Plasmon-Induced Enhancement of Quantum Interference near Metallic Nanostructures

Vassilios Yannopapas,[1,2,*] Emmanuel Paspalakis,[1] and Nikolay V. Vitanov[2,3]

[1]*Department of Materials Science, University of Patras, GR-26504 Patras, Greece*

[2]*Department of Physics, Sofia University, James Bourchier 5 boulevard, 1164 Sofia, Bulgaria*

[3]*Institute of Solid State Physics, Bulgarian Academy of Sciences, Tsarigradsko chaussée 72, 1784 Sofia, Bulgaria*

(Received 5 February 2009; revised manuscript received 10 June 2009; published 6 August 2009)

We show that the quantum interference between two spontaneous emission channels can be greatly enhanced when a three-level V-type atom is placed near plasmonic nanostructures such as metallic slabs, nanospheres, or periodic arrays of metal-coated spheres. The spontaneous emission rate is calculated by a rigorous first-principles electromagnetic Green's tensor technique. The enhancement of quantum interference is attributed to the strong dependence of the spontaneous emission rate on the orientation of an atomic dipole relative to the surface of the nanostructure at the excitation frequencies of surface plasmons.

DOI: 10.1103/PhysRevLett.103.063602 PACS numbers: 42.50.Ct, 32.50.+d, 42.50.Gy, 78.67.Bf

It has been realized for a long time that the quantum interference (QI) and coherence [1] arising from the spontaneous emission (SE) of two closely lying levels to a common level can lead to several fascinating phenomena, such as lasing without inversion [2], coherent population trapping [3], ultranarrow spectral lines and controlled SE in resonance fluorescence spectra [4], phase-dependent line shapes [5], and optical transparency with slow light and enhanced Kerr nonlinearity [6]. For QI effects to occur the corresponding atomic dipoles for the SE process should be nonorthogonal, with the maximum QI effects occurring for parallel (antiparallel) dipoles. This is a condition that is not easy to meet in real systems.

In order to circumvent this condition, Agarwal [7] proposed to place an atom with orthogonal atomic dipoles within or near a modified (relative to the vacuum) reservoir of electromagnetic modes which suppresses SE for a specific atomic dipole orientation. This can be achieved, for example, by embedding the atom within a multilayered dielectric [8], or close to negative-refractive-index metamaterial [9], or in a more complex structure of a one-dimensional photonic crystal that contains negative-refractive-index metamaterials [10]. Specifically, in the latter case, recent calculations have shown that a metamaterial with refractive index $n = -1$ concatenated with a perfect mirror can inhibit SE parallel to the metamaterial surface at a specific distance from the surface [11].

In this Letter we show that SE can be suppressed efficiently without sophisticated experimental setups and materials, e.g., negative-refractive-index metamaterials. Naturally occurring materials exhibiting resonant surface states, e.g., metals exhibiting collective charge oscillations at their surface known as surface plasmons (SPs), offer the necessary anisotropy in the SE rates. By using a rigorous electromagnetic Green's tensor technique we show that the placement of a three-level atom or molecule in the proximity of simple metallic nanostructures, such as a metallic slab or sphere, can boost the degree of QI. QI can be further enhanced with more complex geometries, such as a two-dimensional (2D) lattice of metallic nanoshells. We note that the coherent interaction of SPs in conducting nanowires with optical emitters has been studied recently [12–14].

The quantum system of interest is shown in the inset of Fig. 1(a). We consider a V-type atomic model with two closely lying upper states $|2\rangle$ and $|3\rangle$, and one ground state $|1\rangle$. The atomic dipole moment operator is taken as $\mathbf{d} = d(|2\rangle\langle 1|\hat{\boldsymbol{\epsilon}}_- + |3\rangle\langle 1|\hat{\boldsymbol{\epsilon}}_+) + \text{H.c.}$, where $\hat{\boldsymbol{\epsilon}}_\pm = (1/\sqrt{2})(\mathbf{e}_z \pm i\mathbf{e}_x)$ and d is real. Both excited levels $|2\rangle$ and $|3\rangle$ decay spontaneously to the ground level with decay rates $2\gamma_2$ and $2\gamma_3$, respectively. The above system is studied using a density-matrix approach. By considering solely SE effects, the time-dependent equations describing the interaction of the atom with its environment, in the rotating-wave and Wigner-Weisskopf approximations, are written as [2,4,8,9]

