorbate covered sphere and the naked one in nm. For cases in which the resonance splits in two different excitations the value in the plot corresponds to the plasmon excitation.

the local density of states at energies close to the Fermi level. Within this regime, which corresponds roughly to the lower third of the γ – δ plane in Figs. 3 and 4, the overall dependence on δ is rather small and monotonous, this is not true for larger couplings to the surface, where there is a strong dependence of the adsorbate effect on the molecular characteristics.

Upon increasing the coupling to the surface (given by γ) the scattering effect becomes more pronounced causing a monotonous increase of the resonance width, the extent of which depends non-monotonously on the coupling between the sites of the adsorbate (given by δ). The decohering effect of adsorbates is reflected in the fwhm values. Higher fwhm values imply a more intense decohering effect. This decohering effect has its maximum efficiency at a value of γ of about 1.6 eV at 17% coverage, independent of the diatomic coupling. For higher coverages the maximum effect on the resonance width occurs at smaller values of γ (1.1 eV at 36% coverage).

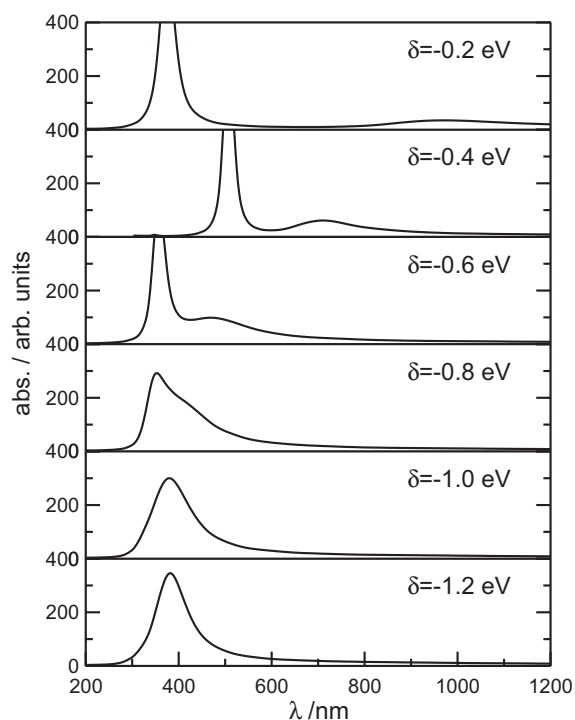


Fig. 5. Splitting of the resonance as a function of the diatomic coupling parameter δ for a fixed value of coupling to the particle $\gamma = -1.4$ eV. The higher energy peak corresponds to a purely plasmonic excitation whereas the lower energy one is located on the adsorbates.

Effects on the resonance energy are much less pronounced than on the resonance width. For the range of parameters that we have explored, changes on the plasmon frequency are always of less than a few nm, however, the resonance width may increase by 200%. As in the case of the resonance width, for the weak adsorption regime the adsorbates have a very small effect on the resonance energy. When γ is over 1 eV, however, both bathochromic and hypsochromic shifts are observed, depending on the value of the δ parameter. For small HOMO–LUMO gaps adsorbates cause a blueshift of the resonance, a trend that is reversed whenever the HOMO–LUMO gap increases.

Our results are qualitatively similar to those found in the literature for adsorbates or environments that interact weakly with the surface such as SO_2 [13] or tetraalkylammonium [26,20] and those corresponding to particles prepared by the citrate method [16]. In these cases adsorbates cause significant broadening of the resonance. Quantitative comparisons, however, are difficult due to the lack of detailed structural and energetic information on the experimental systems. Experimental results show that thiol capped particles possess significantly broadened plasmon resonances, which may even be so wide as to be undetectable [20,26], this is consistent with our results for large values of δ (corresponding to large HOMO–LUMO gaps as those of unsaturated alkyl chains) and strong coupling to the surface via covalent S–Au bonds (corresponding to large values of γ).

For strong coupling to the surface, and sufficiently small values of δ , the renormalized molecular resonance approaches the plasmon energy from above (i.e. from higher energies). When the two excitations are close in energy the plasmon peak is significantly broadened and blueshifted, corresponding to the maximum effect region (red area)¹ in Fig. 3. Effects similar to those we describe

¹ For interpretation of colour in Fig. 3, the reader is referred to the web version of this article.

here have been observed experimentally for molecular excitations in tune with plasmonic excitations in deposited silver nanoparticles [18]. When the excitation of the adsorbates becomes lower in energy than that of the plasmon, the peak splits in two different excitations. This effect can be observed in detail in Fig. 5 where we have plotted the absorption spectra for a fixed value of $\gamma = -1.4$ eV and a series of values of δ ranging from -0.2 eV to -1.2 eV. In Figs. 3 and 4 only the fwhm and energy of the lower λ purely plasmonic peak are plotted.

