Two-Photon Ionization of Silver Clusters

V. Paployan, K. Madoyan, A. Melikyan, H. Minassian

Abstract—In this paper, we calculate the two-photon ionization (TPI) cross-section for pump-probe scheme in Ag neutral cluster. The pump photon energy is assumed to be close to the surface plasmon (SP) energy of cluster in dielectric media. Due to this choice, the pump wave excites collective oscillations of electrons-SP and the probe wave causes ionization of the cluster. Since the interband transition energy in Ag exceeds the SP resonance energy, the main contribution into the TPI comes from the latter. The advantage of Ag clusters as compared to the other noble metals is that the SP resonance in silver cluster is much sharper because of peculiarities of its dielectric function. The calculations are performed by separating the coordinates of electrons corresponding to the collective oscillations and the individual motion that allows taking into account the resonance contribution of excited SP oscillations. It is shown that the ionization cross section increases by two orders of magnitude if the energy of the pump photon matches the surface plasmon energy in the cluster.

Keywords—Resonance enhancement, silver clusters, surface plasmon, two-photon ionization.

I. INTRODUCTION

TWO-PHOTON IONIZATION (TPI) is a valuable technique for the study of small clusters due to its ultrahigh sensitivity. The comparison of the observed TPI spectra with results of calculations allows deducing important information on the shape, rotational and vibrational temperatures of the clusters with high accuracy. Clusters with efficient two-photon absorption can find applications in optical power limiting, nanolithography and biosensing. It is obvious that the TPI process can be enhanced if it is assisted by a resonant transition. In [1] was shown that the Au25 cluster is a very good two photon absorption material with a high cross section due to intermediate resonance with size quantized states. An interesting trend of singularity in TPA cross-section has been observed indicating a transition from cluster to nanoparticle behavior in gold clusters. However, to the best of our knowledge there are no theoretical studies on this subject, whereas e.g. for semiconductors in nanoscale range two photon processes are well studied. Contrary to semiconductor quantum wells where the size-quantization effects are crucial in two-photon processes [2], in large metallic clusters they are negligible because of smallness of the energy quantization intervals.

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It is well known that the cross-section of single-photon ionization of gold nanoparticles with the assistance of surface plasmons increases by two orders of magnitude under the condition of resonance [3], [4]. This effect takes place when the frequency of the external field is close to the frequency of the surface plasmon. In this case, the field inside the particle may significantly exceed the intensity of the external field. It is natural to assume that the described above effect can play important role in TPI.

In this paper, we calculate the probability of TPI of silver clusters. The energy of the first photon (pump wave) is taken to be close to the energy of the SP resonance, and the second photon energy (probe wave) is chosen in such way that the total energy exceeds the ionization threshold. Here we make essential use of the results of [3], as well as the ideology of work [5], which allows us to consider the collective motion of the electrons in the metal separately from motion of single electron.

II. CALCULATION OF TPI PROBABILITY OF SILVER CLUSTER

A. Review Stage

Consider a Silver Cluster (SC) in the field of a monochromatic pump wave, the wavelength of which is much larger than the radius of the sphere. This means that so-called quasi-static approximation can be applied [6]. The field inside the sphere is the sum of the external field and the field created by surface charge. In quasi-static approximation it has the form (see [7])

$$E_{\text{int}}\left(\omega_{pump}\right) = \frac{3\varepsilon_m}{\varepsilon\left(\omega_{pump}\right)+2\varepsilon_m}E_{0\,pump} \qquad (1)$$

where $E_{0\,pump}$ is the amplitude of the external field, $\varepsilon(\omega)$ and ε_m are correspondingly the dielectric constants of the metal and the environment. Therefore the resultant field acting on each electron from the pump field and from the all other electrons now is $E_{\text{int}} = \text{Re}\left[E_i\left(\omega\right)e^{-i\omega t}\right]$. In order to have TPI one needs also a subsequent probe wave $E_{pr}\left(\omega_{pr}\right) = \frac{3\varepsilon_m}{\varepsilon\left(\omega_{pr}\right)+2\varepsilon_m}E_{0\,pr}$. For simplicity, we assume that both pump and probe fields have the same linear polarization.

The crucial point in our study is the existence of significant enhancement of internal field caused by SP resonance. This effect is expressed by sharp resonance in the dependence of $f_{pump}\left(\omega\right) = \left|E_i/E_0\right|^2$ on ω for silver ($\varepsilon(\omega)$ is taken from [8]). Indeed, from (1) for $\varepsilon_m = 1$ we obtain sharp maximum at frequency ~3.5 eV (see Fig. 1), due to which the TPI can be

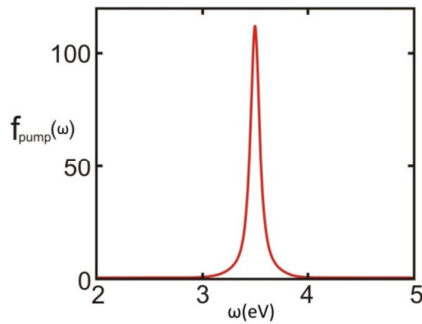significantly enhanced. As it can be seen from Fig. 1, the enhancement factor is 100.

