Activating spin-forbidden transitions in molecules by the highly localized plasmonic field

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Optical spectroscopy has been the primary tool to study the electronic structure of molecules. However the strict spin selection rule has severely limited its ability to access states of different spin multiplicities. Here we propose a new strategy to activate spin-forbidden transitions in molecules by introducing spatially highly inhomogeneous plasmonic field. The giant enhancement of the magnetic field strength resulted from the curl of the inhomogeneous vector potential makes the transition between states of different spin multiplicities naturally feasible. The dramatic effect of the inhomogeneity of the plasmonic field on the spin and symmetry selection rules is well illustrated by first principles calculations of C$_{60}$. Remarkably, the intensity of singlet-triplet transitions can even be stronger than that of singlet-singlet transitions when the plasmon spatial distribution is comparable with the molecular size. This
approach offers a powerful means to completely map out all excited states of molecules and to actively control their photochemical processes. The same concept can also be applied to study nano and biological systems.

Optical excitation is the fundamental process that controls molecular properties and their spectroscopies. In spite of great success, the optical excitation with conventional light sources could only access to very limited number of excited states due to the restriction of the intrinsic symmetry and spin selection rules. It was reported recently that the symmetry selection rule for optical excitations could be softened under the plasmonic field, which takes advantage of its near field characteristic. We will demonstrate here that the use of locality of the plasmonic field could not only further weaken the symmetry selection rule, but also remove completely the much stricter spin selection rule.

Within non-relativistic regime, the light-matter interaction is governed by the minimal coupling Hamiltonian, which is adequate even for plasmonic fields. In this context, the light-matter interaction Hamiltonian, \( \hat{H}' \), can be expressed as the summation of the vector potential component \( \hat{H}'_A \) and magnetic component \( \hat{H}'_B \)

\[
\hat{H}' = \hat{H}'_A + \hat{H}'_B
\]

\[
\hat{H}'_A = \sum_k \frac{1}{2} \left[ \hat{p}_k \cdot A(r_k, t) + A(r_k, t) \cdot \hat{p}_k \right]
\]

\[
\hat{H}'_B = \sum_k \frac{1}{2} \hat{\sigma}_k \cdot B(r_k, t)
\]

where \( \hat{p}_k \) is the momentum operator of the \( k \)th electron, \( A(r_k, t) \) is the vector potential of the light, \( r_k \) is the position of the \( k \)th electron, \( \hat{\sigma}_k \) is the Pauli matrix for the \( k \)th electron, and \( B(r_k, t) \)
is the magnetic field that can be calculated by the curl of the vector potential, i.e., $B(r_k, t) = \nabla_k \times A(r_k, t)$. Here we neglect the high-order $A^2(r_k, t)$ term. Thus, the light-matter interaction can be determined by the vector potential. In general, vector potential could be expressed as (Figure 1a)

$$A(r, t) = A_0 g(r) e^{i\eta_0 k_0 \cdot r} e^{-i\omega t} \hat{n} + \text{c.c.} \tag{2}$$

where $A_0$ is the constant field amplitude, $g(r)$ is the amplitude of the spatial distribution function, $k_0$ is the wave vector in vacuum, $\eta_0$ is the confinement factor for the wave vector caused by surrounding dielectric media, $\omega$ is the frequency of electromagnetic field, $\hat{n}$ is the norm of the vector potential, and c.c. is the complex conjugate. As a result, we have

$$B(r, t) = [i\eta_0 g(r) k_0 \times \hat{n} + \nabla g(r) \times \hat{n}] e^{i\eta_0 k_0 \cdot r} e^{-i\omega t} + \text{c.c.} \tag{3}$$

According to the Fermi’s golden rule, the absorption cross section between molecular initial state $|i\rangle$ and final state $|f\rangle$ caused by the interaction Hamiltonian reads

$$\sigma_{if} = 2\pi \frac{|\langle i| \hat{H}'| f\rangle|^2}{\mathcal{F}} \tag{4}$$

where $\mathcal{F}$ is the flux of the incident light.

