Supporting information: Integrated molecular optomechanics with hybrid dielectric-metallic resonators

Ilan Shlesinger,1 Kévin G. Cognée,1,2 Ewold Verhagen,1 and A. Femius Koenderink1

1 Center for Nanophotonics, AMOLF, Science Park 104, 1098 XG Amsterdam, The Netherlands
2 LP2N, Institut d’Optique Graduate School, CNRS, Univ. Bordeaux, 33400 Talence, France
DERIVATION OF THE EFFECTIVE HYBRID HAMILTONIAN

The optomechanical coupling is described as a shift of the antenna resonance frequency due to the mechanical motion. Introducing the position operator, 
\[ \hat{x}_m = x_{\text{zpf}} (\hat{b}^\dagger + \hat{b}) \]
the frequency shift of an optical mode can be expressed to first order in \( x_m \) as \([1]\):
\[ \omega_a(x_m) = \omega_a - G_m x_m, \]
with the optomechanical coupling rate \( G_a \equiv -\frac{\partial \omega_a}{\partial x_m} \). Crossed optomechanical interaction appears when multiple optical modes interact with the same mechanical resonator \([2, 3]\). The crossed optomechanical rate is proportional to the overlap of the optical fields at the surface of the mechanical resonator. In the case of molecular optomechanics where the mechanical resonator is considered to be a point dipole, the crossed optomechanical coupling simplifies to \( G_{\text{cross}} = \sqrt{G_a^2 G_c} \). Alternatively one can use a dipolar interaction Hamiltonian between the molecule’s Raman dipole \( \hat{p}_R \) and the optical fields at the molecules position \( r_m \) \([4]\),
\[ \hat{H}_I = -\frac{1}{2} \hat{p}_R(t) \cdot \hat{E}(r_m, t). \]
The total field of the antenna and the cavity at molecule’s position, along the dipole of the molecule is
\[ \hat{E}(r_m, t) = \frac{\hbar \omega_c}{2 V_c \epsilon_0} (\hat{a}(t) + \hat{a}^\dagger(t)) + \frac{\hbar \omega_a}{2 V_a \epsilon_0} (\hat{c}(t) + \hat{c}^\dagger(t)). \]
where \( \hat{a} \) and \( \hat{c} \) are the annihilation operators for the plasmonic and the cavity mode respectively. The Raman dipole operator can be written as a function of the Raman tensor as \( \hat{p}_R(t) = \frac{\partial \alpha}{\partial x_m} x_m \hat{E}(r_m, t) \). Inserting this expression and the electric field of Eq. 3 into the interaction Hamiltonian, and discarding non-resonant terms yields the optomechanical interaction Hamiltonian, with the crossed optomechanical coupling. Next, the hybrid coupling between optical modes is obtained through a Green tensor approach \([5]\), which considers the antenna as a single polarizable dipole. This model can directly be mapped on a quantum optics formalism \([6]\). The total Hamiltonian is finally written (\( \hbar = 1 \)):
\[ \hat{H} = \omega_a \hat{a}^\dagger \hat{a} + \omega_c \hat{c}^\dagger \hat{c} + \Omega_m \hat{b}^\dagger \hat{b} \]
\[ - x_{\text{zpf}} \left( G_a \hat{a}^\dagger \hat{a} + G_c \hat{c}^\dagger \hat{c} + G_{\text{cross}} (\hat{a}^\dagger \hat{c} + \hat{c}^\dagger \hat{a}) \right) (\hat{b}^\dagger + \hat{b}) \]
\[ + J (\hat{a}^\dagger \hat{c} + \hat{c}^\dagger \hat{a}) + \hat{H}_{dr}. \]
The annihilation operators for the antenna and cavity modes are \( \hat{a} \) and \( \hat{c} \), and the driving of the antenna or the cavity by a laser is described by \( \hat{H}_{dr} \propto a + a^\dagger \) or \( \propto c + c^\dagger \). The mechanical displacement operator is \( \hat{x} = x_{zpf} (\hat{b} + \hat{b}^\dagger) \), with \( x_{zpf} \) the mechanical zero-point fluctuation. The classical Langevin equations describe the evolution of the expectation values of these three operators. We also consider the high photon number (mean-field) limit where \( \langle \hat{x}_m \hat{a} \rangle = \langle \hat{x}_m \rangle \langle \hat{a} \rangle \) \cite{7}. The resulting classical Langevin equations are given in Eq. 1 of the main text.