Fig. 1 Dependence of internal field enhancement of the pump wave for SC in vacuum

Note that in case of gold clusters enhancing effect is much weaker due to the fact that the electron relaxation time in Au is a third of that in Ag [8]. It should be mentioned, that we consider relatively large clusters for which the 1/R mechanism of relaxation (surface scattering mechanism, see e.g. [6]) does not contribute into the line shape which is formed mainly by Drude mechanism.

The process under consideration is composed of two steps [9]. First, the pump wave induces electron collective oscillations; further the probe wave knocks one of oscillating electrons out of the cluster. It will be shown below that the motion of electrons participating in the first stage of the TPI is classical. Consequently, the field created by collective oscillations of electrons also can be considered as classical. The process of excitation of SP by pump wave described classically can be justified by the following reasoning.

We consider all electrons oscillating in the monochromatic field $E_i \cos(\omega_{pump} t)$ on the basis of quantum theory. We denote the unperturbed wave functions as a $\psi_k(\vec{r}, t)$. Then in the first order of the perturbation theory in the field strength the following expression for the wave function is obtained

$$\psi_k^{(1)}(\vec{r}, t) = \psi_k(\vec{r}, t) + \sum_l c_{kl}(t) \psi_l(\vec{r}, t), \qquad (2)$$

where the coefficients $c_{kl}(t)$ are determined in a usual way in the frame of perturbation theory. The quantum mechanical average of the total dipole moment of all electrons $\vec{p}$ is

$$\langle \vec{p} \rangle = e \sum_k \int \overline{\psi}_k^{(1)}(\vec{r}, t) \vec{r} \psi_k^{(1)}(\vec{r}, t) dV, \qquad (3)$$

where the summation runs over all occupied states (the Fermi distribution at room temperature). This value is of interest because the field inside the sphere can be linked to the dipole moment $\vec{P}$ per unit volume of the sphere as follows (see e.g. [7])

$$\vec{P} = \frac{\varepsilon(\omega) - \varepsilon_m}{4\pi\varepsilon_m} \vec{E}_i, \qquad (4)$$

Note that (4) is valid in both classical and quantum electrodynamics as it expresses a linear relationship between the variables. Since $\vec{P} = \langle \vec{p} \rangle / V$, where V is the sphere volume we obtain for the mean value of $\vec{P}$

$$\langle \hat{\vec{P}} \rangle = \rho \sum_k \int \overline{\psi}_k^{(1)}(\vec{r}, t) \vec{r} \psi_k^{(1)}(\vec{r}, t) dV, \qquad (5)$$

where ρ is the charge density in the SC, and N is the number of electrons in the particle. $\langle \hat{\vec{P}} \rangle$ is the mean value of the operator of the dipole moment over the Fermi distribution (see [10]). This expression can be presented as

$$\langle \hat{\vec{P}} \rangle = \rho \int \Phi^* \frac{\sum_n \vec{r}_n}{N} \Phi \prod_m dV_m, \qquad (6)$$

where Φ is the wave function of the many electron system. Integration is carried out over the coordinates of all electrons. According to the central limit theorem of the probability theory the fluctuation of such quantity is inversely proportional to the number of particles, i.e. it is negligibly small. This allows considering the dipole moment per unit volume and the field inside the particle as classical quantities with a high degree of accuracy determined by the value of the factor of N^{-1}. This means that for large clusters the error conditioned by classical consideration is negligibly small.

Mention that the electron which is emitted from SC during the TPI is usually described by Schrödinger equation. The proposed approach to describe TPI differs substantially from the usual perturbation theory by the following. It was already mentioned that the field inside the sphere $E_{int}(\omega)$ is the sum of the external field and the field created by alternating surface charge containing the electron to be knocked out of nanoparticle. It is clear that emission of one electron does not sufficiently change the charge distribution and consequently the internal field if $N \gg 1$. Thus, we apply perturbation theory with respect to the internal field strength assuming that it remains constant during the ionization process. This allows considering the ionization process separately from the collective motion, in the spirit of theory developed by Bohm and Pines for the collective description of electron interaction in degenerate gas [5]. However, in [5] the case of an alternating external field is not considered. We also use the results of [3] where a single-photon photoemission from metal clusters assisted by surface plasmon is considered.