In general, matrix elements of light-matter interaction Hamiltonian in Eq. 4 between arbitrary state of system are non-vanishing, and the magnitude of these matrix elements depends on the nature of vector potential and magnetic field of electromagnetic field entering $\hat{H}'$. The vector potential component of electromagnetic field governs the behaviour of the first spin-independent term in $\hat{H}'$, and the magnetic field component controls the second spin-dependent term, respectively. This separation in $\hat{H}'$ leads to distinct selection rules for its matrix elements, where the
vector potential component is responsible for selection rules for matrix elements between states of the same multiplicity, while the magnetic field component responsible for selection rules between states of different multiplicities. For instance, for plane wave, \( g(r) = 1 \), the dipole approximation assumes \( e^{i\eta_0 k_0 \cdot r} \approx 1 \). With the help of the quantum mechanical relationship \( \hat{p} = i[\hat{H}_0, \hat{r}] \), where \( \hat{H}_0 \) is the unperturbed molecular Hamiltonian, the absorption between the same multiplicity is proportional to \( |\langle i | \sum_k r_k | f \rangle|^2 \), resulting in the spatial symmetry selection rule (also called as the “dipole selection rule”).\(^{13, 19}\), i.e., only the totally symmetric representation of the direct product of the symmetry irreducible representation of \( r \), initial and final states is allowed. Meanwhile, the involvement of the plan wave (\( g(r) = 1 \)) eliminates the gradient term for the magnetic field (Eq. 3). Moreover, within the dipole approximation, the magnetic field would become zero. As a result, the transitions between different multiplicities are strictly forbidden, i.e. the so-called spin symmetry selection rule. Apparently, there are two ways to break-down the spin symmetry selection rule. One is to go beyond the dipole approximation, while another is to introduce a large confinement factor that can lead to non-zero magnetic field.

It is well established that with the conventional optical excitation sources, none of these two approaches could be utilized. However, the spatially confined plasmon (SCP) generated either by optical excitation or electron current has offered exciting new opportunity. It has been shown that the inhomogeneous plasmonic field can be confined in a nano-cavity.\(^{20, 21}\) With such a highly confined plasmonic field, the inner structure of a porphyrin molecule has been visualised by the tip-enhanced Raman spectroscopy (TERS) with a super high spatial resolution of 0.5 nm.\(^{21}\) Our recent theoretical work has nicely reproduced the experimental Raman images of the molecules by
taking into account the spatial distribution of the SCP in the transition matrix. It was found both theoretically and experimentally that the spatial distribution of the SCP has been confined within the size of 2 nm, which is comparable with the size of many molecules. In principle, the spatial size of the SCP is determined by the Thomas-Fermi screening length, which can be down to, for example, 1 Å for silver and gold. With such a highly localized field, a huge magnetic field is expected to be generated through the curl of its vector potential, as indicated by Eq. In other words, even with vanished spin-orbit coupling, the spin symmetry selection rule can be completely removed. For the sake of the presentation, we name afterwards this new transition as plasmon induced spin transition (PIST).

We will verify the actual magnitude of the effects from the PIST under different confined plasmonic field by calculating the absorption spectrum of a highly symmetric buckminsterfullerene C_{60}. The computational methods are summarized in the Methods section. Due to its very high symmetry I_h, under the dipole approximation, only the {1T_{1u}} excited states of C_{60} are allowed optical transitions, which give rise to only one main absorption band (the C band) above 300 nm in the experimental spectrum. Although the inclusion of the Herzberg-Teller (for singlet) and spin-orbit coupling (for triplet) could break the selection rules, their effects only make very small contribution to the low energy transitions as illustrated in previous experiments (black line in Figure 1b). Without considering both vibronic and spin orbital couplings, our calculated spectrum does well reproduce the experimental one as shown in Figure 1b. The orientation of the molecule is an important fact when it interacts with the highly localized plasmonic field. For the sake of the simplicity, we have adopted the 6-Ring configuration of C_{60} on a spaced substrate (Figure 1a) as
mostly observed in previous experiments\textsuperscript{29}\textsuperscript{29}. The C band is again dominant above 300 nm in the absorption spectrum of C\textsubscript{60} on surface with the 6-Ring configuration with conventional light source shown in Figure 1c. It should be noted that the absorption cross section from single molecules can be experimentally measured through the photoluminescence excitation technique\textsuperscript{21}.