**INPUT AND OUTPUT PARAMETERS**

The source terms for the laser pump have been written such that \( |s_{in,a}|^2 \) and \( |s_{in,c}|^2 \) correspond to the optical power arriving through the free-space and the waveguide. The input coupling efficiencies dictate the portion of the input power that is effectively coupled into each resonator, and are written as a fraction of the total decay rate of each resonator. For the waveguide, the input and output coupling are chosen to be \( \eta_{in,c} = \eta_{out,c} = 1/4 \) (critical coupling). For the antenna we have assumed a diffraction limited focusing of a collimated input beam, from which we can write the incoming photon flux as

\[
|s_{a,in}|^2 = \pi \left( 1.22 \frac{\lambda}{2} \right)^2 \frac{\epsilon_0 c}{2} |E_{inc}|^2,
\]

with \( E_{inc} \) the incoming electric field. By using the equation of motion for the antenna field as a function of the antenna dipole moment \( p \) in the rotating wave approximation obtained from a Green-function based analysis \cite{5}:

\[
(\omega_a - \omega - i \gamma / 2) p - \frac{\beta}{2 \omega} E_{c,c} = \frac{\beta}{2 \omega} E_{inc}
\]

and comparing it to Eq. 1 of the main text one obtains:

\[
\sqrt{\eta_{a,in}} \gamma_{rad} s_{a,in} \equiv -i \sqrt{\frac{\beta}{8}} E_{inc},
\]

where we have used \( \gamma_{rad} = \frac{\beta \omega^2}{6 \pi \epsilon_0 c^3} \) and \( p = \sqrt{\frac{\beta}{\omega}} a \). From this one can express the input coupling efficiency for the antenna

\[
\eta_{a,in} = \frac{\beta}{8 \gamma_{rad} \pi (0.66\lambda)^2 \frac{\epsilon_0 c}{2}} = \frac{27}{32 \pi^2}
\]
which we have approximated to $\eta_{a,\text{in}} = 1/10$ throughout the article. Collection of the emission in the upper half-space yields a collection efficiency of $\eta_{a,\text{out}} = 1/2$. Thus, due to reduced extinction cross section of a dipolar scatterer, the input and output coupling efficiencies are not equal, and collection efficiency is roughly 5 times more efficient than excitation efficiency. It should be noted that it is possible for the input and output efficiencies to be different as the free-space radiation channel is in fact composed of a continuum of modes, and the input field and radiation (output) fields are not distributed over those modes equally.

**INFLUENCE OF ANTENNA FIELD CONFINEMENT**

The antenna field confinement, characterized by the mode volume $V_a$, determines the optomechanical coupling strength to the molecule’s vibration through $G_a = \frac{\omega_a}{2\varepsilon_0\varepsilon_0} \partial x_m \partial x_m$. In the main text we have chosen a very conservative value for $V_a = 3 \left( \frac{\lambda}{10} \right)^3$, corresponding to a molecule placed at 10 nm from a gold sphere with a radius of 50 nm [8]. The antenna mode volume does not modify any other parameter in the model, since the hybrid coupling is only determined by the antenna polarizability (or oscillator strength) and the cavity mode volume at the antenna position. Hence the antenna mode volume will only modify the overall Raman enhancement of the system, which due to the 2-step process will be proportional to $1/V_a^2$. Hence for molecules closer to the antennas (such as obtained in self-assembled procedures [9]), or for state-of-the art nm-sized gap antennas [10] with mode volumes in the order of $V_a \sim 10^{-6}\lambda^3$, a thousand times smaller than what is used here, the Raman enhancements that we presented will scale by a factor $10^6$. This is shown in figure S1 where we compared both cases. Small deviations from the simple $10^6$ factor are due to the increasing influence of direct optomechanical coupling from the molecule to the cavity slightly modifying the effective coupling rate $G_{a,c}^{\text{eff}} = G_{a,c} \tilde{\alpha}_{a,c} + G_{\text{cross}} \tilde{\alpha}_{c,a}$. These become negligible once the confinement of the antenna is significantly larger than the cavity.

