

Picocavities: a primer

Jeremy J. Baumberg^{1*}

¹ *Nanophotonics Centre, Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, UK.*

Abstract

Picocavities are sub-nm scale optical cavities recently found to trap light, which are formed by single-atom defects on metallic facets. Here we develop simple picocavity models and discuss what is known and unknown about this new domain of atom-scale optics, as well as the challenges for developing comprehensive theories. We provide simple analytic expressions for many of their key properties, and discuss a range of applications from molecular electronics to photocatalysis where picocavities are important.

keywords: picocavity, nanocavity, plasmonics, SERS, Raman scattering, adatoms

Introduction to picocavities

The observation of clear and persistent transient vibrational lines in surface-enhanced Raman spectra (SERS) has opened up a new domain of spectroscopy for single molecules and their interactions with metal surfaces. While fleeting phenomena have been seen since the 1990s, measurements of vibrational pumping in 2016 finally allowed a rigorous evaluation of the optical mode volume,¹ which was found to be below 1nm^3 . These modes are thus called picocavities, and are formed by single atom surface defects known as adatoms.

Surprisingly, the ability to confine visible light to such scales had not previously been considered feasible, even though it is likely a frequent phenomenon. Nano-scale crevices in typical gold or silver jewellery harbour these modes, but to efficiently couple in light of thousand-fold larger free-space wavelength requires more sophisticated nano-scale structuring. Many plasmonic geometries such as metal nanorods or near-field tips provide field concentration. A consistent architecture that has proved a useful workhorse for picocavities is the nanoparticle-on-mirror (NPoM). This conveniently combines an antenna with a metal-insulator-metal (MIM) nano-thick waveguide between a nanoparticle facet and a metal mirror (Fig.1a). The MIM spacing is set by a dielectric molecular (or crystalline) layer which scaffolds the gap, while the nanoparticle image-dimer from the mirror provides the antenna resonance that couples efficiently to free space photons. However picocavities may occur in any geometry where the internal optical field is large enough to move single atoms out of the facets.

Simple model of picocavities

In this section a simple analytic model for picocavities is developed, that can be widely used to evaluate different concepts. This model of the picocavity field in the nanogap matches full theories and simulations reasonably well and is based on an atom-size metallic ellipsoid in a quasi-uniform field $\mathcal{E}_{\text{nano}}$ inside the gap (Fig.1b). This arises from each nanogap plasmonic mode inside the MIM (Fig.1a), where for small gaps

$d < 10\text{nm}$ the perpendicular field (\mathcal{E}_z) in the gap dominates. The normalised polarizability of the metallic ellipsoid in a dipole approximation is given by

$$\tilde{\alpha}_j(\lambda) = \frac{\alpha_j(\lambda)}{\epsilon_0 V} = \frac{1}{[\epsilon_m(\lambda)/\epsilon_g - 1]^{-1} + L_j L_s(\lambda)}, \quad j = \{x, y, z\} \quad (1)$$

where V is the volume of the half-ellipsoid with semi-axes a_j , ϵ_m is the metal's permittivity (typically Au) and ϵ_g the permittivity of the gap medium (eg. molecular monolayer),² with z perpendicular to the metallic facet (Fig. 1). L_j are structure parameters accounting for the polarisation anisotropy of the ellipsoid with $\sum_{j=1}^3 L_j = 1$. The dominant polarizability here is α_z , for which L_z depends simply on aspect ratio $\varphi = a_z/a_{x,y}$ (see Eqn.S1).³ To account for half-embedding the elliptical asperity in metal (Fig. 1c) using image charges (valid for atomic-scale structures), we include the multiplicative structure factor⁴

$$L_s(\lambda) = 1 - \aleph \frac{\epsilon_m - \epsilon_g}{\epsilon_m + \epsilon_g} \quad (2)$$

where $\aleph=0.19$ (see SI).

