Density-Matrix Approach for the Electroluminescence of Molecules in a Scanning Tunneling Microscope

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The electroluminescence (EL) of molecules confined inside a nanocavity in the scanning tunneling microscope possesses many intriguing but unexplained features. We present here a general theoretical approach based on the density-matrix formalism to describe the EL from molecules near a metal surface induced by both electron tunneling and localized surface plasmon excitations simultaneously. It reveals the underlying physical mechanism for the external bias dependent EL. The important role played by the localized surface plasmon on the EL is highlighted. Calculations for porphyrin derivatives have reproduced corresponding experimental spectra and nicely explained the observed unusual large variation of emission spectral profiles. This general theoretical approach can find many applications in the design of molecular electronic and photonic devices.

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Light emission of molecules induced by the localized tunneling current in a scanning tunneling microscope (STM) has been studied for almost two decades [1–12], owing to its rich new physics and fascinating potential applications in molecular scale optics and electronics [6–8,10,13]. In principle, the electroluminescence (EL) of a molecule can be generated once an electron-hole pair is formed inside the molecule. This could happen when the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) enter into the window of the external bias [6,7]. Such an electron driven mechanism has been explained by several groups using different theoretical methods [9,11]. Very recently, a fascinating new experimental study by Dong *et al.* [13] has shown that the EL spectra of tetraphenyl porphyrin (TPP) molecules can be effectively modified by tuning the energy profile of the resonant nanocavity plasmons (NCPs) in a STM. The resonant hot EL arising directly from higher vibronic levels of the singlet excited state for porphyrin molecules, even up-conversion luminescence, have been observed for the first time. It was suggested that the local nanocavity plasmons behave like a strong coherent optical source with a tunable energy [13]. However, there is no fully developed theoretical model ready to describe these new phenomena.

It was known that the light induced fluorescence and Raman scattering of molecules in the metallic nanogap could be uniformly treated by the density-matrix approach [14,15]. Generalized Bloch equations have also been used to study the optical interactions in confined geometries [16]. In this Letter, we will show that the density-matrix formulation can be generalized to describe the EL from molecules near a metal surface in a STM. In our model, the surface plasmons are regarded as strong coherent electromagnetic sources, the electron tunneling rates are determined by Fermi's golden rule, and the finite lifetimes of the energy levels are introduced phenomenologically into the density-matrix equations as relaxations. In other words, the spontaneous, electron tunneling induced, and stimulated emissions can be uniformly described by this newly proposed approach.

The equation of motion of the density matrix is

$$\frac{\partial\rho}{\partial t} = -\frac{i}{\hbar}[\hat{H}, \rho] + \Gamma_{\mathrm{tr}}\rho + \Gamma_{\mathrm{ph}}\rho + R\rho. \tag{1}$$

Here ρ is the Hermitian density operator, its diagonal matrix element ρ_{nn} gives the probability of the molecule in the level n. Within the electric dipole approximation, the total Hamiltonian of the system $\hat{H}$ is the sum of the free system Hamiltonian $\hat{H}_0$ and the interaction Hamiltonian of the system and the plasmon, $\hat{V}(\boldsymbol{r}, t) = -\boldsymbol{\mu}\cdot\boldsymbol{\varepsilon}$. Considering the surface plasmon as a linearly polarized electromagnetic field, we have $\boldsymbol{\varepsilon}(t) = \mathbf{e}E(t)\cos(\omega t)$. Here $\mathbf{e}$, $E(t)$, and ω are the polarization vector, the envelope, and the resonant frequency of the surface plasmon, respectively. $\boldsymbol{\mu}$ is the electric dipole moment operator of the molecule. Γ_{tr} is the population decay operator with [14]

$$\Gamma_{\mathrm{tr}}\rho = -\sum_{ij}\frac{\Gamma_{i\leftarrow j}}{2}[a_{ji}a_{ij}\rho - 2a_{ij}\rho a_{ji} + \rho a_{ji}a_{ij}]. \tag{2}$$

Here $\Gamma_{i\leftarrow j}$ is the decay rate from the level j to the level i. a_{ij} is a matrix with element (i, j) equal to 1 and all other elements equal to 0. Γ_{ph} is the dephasing operator which is introduced into the density matrix to describe the broadening of the emission spectrum caused by the surroundings. It is noted that a large dephasing factor can lead to the quenching of the luminescence [17].

