Optical Generation of Collective Plasmon Modes in Small Gold Chains Induced by Doping Transition-Metal Impurities

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Transition metal impurity-induced generation of plasmonic collective modes in small gold clusters

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Our examination of the optical properties of small gold chains containing up to 24 atoms doped with a transition metal (TM) atom (Ni, Rh, Fe), using the time-dependent density functional theory, show the splitting of the collective plasmon peak. We associate the additional peak with a local plasmonic mode which corresponds to charge oscillations around the potential created by the d-orbitals of the impurity atoms. The effect is almost independent of the position of the TM atom in the chain, as long as it is not at the chain edge. This behavior is opposite to that of larger noble-metal-TM clusters (radius >1nm), in which doping with TM atoms does not lead to generation of new modes, and often produces a suppression of the main plasmon peak.

Introduction.–The characteristics of bimetallic nanostructures consisting of a noble and a transition metal is an active area of both experimental and theoretical study, owing to their great potential for application in modern technology, including catalysis[1], biomedicine [2], photophysics [3], and photonics [4]. One of the main reasons is that bulk noble metals such as Au and Ag and their extended layered structures display plasmon excitations in the visible frequency range which may be further tuned by changing either the geometry or chemical composition via doping with TM atoms. Since the TM atoms have both extended s- and localized d-states, one may expect interesting and unusual interplay of the role of these two types of states in determining the properties of noble-metal-TM systems, particularly at the nanoscale.

Collective excitations in few-atom clusters shown initially by Kummel et al.[5] have been the subject of several theoretical investigations following recent Scanning Tunneling Microscope (STM) observations showing development of 1D band structure when the number of atoms in Au chains on NiAl(110) exceeds 10 [6]. Subsequent theoretical calculations at the same time confirmed the presence of collective plasmon mode for Na[7], Ag[8], and Au [9, 10] chains containing more than 10 atoms. More germaine to our interest, is the experimental study of TM(Pd) doped small Au chains on NiAl(110) [11] which were found to display local electronic resonances around the dopant atom. As for optical properties of TM doped noble metal chains, we are not aware of any previous study. In this Letter, we present results of theoretical calculations of the optical properties of Au chains, $Au_{n-m}X_m$, consisting of n=2 to 24 atoms and weakly doped with different TM atoms (X= Ni, Rh and Fe and m=1 to 4) which demonstrate an unusual response of the system, including generation of extra plasmon peaks.

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Computational details.–We have applied the Time Dependent Density Functional Theory (TDDFT) approach as employed in the Gaussian 03 code [12] with a B3PW91 hybrid functional [13, 14] and a LanL2DZ basis set [15]. This choice of potential and basis set allowed us to reproduce reasonably well the experimental results for the lowest excited states of the Au dimer [16, 17]. For pure Au chains, we reproduce the results from previous TDDFT calculations [9]. The slight shift in plasmon frequency is attributed to differences in the functionals. Calculations of optimized Au-Au bond lengths show that the optical absorption spectrum does not depend significantly on the interatomic distance d in the range $2.5\mathring{A}$ (optimized bond length for the chains) and $2.89\mathring{A}$ (the experimental interatomic distance corresponding to Au chains on NiAl(110) substrate[6]). We have set the Au-Au distance as the latter to mimic the experimental setup, while cognizant of the fact that even though NiAl(110) surface does not affect the electronic properties of the Au chains [18], it can have strong implications for its optical properties. For doped chains, we optimized the bond lengths in the Au-X dimer and Au-X-Au trimer. To both focus our attention on the response of the system in the visible spectrum and to make the computation of excited states feasible, we consider states below 5eV. This choice allowed as to study the longitudinal plasmon modes in all cases, but not the transverse plasmon modes (ultra-violet) found in Au chains [10]. After obtaining the energy levels E_i and the transition dipole moments $\langle i|\hat{D}|j\rangle$, we calculated the absorption spectrum

$$A(\omega) = \sum_{i \neq j}(E_i - E_j)|\langle i|\hat{D}|j\rangle|^2 e^{-|E_i - E_j - \omega|/\Gamma}, \quad (1)$$

where ω is the frequency and Γ is the peak broadening. For clarity, in plotting $A(\omega)$ we neglected the contribution of dipole moments whose intensity was <1% of main plasmon peak.