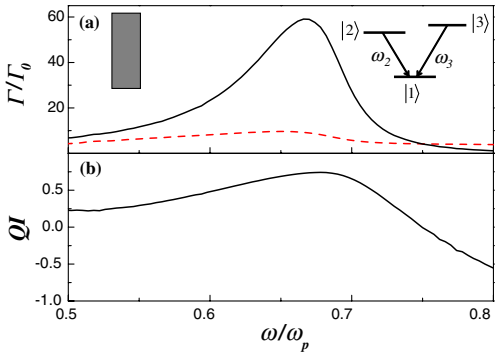

FIG. 1 (color online). (a) The SE rate as a function of the atomic frequency close to an absorbing metal surface $[(\omega_p\tau)^{-1} = 0.05]$ for an atomic dipole which is normally ($\Gamma_\perp$, solid line) and parallel ($\Gamma_\parallel$, dashed line) oriented with respect to the metal-air interface. The atom is placed at a distance $d = 0.5c/\omega_p$ from the metal surface. (b) The corresponding QI factor.

$$\dot{\rho}_{22} = -2\gamma_2\rho_{22} - \kappa_3\rho_{23} - \kappa_3\rho_{32}, \quad (1)$$

$$\dot{\rho}_{33} = -2\gamma_3\rho_{33} - \kappa_2\rho_{32} - \kappa_2\rho_{23}, \quad (2)$$

$$\dot{\rho}_{23} = -[\gamma_2 + \gamma_3 + i(\omega_2 - \omega_3)]\rho_{23} - \kappa_2\rho_{22} - \kappa_3\rho_{33}, \quad (3)$$

with $\rho_{11} + \rho_{22} + \rho_{33} = 1$ and $\rho_{nm} = \rho^*_{mn}$. If the orientation of the atomic dipoles for the transitions $|2\rangle \rightarrow |1\rangle$ and $|3\rangle \rightarrow |1\rangle$ is defined in terms of a nearby material surface, then the SE rates are given as $\gamma_{2,3} = m^2\omega_{2,3}\,\mathrm{Im}[G_\perp(\mathbf{r},\mathbf{r};\omega_{2,3}) + G_\parallel(\mathbf{r},\mathbf{r};\omega_{2,3})]$ where the symbol $\perp$ ($\parallel$) refers to a dipole oriented normal—along the z axis (parallel—along the x axis)—to the surface. Also, $\mathbf{r}$ refers to the position of the atom, and m is the atomic dipole moment. The coefficients κ_2 and κ_3 express the QI between the two spontaneous emission channels $|2\rangle \rightarrow |1\rangle$ and $|3\rangle \rightarrow |1\rangle$, and are given by $\kappa_{2,3} = m^2\omega_{2,3}\,\mathrm{Im}[G_\perp(\mathbf{r},\mathbf{r};\omega_{2,3}) - G_\parallel(\mathbf{r},\mathbf{r};\omega_{2,3})]$.

For simplicity, we assume that the two upper levels $|2\rangle$ and $|3\rangle$ are almost degenerate, i.e., $\omega_2 \approx \omega_3 = \omega_0$. In this case, $\gamma_2 \approx \gamma_3 = \gamma = \Gamma_\perp + \Gamma_\parallel$ and $\kappa_2 \approx \kappa_3 = \kappa = \Gamma_\perp - \Gamma_\parallel$, where we define the SE rates normal and parallel to the surface as $\Gamma_{\perp,\parallel} = m^2\omega_0\,\mathrm{Im}[G_{\perp,\parallel}(\mathbf{r},\mathbf{r};\omega_0)]$. The degree of QI is defined as $p = (\Gamma_\perp - \Gamma_\parallel)/(\Gamma_\perp + \Gamma_\parallel)$ [9]. Obviously, for $p = 1$ we have maximum QI, which can be achieved if we place the atom close to a structure that completely quenches $\Gamma_\parallel$.