The electron tunneling process can only affect the population of the molecule through the diagonal terms of the density matrix (tunnel into and out of a particular level). The last term in Eq. (1) has the form

$$R\rho = -\sum_{ij}[R_{j\to i}a_{jj}\rho a_{jj} - R_{i\to j}a_{ji}\rho a_{ij}]. \tag{3}$$

Here $R_{i\to j}$ ($R_{j\to i}$) is the electron tunneling rate from level i to j (j to i). Under the approximation of weak coupling between the molecule and the STM tip and substrate, these rates can be calculated according to Fermi's golden rule as widely used in the rate equation method [11,18,19]. If we assume the STM tip as the left lead and the substrate as the right lead related to the molecule, the tunneling rates between two relevant levels i and j ($E_i < E_j$) could be obtained: [19–21],

$$\begin{aligned} R_{i\to j} &= F_{ij}[\gamma^L f(\delta E^L) + \gamma^R f(\delta E^R)],\\ R_{j\to i} &= F_{ji}\{\gamma^L[1 - f(\delta E^L)] + \gamma^R[1 - f(\delta E^R)]\}, \end{aligned} \tag{4}$$

with $\delta E^L = E_j - E_i - e\alpha V$ and $\delta E^R = E_j - E_i - e(\alpha - 1)V$. F_{ij} is the transition probability between the levels i and j. γ^R and γ^L are the bare tunneling rates between a particular level of the molecule and the left and right leads (for the simplicity, we assume different levels have the same bare tunneling rates), α is the bias coupling over the leads, f is the Fermi distribution at the temperature T, $f(E) = 1/[1 + \exp(E/k_BT)]$.

Relative to the level i in the ground state, the probability of radiative population or depopulation of the level j in the excited state induced by the plasmon is depicted by the work of the field $W^p_{ji}(t)$,

$$W^p_{ji}(t) = \mathrm{Im}[H_{ji}\rho_{ij} - \rho_{ji}H_{ij}]. \tag{5}$$

Determined by the instantaneous Rabi frequency, $W^p_{ji}(t)$ shows a sign-changing property with its positive $[W^{pA}_{ji}(t)]$ and negative $[W^{pE}_{ji}(t)]$ parts representing, respectively, the absorption and the stimulated emission induced by the plasmon. Correspondingly, the work done by the electron tunneling process at time t can be calculated as

$$W^e_{ji}(t) = W^{eA}_{ji}(t) + W^{eE}_{ji}(t) = R_{i\to j}\rho_{ii} - R_{j\to i}\rho_{jj}. \tag{6}$$

The contributions of spontaneous emissions to the total emission spectra are described by the radiative decay from level j in the excited state to the level i in the ground state, $W^{sE}_{ji}(t) = -\Gamma_{i\leftarrow j}\rho_{jj}$. All of these quantities can be calculated by solving the density-matrix equation of the system, and the emission cross section for the transition between the level j and the level i can then be obtained from

$$\sigma_{ji} = A\int_{-\infty}^{\infty}[W^{pE}_{ji}(t) + W^{eE}_{ji}(t) + W^{sE}_{ji}(t)]dt. \tag{7}$$

A at the right-hand side of the equation is a constant prefactor. The photon emission process can be described by a Lorentzian function; the power spectrum is then obtained as

$$\sigma(\omega) = \frac{1}{\pi}\sum_j\sum_i\frac{\sigma_{ji}\tau_{ji}}{(\omega_{ji} - \omega)^2 + \tau_{ji}^2}. \tag{8}$$

Here τ_{ji} is the half width at half maximum (HWHM) of the emission line, and ω_{ji} is the resonant frequency between the levels j and i. It is noted that the system can reach its steady state in several nanoseconds for all the cases studied here, which is several orders of magnitude shorter than the time of the experimental measurements. Thus the contribution from the transient states can be averaged out.

