Two-photon molecular emitters enhanced with nanoantennas

Steve Smeets[1], Bjorn Maes[1], Gilles Rosolen[1], and Colin Van Dyck[2]

[1] Micro- and Nanophotonic Materials Group, [2] Theoretical Chemical Physics Group,
Research Institute for Materials Science and Engineering, University of Mons

Abstract

Although two-photon spontaneous emission (TPSE) is the reverse process of two-photon absorption (TPA), the design of efficient emitters follows different rules. We design two-photon emitters by: 1) employing TD-DFT to compute transition moments 2) designing a hybrid nanoantenna to enhance the radiative TPSE rate. The enhancement is calculated using our framework based on the numerical calculation of one-photon Purcell factors [1]. We design a molecular emitter emitting 30 times more than a dipole in vacuum.

Design rules for two-photon emitters

- **Two-photon spontaneous emission (TPSE):** second-order process, 8 to 10 orders of magnitude slower than one-photon emission [2], entangled photons
- **For degenerate processes** (higher TPSE rate):

Vacuum TPSE rate

$$\phi_0^{(2)}(y=0.5) \propto \left\| \sum_{|m\rangle} \frac{\mathbf{d}^{em}\mathbf{d}^{mg}}{\boxed{y_{em}} - 0.5} \right\|^2$$

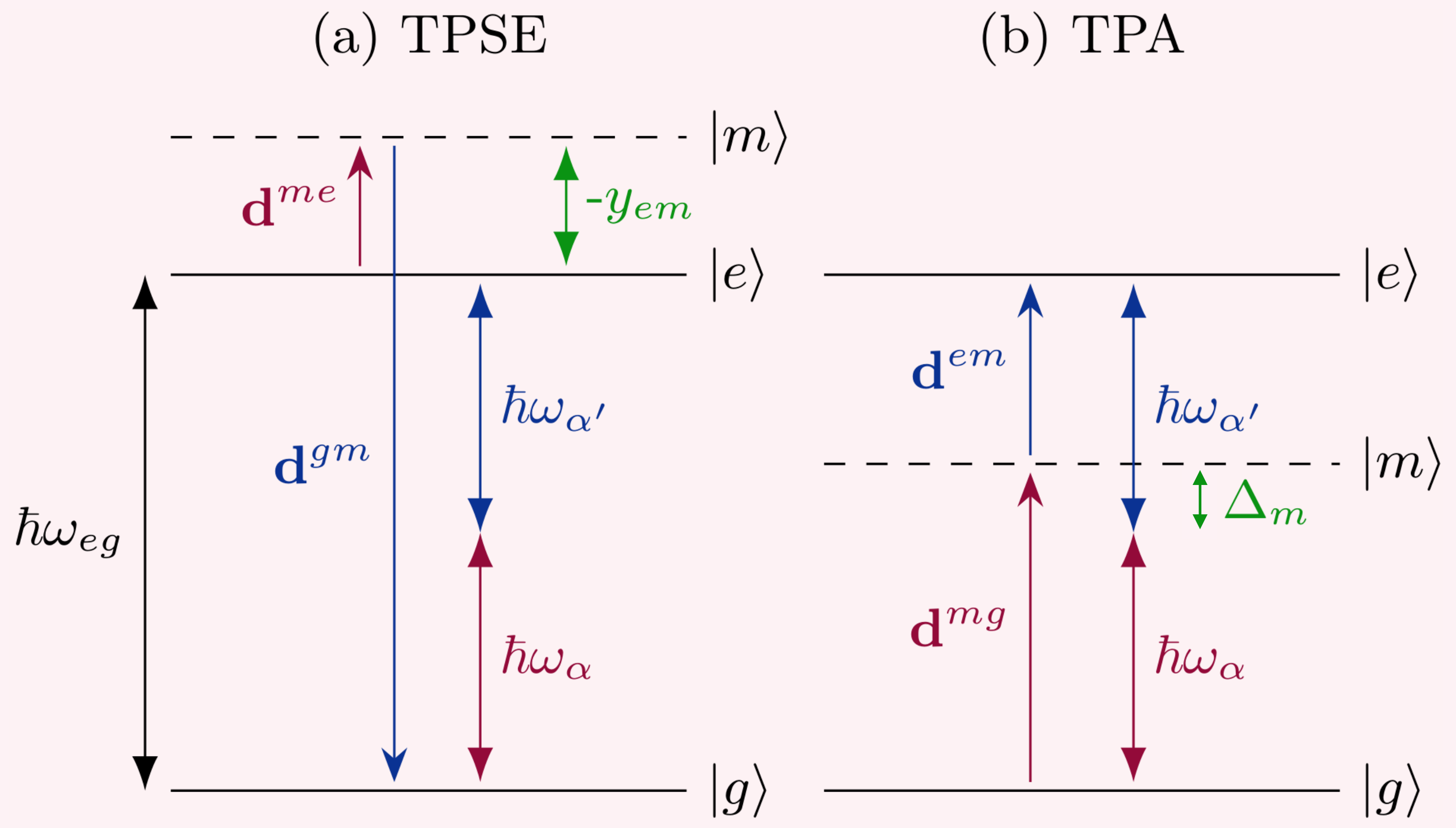
Negative value

TPA cross-section [3]

$$\delta \propto \left\| \sum_{|m\rangle} \frac{\mathbf{d}^{em}\mathbf{d}^{mg}}{\Delta_m} \right\|^2$$

