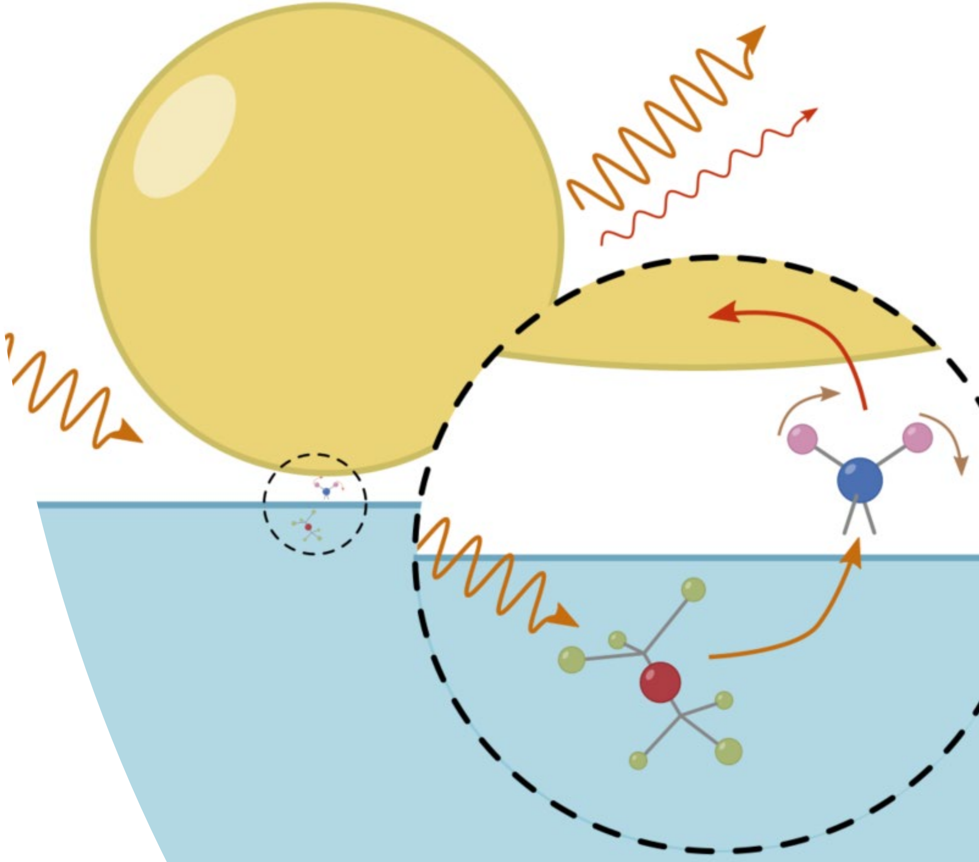
Molecular optomechanics with atomic antennas



Mikołaj K. Schmidt
School of Mathematical and Physical Sciences
Macquarie University, Sydney

Alexander A. High
Pritzker School of Molecular Engineering, University of Chicago
Centre for Molecular Engineering and Materials Science Division, Argonne National Laboratory

Michael J. Steel
School of Mathematical and Physical Sciences
Macquarie University, Sydney

Quantum Nanophotonics 2025

MACQUARIE University

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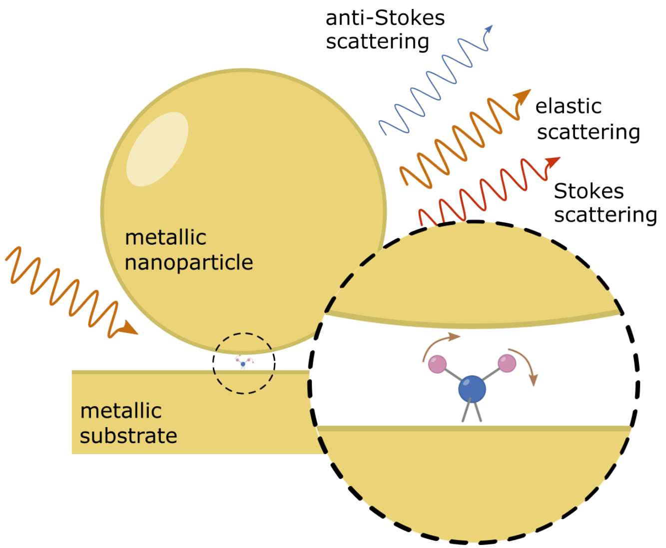
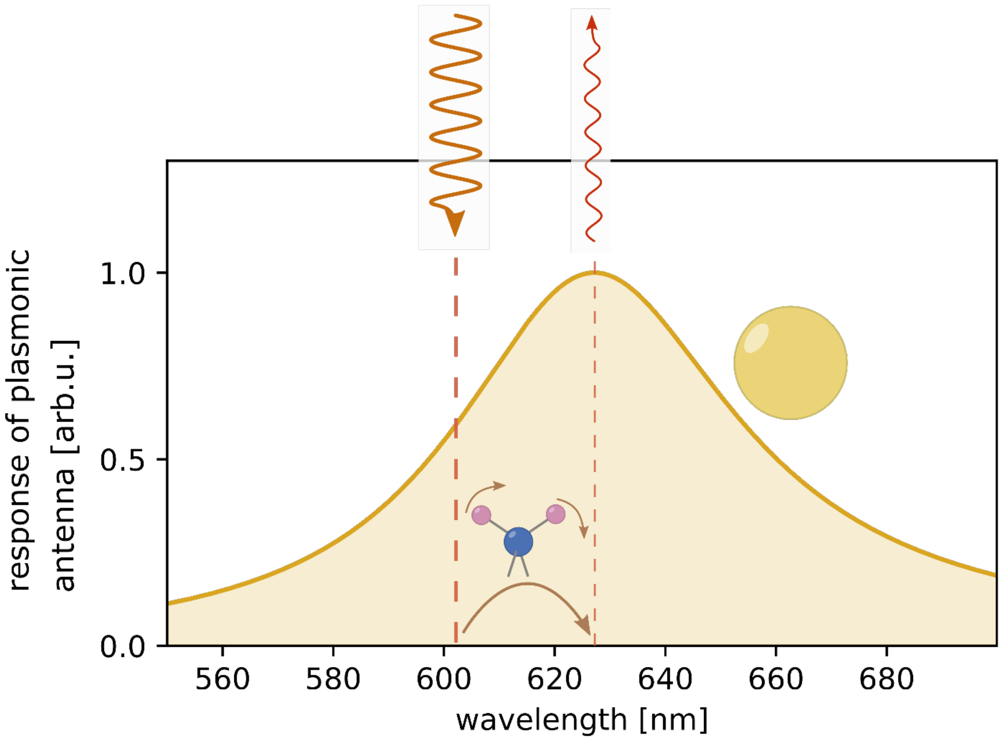
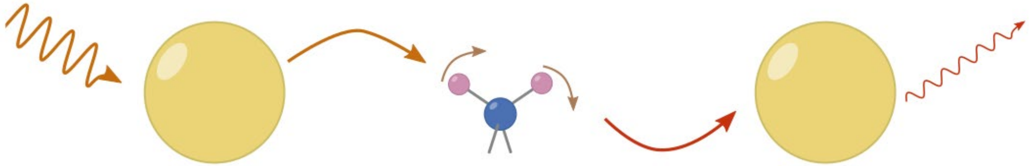
SURFACE-ENHANCED RAMAN SCATTERING – double role of cavities





$$\mathrm{EF} = \left|\frac{\boldsymbol{E}(\boldsymbol{r}_m, \omega_p)}{\boldsymbol{E}_0}\right|^2 \times \frac{\rho_{\mathrm{SERS}}(\boldsymbol{r}_m, \omega_{S/aS})}{\rho_0(\omega_{S/aS})}$$

