Raman Images of a Single Molecule in a Highly Confined Plasmonic Field

Sai Duan,1,2 Guangjun Tian,2 Yongfei Ji,2 Jiushu Shao,3 and Yi Luo1,2,*

1 Hefei National Laboratory for Physical Science at the Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei, 230026 Anhui, P. R. China.
2 Department of Theoretical Chemistry and Biology, School of Biotechnology, Royal Institute of Technology, S-106 91 Stockholm, Sweden.
3 Key Laboratory of Theoretical Computational Photochemistry, Ministry of Education, College of Chemistry, Beijing Normal University, Beijing 100875, P. R. China.

(Dated: June 19, 2014)

Under the local plasmonic excitation, the Raman images of a single molecule can now reach sub-nm resolution. We report here a general theory to describe the interaction between a molecule and a highly confined plasmonic field. It is shown that when the spatial distribution of the plasmonic field is comparable with the size of the molecule, the plasmonic field needs to be treated quantum mechanically. The resonant Raman image of a molecule is found to be strongly associated with the density of the electronic transition. In combination with the first principles calculations, the simulated Raman image of a porphyrin derivative adsorbed on the silver surface nicely reproduces its experimental counterpart. It reveals that the quantum nature of the highly confined plasmonic field offers a new way to modify the wavefunction of the molecule. The present theory provides the basic framework for describing linear and nonlinear responses of molecules under the non-uniform quantized field.

The development of tip enhanced Raman scattering (TERS) technique has significantly increased the spatial resolution of Raman images for molecules[1–3]. Under the low temperature and ultrahigh vacuum conditions, the resolution has amazingly reached a sub-nanometer level for a porphyrin derivative adsorbed on the silver surface[3]. It is anticipated that the spatial confinement of the tip-induced plasmon has played a decisive role in achieving such a high resolution. In this case, the spatial distribution of the plasmonic field has to be comparable with the size of the molecule, even with the inclusion of possible nonlinear processes[3]. This situation presents a great challenge to the conventional theory, which always assumes that the electromagnetic (EM) field is a classical field that uniformly interacts with the molecule[4]. A new theory that takes into account the locality of the EM thus needs to be developed. Moreover, what a Raman image really tells about the molecular structure is another important issue that has not yet been discussed in the literature.

In this work, we have derived a general theory to describe the interaction between a molecule and a highly confined EM field. In this new framework, the EM field is treated quantum mechanically and acts as an operator to directly interact with the wavefunction of the molecule. In combination with the first principles calculations, we have successfully reproduced experimental Raman image of the porphyrin derivative adsorbed on the silver surface. It is found that within the Born-Oppenheimer (BO) approximation, the resonant Raman image reflects the density of the electronic transition between the ground and the excited states. The effects of nonlinear processes on the Raman images have also been briefly discussed.

The highly confined plasmon can be regarded as a non-uniform monochrome EM field. The operator related to the vector potential is written as[5, 6]

\[
\hat{A}(r, t) = \sqrt{\frac{2\pi \hbar c^2}{\omega}} \left( \hat{a}(r) e^{i(k \cdot r - \omega t)} + \hat{a}^\dagger(r) e^{-i(k \cdot r - \omega t)} \right),
\]

where \(\hbar\) is the reduced Planck constant, \(c\) is the speed of light, \(\omega\) is the frequency of the EM field, \(\epsilon\) is the unit vector of electric polarization, \(k\) is the wave vector, \(\hat{a}\) and \(\hat{a}^\dagger\) are annihilation and creation operators for the photon, respectively. Notice that, here, the annihilate and create operators depend on the position, which represent the non-uniform number density of photon, i.e.[4, 5]

\[
\begin{align*}
\hat{a}(r)|n\rangle &= \sqrt{n(r)}|n - 1\rangle \\
\hat{a}^\dagger(r)|n\rangle &= \sqrt{n + 1(r)}|n + 1\rangle,
\end{align*}
\]

where \(n(r)\) and \(n+1(r)\) are number densities of photon related to states \(|n\rangle\) and \(|n + 1\rangle\), respectively. According to the energy conversation of the light,[4–6] we have

\[
n(r) = \frac{\epsilon_0|E_0(r)|^2}{\hbar \omega},
\]

where \(\epsilon_0\) is the vacuum permittivity and \(E_0\) is the amplitude of the non-uniform electric field. The plasmonic frequency often falls into the visible or UV region and the electric dipole approximation still holds[5]. Based on Fermi’s Golden rule, the transition rate for the absorption between two molecular states may be expressed as