- Search for molecules having an intermediate state:
  - → Close in energy to the excited state for TPSE
  - → Near the middle of the gap for TPA

Different design rules for TPSE and TPA

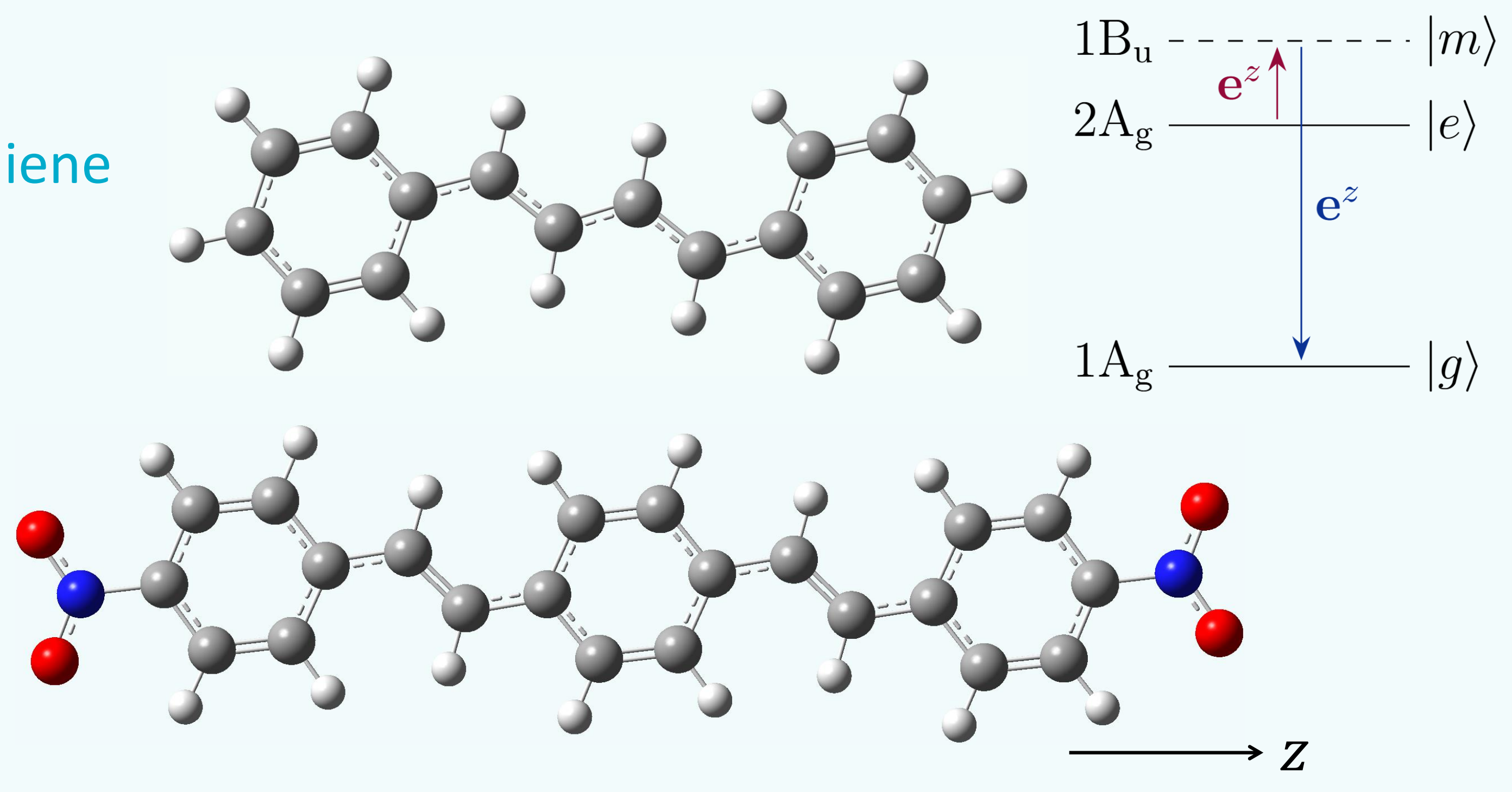


Calculation of TPSE in molecules

Two candidates

Diphenyl butadiene (DPB)