Results.–In accordance with the finding of Lian et.al. [9], we show in Fig.1a that a new collective (longitudi-
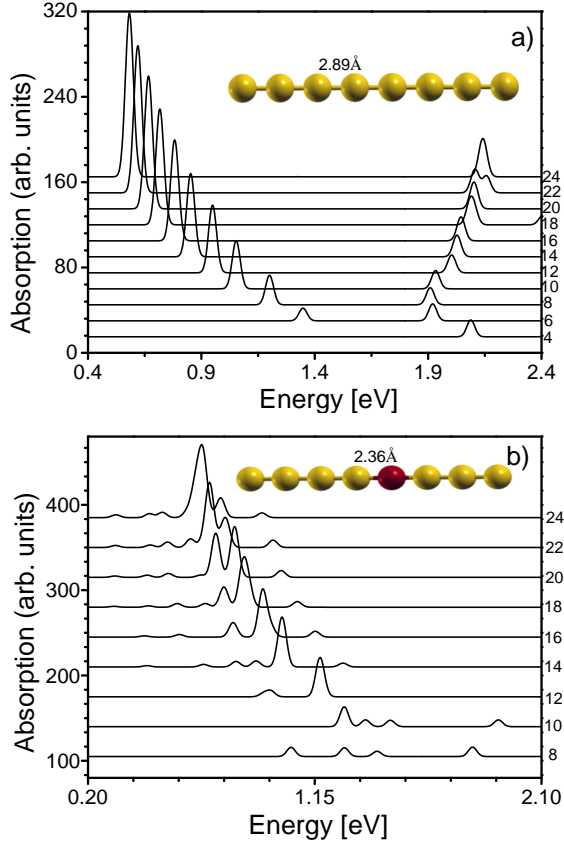
FIG. 1: The optical absorption spectrum of the Au_n (n=4-24) (a) and $Au_{n-1}Ni$ (n=8-24) (b) chains.

nal) plasmonic mode emerges in the optical absorption spectrum when the number of atoms n is of order 10. Similar to inter-band transitions, the magnitude of the plasmonic peak grows with increasing number of atoms. While peaks related to atomic levels shift only slightly as the number of atoms in the chain increases (peaks on the right in Fig.1a), plasmonic peaks emerge only beyond a certain number of atoms in the chain (here $n \sim 10$), at which point we have "an extended system" necessary for plasmon excitations (see also Ref. [9]). The position of the peaks moves into the infrared region with increasing n and becomes close to the asymptotic value ~ 0.6eV when n=20. The redshift of the plasmon energy with increasing n is related to the reduction in the energy gap (the bandgap in the many-atom case) involved in the dipole excitation.

The interesting result for the Au chains doped with one Ni atom is the presence of an additional plasmon peak close in energy to that of the main peak (Fig 1b). Since this additional peak does not exist in the case of short chains (n<12), it must originate from a collective behavior of the chain i.e. the presence of plasmon resonance in the entire chain. The fact that this peak appears when the Au chain is doped with one TM atom and that its position is independent of the position of the doping atom

in the chain (except when it is very close to the chain edge) suggests that it itself is localized in the region near the TM atom (see below). This localized plasmon mode also appears when the doping atom is Fe, Cu and Pt , although subtle differences in the spectrum appear in each case. Somewhat different is the case of Rh as a dopant (Fig.2a) in which the localized peak is not prominent. As we shall see, the presence of the extra peak may be closely related to the charge redistribution in the doped chains, which is expected to be much larger for Ni or Fe atoms, with unfilled d orbitals, than for Rh, the d-levels of which are filled. In other words, the effective attraction potential created by the impurity atom forces the electrons to oscillate around it. Since the second peak appears at chain lengths of approximately 12 atoms, it means that this strong local potential affects only electrons within the radius of 6 inter-atomic distances around it. Therefore, "the collective" nature of the local plasmon comes from the fact that it exists only when ~ 12 electrons are involved in these oscillations. However, it can be regarded as "local" compared to the main extended mode, since the local potential affects only these twelve electrons involved in the oscillations around the impurity and further increase of the chain length does not affect significantly this plasmon mode (see also Discussion below).