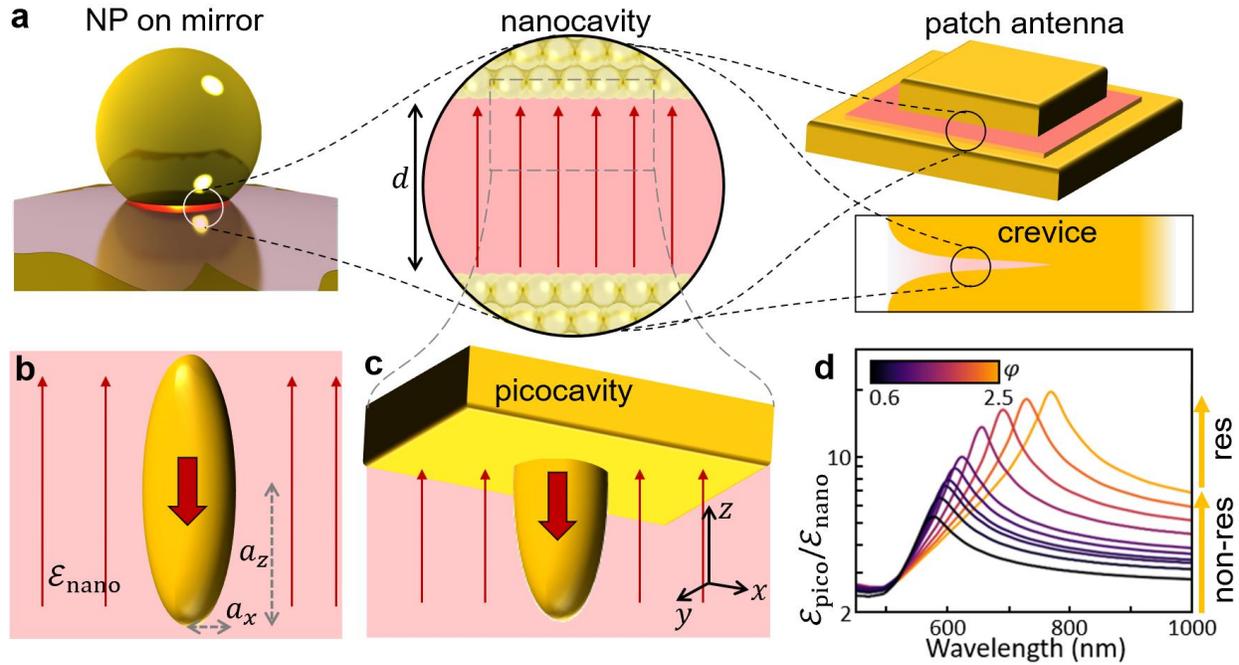


Figure 1. Picocavity analytic polarizability. (a) Plasmonic nanogap confined optical field, in NPoM, patch antenna, or crevice. (b) Schematic metallic ellipsoid in uniform nanogap field, showing induced dipole (solid arrow). (c) Half-ellipsoid embedded in metal facet, axes as marked. (d) Analytic field enhancement at the sharp tip vs aspect ratio φ for a Au picocavity, showing broadband (non-resonant lightning rod) and resonant contributions (adapted from [6], copyright 2021 American Chemical Society).

This picocavity plasmon combines a non-resonant ‘lightning rod’ part with a similar-sized resonant part (Fig.1d). Resonances occur when the denominator of Eqn.(1) is zero, and using a simple Drude model for the plasmonic metal, $\epsilon_m = \epsilon_\infty - \lambda^2/\lambda_p^2$ leads to

$$\lambda_{\text{pico}} = \lambda_p \sqrt{\epsilon_\infty + \epsilon_g \gamma(\varphi)} \quad (3)$$

where

$$\gamma(\varphi) = [2L_z(1 - \kappa)]^{-1} \left\{ 1 + 2L_z\kappa + \sqrt{1 + 4L_z(L_z + 2\kappa - 1)} \right\}$$

This analytic expression for λ_{pico} matches full theories well (Fig.2a). Maximum field enhancements at the picocavity tip (on resonance) from Eqn.(1) are $EF_{\text{pico}} = |\tilde{\alpha}_z(\lambda_{\text{pico}})|$, set by the imaginary part of the denominator evaluated at λ_{pico} (Fig.2b). Given nanocavity enhancements $EF_{\text{nano}} = 300\text{-}500$ in NPoM structures,⁵ the total field strength in picocavity hot-spots easily exceeds $EF_{\text{tot}} = EF_{\text{nano}} \cdot EF_{\text{pico}} > 1000$.