NO_2 – OPPV



Method

- **TD–DFT:** B3LYP/6-31G*, optimization in the first excited state
  - → Misses double excitations → incorrect state ordering
  - → Computes transition moments (via Gaussian)
- **PPP Theory** (semi-empirical method for π − electrons systems)
  - → Computes excited-state energies

Results

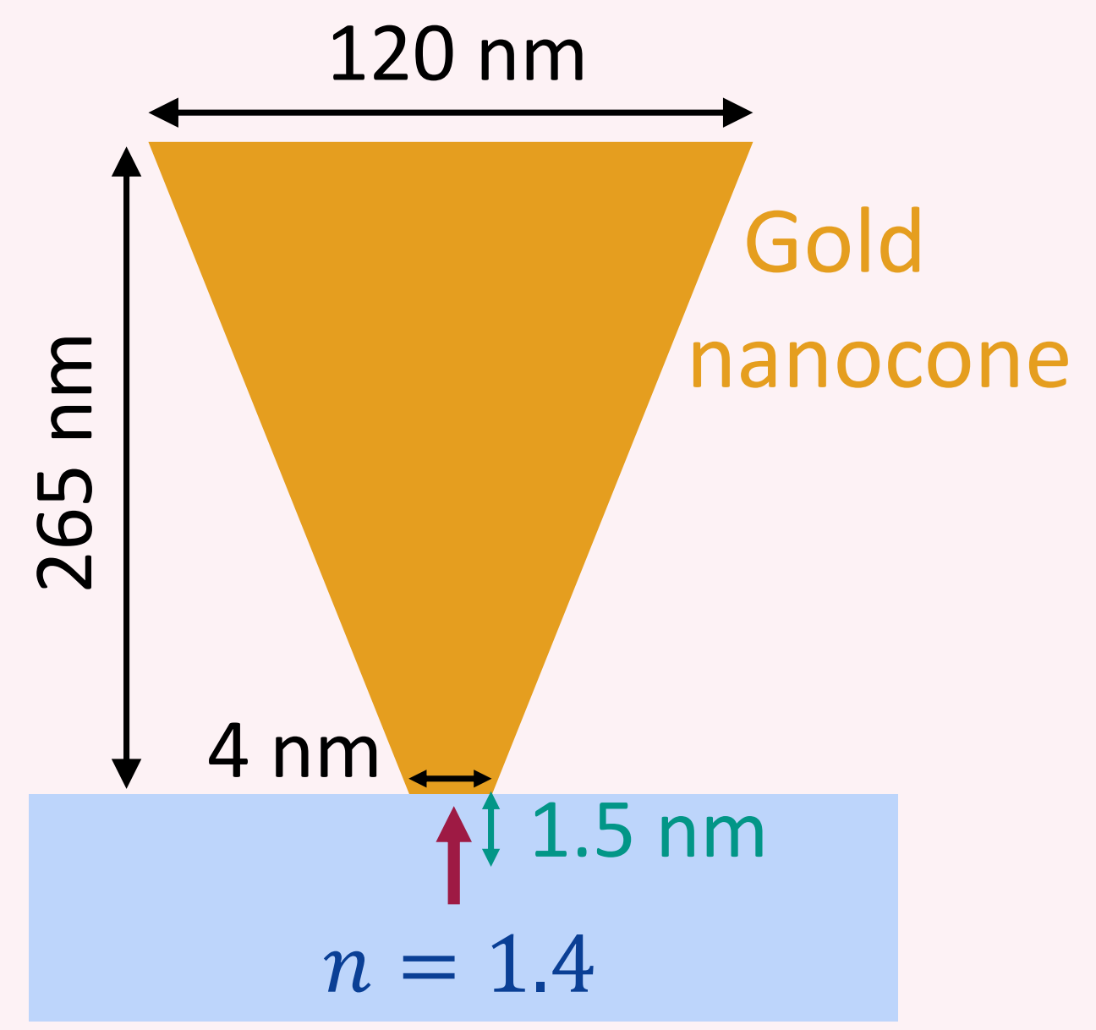
Molecule	E_{2A_g} [eV]	E_{1B_u} [eV]	$D^{eg}(0.5)$ [a.u.]	$\phi_0^{(2)}(0.5)$ [s^{-1}]
DPB	2.98	3.15	30.2	0.12
NO_2 – OPPV	2.44	2.54	**117**	**2.19**

- ✓ Small energy gap between 1st and 2nd excited states
- ✓ High second-order transition moments D^{eg}

Enhancement with a hybrid nanoantenna

System

- **Highly radiative in perpendicular direction**
- **Emitter:** NO2 – OPPV (2 nm)