\[
\Gamma_{\text{abs}}^{\text{1\rightarrow f}} = \frac{4\pi^2 c^3 \omega^2 \hbar}{\lambda^2} \left| \epsilon \cdot \langle \Psi_f | \sqrt{n(r)\hat{r}} | \Psi_i \rangle \right|^2 \delta(E_f - E_i + \hbar \omega)
\]

where \(\epsilon\) is the elementary charge, \(E_i\) and \(E_f\) are the energies related to the initial and final molecular states \(|\Psi_f\rangle\)
and $|\Psi_i\rangle$, respectively, and $\omega_{fi}$ is the corresponding frequency difference. With BO approximation, the molecular state can be rewritten as $|\Psi_i\rangle = |\psi_i\rangle|v\rangle$, where $|\psi_i\rangle$ and $|v\rangle$ are electronic and nuclear components, respectively.

A Raman process is described by the polarizability of the molecule and it is a combination of the absorption and emission processes. Since the plasmonic excitation mainly involves in the absorption process, analogy to the Albrecht’s theory[7], the polarizability can thus be written as

$$
\alpha_{pq} = A_{pq} + B_{pq},
$$

where

$$
A_{pq} = \frac{1}{\hbar} \langle \psi_g | \hat{p} | \psi_r \rangle \langle \psi_r | \sqrt{n(r)} \hat{q} | \psi_g \rangle
\times \sum_{v'=0}^{\infty} \frac{\langle v' | Q_k | v \rangle \langle v' | v \rangle}{\omega_{v' - v} - \omega - i\Gamma} + \text{NRT},
$$

and

$$
B_{pq} = \frac{1}{\hbar} \langle \psi_g | \hat{p} | \psi_r \rangle \langle \psi_r | \sqrt{n(r)} \hat{q} | \psi_g \rangle
\times \sum_{v'=0}^{\infty} \frac{\langle v' | Q_k | v \rangle \langle v' | v \rangle}{\omega_{v' - v} - \omega - i\Gamma} + \frac{1}{\hbar} \langle \psi_g | \hat{p} | \psi_r \rangle \frac{\partial}{\partial Q_k} \langle \psi_r | \sqrt{n(r)} \hat{q} | \psi_g \rangle
\times \sum_{v'=0}^{\infty} \frac{\langle v' | Q_k | v \rangle \langle v' | v \rangle}{\omega_{v' - v} - \omega - i\Gamma} + \text{NRT}.
$$

Here $p$ and $q$ are the Cartesian coordinates, $|\psi_g\rangle$ and $|\psi_r\rangle$ are the electronic ground and resonant excited states, $Q_k$ is the corresponding normal mode, $|v\rangle$ and $|v'\rangle$ are initial and final vibrational states in $|\psi_g\rangle$, $|v'\rangle$ is vibrational state in $|\psi_r\rangle$, $\omega_{v' - v}$ is the frequency difference between $|\psi_r\rangle|v'\rangle$ and $|\psi_g\rangle|v\rangle$, $\Gamma$ is the damping factor, and NRT is the non-resonant term. We notice that the electronic part of $A$ term in Eq. 6 is independent of $Q_k$, which provides a universal contribution to all normal modes. On the other hand, the derivatives in $B$ term in Eq. 7 are related to individual $Q_k$, which have different values for each vibrational mode. From the polarizability, the Raman intensity can be calculated directly[4, 7, 8].

Interestingly, we can rewrite Eqs. 6 and 7 as

$$
A_{pq} = \frac{1}{\hbar} \langle \psi_g | \hat{p} | \psi_r \rangle \langle \psi_r | \sqrt{n(r)} \hat{q} | \psi_g \rangle
\times \sum_{v'=0}^{\infty} \frac{\langle v' | v' \rangle \langle v' | v \rangle}{\omega_{v' - v} - \omega - i\Gamma} + \text{NRT},
$$

and

$$
B_{pq} = \frac{1}{\hbar} \frac{\partial}{\partial Q_k} \langle \psi_g | \hat{p} | \psi_r \rangle \langle \psi_r | \sqrt{n(r)} \hat{q} | \psi_g \rangle
\times \sum_{v'=0}^{\infty} \frac{\langle v' | v' \rangle \langle v' | Q_k | v \rangle \langle v' | v \rangle}{\omega_{v' - v} - \omega - i\Gamma} + \frac{1}{\hbar} \langle \psi_g | \hat{p} | \psi_r \rangle \frac{\partial}{\partial Q_k} \langle \psi_r | \sqrt{n(r)} \hat{q} | \psi_g \rangle
\times \sum_{v'=0}^{\infty} \frac{\langle v' | Q_k | v \rangle \langle v' | v \rangle}{\omega_{v' - v} - \omega - i\Gamma} + \text{NRT}.
$$