Fields around the picocavity have been calculated in many approximations including finite-difference time-domain simulations (FDTD),⁶ quantum time-dependent DFT,^{7,8} quasi-normal mode (QNM) solutions,⁹ finite-element methods (FEM),¹⁰ and quantum hydrodynamic models (QHDM)¹¹ among others. In all, the field resembles our dipolar model (Eqn.1).⁸ For the spherical picocavity ($\varphi=1$, for $\varphi \neq 1$ see SI), the absence of field parallel to the metal surface sets the central dipole $\mathbf{p} = \alpha_z \mathcal{E}_{\text{nano}} \hat{z}$, with the outside picocavity field $\mathcal{E}_{\text{pico}}(\hat{\mathbf{r}}) = \mathcal{E}_{\text{nano}} + [(\mathbf{p} \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} - \mathbf{p}]/(4\pi\epsilon_0 r^3)$ or

$$\frac{\mathcal{E}_{\text{pico}}}{\mathcal{E}_{\text{nano}}} = \epsilon_{\text{nano}}^{-1} \begin{pmatrix} \mathcal{E}_x \\ \mathcal{E}_z \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} + \frac{1}{(1 + \delta/a)^3} \left[\tilde{\alpha}_z \cos \theta \begin{pmatrix} \sin \theta \\ \cos \theta \end{pmatrix} - \begin{pmatrix} 0 \\ 1 \end{pmatrix} \right] \quad (4)$$

where $r = a + \delta$ (the distance outside the metal atom of radius a), and $\mathcal{E}_{\text{nano}} \hat{z}$ is the quasi-uniform nanocavity field in the gap (Fig.2c). We note that $\mathcal{E}_{\text{nano}}(\lambda)$ has its own resonant spectrum (see below). The decay length of this enhanced field away from the adatom surface is 0.7\AA for a dipolar field distribution (and 1.1\AA if monopolar, Fig.2d), while the on-resonance decay length estimated using quantum hydrodynamics for a cone of base 1.2nm and height 0.3nm is 2\AA (Fig.2d). Although electron spill-out and Landau damping have some contribution (QHDM, Fig.2d), the ellipsoidal dipolar model (SI) captures the decay length of 1.6\AA reasonably well for this flattened cone.

