Light-Matter Interaction at the Nano Scale

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Elastic and Inelastic Electron/Photon Scattering

Electron Transport in Molecules

- Elastic
- Inelastic

- Electronic excitation
- Vibrational excitation

Energy loss

- Raman
- Luminescence
**Surface plasmon**

**Electromagnetic field:**

\[ \mathbf{E}(\mathbf{r}, t) = E_0(\mathbf{r}, t)W_k(\mathbf{r})e^{-i\omega t} \]

- Field Strength
- Time Structure
- Spatial Distribution

\( W_k \): node function


High intensity of the plasmon enables to achieve effective detection of a very small numbers of molecules.
Electro-luminescence of molecules in a nano-cavity (time-structure)

Plasmon assisted electro-luminescence of molecules

Beyond the Kasha’s rule

Simulation of vibronic coupling in polyatomic molecules

Transition dipole moment

\[ \mu = \langle g, \nu | \hat{\mu} | e, \mu \rangle \]

Apply *BO approximation* and including the non-Condon effect

\[ \mu = \mu^e(q_0) \langle \nu | \mu \rangle + \sum_a \frac{\partial \mu^e}{\partial q_a} \langle \nu | q_a | \mu \rangle \]

\[ \mu^e(q_0) \text{ is the electronic transition dipole moment at } q_0 \]

Franck-Condon term

Herzberg-Teller term

\[ \langle \nu | q_a | \mu \rangle = \sqrt{\frac{\hbar}{2\omega_a}} \left[ \sqrt{\mu_a} \langle \nu | \mu - 1_a \rangle + \sqrt{\mu_a + 1} \langle \nu | \mu + 1_a \rangle \right] \]

Remaining problem is to calculate the Franck-Condon integral
Simulation of vibronic coupling in polyatomic molecules

Duschinsky Transformation\textsuperscript{[1]}:

\[ Q' = JQ + K \]

\[ J = (L')^T L \quad K = (L')^T M^{1/2} (X - X') \]

\( <0|0> \) can be calculated analytically as\textsuperscript{[2]}:

\[
\langle 0|0 \rangle = \left( \frac{2^N \det(\Gamma'\Gamma)^{1/2}}{\det(J(J^T\Gamma'J + \Gamma))} \right)^{1/2} \times \exp\left( \frac{1}{2} K^T [\Gamma'J(J^T\Gamma'J + \Gamma)^{-1} J^T - 1]\Gamma'K \right)
\]

All other terms can be computed recursively\textsuperscript{[3]}, for example, at 0K we have:

\[
\langle 0|\mu \rangle = \frac{1}{\left( 2\mu_a \right)^{1/2}} \left[ d_a \langle 0|\mu - 1_a \rangle + \sqrt{2(\mu_a - 1)}C_{aa} \langle 0|\mu - 2_a \rangle \right] \\
+ \sum_{b=a+1}^{N} \left( C_{ab} + C_{ba} \right) \langle 0|\mu - 1_a - 1_b \rangle
\]

\textsuperscript{[1]} F. Duschinsky, \textit{Acta Physicochimica URSS} 7, 551 (1937)
Simulation of vibronic coupling in polyatomic molecules

Convergence of the calculation can be checked by the intensity sum rule:

\[ I^{tot} = \left| \mu^e (q_0) \right|^2 + \sum_a \sum_v p_v \left( \frac{\partial \mu^e}{\partial q_a} \right)^2 \frac{\hbar}{2 \omega_a} (2\nu_a + 1) \]

\( p_v \) is the population of initial states.

Implemented in DynaVib software package with applications in the following areas:

(1) STM induced electroluminescence from single molecules
(2) Vibrationally-resolved optical and X-ray spectroscopy
(3) Electron transport properties of single molecules with the inclusion of electron-vibration coupling

Theoretical model: electron tunneling induced photon emission

Schematic picture of the electron tunneling induced photon emission process.