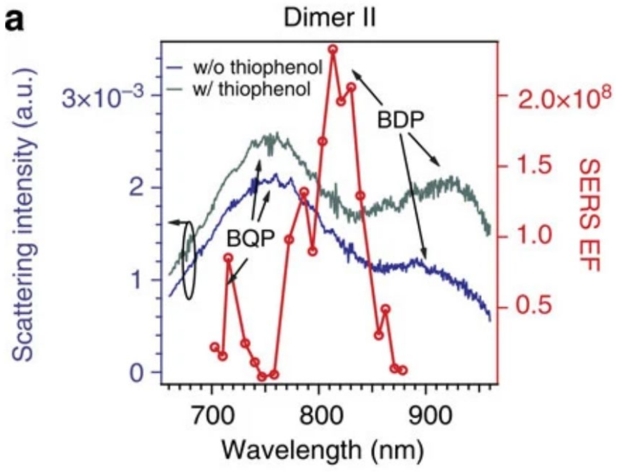
1. enhance the EM field from the laser driving the molecule
2. modify the LDOS for the Stokes and anti-Stokes emission

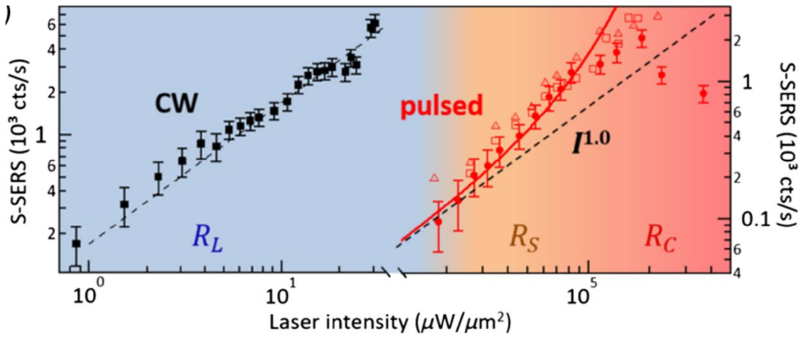


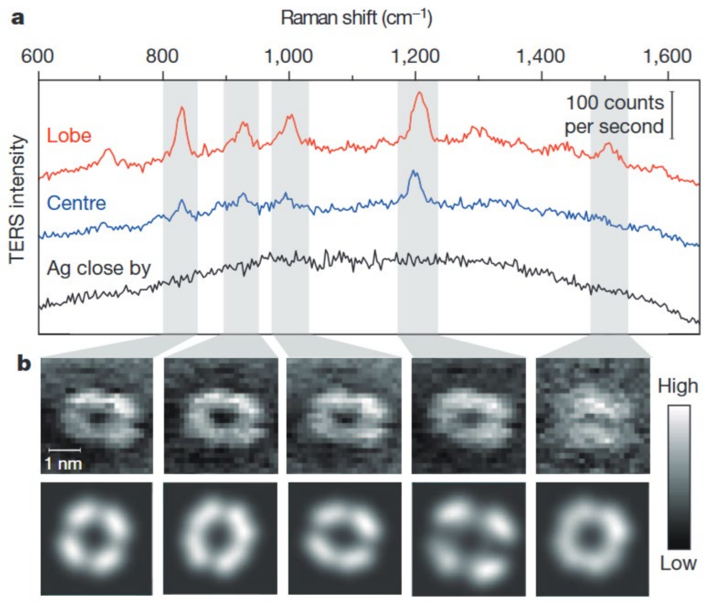
PUZZLING FEATURES OF RAMAN SCATTERING EXPERIMENTS

power- and spectral dependence of Raman emission

spatial resolution in Raman microscopes





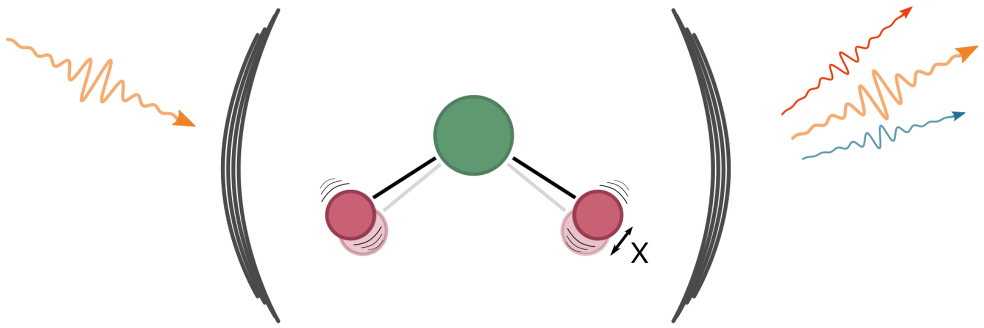


Zhu and Crozier, Nat. Commun. 5, 5228 (2014)

Lombardi et al., Phys. Rev. X 8, 011016 (2018)

Zhang et al., Nature 498, 82 (2014)

QUANTUM THEORY OF RAMAN SCATTERING



electric dipole in E field

$$U = -\boldsymbol{d} \cdot \boldsymbol{E}(\boldsymbol{r}_d)$$

…induced dipole with polarisability α ($\boldsymbol{d} = \alpha \boldsymbol{E}$)

$$U = -\alpha[\boldsymbol{E}(\boldsymbol{r}_d)]^2$$

quantise the EM field

$$\boldsymbol{E}(\boldsymbol{r}) \rightarrow \widehat{\boldsymbol{E}}(\boldsymbol{r}) = \boldsymbol{E}_0(\boldsymbol{r})\hat{a}^\dagger + [\boldsymbol{E}_0(\boldsymbol{r})]^*\hat{a}$$

and take polarisability as $\alpha \rightarrow \alpha_0 + R\hat{x}$ dependent on coordinate $\hat{x} = x_{\mathrm{zpf}}(\hat{b}^\dagger + \hat{b})$

$$\widehat{H}_{\mathrm{mo}} \approx -\underbrace{\boldsymbol{E}_0(\boldsymbol{r}){:}\,R{:}\,[\boldsymbol{E}_0(\boldsymbol{r})]^* x_{\mathrm{zpf}}}_{g_0}\,\hat{a}^\dagger\hat{a}(\hat{b}^\dagger + \hat{b})$$

recover the figure of merit:

$$\mathrm{C}_0 = 4g_0^2/\kappa\Gamma \propto Q/V^2$$

resonant laser (I) can drive the optical mode ($\hat{a}$) into a coherent state with amplitude $\alpha \propto \sqrt{I}/\kappa$

$$\widehat{H}_{\mathrm{mo}} \approx -\underbrace{g_{0,a}\alpha}_{g_{\mathrm{eff}}}\,(\hat{a}^\dagger + \hat{a})(\hat{b}^\dagger + \hat{b})$$

groups of Galland, Aizpurua, Esteban, Baumberg, Schmidt, Hughes, Koenderink, Martin-Cano,…