**BENCHMARK WITH FULL-WAVE SIMULATION**

To prove the validity of the model we have proceeded to a comparison with full-wave simulation results obtained using the finite element method (FEM) in COMSOL. The system
FIG. S1. Antenna mode volume $V_a$ influence: Comparing the Stokes enhancement for two different antenna mode volumes: $V_a = 10^{-6}\lambda^3$ in red and $V_a = 10^{-3}\lambda^3$ in blue. The two are exactly proportional to a factor $1/V_a^2$ when no direct optomechanical coupling is taken into account (yellow dashed), and slightly deviate from the scaling law once this direct coupling becomes non-negligible.
FIG. S2. Model benchmark: Comparing the hybrid molecular optomechanics model with FEM simulations. The model uses parameters obtained from fits of the bare constituents FEM simulations and summarized in table S1. The system (b) involves 2 whispering gallery modes of azimuthal number 21 and 22 coupled to an ellipsoid antenna and exhibiting distinct LDOS peaks (a). The FEM results are compared to the predictions of the molecular optomechanics model, which takes only into account parameters from the bare antenna (c) and cavities (d) FEM simulations. The m=22 and m=21 mode cavity modes allow to respectively enhance the pump (e) and the emission (f) in the hybrid system, resulting in Stokes enhancement (g) equal to the product of the two for a mechanical frequency equal to the FSR of the cavity.

quantitative agreement between our model and full-wave simulations.

REFERENCES

[1] P. Roelli, C. Galland, N. Piro, and T. J. Kippenberg, Molecular cavity optomechanics as a theory of plasmon-enhanced Raman scattering, Nat. Nanotechnol. 11, 164 (2016)
TABLE S1. List of parameters obtained from the fit of bare constituents FEM simulations. The pump cavity is the m=22 whispering gallery mode, enhancing the laser pump, whereas the emission cavity (m=21 gallery) is shifted by a mechanical frequency and enhances the Stokes-shifted emission.

| Parameters          | Resonant Freq. [THz] | Mode Volume $[\lambda^3]$ | Decay rate $[\text{THz}]$ | Oscillator Strength $[\text{C}^2 \cdot \text{kg}^{-1}]$ |
|---------------------|----------------------|---------------------------|---------------------------|----------------------------------------------------------|
| Antenna             | 436                  | $5.00 \cdot 10^{-3}$      | $\gamma_i/(2\pi) = 18.3$ | 0.073                                                    |
| Pump Cavity         | 382.584              | 23.5                      | $6.06784 \cdot 10^{-3}$  |                                                          |
| Emission Cavity     | 370.073              | 19.5                      | $10.5584 \cdot 10^{-3}$  |                                                          |

[2] H. K. Cheung and C. K. Law, Nonadiabatic optomechanical hamiltonian of a moving dielectric membrane in a cavity, Phys. Rev. A 84, 023812 (2011).

[3] C. Biancofiore, M. Karuza, M. Galassi, R. Natali, P. Tombesi, G. Di Giuseppe, and D. Vitali, Quantum dynamics of an optical cavity coupled to a thin semitransparent membrane: Effect of membrane absorption, Phys. Rev. A 84, 033814 (2011).

[4] M. K. Schmidt, R. Esteban, F. Benz, J. J. Baumberg, and J. Aizpurua, Linking classical and molecular optomechanics descriptions of SERS, Faraday Discussions 205, 31 (2017).

[5] H. M. Doeleman, E. Verhagen, and A. F. Koenderink, Antenna-Cavity Hybrids: Matching Polar Opposites for Purcell Enhancements at Any Linewidth, ACS Photonics 3, 1943 (2016).

[6] I. Medina, F. J. García-Vidal, A. I. Fernández-Domínguez, and J. Feist, Few-mode field quantization of arbitrary electromagnetic spectral densities, Phys. Rev. Lett. 126, 093601 (2021).

[7] W. P. Bowen, G. J. Milburn, and G. J. Milburn, Quantum Optomechanics (CRC Press, 2015) pp. 37–55.

[8] J. J. Penninkhof, L. A. Sweatlock, A. Moroz, H. A. Atwater, A. van Blaaderen, and A. Polman, Optical cavity modes in gold shell colloids, J. Appl. Phys. 103, 123105 (2008).

[9] C. Vericat, M. E. Vela, G. Benítez, P. Carro, and R. C. Salvarezza, Self-assembled monolayers of thiols and dithiols on gold: New challenges for a well-known system, Chem. Soc. Rev. 39, 1805 (2010).

[10] J. J. Baumberg, J. Aizpurua, M. H. Mikkelsen, and D. R. Smith, Extreme nanophotonics from ultrathin metallic gaps, Nat. Mater. 18, 668 (2019).