We begin first by placing the atom near a metallic slab (Fig. 1), at a distance $d = 0.5c/\omega_p$. The metal is described by a Drude-type dielectric function, i.e., $\epsilon(\omega) = 1 - \omega_p^2/[\omega(\omega + i\tau^{-1})]$, where ω_p is the bulk plasma frequency and τ the relaxation time of the conduction-band electrons of the metal. At frequency $\omega_{\mathrm{sp}} = \omega_p/\sqrt{2}$, the metal-air interface supports a SP which is a bound state of the system since it decays exponentially away from the surface (near-field). At the same time, the charge oscillations taking place at the surface enhance the SE decay of a normally oriented dipole and suppress that of a tangentially oriented one. This results in substantial increase in the QI factor p as is evident from Fig. 1.

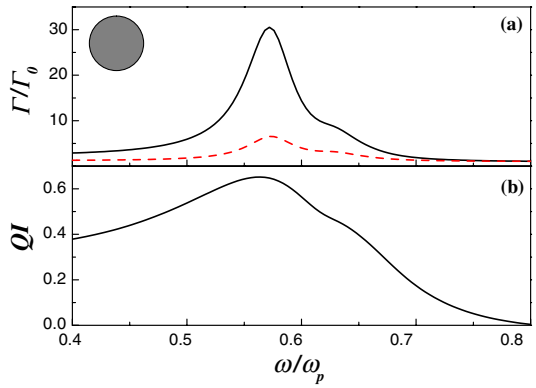

FIG. 2 (color online). (a) The SE rate as a function of the atomic frequency close to an absorbing metallic sphere $[(\omega_p\tau)^{-1} = 0.05]$ for an atomic dipole which is radially ($\Gamma_\perp$, solid line) and tangentially ($\Gamma_\parallel$, dashed line) oriented with respect to the metallic sphere. The atom is placed at a distance $d = 0.5c/\omega_p$ from the surface of the sphere. (b) The corresponding QI factor.

Next, we examine the case where the atom is placed adjacent to a metallic nanosphere (Fig. 2), again, at a distance $d = 0.5c/\omega_p$ from the surface of the sphere. The sphere radius is $S = 0.2c/\omega_p$, and it is described by the same $\epsilon(\omega)$ as the metallic slab. It is obvious that, although the SE rates for both atomic dipole orientations are enhanced relative to the vacuum case, a radially oriented dipole decays much more rapidly. This difference can be explained as follows. Around the surface plasmon frequencies of any type of metallic object, the near-field existing close the surface of the body is greatly enhanced and dominates the far-field components. Therefore, the increased SE rate close to the surface is mainly of nonradiative character and diminishes rapidly as we move away from it. In the near-field limit, a quasistatic description is valid [15] in which case the magnetic field is much smaller than the electric and the EM field is primarily p polarized. The terms comprising the SE rate for a dipole close to a metallic sphere are purely of the p type for a radially oriented dipole, while the corresponding rate for a tangentially oriented dipole contains both s- and p-polarized terms [16]. Moreover, the discontinuity at the metal-air interface shifts the radial decay rate $\Gamma_\perp$ with respect to $\Gamma_\parallel$ for all frequencies. The combined action of the above factors leads to the calculated difference between $\Gamma_\perp$ and $\Gamma_\parallel$ for both geometries (slab and sphere). The maximum value of the QI factor is obtained near the metallic sphere, $p \approx 0.65$, and can be further enhanced if the atom is placed closer to the sphere. We note, however, that if the sphere is put too close to a metallic object, the macroscopic description of the metallic object is no longer valid.