QUANTUM THEORY OF RAMAN SCATTERING

multiple cavity modes $\boldsymbol{E}(\boldsymbol{r}) \rightarrow \sum_i \widehat{\boldsymbol{E}}_i(\boldsymbol{r})$

TH Dezfouli et al., ACS Photonics 6, 1400−1408 (2019)

$$\widehat{H}_{\mathrm{mo}} = -\sum_{ij} g_{0,ij}\, \hat{a}_i{}^{\dagger} \hat{a}_j \left(\hat{b}^{\dagger} + \hat{b}\right)$$

multiple vibrational modes of the same/different molecules $\hat{x} \rightarrow \sum_k \hat{x}_k$

TH Zhang et al., ACS Photonics 7 (7), 1676-1688 (2020)

$$\widehat{H}_{\mathrm{mo}} = -\sum_k g_{0,k}\, \hat{a}^{\dagger} \hat{a} \left(\hat{b}_k{}^{\dagger} + \hat{b}_k\right)$$

anharmonic vibrations! $\hat{x} \neq x_{\mathrm{zpf}}\left(\hat{b}^{\dagger} + \hat{b}\right)$

TH Schmidt et al., New J. Phys. 26 033041 (2024)

TH Moradi Kalarde et al., Nanophotonics 14, 59 (2025)

$$\widehat{H}_{\mathrm{mo}} = -G_0 \hat{a}^{\dagger} \hat{a} \hat{x}$$

pseudo-spin modes $\boldsymbol{E}(\boldsymbol{r}) \rightarrow \widehat{\boldsymbol{E}}(\boldsymbol{r}) = \boldsymbol{E}_0(\boldsymbol{r})\hat{\sigma}^{\dagger} + [\boldsymbol{E}_0(\boldsymbol{r})]^* \hat{\sigma}$

$$\widehat{H}_{\mathrm{mo}} = -g_0\, \hat{\sigma}^{\dagger} \hat{\sigma} \left(\hat{b}^{\dagger} + \hat{b}\right)$$

pseudo-spin ($\boldsymbol{E}_1$) and cavity modes ($\boldsymbol{E}_2$)

TH Neuman et al., Phys. Rev. A. 100, 043422 (2019)

$$\widehat{H}_{\mathrm{mo}} = -g_0\, (\hat{\sigma}^{\dagger} \hat{a} + \hat{a}^{\dagger} \hat{\sigma})\left(\hat{b}^{\dagger} + \hat{b}\right)$$

Z. Physik 237, 224–233 (1970)

Quantum Theory of the Raman Effect

I. Interaction with Phonons

DANIEL F. WALLS*
I. Institut für theoretische Physik der Universität, Stuttgart

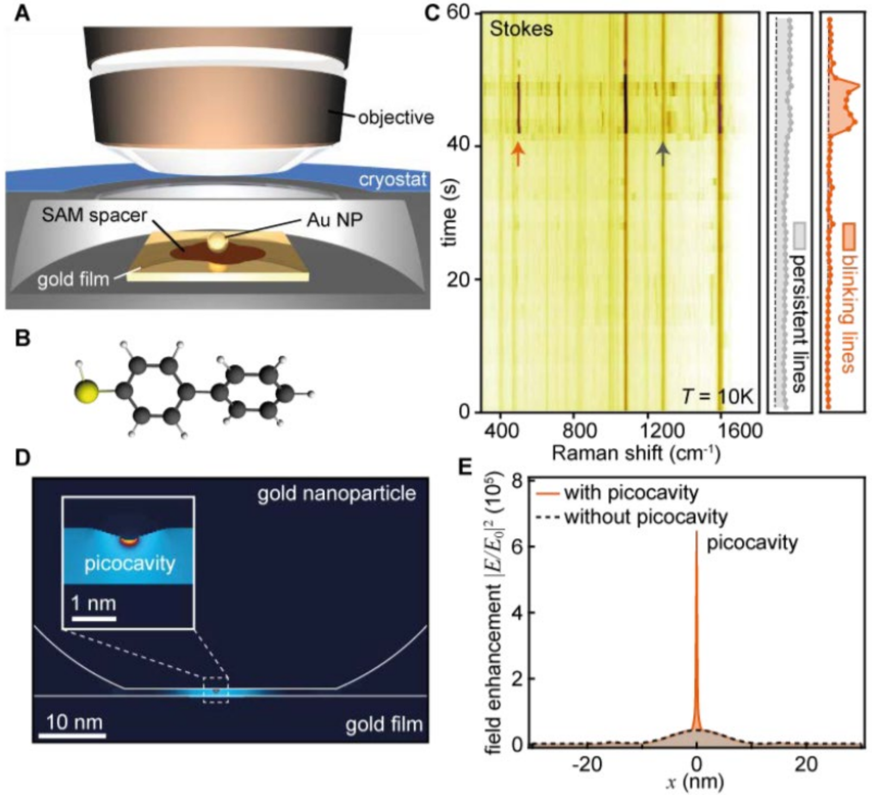
Received April 24, 1970

Considering only near resonance terms (i.e. making the rotating wave approximation) the model Hamiltonian for the process takes the form

$$H = H_0 + H_1$$
$$H_0 = \hbar\omega_L a^+ a + \hbar\omega_s b^+ b + \hbar\omega_{as} c^+ c + \hbar\omega_{ph} d^+ d \qquad (2.3)$$
$$H_1 = \hbar\kappa_s(a\,d^+ b^+ + \text{h.c.}) + \hbar\kappa_{as}(a\,d\,c^+ + \text{h.c.})$$

where κ_s, κ_{as} are the coupling constants for the Stokes and Antistokes processes respectively. They contain the momentum mismatch Δk_s, Δk_{as}