We have solved the related density-matrix equations for a TPP molecule, shown in Fig. 1(a), in a STM as done in the latest experiment of Dong *et al.* [13]. The three processes involved in the EL from the molecule are schematically shown in Fig. 1. The electron tunneling induced emission process is illustrated in Fig. 1(b), in which electrons can tunnel into the LUMO and tunnel out from the HOMO when both orbitals are in the bias window and leave an electronic excited state ready to fluoresce. Because of the relative short lifetime of the vibrational excited state, the system will first relax to the lowest vibrational state of the excited state (S_1) before emitting a photon according to Kasha's rule. In the plasmon-assisted molecular emission process [Fig. 1(c)], a plasmon can be generated by the inelastic tunneling of electrons from the tip to the metal substrate. The plasmon behaves as a strong coherent electromagnetic source and can excite the molecule resonantly into higher vibrational levels in the first excited state following a resonant emission, or stimulated emission, without a nonradiative relaxation [13]. It is noted

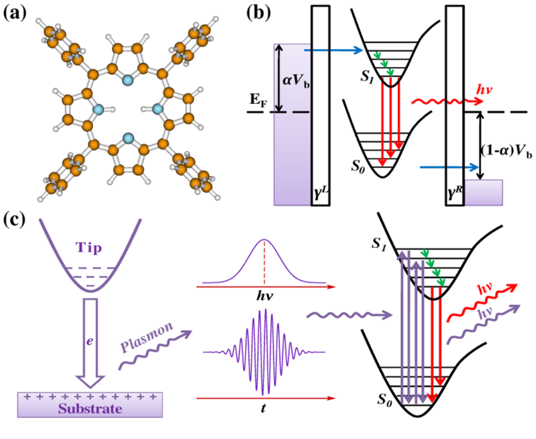

FIG. 1 (color online). (a) The optimized structure of a tetraphenyl porphyrin (TPP) molecule. (b) Electron tunneling induced emission with the inclusion of the internal relaxation. (c) Plasmon-assisted process, including the plasmon generation, the excitation, the stimulated emission, and the spontaneous emission.

that when the plasmonic excitation is relatively weak, the emission will again follow Kasha's rule. Spontaneous emission (fluorescence) has a similar mechanism with the electron tunneling induced emission, and it happens simultaneously with the other two emission processes.

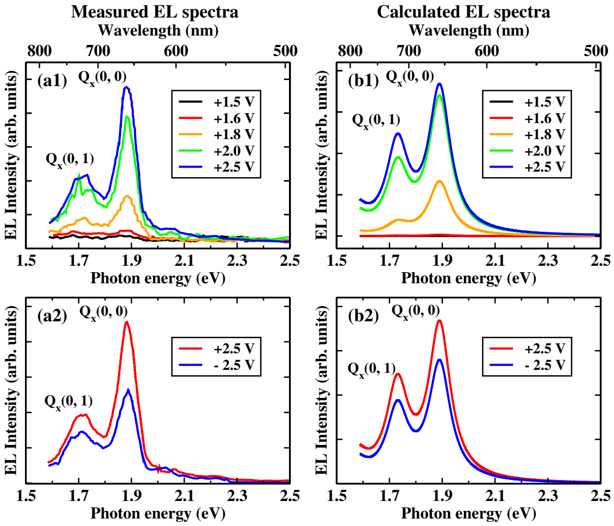

FIG. 2 (color online). (a1),(a2) The measured EL spectra of H_2TBPP molecules at different bias voltages. [Adapted with permission from Z. C. Dong *et al.*, Phys. Rev. Lett. **92**, 086801 (2004). Copyright 2004, The American Physical Society.] (b1), (b2) The calculated EL spectra of TPP molecules at different bias voltages without considering the plasmon excitation. $\gamma^L = 16.40\ \mu\text{eV}$, $\gamma^R = 4.80\ \mu\text{eV}$, $\tau_{ji} = 0.05$ eV, $T = 300$ K.