with $|\psi_g\rangle = \sqrt{n(r)}|\psi_g\rangle$. The whole expressions become the same as the $A$ and $B$ terms of the traditional Albrecht’s theory[7], except that one of the $|\psi_g\rangle$ is now replaced by $|\psi_g\rangle$. This leads to a very important new concept, namely the effect of non-uniform EM can be considered as a quantum modulation of the ground state, resulting in a new wavefunction $|\psi_g\rangle$. For higher order nonlinear processes[9], the excited states could also be modulated by the non-uniform EM as $|\psi_g\rangle = \sqrt{n(r)}|\psi_g\rangle$ and/or $|\psi_g\rangle = \sqrt{n(r)}|\psi_g\rangle$. This will certainly open up an entire new way to manipulate the molecular wavefunctions.

We now focus our attention on the resonant Raman scattering in order to simulate the experimental Raman images. In this case, the $A$ term in Eq. 5 becomes the dominant term[4, 7]. Moreover, for a molecule under the TERS tip, only the zz component in Eq. 6 needs to be evaluated[3]. From Eq. 3, $\sqrt{n(r)}$ has exactly the same distribution as the non-uniform $|E_0(r)\rangle$, which represents the position of the nano-cavity plasmon (NCP). For the sake of computations, we have chosen to expand it in terms of the Gaussian basis sets.

$$
\sqrt{n(r)} = \sum_D \sum_{l,m,n} c_D^{lmn} g_D^{lmn},
$$

where $g_D^{lmn}$ is a Gaussian function localized at the center $r_D$, which can be written as

$$
g_D^{lmn} = (x - x_D)^l(y - y_D)^m(z - z_D)^n e^{-\alpha_D(r - r_D)^2}
$$

and $c_D^{lmn}$ is the corresponding coefficient. Here $r_D$ may represent the position of the NCP. As the first demonstration, only the s-type Gaussian functions are considered for $g_D^{lmn}$, i.e. $c_D^{lmn} = 1$ and $l = m = n = 0$ in Eq. 10. It is noted that within the BO approximation, the calculation of the Raman images is equivalent to the calculation of the absorption images from Eq. 4. We should mention here that the quantization was adopted to describe the generation of the plasmon in a previous study for the surface-enhanced Raman scattering[10]. However, the interaction between the plasmonic field and the molecule was still treated classically[10]. We also notice that the current theory can be connected to the time
FIG. 1. (a) Optimized structures of one H\textsubscript{2}TBPP tautomer adsorbed on the Ag(111) surface for concave, plane, and convex configurations, respectively. Gray, blue, cyan and white balls represent Ag, N, C, and H atoms, respectively. Only the topmost slab layer of the Ag(111) surface as well as all atoms of adsorbates in one supercell are depicted for clarity. (b) Calculated average STM images with the sample biased by 1.0 V for concave, plane, and convex configurations, respectively. The solid lines represent the skeleton of H\textsubscript{2}TBPP. The insert figure shows the experimental STM image under the same condition extracted from Ref. 3.

We put the new theory to the test by directly simulating the system that was measured in a recent study[3], i.e. a single meso-tetrakis-(3,5-di-tertiarybutylphenyl)-porphyrin (H\textsubscript{2}TBPP) molecule adsorbed on the silver (Ag) surface. The high resolution scanning tunneling microscope (STM) and Raman images[3] provide good references for theoretical modeling. The details of the density functional theory calculations are given in the Supplemental Material[12].

Here we considered two degenerate tautomers of H\textsubscript{2}TBPP molecule[13]. The optimized structures of one H\textsubscript{2}TBPP tautomer adsorbed on the Ag(111) surface are depicted in Fig. 1(a)[12]. The optimized structures of the other tautomers are similar except the central hydrogens bonded to different nitrogen atoms. We have considered three configurations: concave, plane, and convex, respectively. The first and last configurations were identified when H\textsubscript{2}TBPP adsorbed on the Cu(111) surface by STM[14] and the second configuration is the minimum of the isolated molecule. Our calculations have shown that the concave is the most stable adsorption configuration, owing to the long range dispersion included in current calculations[15]. Meanwhile, the second stable configuration is the plane and the convex is the least stable one. The calculated STM images[12] of all configurations, together with the experimental result[3] are given in Fig. 1(b). One can immediately see that only the calculated STM image of the concave resembles well the experimental image. It can thus be concluded that H\textsubscript{2}TBPP adsorbed on the Ag(111) surface has the concave configuration under the experimental conditions.