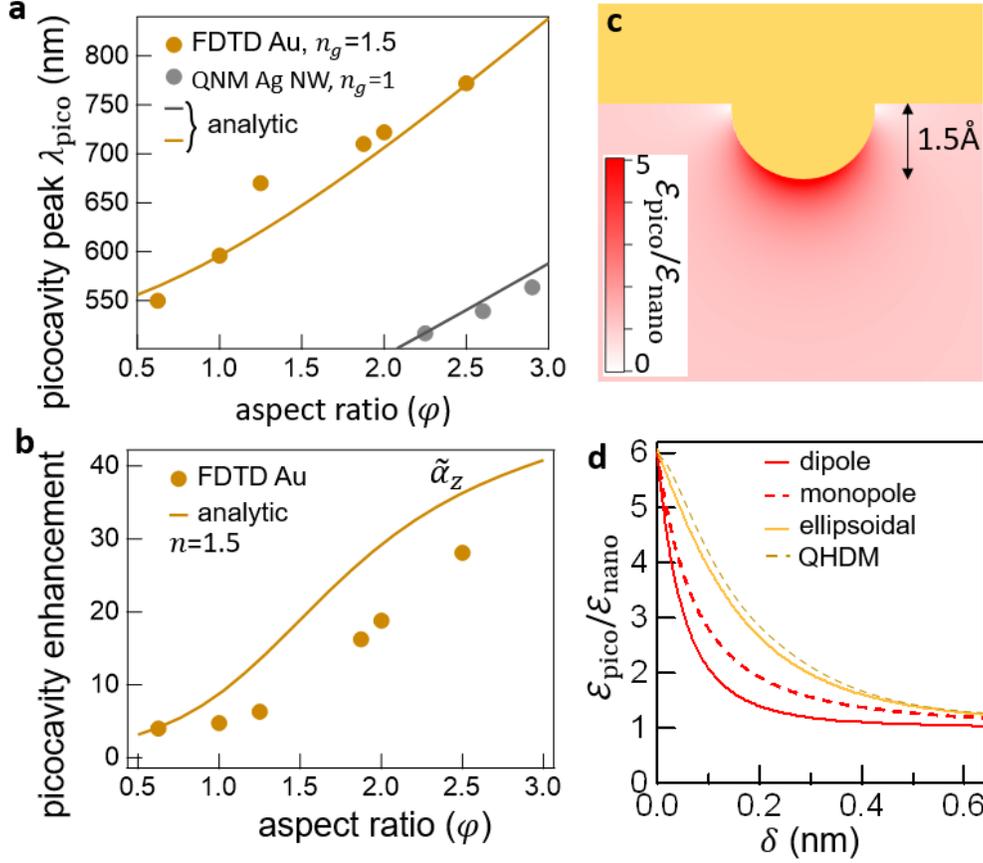


Figure 2. Picocavity spectral tuning and spatial field. (a) Comparison of hemi-ellipsoid picocavity resonant wavelength model (lines using Eqn.3) with FDTD calculations for gold,⁶ and quasi-normal mode calculations for silver nanowires.⁹ (b) Picocavity field enhancement at tip for increasing aspect ratio ϕ of hemi-ellipsoid using FDTD and in analytic model (line using Eqn.1) vs FDTD calculations for gold.⁶ (c) Dipolar field distribution outside Au hemisphere (0.3nm diameter). (d) Spatial decay of near field below the picocavity for distance δ outside Au atom radius, comparing dipolar spherical, dipolar ellipsoidal and monopolar decay with near-field from quantum hydrodynamics model.¹¹

From this field profile, the effective mode volume \tilde{V} of the picocavity can be estimated using

$$\tilde{V} \cdot \text{EF}_{\text{pico}}^2 = \int \left| \frac{\epsilon_{\text{pico}}(\mathbf{r})}{\epsilon_{\text{nano}}} - 1 \right|^2 dV$$

where we take the integral over the gap half-space (Fig. 2c), and exclude the original nanocavity field. This can be simply evaluated using Eqn.(4) in the spherical case to yield

$$\tilde{V} \simeq V(\tilde{\alpha}_z^{-1} - 1)^2$$

which gives $\tilde{V} \simeq \pi a^3 < 0.01 \text{nm}^3$ [see SI §2 in ref ⁹] matching estimates near spherical nanoparticles¹² shrunk to single atoms. With $a=0.15 \text{nm}$ for Au, this classical estimate is too small since full QNM simulations⁹ give 0.25nm^3 , and spill-out effects (Fig.2d) can increase it further. Field inside the metal thus contributes significantly to the mode volume. The ultimate limit to confinement for visible light remains to be clearly theoretically quantified, but is of order 0.1nm^3 .

Given this model for picocavities of different metals, aspect ratios, and gap materials, the coupling to nanocavity plasmon modes needs to be quantified. Electromagnetic models show that when the picocavity mode $\mathcal{E}_{\text{pico}}$ tunes through the nanocavity mode $\mathcal{E}_{\text{nano}}$ (which is little affected by the adatom as it occupies a negligible fraction of the mode volume), they anticross to give mixed states $\mathcal{E}_{\text{eff}}^{\pm}(\mathbf{r}) = \frac{1}{2}\{\mathcal{E}_{\text{nano}}(\mathbf{r}) \pm \mathcal{E}_{\text{pico}}(\mathbf{r})\}$, which are split in energy (Fig.3a).^{9,11} The effective mode volumes of these mixed states at their anticrossing point^{9,11} are given by $\tilde{V}_{\text{eff}}^{-1} = \frac{1}{2}(\tilde{V}_{\text{pico}}^{-1} + \tilde{V}_{\text{nano}}^{-1})$. Since the nanocavity volume is so much larger, the mode volume is then $\tilde{V}_{\text{eff}} = 2\tilde{V}_{\text{pico}} \simeq V$ (the volume of the ellipsoid).