The origin of the extra peak is further delineated in Fig.2a which compares the absorption spectrum of the $Au_{19}Ni$ and $Au_{19}Rh$ chains with those of Au_{20}, Au_{19}, Au_{19} with a hole in the middle. One of the peaks for $Au_{19}Ni$ coincides with that of Au_{19} reflecting that it is indeed the collective excitation of the 19 Au atoms in the chain while the other is inherently linked to the presence of the Ni atom. The absorption spectrum of the $Au_{19}Rh$ chain in Fig.2a asserts that its optical behavior is like the Au_{20} chain with a small lower energy peak revealing the effect of the dopant. On the other hand, a hole in the Au_{19} chain breaks the response into that for a 10-atom and 9-atom chain. A closer look at the plasmonic modes for the Ni doped chains (Fig. 2b) in which the number of Au atoms is close to that for saturation of the plasmon peak (n=18-24) reveals that interchange of the positions of two modes occur when n changes from 18 to 24. The main, collective, higher-energy peak an n=18, shifts to the left with number of atoms increasing (broadening of electronic levels participating in the collective oscillations), while the position of the "local" peak with increasing number of atoms changes relatively little, since a fixed number of electrons participate in these oscillations around the impurity atom, and it is not strongly affected by the increase in the number of atoms. The local maximum of the second peak at n=20 can be explained by a hybridization (or even resonance) of two peaks, since at this length the number of electrons participating in the collective and "local" oscillations is of the same order (20 and 12 correspondingly).

We find that the plasmonic peaks in the optical absorption spectrum disappear when the number of dopant
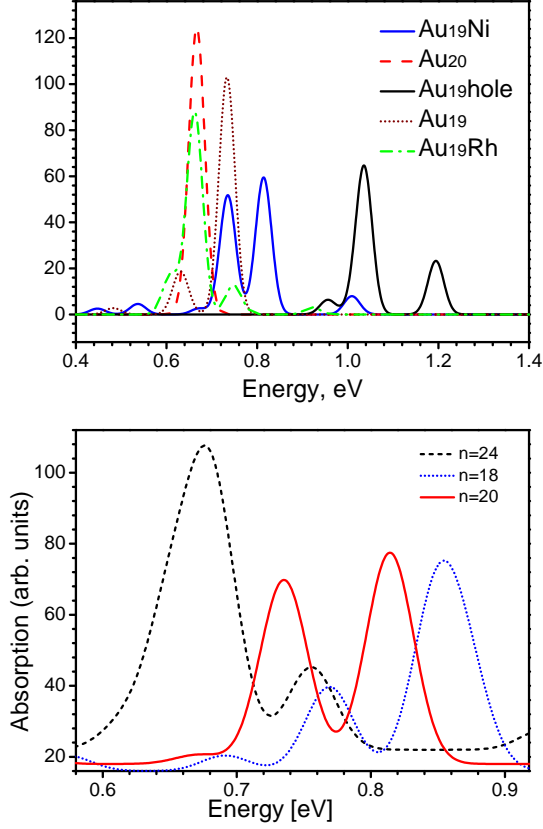
FIG. 4: The Mulliken atomic charge distribution in the case of $Au_{19}X(X = Au, Ni, Rh)$. The impurity atom is put at site 10 from the left.

FIG. 2: (a) The optical absorption spectrum of the Au_{20}, Au_{19}, $Au_{19}Ni$, $Au_{19}Rh$, $Au_{19}hole$ (b) The optical absorption spectrum of the $Au_{n-1}Ni$, n=18, 20, 24, chains.

FIG. 3: The optical absorption spectrum of the $Au_{24-n}Ni_n(n = 1, .., 5)$ chains.