PICOCAVITIES

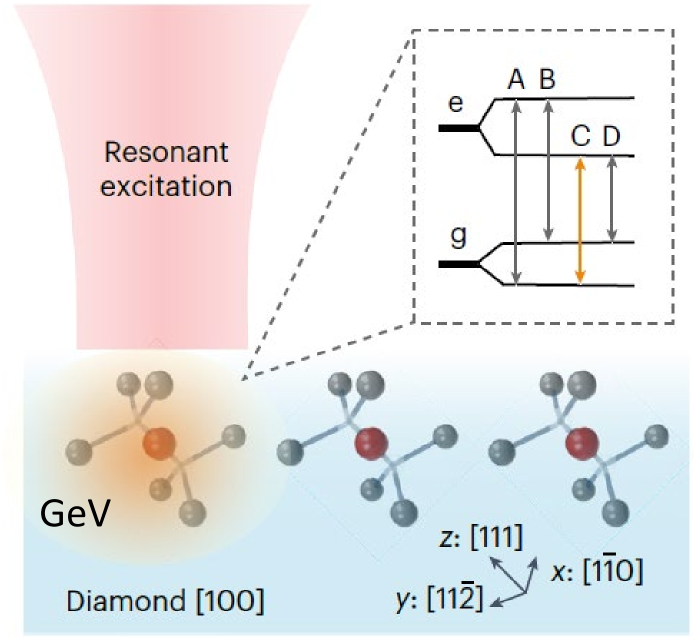


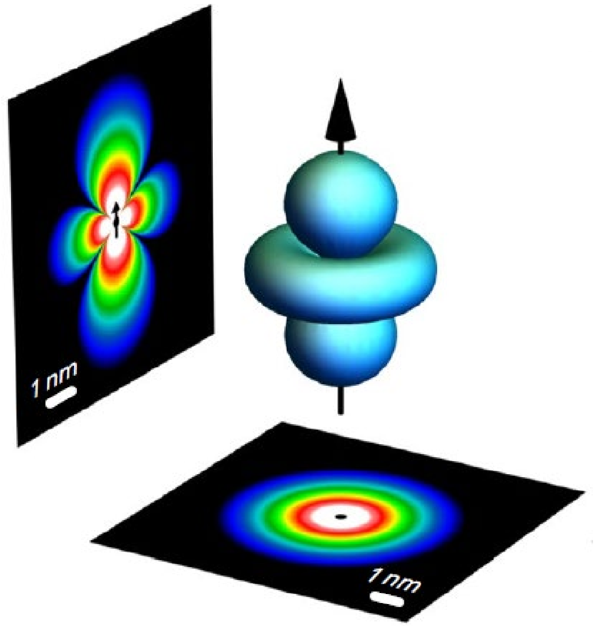
Benz et al., Science 354, 726 (2016)

- inhomogeneous EM field in the cavity – new Raman lines
- extremely high single-photon OM coupling rate $g_0 \sim 2\pi \times 1$ THz:
  - $g_0/\omega_b \sim 0.1$ sets it close to photon blockade regime,
- unstable and hard to pump

IS THERE A BETTER CANDIDATE FOR ATOM-SCALE ANTENNAS?

ATOMIC OPTICAL ANTENNAS (GeV) in solids





protected from electric field noise

$\gamma \sim 4\,\gamma_0 \approx 2\pi \times 100$ MHz

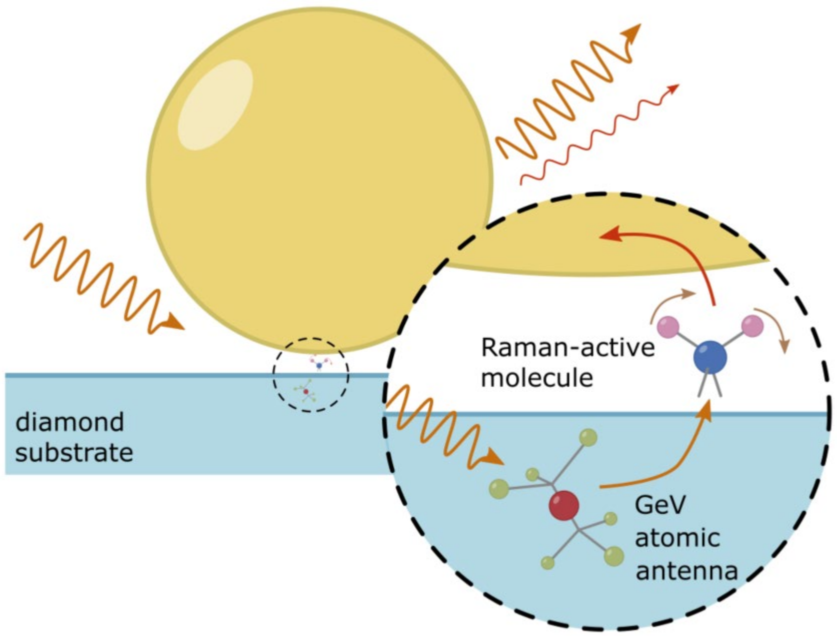
(@ 50 K) for 602 nm transition

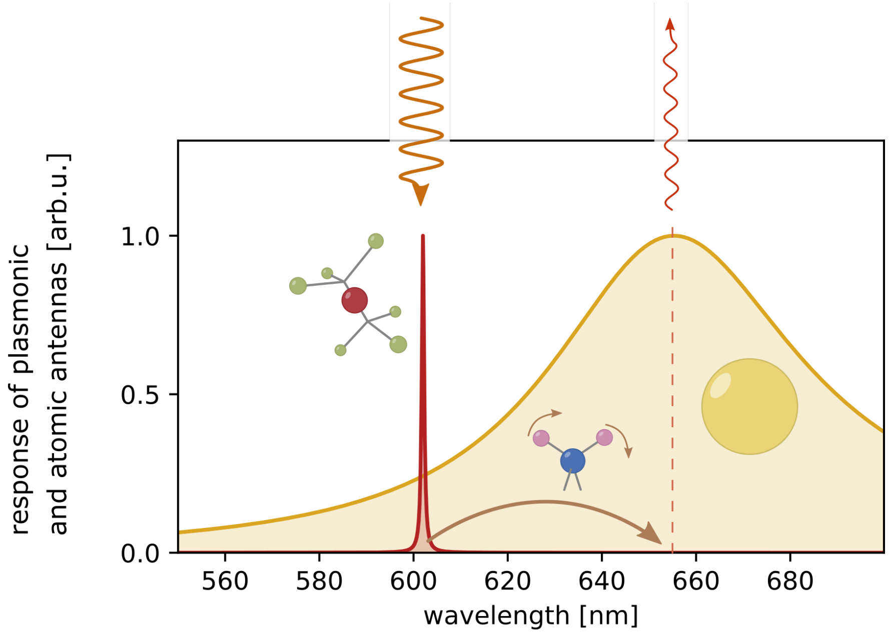
saturates with ~ 10 nW of input power

(similar to other group-IV defects)

Li et al., Nat. Photonics 18, 1113 (2024) – group of Alex High (UChicago)