The energy splitting ΔU between the $\mathcal{E}_{\text{eff}}^{\pm}$ states arises from their coupling strength, which is controlled by the normalised overlap integral¹³

$$\frac{\Delta U}{U} = \int \mathcal{E}_{\text{nano}}(\mathbf{r}) \cdot \mathcal{E}_{\text{pico}}(\mathbf{r}) dV_g / \int \mathcal{E}_{\text{nano}}(\mathbf{r}) \cdot \mathcal{E}_{\text{nano}}(\mathbf{r}) dV_g$$

This integral can be evaluated for hemispherical picocavities to give

$$\frac{\Delta U}{U} \simeq 16 \left(\frac{a^3}{w^2 t} \right) \ln \left(\frac{t}{a} \right) |\tilde{\alpha}_z - 1| \quad (5)$$

for a nanogap thickness t , and facet diameter w . For the parameters used in [9] which give 0.1eV splitting at 2.1eV, using $w=7\text{nm}$, $a=0.2\text{nm}$, $t=1\text{nm}$ in Eqn.(5) yields a 4% splitting in good agreement. For single atom picocavities in NPoM experiments, using $w=20\text{nm}$, $a=0.15\text{nm}$, $t=1\text{nm}$ and $\varphi=1.0-1.3$ (from [6]), we obtain splittings < 1%. Comparing with typical picocavity linewidths (Fig.1d) which exceed 10% of the mode frequency, such splittings will not be spectrally resolved (Fig.3a). The mixing is however important for efficiently coupling light into the picocavity, while ensuring that the mode volume remains small. Picocavity-induced perturbations to nanocavity scattering spectra will thus be only a few %, requiring sensitive experiments to detect them.¹⁴ While desirable to construct larger atomic-scale structures in nanocavities, these are constrained by extremely strong surface forces (see below), and only single (or few) atom picocavities are observed. Recent papers proposing to develop (ultra)strong coupling with single emitter electronic transitions using picocavity fields¹⁵⁻¹⁷ are intriguing but must be treated with caution currently (see SI).

Two resonance conditions must be simultaneously satisfied to observe such tightly confined picocavity modes from free space. The resonant nanocavity modes⁵ (ω_{lm}) must be intense at the spatial location of the picocavity and close in energy (Fig.3a). To also efficiently couple light from free space into the nanocavities requires the antenna mode frequency ω_{ant} of whichever nanostructure used (NPoM, MIM, patch antenna etc., tuning mainly set by height)⁵ to be near-resonant with the same nanocavity modes (ω_{lm}).