The degree of QI can be further enhanced when the three-level atom is placed adjacent to a more complex nanostructure, such as a periodic array of plasmonic nanoscatterers. The EM Green's tensor which provides the corresponding SE rates $\Gamma_\perp$ and $\Gamma_\parallel$ is given by [17]

$$G^{EE}_{ii'} = g^{EE}_{ii'} - \frac{i}{8\pi^2}\iint_{\mathrm{SBZ}} d^2\mathbf{k}_\parallel \sum_{\mathbf{g}} \frac{1}{c^2 K^+_{\mathbf{g};z}}\, v_{\mathbf{g}\mathbf{k}_\parallel;i}(\mathbf{r}) \times \exp(-i\mathbf{K}^+_{\mathbf{g}}\cdot\mathbf{r})\hat{\mathbf{e}}_{i'}(\mathbf{K}^+_{\mathbf{g}}), \quad (4)$$

with $v_{\mathbf{g}\mathbf{k}_\parallel;i}(\mathbf{r}) = \sum_{\mathbf{g}'} R_{\mathbf{g}';\mathbf{g}} \exp(-i\mathbf{K}^-_{\mathbf{g}'}\cdot\mathbf{r})\hat{\mathbf{e}}_i(\mathbf{K}^-_{\mathbf{g}'})$ and $\mathbf{K}^\pm_{\mathbf{g}} = (\mathbf{k}_\parallel + \mathbf{g}, \pm[q^2 - (\mathbf{k}_\parallel + \mathbf{g})^2]^{1/2})$. The vectors $\mathbf{g}$ denote the reciprocal-lattice vectors corresponding to the 2D periodic lattice of the plane of scatterers, and $\mathbf{k}_\parallel$ is the reduced wave vector which lies within the surface Brillouin zone (SBZ) associated with the reciprocal lattice [18]. When $q^2 = \omega^2/c^2 < (\mathbf{k}_\parallel + \mathbf{g})^2$, $\mathbf{K}^\pm_{\mathbf{g}}$ defines an evanescent wave. The term $g^{EE}_{ii'}$ of Eq. (4) is the free-space

Green's tensor, and $\hat{\mathbf{e}}_i(\mathbf{K}_\mathbf{g}^\pm)$ the polar unit vector normal to $\mathbf{K}_\mathbf{g}^\pm$. $R_{\mathbf{g}';\mathbf{g}}$ is the reflection matrix which provides the sum (over $\mathbf{g}$'s) of reflected beams generated by the incidence of plane wave from the left of the plane of scatterers [18]. Also, in Eq. (4), the terms corresponding to s-polarized waves [those containing components with the azimuthal unit vector $\hat{\mathbf{e}}_i(\mathbf{K}_\mathbf{g}^\pm)$ normal to $\mathbf{K}_\mathbf{g}^\pm$] have a small contribution to the decay rates and have been, therefore, neglected. Equation (4) also holds for a homogeneous metallic slab in which case $\mathbf{g} = \mathbf{0}$ and the integral spans over all $\mathbf{k}_\parallel$ space. The corresponding formulas for the Green's tensor of a single sphere or many spheres are given elsewhere [19].

Figure 3 deals with a square lattice of close-packed metal-coated silica nanospheres (nanoshells). The lattice constant of the square lattice is $a = 2c/\omega_p$ and the sphere radius $S = c/\omega_p$ with (silica) core radius $S_c = 0.65c/\omega_p$. It is evident that $\Gamma_\parallel$ is suppressed relative to the vacuum and exhibits a prominent minimum around $\omega/\omega_p \approx 0.65$. The corresponding QI factor is above 0.94 for almost the whole spectral range of Fig. 3, rendering the monolayer of metallic nanoshells an efficient reservoir of modes for the observation of QI phenomena. The near-field nature of the enhancement of QI is clearly illustrated in Fig. 4, which shows the QI factor for different distances of the atom from the monolayer. The QI factor decreases rapidly with distance following the exponential decay of the vacuum near-field fluctuations. The rich structure of the QI factor stems from the variety of dipole and higher-multipole SP photonic bands emerging from the interaction of SP states of neighboring nanoshells [20]. The spectral area of QI enhancement can be tuned in order to overlap with a set of atomic transitions by proper choice of the metal coating due to the strong dependence of the position of the corresponding SP resonances from the coating thickness [20].

