Higher-order effects in extended conjugated molecular emitters near plasmonic nanostructures

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1. Introduction

Spontaneous emission is the process by which an excited emitter emits light.

Usually, we say that it emits light because, in vacuum, it can only couple to the **"**vacuum electromagnetic density of states**"**. [Unless you work in High energy physics]

However, the spontaneous emission, or the spontaneous decay, if you wish, happens **whenever** an excited emitter is in the close vicinity of any continuum density of states.

This is especially true near **Nanoplasmonic** structures, where it decays into **plasmons**. [Plasmon is the quanta for electrons oscillation] → Feel free to ask more about it.

Importantly, the interaction then is more complicated [1], and **you are right** to ask then: is it still a spontaneous ***emission***, or is it now only decaying into **plasmons**, and no longer **photons**?

Interestingly, it is both. You get plasmons, and you get photons. How much is the % of each is my work. In addition, **we see activation** of dark transitions. [Dark transition = Very low probability of emitting a photon]

2. Method

Fermi's Golden Rule: Point-dipole Approximation – Quite BAD ↘

Ask me:
Why?
When?
Where?

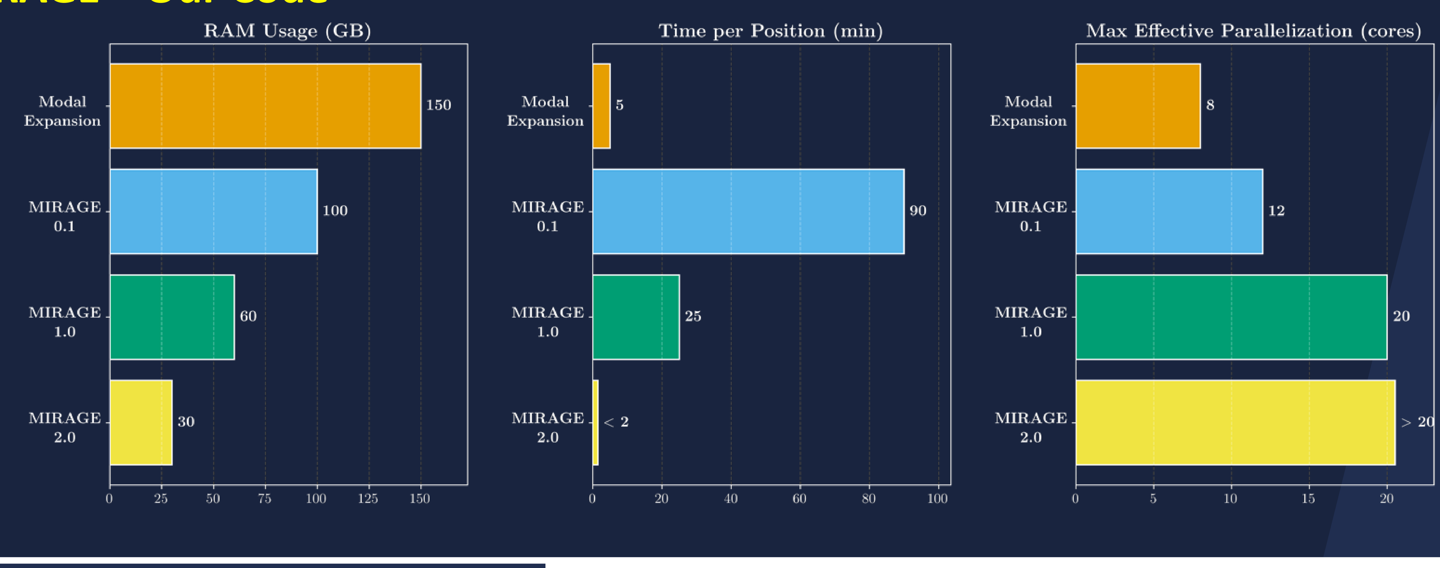
$$\Gamma = \frac{\omega_0^2 |\mathbf{d}|^2}{3\pi\epsilon_0 \hbar c^3}$$

Generalized Fermi's Golden Rule

$$\Gamma = \frac{2\pi}{\hbar^2}\frac{e^2\hbar}{\pi\epsilon_0 m_e^2 c^2}\int\int d\mathbf{r}d\mathbf{r}'\ \psi_e^*(\mathbf{r})\psi_e(\mathbf{r}')\ (\mathrm{Im}\ G_{ij}(\mathbf{r},\mathbf{r}',\omega_0))\ (p_i\psi_g(\mathbf{r}))(p_j^*\psi_g^*(\mathbf{r}'))$$