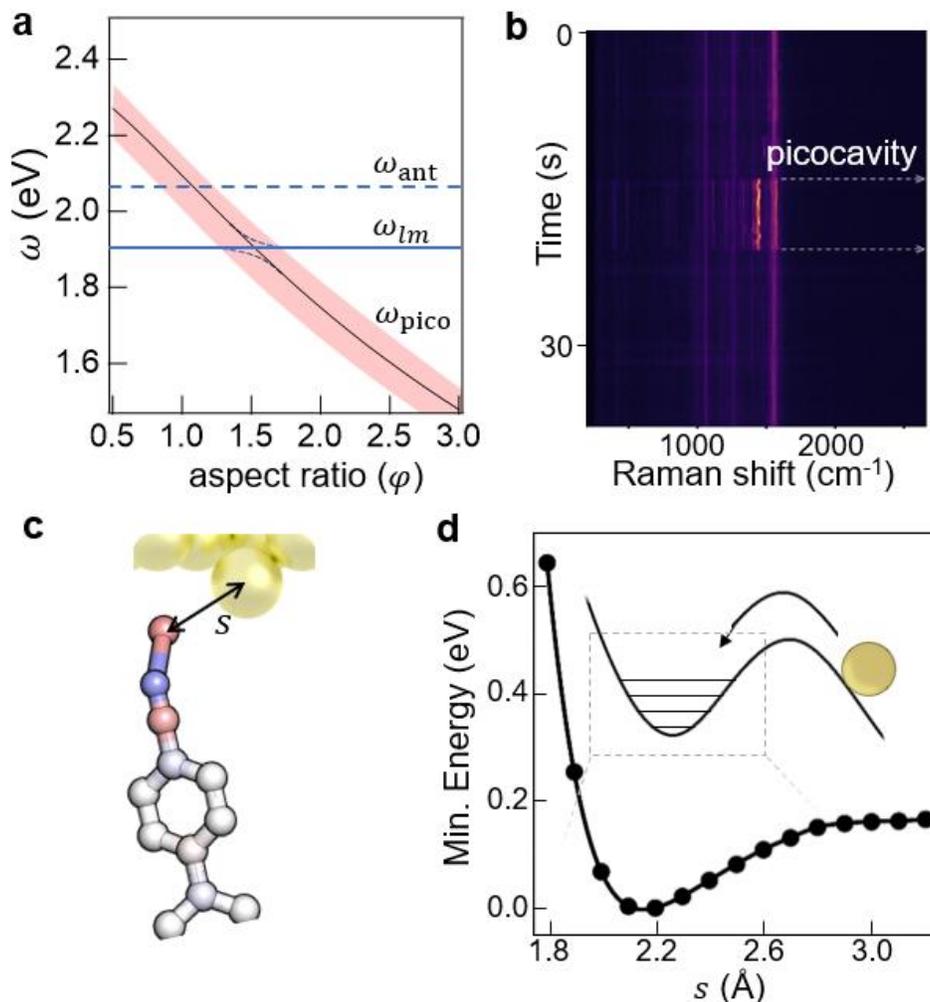


Figure 3. Picocavity, nanocavity, and antenna mode tuning. (a) Picocavity energy tunes with aspect ratio ϕ , crossing nanocavity and antenna plasmons, to give efficient free-space coupling when all are degenerate. (b) SERS spectra of NC-BPT monolayer in the NPoM gap, showing new vibrational lines from a single bond appear when picocavity forms. (c) Coordination bond forming between Au adatom and tip of nearest molecule. (d) Calculated DFT of Au adatom in the vicinity of NC-BPT molecule, showing metastable state at 2.2 Å N-Au separation [from ¹⁸]. Only few Au vibrational states are thermally excited in this coordination bond at room temperature (inset).

How to observe picocavities

Picocavities are seen so far through the enhanced SERS of a molecule in the immediate vicinity of an adatom (Fig.3b). The power dependence of antiStokes to Stokes Raman emission quantifies large optomechanical coupling strengths, giving vibrational pumping¹ even at low CW powers (<100μW) and quadratic power-scaling of antiStokes emission.¹⁹ Picocavity SERS of single molecules is up to tenfold stronger than combined SERS from all other (100-500) molecules giving nanocavity SERS. This is because gold adatoms do not just passively enhance near-field light, but form 'coordination bonds' with atoms at the molecule end. Extensive DFT calculations show that for each molecule there is a stable adatom-molecule position, which in simple cases well-matches picocavity SERS data. For instance, in cyanobiphenyl-4-thiol (NC-BPT) monolayers giving R-C≡N-Au picocavities, the N-Au coordination bond

extracts $0.3e^-$ from the $C\equiv N$ bond, which thus weakens from 2242 cm^{-1} to 2175 cm^{-1} at the stable separation of 2.2 \AA (Fig.3c,d).¹⁸

Variations in the adatom position produce a wandering of picocavity SERS emission, alongside completely stable nanocavity lines. If enough picocavity SERS lines are observed simultaneously, correlating spectral positions allows full reconstruction of the configuration of the single molecule at the metal surface.¹⁸ This promises real-time ambient observations of catalysis, molecular electronics, surface chemistry, electrochemistry, and sensing (see below). It is thus vital to gain full understanding and corroboration of the picocavity geometry, chemistry, and pico-optics. Unfortunately while surface metal adatoms are well known from STM and electron microscopy, observing them in-situ in ambient conditions under optical illumination has proved harder.