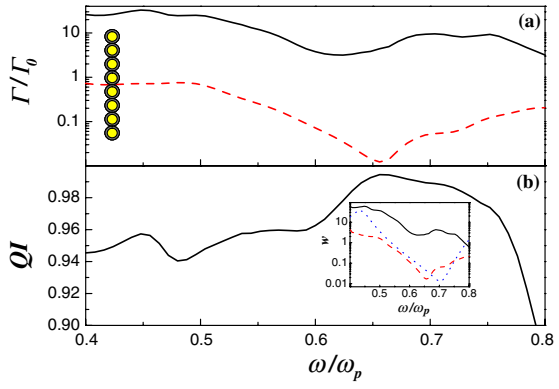

FIG. 3 (color online). (a) The SE rate as a function of the atomic frequency close to a monolayer of plasmonic nanoshells $[(\omega_p\tau)^{-1} = 0.05]$ for an atomic dipole which is normally ($\Gamma_\perp$, solid line) and tangentially ($\Gamma_\parallel$, dashed line) oriented with respect to a plane of spheres. The atom is placed at a distance $d = 0.5c/\omega_p$ from the surface of a sphere of the plane. (b) The corresponding QI factor. Inset: the spectrum of w for a normally (solid line) and tangentially (dashed line) oriented dipole. The dotted line is taken from the formula of Ref. [21].

The inset of Fig. 3(b) shows the ratio $w = \Gamma_{2D}/\Gamma_m$ for a normally (solid line) and tangentially (dashed line) oriented dipole, where Γ_{2D} is the SE rate for the 2D array of coated spheres [those depicted in Fig. 3(a)] and Γ_m for the metallic surface [Fig. 1(a)]. It is evident that for both dipole orientations, the SE rate is much more suppressed close to the 2D array of the metallic nanoshells than to the metallic surface. For a qualitative description of this effect we have used an approximate formula for the spontaneous rate close to a surface of a homogeneous material with permittivity $\epsilon(\omega)$, i.e., $\Gamma/\Gamma_0 \propto \mathrm{Im}\{[\epsilon(\omega) - 1]/[\epsilon(\omega) + 1]\}/(\omega d/c)$ [21]. This formula accounts for the nonradiative decay channel of SE. For the case of the metallic slab, $\epsilon(\omega)$ in the above formula is the Drude-type one used in all previous calculations, while for the 2D array of nanoshells, we have made use of the extended Maxwell-Garnett effective-medium permittivity [22]. We observe that this approximate formula describes quite well the case of the tangentially oriented dipole since the SE through SP channels mostly affects normally oriented dipoles. We stress that for a single metallic nanoshell, the maximum value of p is around 0.3 (for $d = 0.5c/\omega_p$), suggesting that the enhancement of QI for the 2D array of nanoshells is a result of the interference of vacuum fluctuations within the array.

The effect of the presence of a metallic nanostructure can be manifested in the solution of Eqs. (1)–(3) for specific values of $\Gamma_\perp$ and $\Gamma_\parallel$. We have chosen the case of the monolayer of nanoshells for the case where the atom is placed at a (normal) distance $d = 0.8c/\omega_p$ from the surface of a nanoshell, at frequency $\omega/\omega_p = 0.6$. In Fig. 5, we plot the population of state $|3\rangle$ as a function of time (solid line). The dash-dotted line of Fig. 5 refers to an atom without QI ($p = 0$), and the dashed one when the atom decays in a vacuum. It is evident that the presence of the plane of nanoshells delays the SE process as a result of the interference of the two decay channels.