The nature of this two excitations can be elucidated by applying an oscillating external field tuned to each of them. The top panel of Fig. 6 shows the particle dipole moment as a function of time when illuminated at the plasmonic resonance energy (for $\delta = -0.2$ eV and $\gamma = -2.0$ eV). As it can be seen from the figure, the electronic system reaches a quasi-stationary state after 20 fs of constant illumination due to the finite lifetime of the plasmonic excitation. The lower panel of Fig. 6 shows the mean square deviation of atomic charges from their ground state value caused by the excitation as a function of the distance to the center of the particle once the quasi-stationary state has been reached. The inner broad peak maximum is located at the particle surface and corresponds to the higher energy, purely plasmonic excitation.

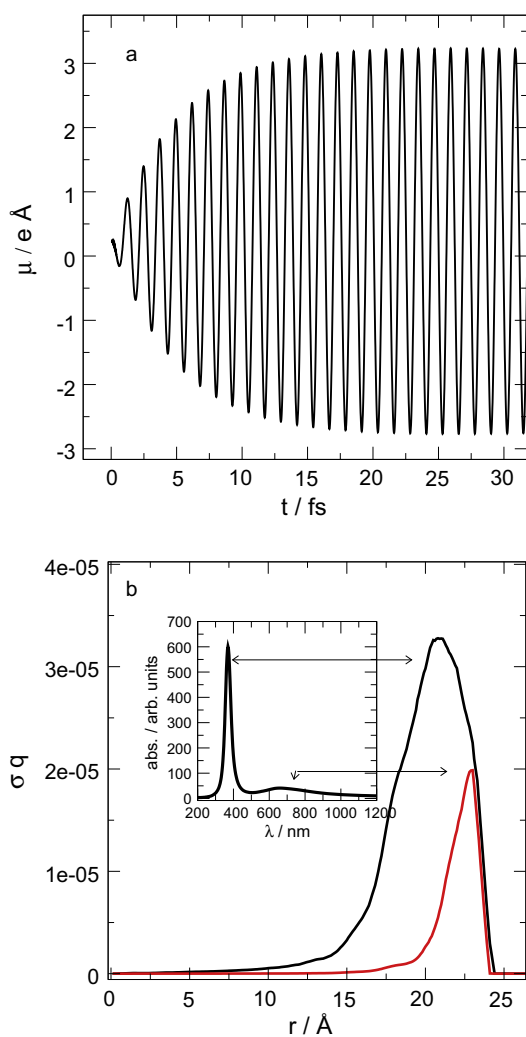


Fig. 6. (a) Time-dependent variation of the dipole moment of a nanoparticle in response to laser illumination in resonance with its plasmon excitation (top figure). (b) Mean square deviation of atomic charges caused by excitation at the energies of the two absorption peaks shown in the inset (bottom figure). The $\delta = -0.2$ eV and $\gamma = -2.0$ eV.

The lower energy excitation is located over the adsorbates. From detailed analysis of the induced charge distributions it can be seen that the lower energy resonance corresponds to an in phase oscillation of molecular dipoles located at opposite sites of the nanoparticle. The molecule excitations couple through the nanoparticle via its conduction electrons, these can only respond to the molecular oscillations if their energy is below the plasmon resonance and therefore the coupling of molecular excitations only occurs whenever these are lower in energy than the plasmon. This new excitation resembles a completely symmetric molecular dimer exciton, in which molecular dipole oscillations couple in phase. In this case, however, the electrostatic coupling between molecular dipoles occurs through the metallic particle, allowing very significant couplings at large distances. The oscillator strength of this excitation is order of magnitudes higher than the bare molecule excitation due to the large distances involved. Similar couplings of adsorbate molecular excitons have been observed experimentally [27].

4. Conclusions

As a first step towards gaining a clear understanding on the effect of chemical surface modification on metal nanoparticle plasmonic excitations we have presented a simple model that can represent a broad range of adsorbates and surface couplings. For small couplings to the surface, adsorbates produce broadening of the plasmonic excitation which even at this coupling regime can be significant without altering the adsorption energy. Upon increasing the coupling to the surface very large broadenings can occur, even when the molecular resonance is far in energy from the plasmonic excitation. Whenever the molecular excitation is in resonance with its plasmonic counterpart the effects are maximal. Adsorbates with excitations below the plasmonic resonance can produce new features in the absorption spectra due to excitonic coupling between adsorbates occurring via the metallic substrate. Due to the extreme simplicity of the model, only a qualitative description of general trends is possible. Further understanding of the complex manifold of influences that adsorbates can have on the plasmonic excitations of nanoparticles would require more detailed models of the electronic structure such as those provided by density functional tight-binding models [28]. Results for realistic molecular adsorbates within this model will be the subject of upcoming work.

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