Molecule Structure

MIRAGE – Our Code



3. Results

3.1. Higher-order effects

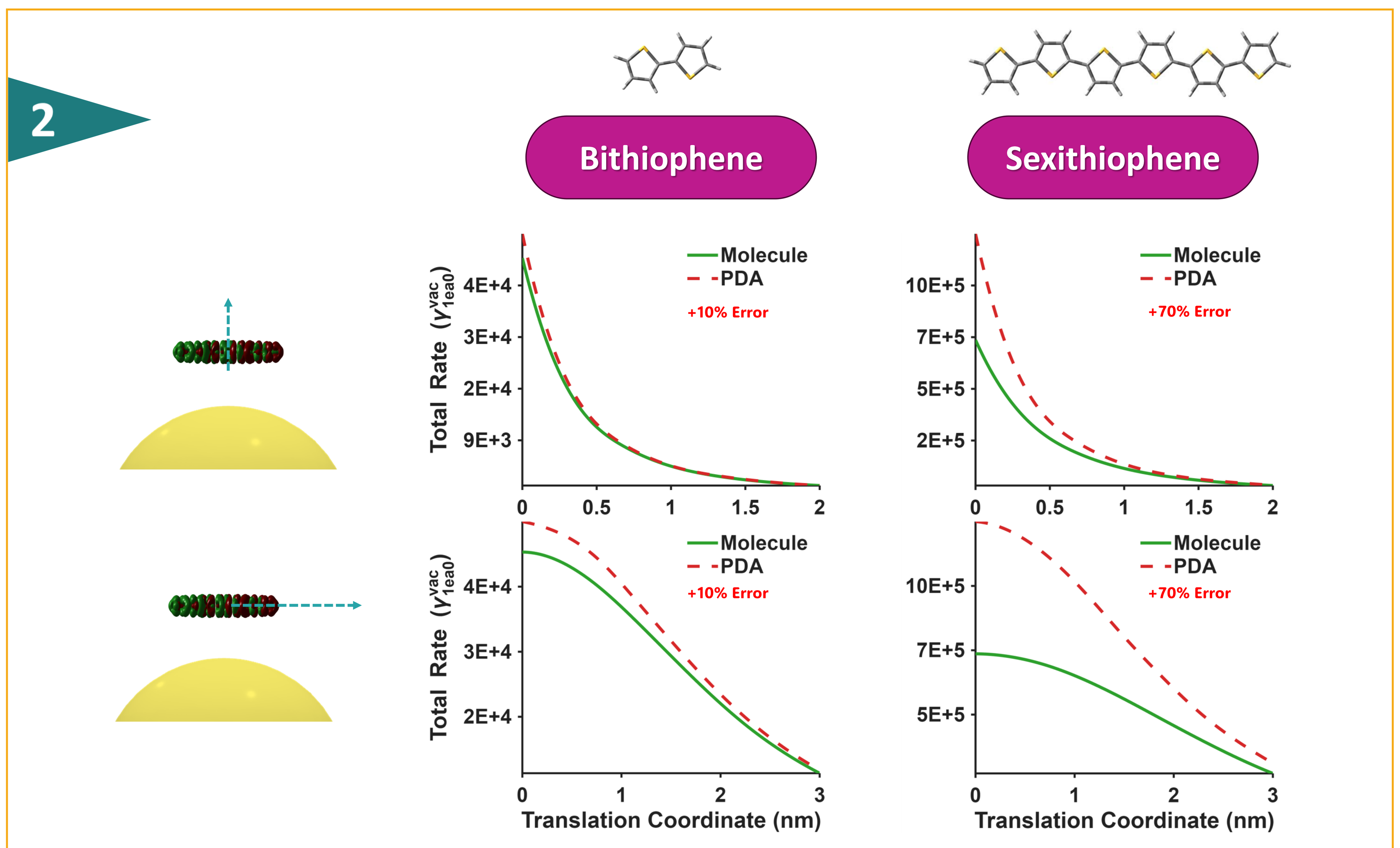


*Figure 1. Molecule suspended on top of a gold nanosphere, and displaced: (**Top**) radially, (**Bottom**) tangentially, with respect to the surface. The graphs show a comparison between the point-dipole approximation (PDA) and the full molecular treatment.*