Method

- **TPSE as a function of one Purcell factors** (emitter along z) [1]

$$\frac{\phi^{(2)}(y)}{\boxed{\phi_0^{(2)}}} = P_z(y)\,P_z(1-y)$$

Vacuum rate — Complementary frequencies

- **Classical computation of Purcell factors** with Comsol

$$\boxed{\frac{W_z}{W_0}} = P_z = \boxed{\frac{\Gamma^{(1)}}{\Gamma_0^{(1)}}}$$

Classical — Quantum

Results

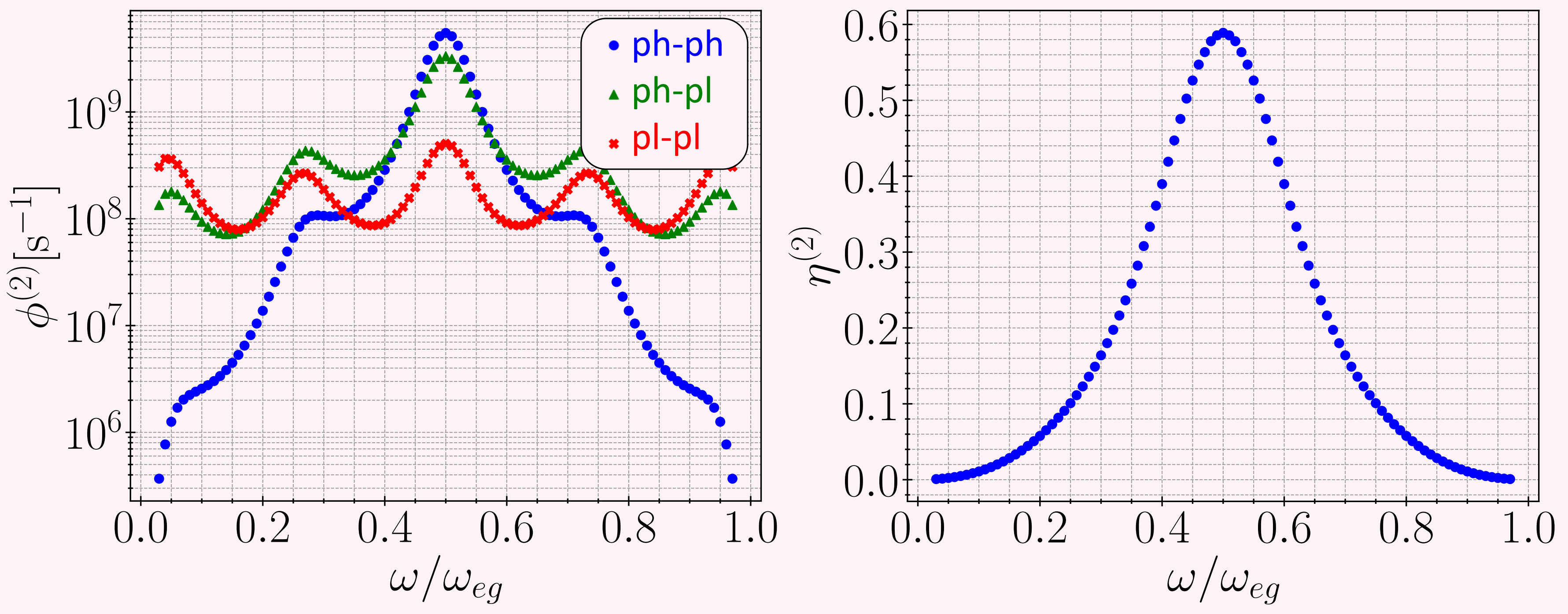


Figure – Two-photon spontaneous emission rate $\phi^{(2)}$and quantum efficiency $\eta^{(2)} \coloneqq \phi^{(2)}_{\text{ph-ph}}/\phi^{(2)}_{\text{tot}}$ for the $2A_g \rightarrow 1A_g$ transition of the NO2 – OPPV molecule placed in the hybrid nanoantenna

Conclusion

- Two-photon molecular emitter **30 times stronger** than a one-photon emitter in vacuum ($d^{eg} = 1$ a.u.)
- **TD-DFT underestimates TPSE rates** for π-conjugated molecules because it fails to account for double excitations
- For a molecule with the same vacuum TPSE rate as NO2 – OPPV near the presented nanoantenna, **TPSE dominates** if the 1st excited state has a transition dipole moment < 0.01 a.u. (verified for dark states)

References

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[3] Pawlicki et al. Two-photon absorption and the design of two-photon dyes. Angew. Chem. Int. Ed. 48, 3244 (2009)

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Contact: Steve.Smeets@umons.ac.be