To simulate the Raman image, H\textsubscript{2}TBPP was extracted from the optimized adsorption structures and its excited states were calculated by the time dependent density functional theory (TD-DFT) at the hybrid B3LYP level[12]. It should be mentioned that it is the compromise that we have to make for such large systems from computational point of view. It is fortunately a reasonable approximation since the molecule is only physisorbed on the Ag(111) surface. The strong absorption states for three configurations are found to be 2.47, 2.36, and 2.25 eV, respectively, in the region of the excitation energy of the experiment (532 nm, 2.33 eV)[3]. We have thus chosen these three excited states to simulate
the resonant Raman images. Consistent with the experimental setup[3, 16], the center of NCP, i.e. \(r_D\), is in the plane which is about 2 Å above the highest position of the adsorbates. Meanwhile, along the \(x\) and \(y\) directions, the full width at half maximum (FWHM) of the plasmonic field, \(g_{D00}\), was set to be 5, 10, 20, and 30 Å, respectively, while the \(z\) component was fixed at 5 Å. We should emphasize that the calculated Raman images are not sensitive to small changes of \(r_D\) and the \(\alpha_D\) in the \(z\) component of \(g_{D00}\).

All simulated Raman images are presented in Fig. 2. It can be seen that the size of the Raman image is dependent on the size of the NCP. This implies that the precondition for the high resolution Raman image is to generate a highly focused plasmonic field. It is nice to observe that different configuration of the molecule gives very different Raman image, indicating that TERS technique is a powerful tool to study the structure of adsorbates. One can notice that the Raman image of the concave with FWHM of 20 Å is in very good agreement with the experimental image, which is consistent with the energy and STM calculations. By definition, Raman images reflect the density change involved in the electronic transition, rather than the local density of state of the adsorbate. This is naturally reflected by the obvious difference between the Raman and STM images.

Under the resonant condition, the \(B\) term often gives a small contribution to the total intensity. We have evaluated numerically the effect of the \(B\) term for two vibrational bands, around 820 and 1200 cm\(^{-1}\), by using the linear coupling model[17]. The calculated Raman images from the total polarizability as well as the \(B\) term alone for these two bands are shown in Fig. 3. One can immediately notice that the \(B\) term is very sensitive to the vibrational models. Its contribution to the total intensity holds the key to distinguish Raman images of different vibrations. For the \(H_2\)TBPP molecule, the contribution of the \(B\) term is very small. Hence, the Raman images from total intensity calculations appear to be identical for two vibrational bands. It should be mentioned that the Raman calculations are performed for the single molecule. The inclusion of the substrate could increase the contribution of the \(B\) term. This could be a reason behind the small variation observed in the experimental Raman images[3].

It was found in the experiment that the observed Raman intensity was cubically dependent on the amplitude of the incident light. A possible involvement of the stim-
ulated Raman process was thus suggested[3]. Although a rigorous theory to describe the nonlinear plasmonic processes is still under development in our laboratory, we can nevertheless estimate the effects of the nonlinearity on the Raman images by simply assuming that it is the cubic of the absolute value of the polarizability. The calculated nonlinear Raman images with the FWHM of 20 Å are depicted in Fig. 4. In general, the nonlinear images have slightly higher spatial resolution than their linear counterparts. It seems like that the inclusion of the nonlinear effects does give a better agreement between the calculated and the experimental images.

In summary, we have proposed a new theory to describe the interaction between a molecule and a highly confined plasmonic field. It shows that the quantized description of the plasmonic field holds the key to simulate super-high resolution molecular Raman images. The usefulness of the new theory is highlighted by reproducing successfully the experimental Raman images of a H$_2$TBPP molecule adsorbed on the Ag(111) surface. The theoretical framework established in this work lays the foundation for the future development of linear and nonlinear plasmonic spectroscopy.

This work was supported by Ministry of Science and Technology of China (Grant No. 2010CB923300), Natural Science Foundation of China (Grant No. 20925311), and Göran Gustafsson Foundation for Research in Natural Sciences and Medicine. The Swedish National Infrastructure for Computing (SNIC) was acknowledged for computer time.

* yiluo@ustc.edu.cn

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