ATOMIC OPTICAL ANTENNAS (GeV) for RAMAN SCATTERING



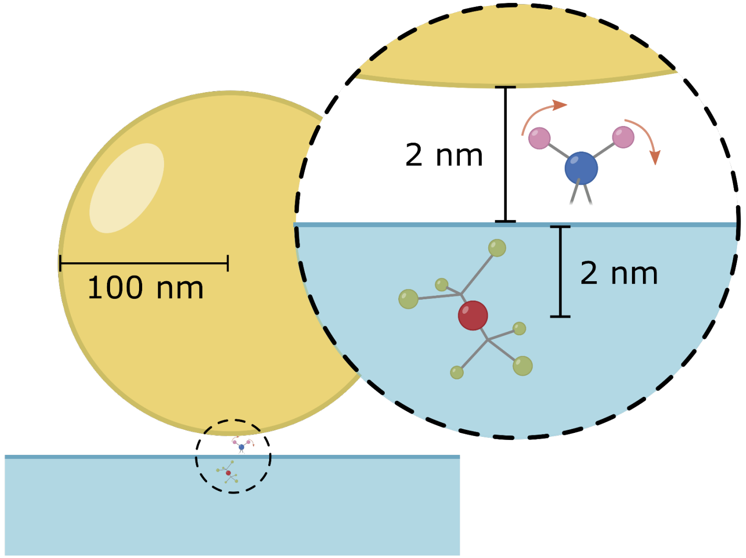


Schmidt, High, Steel, arXiv:2412.02106 (2024)

ATOMIC OPTICAL ANTENNAS (GeV) for RAMAN SCATTERING

resonant laser (I) will drive the pseudo-spin GeV ($\hat{\sigma}$) into a coherent state with amplitude $\alpha \propto \sqrt{I}/\gamma$

$$\hat{H}_{\mathrm{mo}} = -g_{0,\sigma}\,(\hat{\sigma}^{\dagger}\hat{a} + \hat{a}^{\dagger}\hat{\sigma})(\hat{b}^{\dagger} + \hat{b}) \approx -\underbrace{g_{0,\sigma}\alpha}_{g_{\mathrm{eff}}}\,(\hat{a}^{\dagger} + \hat{a})(\hat{b}^{\dagger} + \hat{b})$$

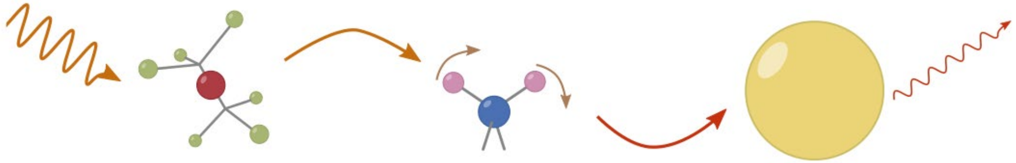


optomechanical coupling $g_{0,\sigma} \sim 2\pi \times 0.2$ GHz

laser intensity required for α=1 $I \sim 10^{-2}\ \mu\mathrm{W}/\mu\mathrm{m}^{-2}$

conversion efficiency at $I = 10^{-2}\ \mu\mathrm{W}/\mu\mathrm{m}^{-2}$:

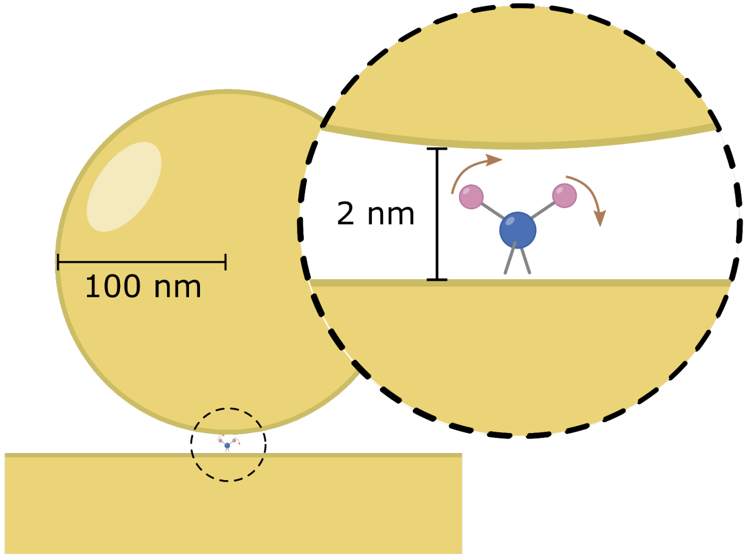
$\eta_{\sigma} \sim 3 \times 10^{-8}$



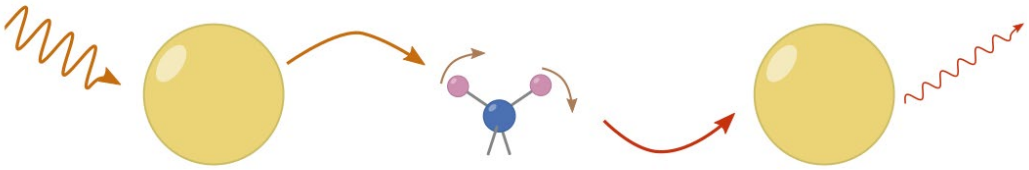
PLASMONIC ANTENNAS for RAMAN SCATTERING

resonant laser (I) will drive the optical mode ($\hat{a}$) into a coherent state with amplitude $\alpha \propto \sqrt{I}/\kappa$

$$\hat{H}_{\text{mo}} \approx -\underbrace{g_{0,a}\alpha}_{g_{\text{eff}}}\left(\hat{a}^\dagger + \hat{a}\right)\left(\hat{b}^\dagger + \hat{b}\right)$$

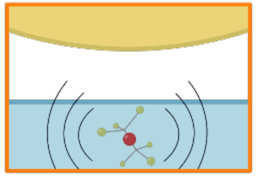


optomechanical coupling	$g_{0,a} \sim 2\pi \times 3$ GHz
laser intensity required for α=1	$I \sim\ 10^3\ \mu\text{W}/\mu\text{m}^{-2}$
conversion efficiency	$\eta_a \sim 5 \times 10^{-11}$

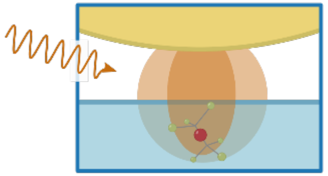


ATOMIC ANTENNAS for RAMAN SCATTERING: additional effects

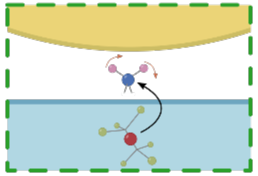
Plasmon enhancement of antenna decay rate