What is known about picocavities

To prove picocavity SERS phenomena come from single metal adatoms, coordination-bonded to single-molecules, several pieces of evidence are important:

- (A) measured picocavity formation energies¹ match adatoms ($\sim 1\text{eV}$) for both Ag and Au (extracting more atoms requires more energy);
- (B) adatom symmetry-breaking alters the Raman selection rules, as observed¹ (since picocavity optical fields significantly vary along a single bond, Fig.2b,d);
- (C) adatom-molecule coordination bonds seen in SERS are transient and fluctuate in time;
- (D) adatoms only amplify the SERS of a single neighbouring molecule, as observed from its vibrational wandering in time (though occasionally 2 molecules with correlated wandering are seen);
- (E) simulations show only single atom features can reduce the optical field volume below 1nm^3 as experimentally measured.

Theory shows that light is localized to mode volumes $<1\text{nm}^3$, perfectly consistent with Maxwell's equations in a quantum description. Given this, it is puzzling why picocavities are not seen initially, when laser irradiation starts. Both upper and lower Au facets of the MIM are not typically single-crystal or defect-free, but picocavities are never observed without light irradiation (and only then, for intensities above a threshold). Since typical Au mirrors used have atomic steps every 5-10nm, this is surprising. The only conclusion is that reconstruction must take place whenever AuNPs bind to a molecular layer on mirror. Estimating the Van der Waals (VdW) force²⁰ $F_{VdW} = Aa_{NP}/3d^2$ for Au Hamaker constant $A\sim 1\text{eV}$, suggests for $d=1\text{nm}$ gaps and $a_{NP}=40\text{nm}$ NPs that $F_{VdW} \sim 3\text{nN}$ over a 20nm wide facet. This corresponds to 10 MPa (100 atmospheres) $\sim 1\text{ pN/Au atom}$, or 40meV per close-packed molecule in a self-assembled monolayer (SAM) nanogap spacer (typically attaching to 11% of Au sites). While SAM Young's moduli are 0.1-1 GPa, metal facets are ductile enough to rearrange under this pressure giving single-crystal facets no matter what their initial state.

Picocavities are subsequently created by light (though potentials can also be used²¹). Such optical forces are puzzling since the fields (Fig.2) at these laser powers give optical tweezer forces $\propto \nabla \mathcal{E}_{\text{pico}}^2$ of $\sim 1\text{pN}$, while pulling the adatom out by $\Delta z=0.3\text{nm}$ costing $\Delta U=1\text{eV}$ requires $F\sim \Delta U/\Delta z\sim 1\text{nN}$.²² This thousand-fold greater force demands new theory. Experiments show a universal power dependence to the picocavity generation rate, that scales with the static polarizability of the atom at the molecule tip.²² The

optical forces thus involve not the molecular refractive index but its quantum-mechanical polarizability. Several observations are important²²:

- (F) adatom generation is probabilistic not deterministic,
- (G) adatom decay is also induced by light, at similar rates to formation (adatoms are stable in the dark),
- (H) adatoms are harder to generate at lower temperatures, and
- (I) adatom formation rates saturate at higher laser power.

Alternatives rejected include:

- (I) Hot-atom effects where a 2eV plasmon is deposited at a single surface atom to kick it out (analogous to hot-electrons, but should not depend on lattice temperature);
- (II) Optical forces which tilt the surface potential to drive out surface atoms but would prevent them returning, instead exponentially inducing roughening;
- (III) Light-induced Au atom quantum tunnelling through the surface barrier has negligible probability;
- (IV) Melting of NPs is excluded by measuring their temperature from antiStokes:Stokes ratios of nanocavity SERS lines, typically heated by ~ 10 K.