3.2. Allowed vs Forbidden

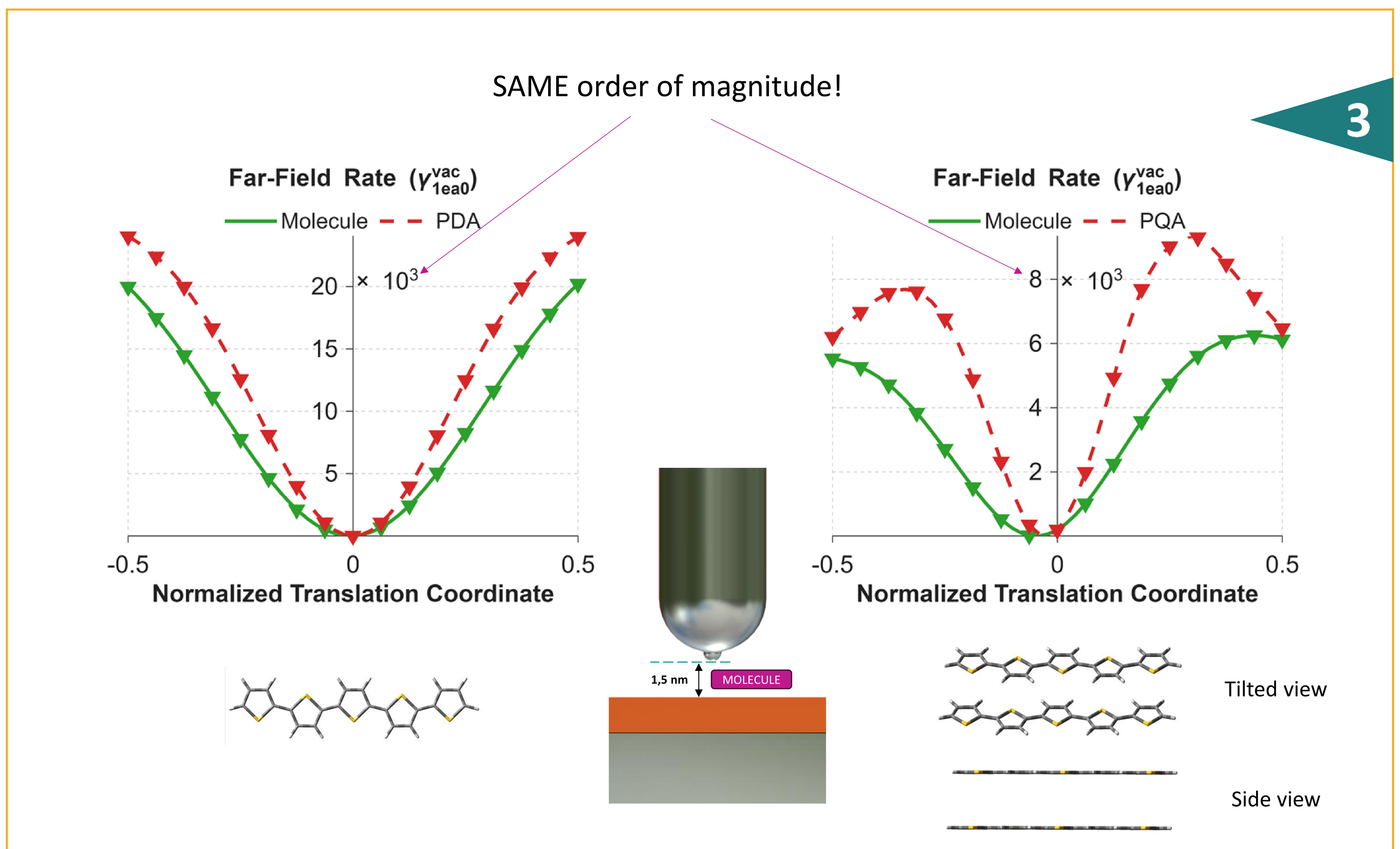


*Figure 2. Molecule sitting in the gap between the STM-tip and the substrate. It is displaced horizontally under the tip along its long axis. On the **left**, is an α-quinquethiophene monomer (dipole-allowed emitter). On the **right**, is an α-quinquethiophene H-aggregate (dipole-forbidden).*

4. Conclusion

1. Full molecular treatment is essential for quantitative results, and even at times, qualitative ones.

1. Dark emitters can exhibit huge enhancements that put them on par with their bright counterparts.
2. A new code MIRAGE was developed capable of providing full molecular treatment at the time complexity of the usual approximations, making them obsolete for all practical purposes.

Acknowledgments

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CÉCI

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