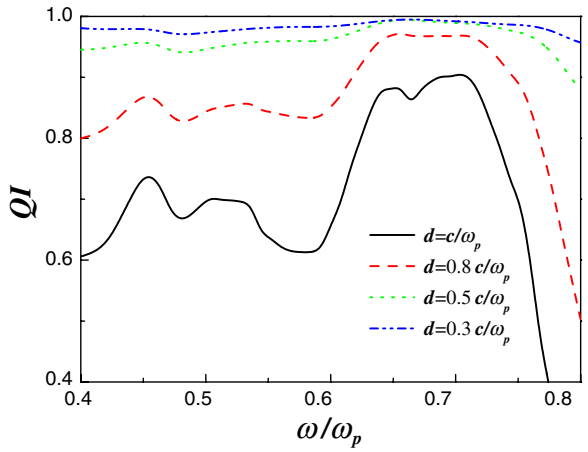

FIG. 4 (color online). The QI factor for various distances (shown in the legend) of the atom from the monolayer of plasmonic nanoshells.

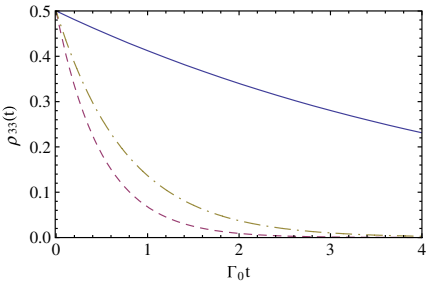

FIG. 5 (color online). Population of the excited state $|3\rangle$ as a function of time, when the atom decays in free space (dashed line) and near the monolayer of metal-coated silica spheres for $d = 0.8c/\omega_p$, $\omega/\omega_p = 0.6$ with (solid line) or without (dash-dotted line) the presence of QI. The corresponding QI factor is $p = 0.851$, and the atom is initially in an antisymmetric superposition of the upper states.

A possible experimental measurement of the reported results requires that the atoms be trapped in the vicinity of the metallic nanostructures reported. This possibility is offered by the near-field generated by illumination of the nanostructure. The near-field is essentially an optical potential landscape which exerts a gradient trapping force on a residing atom. Vertical trapping of neutral particles in the near-field of an illuminated silica-air interface has already been demonstrated [23], while the trapping near a monolayer of metallic nanospheres has been predicted theoretically [24]. In addition, a possible experimental demonstration of the presented phenomena can be achieved with molecules or quantum dots near metallic nanostructures. Actually, several recent experiments exist, where the decay of quantum emitters near metallic nanostructures has been studied [25].

In conclusion, we have shown by rigorous electrodynamic calculations that quantum processes related to the quantum interference of SE channels can be greatly enhanced when the atoms are placed near nanostructures exhibiting SP resonances in a given spectral region. The enhancement of the quantum interference stems from the intrinsic quenching of the SE of atomic dipoles oriented parallel to metallic surfaces. The degree of quantum interference is maximized near nanostructured metallic surfaces, such as a periodic array of metallic nanoshells.

This work has been supported by EC projects EMALI and FASTQUAST; and the Bulgarian NSF Grants No. VU-F-205/06, No. VU-I-301/07, and No. D002-90/08; and the ''K. Karatheodoris'' Project No. B.699 of the University of Patras.

*vyannop@upatras.gr

[1] Z. Ficek and S. Swain, *Quantum Interference and Coherence: Theory and Experiments* (Springer, New York, 2004).

[2] A. Imamoglu, Phys. Rev. A **40**, R2835 (1989); P. Zhou and S. Swain, Phys. Rev. Lett. **78**, 832 (1997); E. Paspalakis, S.-Q. Gong, and P. L. Knight, Opt. Commun. **152**, 293 (1998); S. Menon and G. S. Agarwal, Phys. Rev. A **57**, 4014 (1998); J. H. Wu, H. F. Zhang, and J. Y. Gao, Opt. Lett. **28**, 654 (2003).

[3] S.-Y. Zhu, R. C. F. Chan, and C. P. Lee, Phys. Rev. A **52**, 710 (1995); S.-Y. Zhu and M. O. Scully, Phys. Rev. Lett. **76**, 388 (1996).

