Supporting information

Numerical Calculations of Radiative and Non-Radiative Relaxation of Molecules Near Metal Particles

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Here we present some comparisons between our numerical results and the analytical results of the Gersten-Nitan (GN) theory[1,2] that are valid in the electrostatic limit. Figures 1 and 2 compare our numerical results for the non-radiative relaxation (that is, dipole to metal energy transfer) rate (blue) and the corresponding calculation based on the analytical theory (red), for a system comprising of a metal sphere of radius 20 nm and a point dipole perpendicular to the sphere surface at distance of 10 nm from the sphere surface (see the inset in Fig. 2 of the manuscript). In Fig S1 we use a Drude metal with dielectric function that yields a plasmon resonance at 1eV, while in Fig S2 a Drude model for silver (same parameters as in the manuscript) was used. The better agreement between theory and experiment in Fig. 1 reflects the better performance of the electrostatic approximation used in the GN theory as well as the spatial resolution (here taken with grid step 0.5 nm) for the longer wavelength radiation. We have verified that the distance dependence reported in the paper does not change appreciably by increasing the grid resolution up to 2 nm.

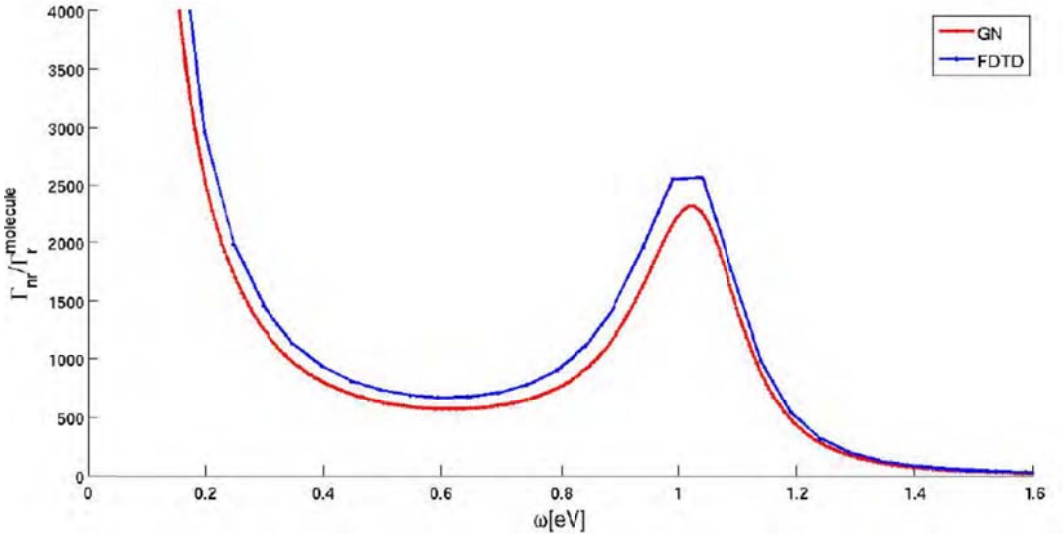
GN
FDTD
$\Gamma_{nr}/\Gamma_r^{molecule}$
ω[eV]

FIG. S1

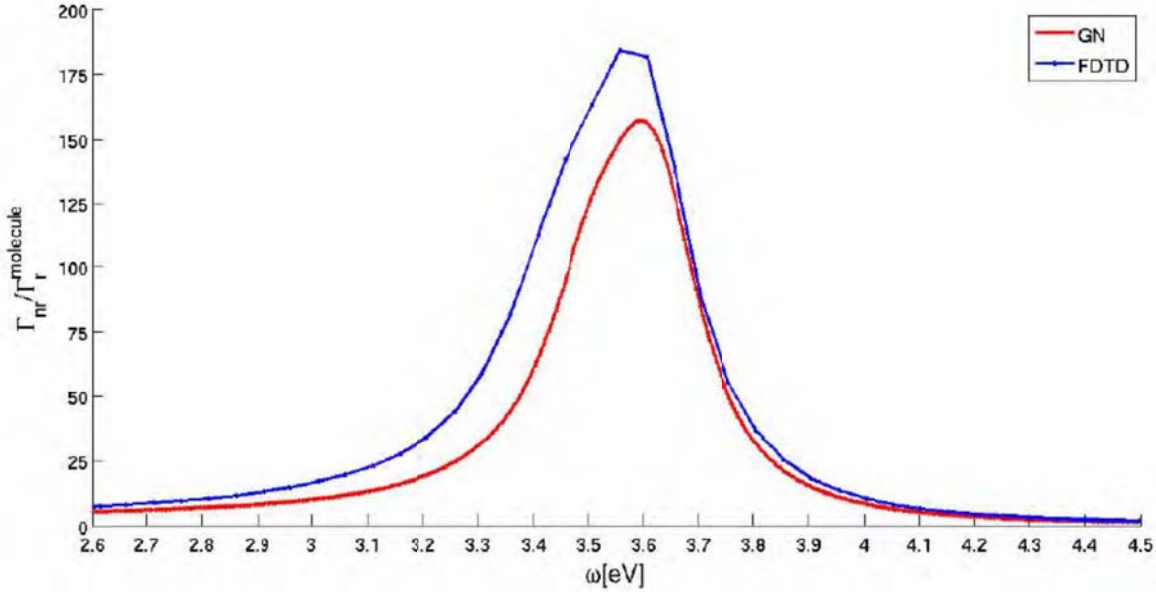
GN
FDTD
$\Gamma_{nr}/\Gamma_r^{molecule}$
ω[eV]

Fig. S2

References

(1) Gersten, J.; Nitzan, A., Spectroscopic Properties of Molecules Interacting with Small Dielectric Particles, *J. Chem. Phys.* **1981**, *75*, 1139-52.

(2) Gersten, J. I.; Nitzan, A., Photophysics and Photochemistry near Surfaces and Small Particles, *Surf. Sci.* **1985**, *158*, 165-89.