Both HOMO and LUMO in the bias window, electron tunneling leaves a molecular excited state for photon emission.

Photon emission from the ground vibrational level due to the fast internal decay rate.
**Theoretical model: Plasmon-assist emission**

Plasmons behave like strong electromagnetic sources and can excite the molecule resonantly into higher vibrational levels in the first excited state following a resonant emission.

Remaining question, how to describe all the processes?

\[
\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} \left[ \hat{H}, \rho \right] + \Gamma_{tr} \rho + \Gamma_{ph} \rho + R \rho
\]

Description of the plasmon

Plasmon-molecule interaction

\[ \hat{H} = \hat{H}_{mol} + \hat{V}(r, t) \]

\[ \hat{V}(r, t) = -\mu \cdot \varepsilon(t) \quad \varepsilon(t) = eE(t) \cos(\omega t) \]

\[ E(t) = E_0 \exp \left[ -2 \ln 2 \left( \frac{t - t_0}{\tau} \right)^2 \right] \]
EL spectra for TPP molecules

EL spectra modified by the resonant plasmonic excitation. (Left) Measured EL spectra of TPP molecules together with the corresponding NCP modes (black dashed line). (Right) Calculated EL spectra together with the contributions from the three processes.

\[ \gamma^L = 4.1 \, \mu eV, \quad \gamma^R = 1.2 \, \mu eV, \quad \alpha = 0.5, \quad T = 80 \, K \]

\[ E(t) = E_0 \exp \left[ -2 \ln 2 \left( \frac{t - t_0}{\tau} \right)^2 \right] \]

Photo-images:
Inter- Molecular Energy Transfer

Single Molecule

Molecular dimer
Electroluminescence of a single Zn-Porphyrin molecule

Photo-images

STM images
Evolution of Intermolecular interaction

Dipolar Interaction

Excited Wavefunction:

\[ \Psi_{\text{dim},e} = \left( \psi_{1,e,2,g} \pm \psi_{1,g,2,e} \right) / \sqrt{2} \]

Interactive energy of two dipoles

\[ J = \frac{\mathbf{r}_1 \cdot \mathbf{r}_2}{4\pi\varepsilon_0 r^3} - \frac{3(\mathbf{r}_1 \cdot \mathbf{r})(\mathbf{r}_2 \cdot \mathbf{r})}{4\pi\varepsilon_0 r^5} \]
Orbital-like Dipolar Interaction

ZnPc transition dipoles

Mode-1

Y

Mode-2

Mode-3

Mode-4

Mode-5

dipole phase relation

ZnPc transition dipoles

Experiment

Simulation

Molecular Orbitals

σ

σ^*

π

π^*

+  

+  

= 2x

= 2x

+  

+  

= 2x
Extension to multi-molecule entangled systems — Superradiant mode-1

Superradiant mode-1: In-line in-phase coupling!
Visualizing coherent intermolecular dipole–dipole coupling in real space

Electron energy loss spectroscopy

a) Diagram of electron energy loss spectroscopy setup with a tip, toroidal deflector, and position sensitive detector.

b) Image of a tip on HOPG (Hexagonal Organic Phthalocyanine Graphite) substrate with a scale bar of 100nm.

c) Graph showing normalized intensity vs. energy loss (eV) with data points labeled Palmer et al and Present work, with a magnification factor of 5.
First observation of nonlinear electron scattering

Nonlinear Electron Scattering Spectroscopy (NESS)

Xu et al., Nature Physics, 10 (2014) 753
in the present work, the probability of SPR excitation is enhanced when an external electric field is introduced by the incident electron. Under normal conditions, we have observed no enhancement of SPR excitation on the Ag surface due to the diode formed by the Ag surface and the Au tip. In their experiments was much larger than ours. This might be due to the diode formed by the Ag surface and the Au tip.