[4] P. Zhou and S. Swain, Phys. Rev. Lett. **77**, 3995 (1996); B. M. Garraway and P. L. Knight, Phys. Rev. A **54**, 3592 (1996); H.-R. Xia, C.-Y. Ye, and S.-Y. Zhu, Phys. Rev. Lett. **77**, 1032 (1996);P. R. Berman, Phys. Rev. A **58**, 4886 (1998); E. Paspalakis, C. H. Keitel, and P. L. Knight, Phys. Rev. A **58**, 4868 (1998); C. H. Keitel, Phys. Rev. Lett. **83**, 1307 (1999); M. Macovei and C. H. Keitel, Phys. Rev. Lett. **91**, 123601 (2003); C.-L. Wang *et al.*, Opt. Lett. **33**, 687 (2008); Phys. Rev. A **79**, 043810 (2009).

[5] E. Paspalakis and P. L. Knight, Phys. Rev. Lett. **81**, 293 (1998); M. Macovei, J. Evers, and C. H. Keitel, Phys. Rev. Lett. **91**, 233601 (2003).

[6] E. Paspalakis, N. J. Kylstra, and P. L. Knight, Phys. Rev. Lett. **82**, 2079 (1999); D. Bortman-Arbiv, A. D. Wilson-Gordon, and H. Friedmann, Phys. Rev. A **63**, 043818 (2001); M. V. G. Dutt *et al.*, Phys. Rev. Lett. **94**, 227403 (2005); Y.-P. Niu and S.-Q. Gong, Phys. Rev. A **73**, 053811 (2006).

[7] G. S. Agarwal, Phys. Rev. Lett. **84**, 5500 (2000).

[8] G. X. Li, F.-L. Li, and S.-Y. Zhu, Phys. Rev. A **64**, 013819 (2001).

[9] Y. Yang *et al.*, Phys. Rev. Lett. **100**, 043601 (2008).

[10] J.-P. Xu *et al.*, Opt. Lett. **33**, 2005 (2008).

[11] J. Kästel and M. Fleischhauer, Phys. Rev. A **71**, 011804(R) (2005).

[12] D. E. Chang *et al.*, Phys. Rev. Lett. **97**, 053002 (2006); Nature Phys. **3**, 807 (2007).

[13] G.-Y. Chen, Y.-N. Chen, and D.-S. Chuu, Opt. Lett. **33**, 2212 (2008).

[14] S. -D. Liu *et al.*, Opt. Lett. **33**, 851 (2008); A. Trügler and U. Hohenester, Phys. Rev. B **77**, 115403 (2008).

[15] J. Gersten and A. Nitzan, J. Chem. Phys. **75**, 1139 (1981).

[16] H. Chew, J. Chem. Phys. **87**, 1355 (1987); Phys. Rev. A **38**, 3410 (1988).

[17] R. Sainidou, N. Stefanou, and A. Modinos, Phys. Rev. B **69**, 064301 (2004).

[18] N. Stefanou, V. Yannopapas, and A. Modinos, Comput. Phys. Commun. **113**, 49 (1998); **132**, 189 (2000).

[19] V. Yannopapas and N. V. Vitanov, Phys. Rev. B **75**, 115124 (2007); J. Phys. Condens. Matter **19**, 096 210 (2007).

[20] C. Tserkezis, G. Gantzounis, and N. Stefanou, J. Phys. Condens. Matter **20**, 075 232 (2008).

[21] G. W. Ford and W. H. Weber, Phys. Rep. **113**, 195 (1984).

[22] R. Ruppin, Opt. Commun. **182**, 273 (2000).

[23] C. D. Mellor, T. A. Fennerty, and C. D. Bain, Opt. Express **14**, 10 079 (2006).

[24] V. Yannopapas, Phys. Rev. B **78**, 045412 (2008).

[25] P. Anger, P. Bharadwaj, and L. Novotny, Phys. Rev. Lett. **96**, 113002 (2006); Y. Fedutik *et al.*, Phys. Rev. Lett. **99**, 136802 (2007); T. Pons *et al.*, Nano Lett. **7**, 3157 (2007); P. Vasa *et al.*, Phys. Rev. Lett. **101**, 116801 (2008); M. Ringler *et al.*, Phys. Rev. Lett. **100**, 203002 (2008); C. W. Chen *et al.*, Appl. Phys. Lett. **94**, 071 906 (2009).