The first consideration is the effects of the going beyond the dipole approximation in wavevector expansion. The SCP is squeezed within a cavity of nanometer size, which is equivalent to the shrinking of the wavelength\textsuperscript{11}. The calculated cross sections as shown in Figure 2a clearly indicate that the shrinking of the wavelength can significantly break the spatial symmetry selection rule, which is consistent with what was proposed by Rivera et al.\textsuperscript{11} It comes from the multipole contributions in the expansion of $e^{i\eta_0\mathbf{k}\cdot\mathbf{r}}$ (Figure 2b). For instance, two $^1T_{1g}$ states from the electric quadrupole contribution emerge when the wavelength is only shrunk by a factor of 50. When $\eta_0 = 100$, the absorptions of $^1T_{1g}$ bands are even larger than the dipole allowed C band transition. It is noted that, with $\eta_0$ less than 100, the breakdown of the spin selection rule shows a very weak sign, resulting in negligible PIST. Again, these observations are consistent with the previous theoretical prediction\textsuperscript{11}. It is interesting to note that the further shrinking of the wavelength by a factor of 300 can generate strong PIST of the triplet $^3T_{1u}$ state caused by the magnetic dipole, which drastically breaks down the spin selection rule. It should be noted that, even when $\eta_0$ equals 500, the dipole-forbidden singlet $^1T_{1g}$ state around 600 nm is still the most intense band, although more PISTs, for instance the magnetic quadrupole allowed $^3H_g$, emerge.

The highly localized plasmonic field can result in a huge gradient of the amplitude distribu-
tion of vector potential that is strongly depended on the spatial distribution of the field, leading to
the generation of a much enhanced magnetic field. Our calculated absorption cross sections of $C_{60}$
excited by the plasmon of different spatial size without shrinking the wavelength are depicted in
Figure 3a. Here the plasmonic size ($\Gamma$) is determined by the full width at half-maximum of field
distribution (see the Methods section). It is found that for the plasmonic size of 20 Å, the absorp-
tion spectrum is almost identical to that from the plan wave excitation except a very weak signal
from the $^3T_{1u}$ state around 427 nm. This is reasonable since the size of the plasmonic field is about
3 times of the size of $C_{60}$ around 7 Å\textsuperscript{10}. When the plasmonic size approaches the molecular size, for
example 10 Å, the PISTs of $^3T_{1u}$ and $^3H_g$ states become significant, nicely illustrating the break-
down of the spin symmetry selection rule. Meanwhile, the appearance of the singlet transitions to
the $^1H_g$ states also indicates that the symmetry selection rule is broken as well. When the molecule
interacts with a highly localized plasmonic field, the symmetry of the whole interactive system is
significantly reduced in comparison with the molecule itself, which results in the breakdown of the
symmetry selection rule. As shown in Figure 3c, the symmetry of the whole interactive system
reduces from $I_h$ to $C_{3v}$. When the plasmonic size sets to be the same of the $C_{60}$ size (7 Å), the $^3T_{1u}$
state around 427 nm gains huge intensity and becomes the most intense absorption band. Under
this condition, the much enhanced magnetic field induced by the gradient term in Eq. 3 kicks in
(Figure 3b). Due to the same reason, all singlet absorption transitions are suppressed by the intense
PISTs when the plasmonic size is set to 5 Å. It should be stressed that the small shrink of wave-
length, for example setting $\eta_0 = 50$, only gives minor affect for the absorption cross sections when
the inhomogeneity is also taken into account. Further shrinking ($\eta_0 = 100$) could indeed enhance
the singlet transitions but does not much affect PISTs (Figure 4a and Figure S1).