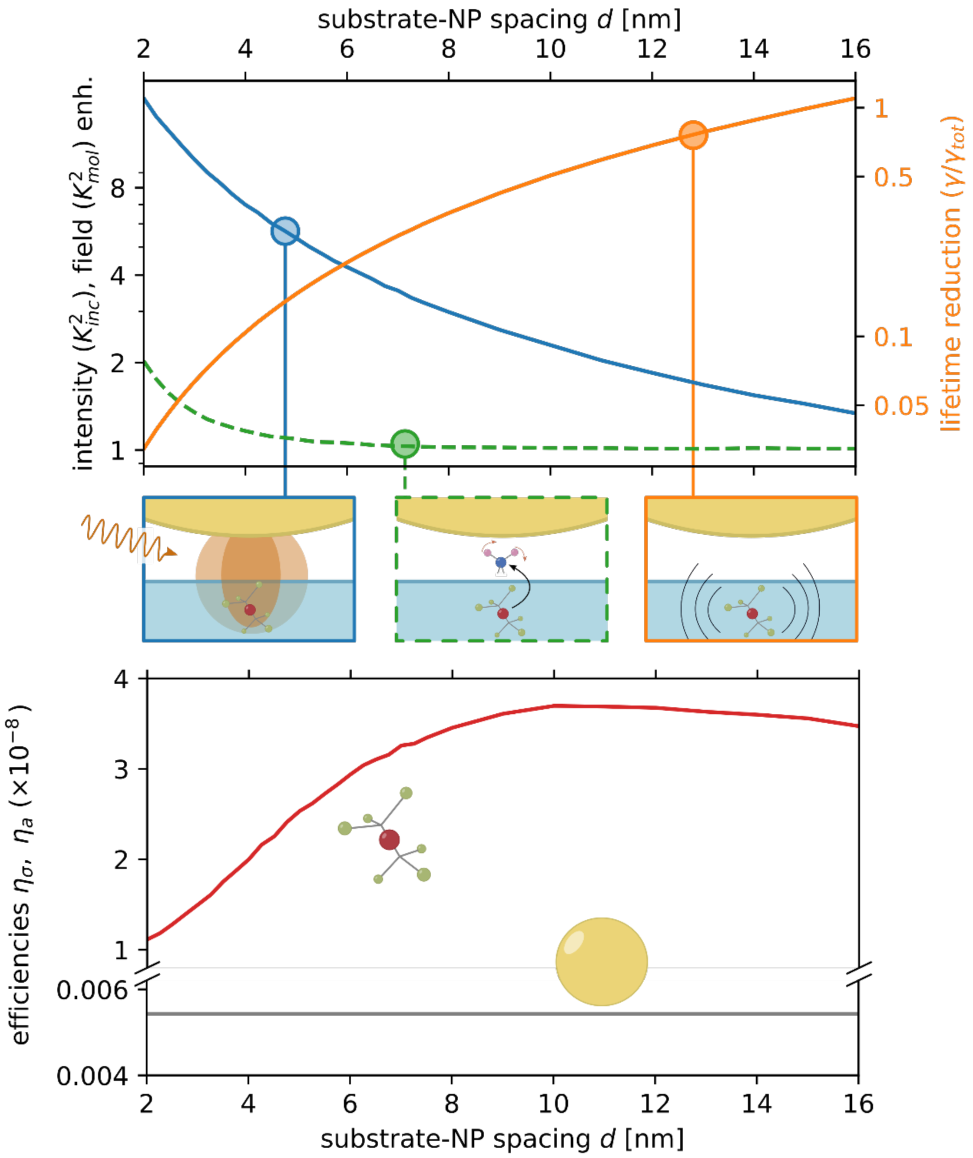


Plasmon-enhanced driving

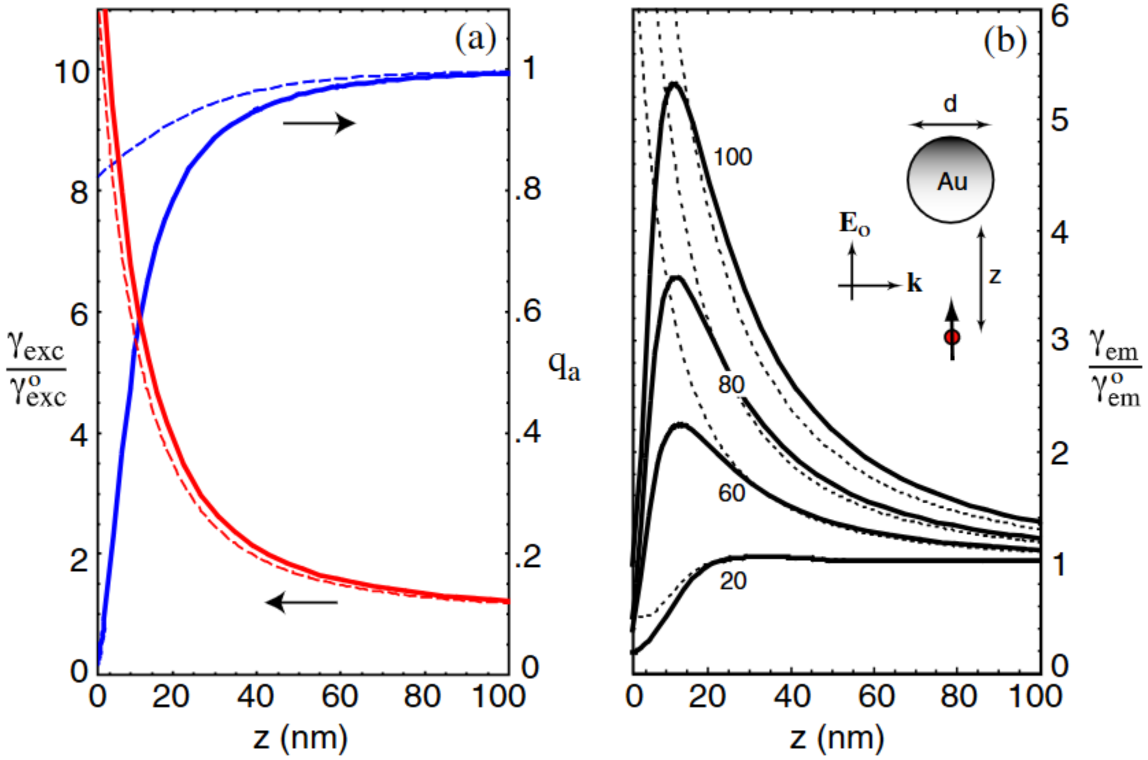


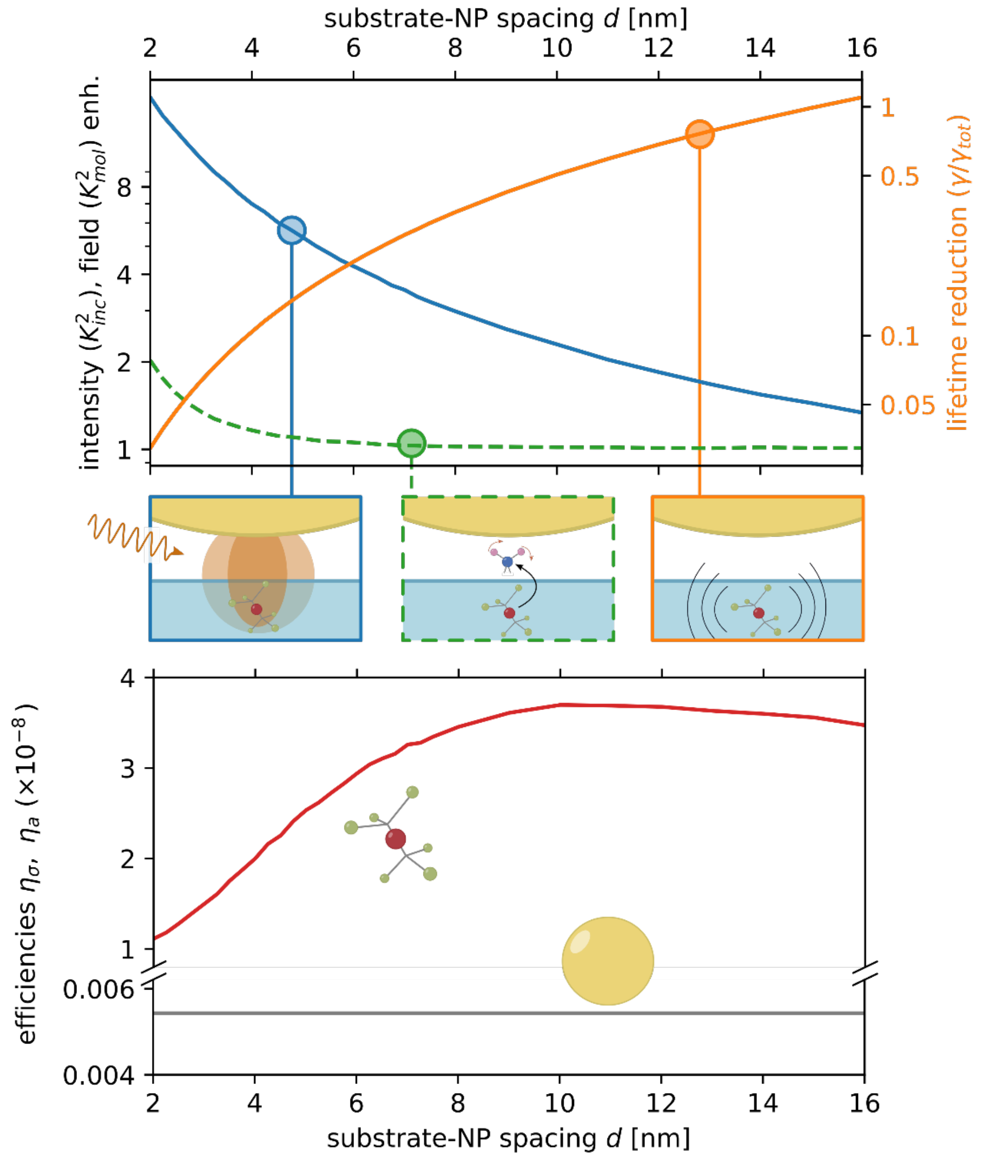
Modification of electric field from the atomic antenna





ATOMIC ANTENNAS for RAMAN SCATTERING: additional effects



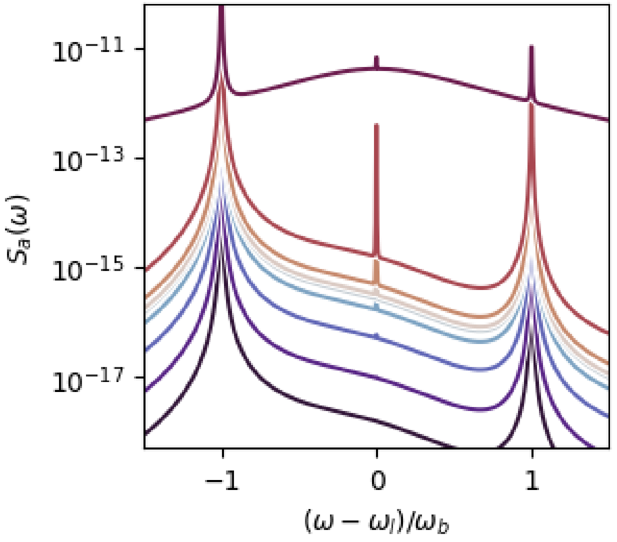


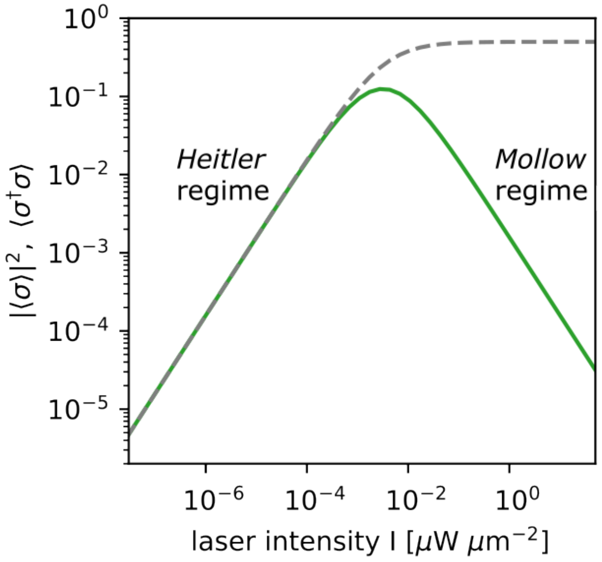