(clubbed together, as it were) at the very end of chain the main plasmon peak survives but the local peak disappears. In particular, with $Au_{18}Ni_2$, there are two plasmon peaks in both the separated and the clubbed cases, separated by $\sim 0.1eV$, though the center of the peak positions is different in the two cases. This result also suggests that there are two kinds of excitations in the system: collective motion in subchains and local-charge oscillations near the Au-Ni border.

Discussion.– We turn now to an analysis of the Mulliken atomic charge distributions these chains. The results for the Au_{20}, $Au_{19}Ni$ and $Au_{19}Rh$ are presented in Fig.4. Since the charge distribution on the edges is almost identical in all three cases and the fact that there is no second plasmon peak in the pure Au chain, we infer that the edge oscillations are not responsible for the second peak in the doped chains. On the other hand, among the three cases there are quite strong differences in charge distribution near the impurity atom at the center of the chain. One can think of this situation as a jellium-electron model (Fig.5) in the presence of one high potential wall and two neighboring valleys; the rest of the chain can be considered as the positive background as in classical plasmon description. To understand the difference between the results for Rh as an impurity, on one hand, and Ni and Fe on the other, one should note that in Fig.4 the height of the potential wall and the depth of the valleys are much smaller for Rh. In the latter case, when the part of the charge from the right subchain in the "impurity" valley moves to the right, it cannot move back because of weak restoring force, and hence no local oscillations result. For the other cases the plasmon oscillations can be modeled as a local mode and an extended mode (Fig.5d and 5e). As our calculations show the magnitude of the corresponding local peak does not grow with increasing number of chain atoms, in contrast to the collective peak (Fig.1), which again confirms that when the subchains are longer than 4-5 atoms, the additional charge (beyond 4-atom region) is much less in-

atoms is around 5 as seen in Fig.3 for the 24-atom chain. Indeed, in the case of 5 impurities, consisting of five 3-atom and one 4-atom Au chains separated by the TM atoms, the constituent chains are too short to excite either collective or local plasmons (see Fig.1). However when the 5 Ni atoms are situated next to each other
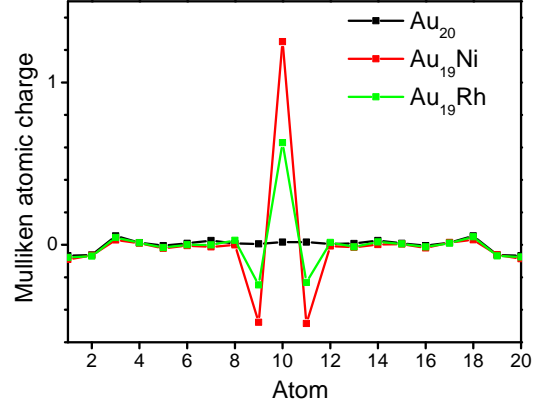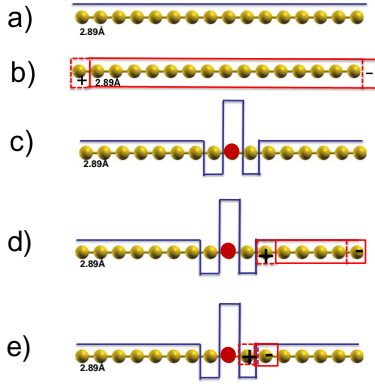
FIG. 5: Schematic form of the positive charge background potential for the Au$_{16}$ (a) and Au$_{15}$X (c) chains. In the case of Au$_{16}$, the plasmon excitation corresponds to the charge oscillation along all the chain (b). In the case of Au$_{15}$X chains, there are possible two kinds of plasmonic oscillations: collective plasmon excitations in each half of the chain (d) and local plasmon oscillations on both sides of the impurity atom potential wall (e).