Noteworthy, when different positions of plasmon are adopted, the symmetry of the whole system could be further reduced to even $C_1$, where all transitions are allowed in principle. Thus, the position-dependent absorption is expected. We depicted the absorption cross sections under a 7 Å plasmon without shrinking the wavelength at different positions in Figure 4b for the most three intense transitions mainly contributed by the transitions from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) of $C_{60}$. It should be noted that, all three states are near degenerate (Table S2, the maximum energy difference is 0.24 eV, which is less than the experimental resolution of the C band, i.e., 0.3 eV \cite{27}, Figure 1b). It is nice to observe the complementary patterns between different states. Specifically, the $^3H_g$ and $^1H_g$ have a bright triangle and quasi-circular pattern located at the center six-member ring, respectively. On the other hand, the central pattern of the $^1T_{1g}$ state is dark. The bright patterns separated in real space (Figure 4b and Figure S2) reveal that different states could be selectively excited by precisely controlling of the plasmonic position.

In summary, we theoretically demonstrate an efficient spin breaking router by inhomogeneous plasmonic fields from the minimal coupling Hamiltonian in non-relativistic regime. Taking the transitions for singlet and triplet excited states of $C_{60}$ under plasmonic fields as an example, we find that the breakdown of the spin symmetry rule is highly dependent on the size of the plasmons. When the size of plasmon approaches to the molecular size, the transitions to triplet excited states could be largely increased because of the enhanced magnetic field contributed from plasmonic
inhomogeneity. As a result, the absorption cross sections of triplet transitions become comparable to or even larger than that of the conventional dipole allowed singlet transitions. In addition, the plasmonic position dependence of the absorption opens a new pathway to manipulate different molecular quantum states in real space. Our findings could be easily extended to Raman scattering, as well as other linear and nonlinear optical processes, which could have strong impact on different applications in chemistry, material science, physics, and biology.

Methods

Density functional theory calculations A single C\textsubscript{60} was optimized in its ground X\textsuperscript{1}A\textsubscript{g} state by the GAUSSIAN 09 suite of program\textsuperscript{31} at the first-principles level with the Perdew-Burke-Ernzerhof exchange-correlation functional and the Pople’s 6-31+G(d) basis set. Because we considered physisorption of C\textsubscript{60} (Figure 1a) \textit{i.e.}, weak interaction limit between surface and C\textsubscript{60}, during the optimization, the symmetry of C\textsubscript{60} was constrained to I\textsubscript{h}. The optimized structure is in excellent agreement with the experimental observation in gas phase (Figure S3). Based on the optimized structure, adequate singlet and triplet excited states were calculated by the time-dependent density functional theory method at the same computational level. All calculated vertical excitation energies were shifted by 0.35 eV to eliminate the systematic error of the approximate functional\textsuperscript{32}.

Absorption cross section The vector potential of plasmonic field was considered as a field along z-axis with Gaussian distribution\textsuperscript{33} for the calculations of the absorption spectra. Specifically, we assume

\[ A(\mathbf{r}, t) = A_0 e^{i\mathbf{k}_0 \cdot \mathbf{r}} e^{-i\omega t} \hat{z} + c.c., \]  