\[
W_{ba} = W_{ba}^{(1)} + W_{ba}^{(2)} \propto |\langle b|E_1 \cdot D_{ba}|a\rangle|^2 + \left| \sum_n \frac{\langle b|E_2 \cdot D_{bn}|n\rangle \langle n|E_1 \cdot D_{na}|b\rangle}{\Gamma_n/2} \right|^2
\]

\[
W_{ba}^{(1)} \propto |\langle b|E_1 \cdot D_{ba}|a\rangle|^2 \propto (\mu_{ba}E_1)^2
\]

\[
W_{ba}^{(2)} \propto \left| \frac{\langle b|E_2 \cdot D_{b}|b\rangle \langle b|E_1 \cdot D_{ba}|a\rangle}{\Gamma_b/2} \right|^2 \propto \left( \frac{2\mu_b E_2}{\Gamma_b} \right)^2 W_{ba}^{(1)}
\]

\[
W_{ba} = (1 + \beta)W_{ba}^{(1)} \quad \beta \propto \left( \frac{2\mu_b E_2}{\Gamma_b} \right)^2
\]

Xu et al., *Nature Physics*, 10 (2014) 753
Electric field effects

\[
\frac{n_{SPR}}{n_{els}} = RI
\]
Hot spots

10nm
30nm
100nm
How about the spatial distribution?

Nonlinear effects?
Super-high spatial resolution?

Advantages of near field images: Beyond the diffraction limit
Tip Enhanced Raman Scattering (TERS)


H2TBPP on Ag(111)
Sub-nm resolution of optical Raman mapping of a single molecule: structure details

**Light-matter interaction**

\[ \hat{V}(r,t) = -\mu \cdot E(r,t) \]

\( \mu \) is a position \( (r) \) operator, the electric field is position independent.

Fine with light: 530nm light, the focusing spot size less than 265nm, much larger than the size of the molecule

\[ \Delta x \cdot \Delta p \geq \frac{\hbar}{2} \]

Plane Wave (Uniform)

Plasmon???

Calling for new theory!!!
Theory: Uniform EM

\[ E_p = E_p^0 e^{-i \omega_p t} \]

The Albrecht's theory for Raman Intensity

A term:

\[ P_{0L}^L (A) = \frac{E_p^0}{\hbar} \langle \psi_g | \mu | \psi_r \rangle \langle \psi_r | \mu | \psi_g \rangle \sum_{v' = 0}^{\infty} \frac{\langle v^f | v^r \rangle \langle v^r | v^i \rangle}{\omega_{e^r v^r : e^g v^i} - \omega_p - i \Gamma} + \text{NRT} \]

B term:

\[ P_{0L}^L (B) = \frac{E_p^0}{\hbar} \left[ \frac{\partial \langle \psi_g | \mu | \psi_r \rangle}{\partial Q_k} \langle \psi_r | \mu | \psi_g \rangle \sum_{v' = 0}^{\infty} \frac{\langle v^f | Q_k | v^r \rangle \langle v^r | v^i \rangle}{\omega_{e^r v^r : e^g v^i} - \omega_p - i \Gamma} \right] + \text{NRT} \]
The Raman Intensity is given by:

\[ E_p = M_i E_p^0 g(r) e^{-i\omega_p t} \]

**Raman Intensity:**

A term:

\[
P_L^0 (A) = \frac{\sqrt{F_p M_i E_p^0}}{\hbar} \left[ \langle \psi_g | \mu | \psi_r \rangle \langle \psi_r | \mu g(r) | \psi_g \rangle \sum_{v'=0}^{\infty} \frac{\langle v^f | v^r \rangle \langle v^r | v^i \rangle}{\omega_{e^v v^r e^g v^i} - \omega_p - i\Gamma} \right] + \text{NRT}
\]