In principle, our formulation allows us to include as many electronic states and vibrational levels as one wants to. However, for the relevant emission processes of the TPP molecule, it is enough to consider two electronic states, S_0 and S_1 (Q band), each with three vibrational levels. The transition probability between different vibrational levels is governed by the Franck-Condon factors that can be calculated using the standard harmonic model. The calculated energy gap between the two vibrational bands, $Q(0, 0)$ and $Q(0, 1)$, is scaled to the experimental value of 0.16 eV and the excitation energy between two molecular states is set to the experimental value of 1.89 eV [13] for the sake of a better presentation. The initial condition for the population is $\rho_{0,0} = 1$ and $\rho_{n,n} = 0$, $n \neq 0$; i.e., the electrons rest at the lowest vibrational level of the ground state. Normally, the radiative lifetime of the state is about 3 orders of magnitude longer than those of nonradiative relaxations [22]. In this work the radiative lifetime τ_r is set to be 2 ns and the radiative decay rate between level j in S_1 and i in S_0 is calculated as $\Gamma_{i\leftarrow j} = F_{ji}/\tau_r$. The nonradiative decay rates between the vibrational levels are set to be $(2\text{ ps})^{-1}$. In our simulations we have assumed that $\mathbf{e}$ is parallel to $\boldsymbol{\mu}$, which results in the largest plasmon enhancements of the EL. It might be more general if the averaged effect of the polarization is taken into account. The density-matrix equations are solved using an iterative predictor-corrector method. The dephasing factor enters the calculated spectrum through the HWHM (τ_{ji}, derived from the experimental spectra) of the convoluted Lorentzian profile [Eq. (8)]. All the calculations are performed with a bias coupling constant (α) of 0.50.

We first simulate the EL spectra of a TPP molecule in a STM induced by the electron tunneling process only. The bias voltage dependence of EL spectra for different porphyrin molecules was experimentally observed by Qiu *et al.* [6] and Dong *et al.* [7]. It was found that the spectral peaks under different bias voltages remain unchanged with enhanced intensities at higher bias voltages. Dong *et al.* also reported bipolar EL spectra at ±2.5 V. In a very recent theoretical study by Seldenthuis *et al.* [11], the bias voltage dependence of EL spectra measured by Qiu *et al.* as well as the bipolar molecular fluorescence observed by Dong *et al.* has been successfully analyzed using a rate equation method. We focus our attention on the results for the *mesotetrakis* (3,5-di-terbutylphenyl) porphyrin (H_2TBPP) molecules [7]. Our simulated spectra under different bias voltages from the density-matrix approach are illustrated in Fig. 2(b1), which have largely reproduced the corresponding experiments as recaptured in Fig. 2(a1). The peak positions of the calculated EL spectra all remain the same simply due to Kasha's rule. A clear enhancement of the spectral intensities at higher bias voltages is revealed, which arose from the increased number of vibronic levels entering in the bias window. One interesting experimental observation is that the EL can still be observed when the excitation voltage is less than the energy of the emitted photon around 1.9 eV. Such "energy forbidden" transitions were suggested to be a result of either the thermally assisted tunneling injection of holes or the shift of energy levels due to the charging of the molecules [7]. Our simulations have shown that the thermally assisted electron tunneling is the reason for such transitions because of the broad Fermi-Dirac distribution at 300 K. Moreover, the experimentally observed bipolar spectra at ±2.5 V in Fig. 2(a2) are also well reproduced by our calculations [Fig. 2(b2)] as a result of the weak couplings between the leads and the molecules. The intensity difference in the bipolar spectra is due to the slight asymmetric coupling between the molecule and the two leads [11].

It can be seen that the electron tunneling induced EL strictly follows Kasha's rule; i.e., only the emission from the lowest vibrational level of the excited state is possible. In the latest experiment, the EL from higher vibrational levels was observed, which suggests that a new mechanism must be involved [13]. One of the possible candidates is certainly the plasmonic excitation. In order to be consistent with the experiment, the actual energy profiles of the five NCP modes (dashed lines in the left of Fig. 3) are fitted by Gaussian functions which are then Fourier transferred to the time domain, resulting in the pulses of different duration τ. The obtained time dependent field $E(t)$ is used in the density-matrix equations to simulate the spectra. The frequencies and the durations of the pulses can be found in