(5)
where \( g = e^{-\alpha (r-r_D)^2} \) is a Gaussian function located at \( r_D \) with exponent of \( \alpha \) and \( \hat{z} \) is the normal of the substrate surface. For plane wave plasmonic field, we set \( \alpha \) to zero. For localized plasmonic field, the size of plasmon is determined by the full width at half-maximum of the Gaussian function \( (\Gamma) \). In practical simulations, we set \( k_0 \) in the \( xy \) plane pointing to the observer and the angle between \( k_0 \) and \( x \)-axis is set to \( 45^\circ \). As a result, we have

\[
\nabla \times A = [\eta_0 k_y - 2\alpha (y - y_D)] A_0 g e^{i\eta_0 k_0 \cdot r} e^{-i\omega t} \hat{x} - [\eta_0 k_x - 2\alpha (x - x_D)] A_0 g e^{i\eta_0 k_0 \cdot r} e^{-i\omega t} \hat{y} + \text{c.c.},
\]

(6)

where \( |k_x| = |k_y| = \frac{|k_0|}{\sqrt{2}} \), \( \hat{x} (\hat{y}) \) is the unit vector along the \( x (y) \) direction, and \( x_D (y_D) \) is the \( x (y) \) component of \( r_D \). Thus, according to the Fermi’s golden rule and the Wigner-Eckart theorem\(^{34} \), we could calculate the cross section for singlet to singlet and singlet to triplet by

\[
\sigma_{S \rightarrow S} \propto \frac{A_0^2}{\Delta E_{rg}} \left| \langle \Psi_g | \frac{1}{2} \sum_k (\hat{p}_{k,z} g_k e^{i\eta_0 k_0 \cdot r_k} + g_k e^{i\eta_0 k_0 \cdot r_k} \hat{p}_{k,z} ) | \Psi_r^S \rangle \right|^2
\]

\[
\sigma_{S \rightarrow T} \propto \frac{A_0^2 g_e^2}{4\Delta E_{rg}} \left( \left| \langle \Psi_g | \sum_k [\eta_0 k_y - 2\alpha (y_k - y_D)] g_k e^{i\eta_0 k_0 \cdot r_k} \hat{s}_{z,k} | \Psi_r^T \rangle \right|^2 + \left| \langle \Psi_g | \sum_k [\eta_0 k_x - 2\alpha (x_k - x_D)] g_k e^{i\eta_0 k_0 \cdot r_k} \hat{s}_{z,k} | \Psi_r^T \rangle \right|^2 \right),
\]

(7)

where \( |\Psi_g \rangle \) is the \( X^1A_g \) ground state, \( |\Psi_r^S \rangle \) and \( |\Psi_r^T \rangle \) are the singlet and triplet excited states obtained by time-dependent density functional theory calculations, respectively, \( \Delta E_{rg} \) is the vertical energy between ground and excited states, \( \hat{s}_{z,k} \) is the spin operator component along the \( z \)-axis for the \( k \)th electron, and \( g_e \) is the electron \( g \)-factor. In practical calculations, the \( z \) component of \( r_D \) is around 2 Å above the topmost position of \( C_{60} \). All cross sections were calculated by the FASTERS program\(^{35} \).
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Figure 1  **Schematic illustration for C\textsubscript{60} model system.**  
\textbf{a}, Schematic figure for general vector potential of plasmonic field confined in a nano-cavity formed between the tip and spaced substrate. The insert shows the 6-Ring configuration of C\textsubscript{60} adsorbed on the substrate.  
\textbf{b}, Comparison between experimental (black line) and theoretical (red line) absorption cross sections of C\textsubscript{60} in vacuum. The experimental data were obtained after solid-vapour equilibrium under a stable temperature of 858 K by Coheur \textit{et al}\textsuperscript{[27]} The theoretical spectrum was convoluted by the Lorentzian function with a full width at the half-maximum of 0.3 eV. The gray zone indicates the dipole and spin forbidden region for absorption of C\textsubscript{60}.  
\textbf{c}, Calculated absorption cross sections of a single C\textsubscript{60} adsorbed on a spaced substrate with the 6-Ring configuration under the dipole approximation, \textit{i.e.}, set the confinement factor (\(\eta_0\)) to zero, meanwhile, the full width at half-maximum of the amplitude distribution function (\(\Gamma\)) to infinity. The red and blue bars on the top of x-axis indicate the triplet and single transition energies, respectively. The symmetry irreducible representations of all triplet and singlet states mainly contributed by the transitions from highest occupied molecular orbital to lowest unoccupied molecular orbital of C\textsubscript{60} are labeled in red and blue fronts, respectively. All calculated cross sections were convoluted by the Lorentzian function with a full width at half-maximum of 0.05 eV. All calculated transition energies in \textbf{b} and \textbf{c} were shifted by 0.35 eV to compare the experimental observations.