Anger, Bharadwaj, Novotny, Phys. Rev. Lett. 96, 113002 (2006)

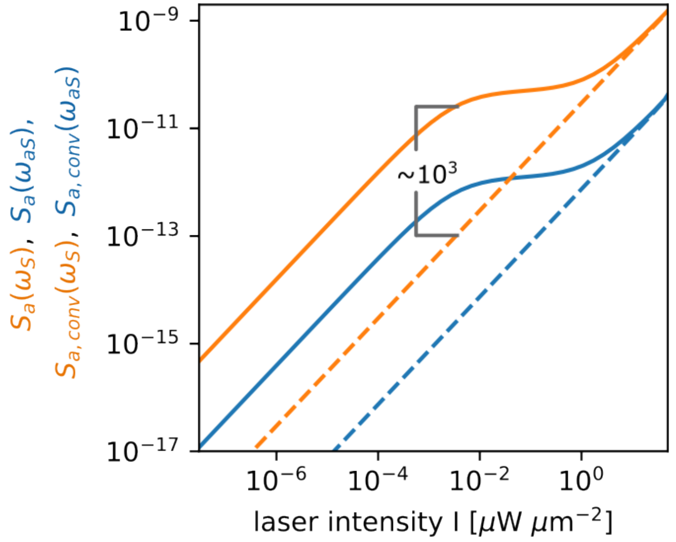
POWER DEPENDENCE OF RAMAN SCATTERING

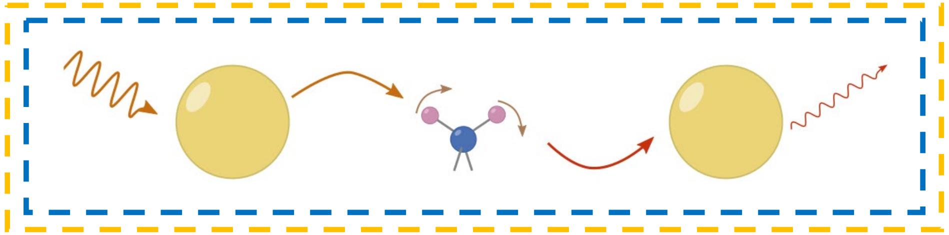
beyond the linearisation regime!

$$\hat{H}_{\mathrm{mo}} \approx -g_{0,\sigma}\langle\hat{\sigma}\rangle(\hat{a}^\dagger + \hat{a})(\hat{b}^\dagger + \hat{b})$$