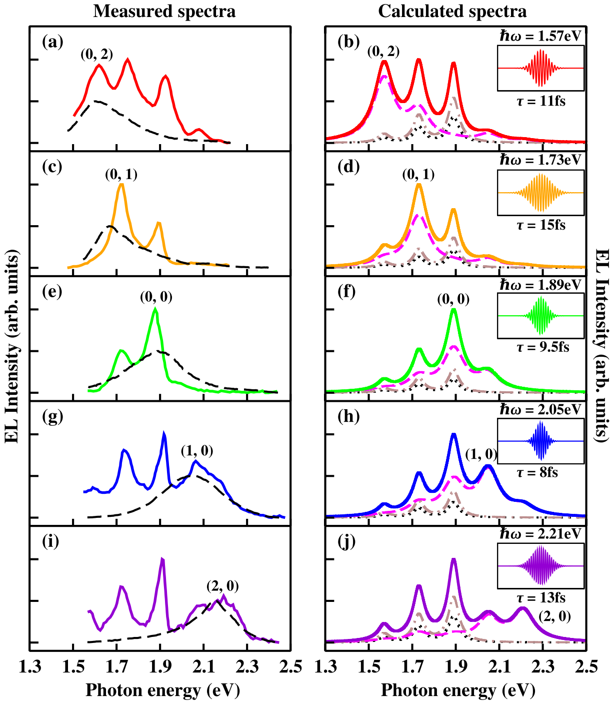

FIG. 3 (color online). EL spectra modified by the resonant plasmonic excitation. Left: Measured EL spectra of TPP molecules together with the corresponding NCP modes (black dashed lines). [Adapted by permission from Z. C. Dong *et al.*, Nat. Photon. **4**, 50 (2009). Copyright 2010, Macmillan Publishers Ltd.] Right: Calculated EL spectra together with the plasmon-assisted (dashed lines), electron tunneling induced (dotted lines), and spontaneous (dash-dotted lines) emissions. The insets show the pulse shape for the corresponding NCP modes. The plasmon resonant energy is 1.57, 1.73, 1.89, 2.05, and 2.21 eV with the corresponding pulse duration of 11.0, 15.0, 9.5, 8.0, and 13.0 fs, respectively. The field strength of the plasmon is 7.0×10^7 V/m. $\gamma^L = 4.10\ \mu$eV, $\gamma^R = 1.20\ \mu$eV, $V_b = 2.5$ V, $T = 80$ K. τ_{ji} is 0.06 eV for the plasmon-assisted process and 0.03 eV for the other processes.

Fig. 3 (right). It is interesting to see that all NCP modes behave similarly to the femtosecond laser (with durations around 10 fs). The field strength of the plasmon is set to 7.0×10^7 V/m for all the calculations. Since the plasmon is generated by inelastic electron tunneling, a sequence of pulses has been used in the simulations.

The simulated EL spectra with the inclusion of both electron tunneling and plasmonic excitation are given in Fig. 3 to directly compare with their experimental counterparts. One can immediately notice that the spectral feature is drastically changed by the inclusion of the plasmonic resonant excitations. In other words, all the non-Franck-Condon features in Fig. 3, such as new peaks, (1, 0) in 3(h) and (1, 0) and (2, 0) in 3(j), the enhanced peaks, (0, 2) and (0, 1) in 3(b), (0, 1) in 3(d), and (0, 0) in 3(f), are contributed from the plasmonic excitation. We have also plotted out the contributions from three individual emission processes in Fig. 3 (right). It can be found that the electron tunneling induced emission and the spontaneous fluorescence always follow Kasha's rule and give the conventional double-peak Q profile. The plasmon-assisted molecular emission is a stimulated process directly from the resonantly excited vibrational levels. The position of such a stimulated emission is controlled by the plasmonic resonant energy and its energy width (or the related time duration of the plasmon pulse).

In summary, we have presented a generalized density-matrix formalism to successfully describe the EL from molecules near a metal surface in a STM. Both the electron tunneling and local surface plasmon induced excitation and emission are treated on an equal footing. Model calculations for porphyrin derivatives have reproduced corresponding experimental spectra and nicely explained the observed unusual large variation of emission spectral profiles in recent experiments.

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