volved in the local (or quasi-local) plasmonic oscillations. Also, since the removal of the Ni atom from the middle of the chain in the case of long (~ 20 atom) chains (leaving a hole) shows no second peak in the absorption spectrum, the second peak cannot be the result of two subchain-plasmon interaction. Thus, the local plasmon oscillations are charge oscillations around the local electrostatic ionic potential created by the impurity atom due to the corresponding redistribution of the equilibrium electric charge. A rough estimate of the strength of the potential necessary for causing local oscillations is that the restoring energy should be at least of the order of the kinetic energy in the system. The kinetic energy of electrons, on the other hand, may be assumed to be twice the nearest-neighbor hopping energy. We approximate the latter by the expression for the Slater-Koster parameter $V_{ss\sigma} = 1.32/md^2$, where m is the electron effective mass, which for simplicity we put equal to the free electron mass m_e[6] and $d = 2.89\mathring{A}$ is the inter-atomic distance (here and below we put $\hbar = 1$). This gives $E_{kin} = 1eV$. The potential energy is thus of the order of the local plasmon energy ω_{lp}, which can be estimated from the bulk formula $\omega_{lp} = \sqrt{4\pi ne^2/m}$, where n is the electron density. We can further model the chain as a tube of radius r and length ($(N_{atoms} - 1) \times 2.89\mathring{A} + 2r$). We estimate the radius of the tube as such that it contains 90% of the Au 6s electronic charge, which corresponds to 21.07Å. This gives the potential energy of the chain as 0.638eV, which is in good agreement with what we obtain from our calculations(0.66eV). When an impurity is introduced, its charge shifts to its neighboring Au atoms. This charge density increase in turn causes the plasmon frequencies to increase. From the estimations above, to excite the local plasmon oscillations $\omega_{pl} \sim E_{kin} \sim 1eV$, which cor-

responds to $(1eV/0.66eV)^2 \sim 2$ electrons per atom. In other words, the Au atoms nearest to the impurity atoms receive one extra electron – and in doing so generate local plasmons. As we see from Fig.4, this analysis gives semi-quantitatively correct results in the case of Ni and Rh atoms. In the first case, the extra charge is ~ 0.5 electrons, i.e., on the order of one electron, while in the case of Rh atom the charge received is almost an order of magnitude smaller.

The hybridization of the atomic orbitals between the Au s- and TM d-orbitals may also result in electron density pinning on the impurities. Since there is only one valence s-electron in the case of the Rh atom, this electron participates in σ bonding, while the eight d-electrons are not chemically very active. Thus, one can assume that the charge of the Rh core is +1, similar to that for the Au atoms, with the result that the positive and negative charges of the Au$_{n-1}$Rh and Au$_n$ plasmas are almost the same(Fig.2a). Hence, the type of the excitations in these chains will be similar, i.e. a single plasmon peak. In the case of Ni and Fe atoms, the valence s-state is doubly occupied which means that it is mainly the d-states that contribute to atomic bonding. A more precise look shows that d_z^2, d_{xz} and d_{yz} orbitals donate most of the charge to the bonding, resulting in a positively charged core with charge $Z > +1$. This is the main reason for the potential well at the impurity atom. The arguments above further substantiated by quantitative results from TDDFT calculations, thus provide measures for determining a priori the absorption spectrum of a TM doped Au chain.

To summarize: We have shown that a weak doping of Au chains with TM atoms may lead to generation of local plasmonic modes. This effect is a result of a delicate balance between the s- and d-states of TM atoms, a situation that may lead to strong charge redistribution in the chain near the impurity atom. We have also proposed a simple criterion for determining (in advance of experiment and engineering) the likelihood that a given potential dopant will generate a local plasmon, namely, the nature of the charge redistribution between it and the nearest host atoms. Specifically, our results show that TM atoms can be used to tune the optical properties of nanostructures – welcome news for many potential applications (solar cells and sensors being two key areas). Several important questions related to this project remain open, including the role of the substrate in the optical response of the chains and the possibility of generating magneto-plasmons by tailoring ferromagnetically-ordered TM impurities (see, e.g., Ref. [19]). Of course, experimental verification of the prediction here will provide further motivation for detailed examination of these and related issues.

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