Figure 2  **Absorption under the plane wave plasmonic field.**  
\textbf{a}, Calculated absorption cross sections of a single C\textsubscript{60} adsorbed on a spaced substrate with the 6-Ring configuration under the plane wave plasmonic field with different confinement factor \(\eta_0\) from 50 to
The red and blue areas in absorption cross sections represent the contributions from triplet and single excited states, respectively. The symmetry irreducible representations of all significant triplet and singlet transitions are labeled in red and blue fronts, respectively. All calculated transition energies were shifted by 0.35 eV and cross sections were convoluted by the Lorentzian function with the full width at half-maximum of 0.05 eV.

Figure 3  Absorption under the localized plasmonic field. a, Calculated absorption cross sections of a single $C_{60}$ adsorbed on a spaced substrate with the 6-Ring configuration under the localized plasmonic field without shrinking wavelength at different plasmonic size from 20 to 5 Å (bottom to top). The plasmons are placed on around 2 Å above the center of the center six-member ring and the size of the plasmon is determined by $\Gamma$ (the full width at half-maximum of the amplitude distribution function). The red and blue areas in absorption spectra represent the contributions from triplet and single excited states, respectively. The symmetry irreducible representations of all significant triplet and singlet transitions are labeled in red and blue fronts in the spectra, respectively. All calculated transition energies were shifted by 0.35 eV and cross sections were convoluted by the
Lorentzian function with the full width at half-maximum of 0.05 eV. 

b, Schematic illustration of vector potential (blue) and corresponding magnetic field (red) for infinite and finite plasmons without shrinking wavelength. 

c, Schematic illustration of point group changes of the whole system (including adsorbate and plasmon) from infinite plasmon to finite plasmon. All symmetrical operators for the finite plasmon case are depicted. The reduction of symmetry irreducible representations from infinite plasmon ($I_h$) to finite plasmon ($C_{3v}$) is also included. The symmetry irreducible representations for both allowed triplet and singlet final states for infinite plasmon are labeled in magenta fonts, meanwhile, the symmetry irreducible representations for allowed triplet and singlet final states for finite plasmon are labeled in red and blue fonts, respectively.

Figure 4  Absorption under 7 Å plasmon  
a, Calculated absorption cross sections of a single $C_{60}$ adsorbed on a spaced substrate with the 6-Ring configuration under a 7 Å plasmon with confinement factor $\eta_0$ of 50 (bottom) and 100 (top). In calculated spectra, the red and blue areas represent the contributions from triplet and single excited states, respectively. The symmetry irreducible representations of all significant triplet and singlet transitions are labeled in red and blue fronts, respectively, in the spectra. All calculated transition energies were shifted by 0.35 eV and cross sections were convoluted by the Lorentzian function with the full width at half-maximum of 0.05 eV. 

b Calculated absorption images for $1^3H_g$, $1^1T_{1g}$, and $1^1H_g$ (from left to right) excited states mainly contributed by the transitions from highest occupied molecular orbital to lowest unoccupied molecular orbital of a single $C_{60}$ adsorbed on a spaced substrate with the 6-Ring configuration under
a 7 Å plasmon without shrinking wavelength. The scanning plane is around 2 Å above the C\textsubscript{60}. The solid lines represent the skeleton of C\textsubscript{60} and the values are the relative maximum absorption with respect to the maximum absorption from $^3$H\textsubscript{g}. 