B term:

\[
P_L^0 (B) = \frac{\sqrt{F_p M_i E_p^0}}{\hbar} \left[ \frac{\partial \langle \psi_g | \mu | \psi_r \rangle}{\partial Q_k} \langle \psi_r | \mu g(r) | \psi_g \rangle \sum_{v'=0}^{\infty} \frac{\langle v^f | Q_k | v^r \rangle \langle v^r | v^i \rangle}{\omega_{e^v v^r e^g v^i} - \omega_p - i\Gamma} \right] + NRT
\]

\[
+ \langle \psi_g | \mu | \psi_r \rangle \frac{\partial \langle \psi_r | \mu g(r) | \psi_g \rangle}{\partial Q_k} \sum_{v'=0}^{\infty} \frac{\langle v^f | v^r \rangle \langle v^r | Q_k | v^i \rangle}{\omega_{e^v v^r e^g v^i} - \omega_p - i\Gamma} \]

**Uniform**  **Confined**

\[
\langle \psi_r | \mu | \psi_g \rangle \rightarrow \langle \psi_r | \mu g(r) | \psi_g \rangle
\]

---

Theory: Confined localized field induced nonlinear effects

\[ E_p = M_i E_p^0 g(\mathbf{r}) e^{-i\omega_p t} \]
\[ E_s = M_s E_p^0 g(\mathbf{r}) e^{-t^2/2\tau_s^2} e^{-i\omega_s t} \]

Induced nonlinear polarization:

A term:
\[ P_{0}^{NL}(A) = \frac{M_i^2 M_s \left| E_p^0 \right|^2 E_s^0 \sqrt{2\pi \tau_s}}{\hbar^3} \langle \psi_r | \mu | \psi_g \rangle \langle \psi_r | \mu g(\mathbf{r}) | \psi_g \rangle^3 \]
\[ \times \sum_{v^i, v^{i'}} \langle v^f | v^r \rangle \langle v^r | v^i \rangle \langle v^i | v^{r'} \rangle \langle v^{r'} | v^f \rangle \lambda^{(3)} + \text{NRT} \]

B term:
\[ P_{0}^{NL}(B) = \frac{M_i^2 M_s \left| E_p^0 \right|^2 E_s^0 \sqrt{2\pi \tau_s}}{\hbar^3} \left[ \frac{\partial \langle \psi_r | \mu | \psi_g \rangle}{\partial Q_k} \langle \psi_r | \mu g(\mathbf{r}) | \psi_g \rangle^3 \right. \]
\[ \times \sum_{v^i, v^{i'}} \langle v^f | v^r \rangle \langle v^r | v^i \rangle \langle v^i | v^{r'} \rangle \langle v^{r'} | v^f \rangle \lambda^{(3)} \]
\[ + \langle \psi_r | \mu | \psi_g \rangle \frac{\partial \langle \psi_r | \mu g(\mathbf{r}) | \psi_g \rangle}{\partial Q_k} \langle \psi_r | \mu g(\mathbf{r}) | \psi_g \rangle^2 \]
\[ \left. \times \sum_{v^i, v^{i'}} \left( \langle v^f | v^r \rangle \langle v^r | Q_k | v^i \rangle \langle v^i | v^{r'} \rangle \langle v^{r'} | v^f \rangle \right) \right] + \text{NRT} \]
Possible structures of H2TBPP on Ag(111)
**Energies (in eV)**

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<th>Conf.</th>
<th>Concave</th>
<th>Plane</th>
<th>Convex</th>
</tr>
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<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td>$E_{ads}$</td>
<td>4.17</td>
<td>4.19</td>
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<td>$E_{s1}$</td>
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<td>$E_{s2}$</td>
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<td>$E_{s3}$</td>
<td><strong>2.47</strong></td>
<td><strong>2.48</strong></td>
<td>3.11</td>
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<tr>
<td>$E_{s4}$</td>
<td>2.57</td>
<td>2.56</td>
<td>3.20</td>
</tr>
</tbody>
</table>

- Experimental excitation energy is 2.33 eV
Calculated STM images

(a) Sideview

(b) Topview

- Concave
- Plane
- Convex
Calculated Raman images

<table>
<thead>
<tr>
<th>Concave</th>
<th>Plane</th>
<th>Convex</th>
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<tbody>
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<tr>
<td>1.0nm</td>
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</tr>
<tr>
<td>2.0nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0nm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Raman shift (cm$^{-1}$)

Intensity (a.u.)