To calculate the TPI, we write the Schrödinger equation for an electron in the field of two waves and solve it in a second-order of perturbation theory. This approximation is valid if the electric field strengths of pump and probe waves are small enough so that the interaction energy of an electron with these

fields are much smaller than $\hbar \tau_D^{-1}$, where τ_D is Drude relaxation time in Ag. Thus, the TPI probability W_{TPI} can be expressed as

$$W_{TPI} = g\left(\omega_{pump}, \omega_{probe}\right) \cdot W_{TPI}^0, \qquad (7)$$

where W_{TPI}^0 is the TPI probability per unit time in the absence of SP resonance. The sought probability of the TPI turns to be proportional to $\left|E_{pr} E_{pump}\right|^2$ through the factor $g\left(\omega_{pump}, \omega_{probe}\right)$ which is determined as

$$g\left(\omega_{pump}, \omega_{pr}\right) = \left|\frac{3\varepsilon_m}{\varepsilon\left(\omega_{pump}\right) + 2\varepsilon_m}\right|^2 \left|\frac{3\varepsilon_m}{\varepsilon\left(\omega_{pr}\right) + 2\varepsilon_m}\right|^2. \qquad (8)$$

The main effect in the process under consideration is enhancing of E_{pump} due to the smallness of the denominator in (1), which does not vanish for any real ω because $\varepsilon(\omega)$ is a complex function. Obviously, factor $g\left(\omega_{pump}, \omega_{probe}\right)$ in (8) can be expressed by the enhancement factors

$$g\left(\omega_{pump}, \omega_{probe}\right) = f_{pump}\left(\omega_{pump}\right) f_{pr}\left(\omega_{pr}\right), \qquad (9)$$

where $f_{pr}\left(\omega_{pr}\right)$ is determined in analogous of $f_{pump}\left(\omega_{pump}\right)$ as

$$f_{pr}\left(\omega_{pr}\right) = \left|\frac{3\varepsilon_m}{\varepsilon\left(\omega_{pr}\right) + 2\varepsilon_m}\right|^2. \qquad (10)$$

Thus, the probability of TPI strongly depends on the dispersion of dielectric function of Ag. For this reason, the efficiency of this process can be optimized by proper choice of dielectric environment of SC.

III. RESULTS AND DISCUSSION

Our study of factor $g\left(\omega_{pump}, \omega_{probe}\right)$ shows that the high refractive index materials are suitable environments for effective TPI in SC. The calculations are performed for the SC in the environment with refractive index $n = 1.6$ $\left(\varepsilon_m = 2.56\right)$, that is common for high index glasses as well as for organic materials such as proteins [11]. In this case using data of [8] we obtain for the SP energy $\hbar\omega_{SP}$ the value of $\approx 3.0\,eV$, and consequently the pump wave photon energy falls in the short wave limit of visible range. In Fig. 2, the dependence of the enhancement factor for the pump wave for the chosen refractive index value is presented.

As it can be seen for the pump, the enhancement factor exceeds one thousand due to SP resonance. Since the ionization potential of Ag cluster is about 5 eV [12] photon energy of probe wave exceeds 2 eV. Under these conditions we obtain for the enhancement factor the value of 0.4 (see the inset of Fig. 2). Thus, the net enhancement of TPI makes 400.
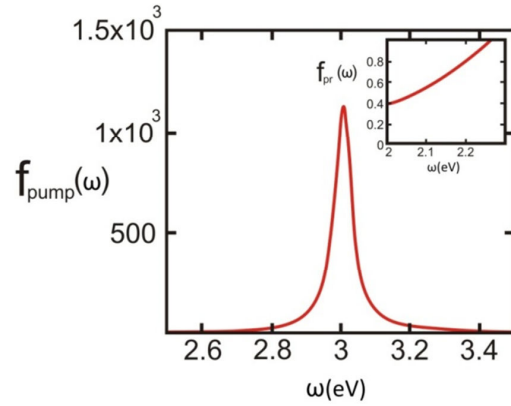

Fig. 2 Dependence of internal field enhancement of the pump wave frequency for SC in the medium with $n = 1.6$. The inset shows the same for the probe wave

Obviously, besides the TPI conditioned by the frequency summation there may occur two-photon ionization at the frequency $2\omega_{pump}$. However, we will not consider this channel of TPI because it falls far from ionization threshold.

Possible application of proposed mechanism is conditioned by high quality factor of TPI process $Q = \omega_{SP}/\gamma$, where γ is the FWHM of the resonance. Indeed from the Fig. 2 we have for $\hbar\gamma \approx 0.04\,eV$, which gives for Q rather high value - 75.

IV. CONCLUSION

For the first time two-photon ionization is investigated theoretically in Ag clusters. It is shown that in large clusters with $N \gg 1$ the field created by the electron collective oscillations can be described classically. Since the pump photon energy is close to SP energy, the first step of the TPI process runs with high probability. Thanks to this resonance, the cross section of whole ionization process increases. It is shown, that considered process is less effective in other noble metals – Au and Cu that do not possess sharp SP resonance. We prove that in dielectric media with refractive index of $n = 1.6$ the TPI probability for Ag clusters increases by one hundred times as compared to non-resonant case. We demonstrate that the quality factor of the considered process reaches the value of 75.

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