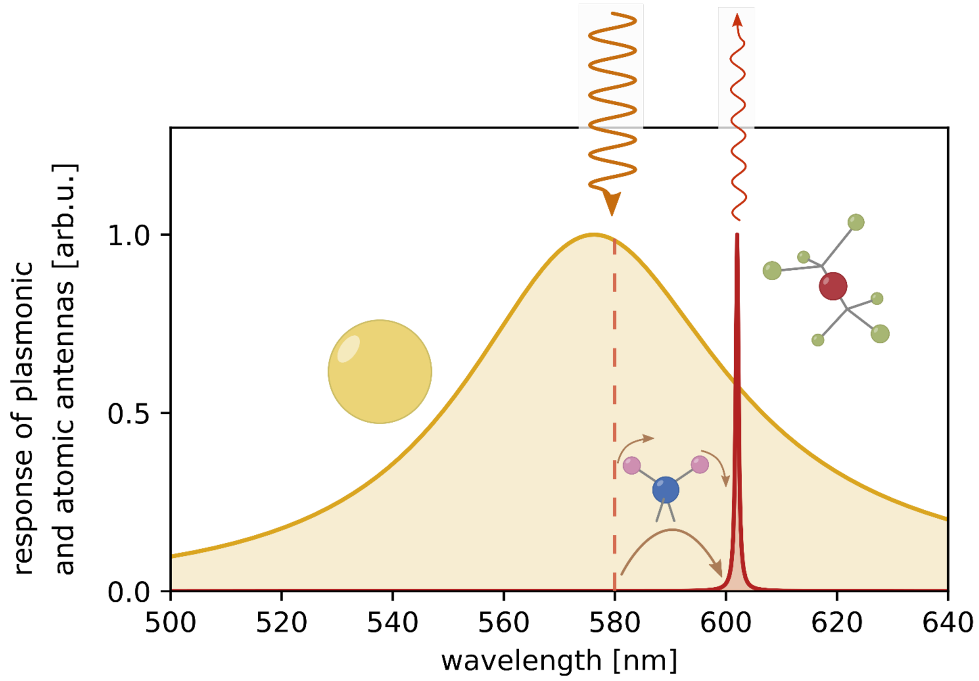


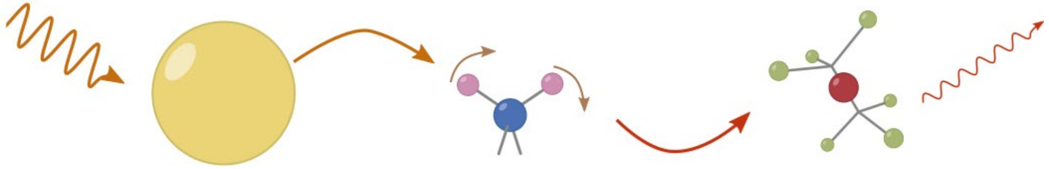






CAN ATOMIC ANTENNAS COLLECT THE STOKES PHOTONS INSTEAD?





- plasmon is hard to pump, so
  - low plasmon population,
  - low conversion efficiency :(
- GeV linewidth is smaller than phonon linewidth – non-Markovian effects!

SUMMARY

» atomic antennas offer 1000-fold enhancement in (pump to Stokes) conversion efficiency,

» picocavity-like fields:

  - inhomogeneous, atom-scale localised field distribution,
  - but stable!

» clear signature of GeV-mediated RS in power dependence,

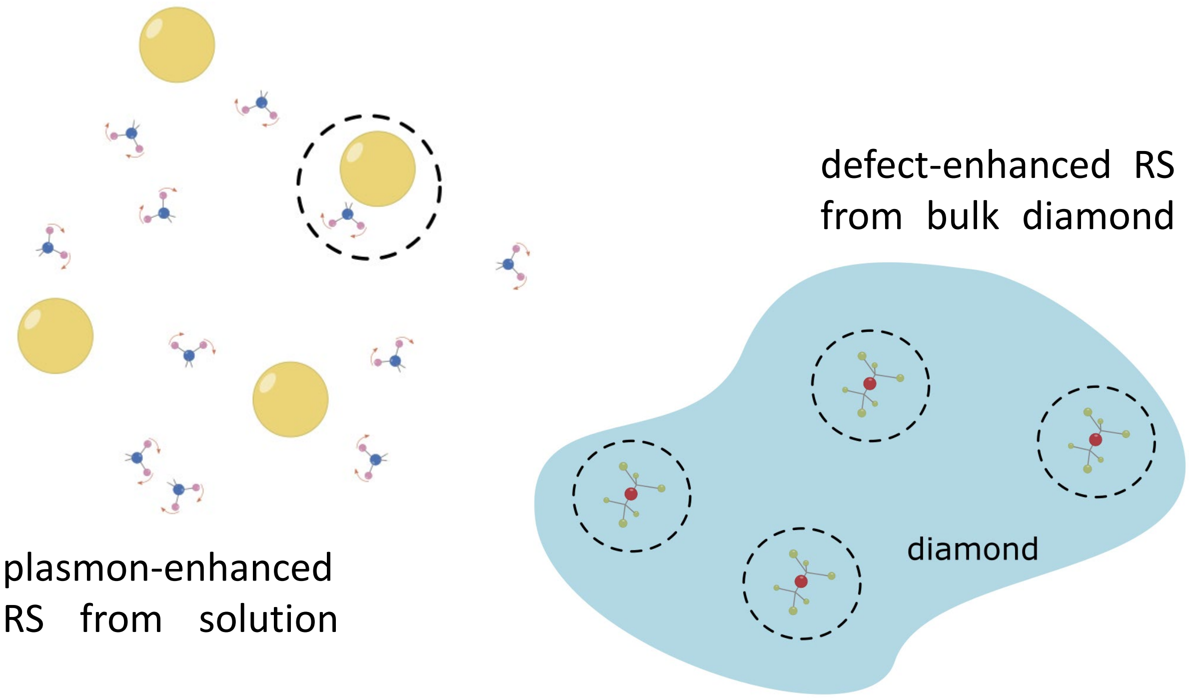
» weak emission, limited by GeV saturation

Schmidt, High, Steel, arXiv:2412.02106 (2024)

OUTLOOK

» can atomic antennas enhance fluorescence?

» can atomic antennas locally boost the Raman processes?



w/ Rogers (U. Newcastle), Volz&Nair (Macquarie U.)

Australian Government
Australian Research Council

SYDNEY QUANTUM ACADEMY

MACQUARIE University

mikolaj.schmidt@mq.edu.au

https://mkschmidtphysics.blog

Aizpurua, Esteban, Giedke, Roelli (University of the Basque County, DIPC, CIC nanogune)
Huang, Raman Nair, Volz, Mildren (Macquarie University)
Rogers (University of Newcastle)
Slim (University of Queensland)
Neuman (Czech Academy of Sciences)
Galland (EPFL)
Gonzalez-Tudela (IFF CSIC)

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