B term

Total

A term

Expt., Concave, Convex, Plane

800 900 1000 1100 1200 1300 1400 1500 1600

Calculated Raman images
Distinguishing adjacent molecules on a surface

Distinguishing between ZnTPP and H2TBPP domains. a, STM topograph of two separated molecular islands (1 V, 100 pA). b, Corresponding spectral evolution for ten sequential TERS measurements along the line trace marked in a (0.1 V, 1 nA, 30 s) with a step size of 1 nm. c, Fine details of spectral evolution across the molecular island edge for ZnTPP molecules with a step size of 0.25 nm. Top: height profile for the line trace marked in the right inset (0.75 V, 10 pA). Bottom: corresponding TERS intensity profile for the 700 cm−1 mode (integrated over 670–730 cm−1) shown in the right inset (0.1 V, 1 nA, 10 s). d, STM topograph of two adjacent molecular islands (0.6 V, 10 pA). e, Corresponding spectral evolution for 15 sequential TERS measurements along the line trace marked in d (0.1 V, 1 nA, 10 s) with a step size of 0.75 nm.
Distinguishing adjacent molecules on a surface

The spatial distribution of the plasmonic field should be localized within 2nm

Nonresonant Raman: Theory

- Sum over all possible states
- Take care of prior summation of the vibrational states

Linear:

$$P_0^L = 2\sqrt{F_p M_i E_i^0} \frac{\partial \alpha_{\text{eff}}}{\partial Q_k} \langle v^f | Q_k | v^i \rangle$$

Nonlinear:

$$P_0^{NL} = \lambda \frac{\partial \alpha_{\text{eff}}}{\partial Q_k} \frac{\partial \alpha'_{\text{eff}}}{\partial Q_k} \langle v^f | Q_k | v^i \rangle^2$$

where

$$\alpha_{\text{eff}} = \sum_r \frac{\langle \psi_g | \mu | \psi_r \rangle \langle \psi_r | \mu g | \psi_g \rangle}{E_{e^r:e^g}}$$

$$\alpha'_{\text{eff}} = \sum_r \frac{\langle \psi_g | \mu g | \psi_r \rangle \langle \psi_r | \mu g | \psi_g \rangle}{E_{e^r:e^g}}$$

Nonresonant Raman: Water monomer

1 Å
Nonresonant Raman: Water dimer

Figure 1. (a) Topview (left) and sideview (right) of the optimized geometry for water monomer adsorbed on the Au(111) surface. (b) Simulated non-resonant Raman images on Au(111) surface (top) and in vacuum (bottom) for water vibrational modes.

Figure 2. (a) Topview (left) and sideview (right) of the optimized geometry for water dimer adsorbed on the Au(111) surface. (b) Simulated non-resonant Raman images for water trimer of hydrogen bonding, bending, and stretching modes. The labeled values are the corresponding frequencies in cm$^{-1}$. It is interesting to remark the phase of image's pattern, which represents the sign of $\partial\psi/\partial Q$. For instance, the ribbon and the bell-shaped parts in the $\tilde{\nu}_2$ image have different phases, while, all parts in the $\tilde{\nu}_1$ image have the same phase. In addition, the phases of four parts in the $\tilde{\nu}_3$ image (including two strong lobes and two weak lobes) are the same of those in the $d_{xy}$ atomic orbital (Figure S1).
Nonresonant Raman: Water trimer

(b) 

231.8 238.7 289.5

1616.0 1617.9 1627.6

Figure 3. Simulated non-resonant Raman images for water trimer of hydrogen bonding, bending, and stretching modes. The labeled values are the corresponding frequencies in cm$^{-1}$.
Nonresonant Raman: Water trimer

![Image of Nonresonant Raman: Water trimer]
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