The sole explanation identified is that light decreases the barrier for adatom formation. This happens through light-induced VdW attraction between the molecule tip atom in the most intense light and the weakest-bound Au surface atom. The picocavity field (Fig.2b) polarizes the electron cloud around the molecule tip, which induces free electron currents in the metal surface. Solving self-consistently gives strongly-enhanced attractive forces.²² We emphasise the theory breakthroughs required for integrating photons into DFT calculations,²³ not yet realistically feasible. However this does explain all observations noted above, and why picocavity formation rates depends on molecule, laser power, laser wavelength, gap size, facet (*hkl*) plane,²⁴ facet metal (Au,Ag,Pd), and temperature. Further experiments with multiple laser wavelengths that identify where on each facet picocavities are pulled out, agrees with this mechanism.⁶ Such experiments also suggest that $\varphi=1.0-1.3$ (*cf.* Fig.2), consistent with the predicted adatom site on the (111) surface. They also imply reduced adatom barriers near facet edges, expected since the coordination number is lower there.

We note that picocavities do not only form in nanocavities (likely even existing on jewellery), however optical forces must be strong enough. In nanocavities these are enhanced by $EF_{\text{nano}}^2 \sim 10^5$, so light intensities $\sim 1\text{W}/\mu\text{m}^2$ are required outside nanocavities.

Picocavity effects in technology applications

A number of implications from the optical (or electrical) creation of picocavities follow.

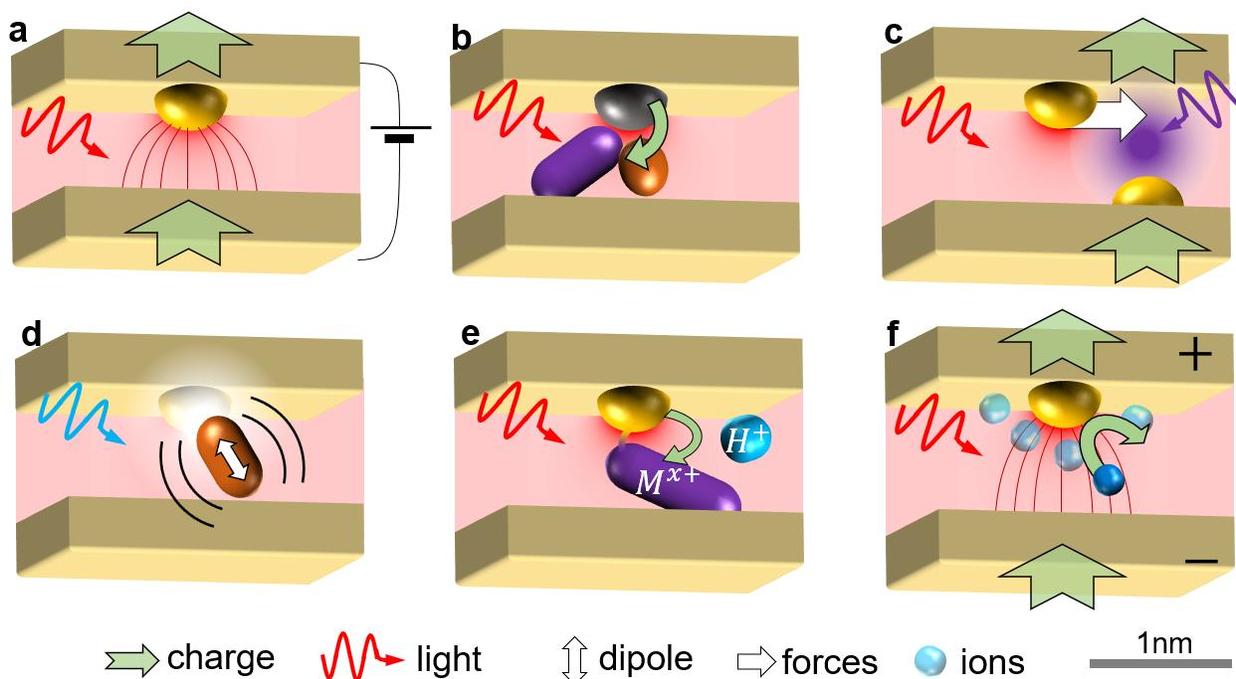


Figure 4. Picocavity-influenced devices. (a) Electron tunnelling at asymmetries. (b) Catalytic reactions. (c) Light-driven lateral atomic switching of electrical conduction. (d) Light emission and strong coupling. (e) Light-induced redox chemistry. (f) Surface electrochemistry and ion shell structures.

(i) **Quantum tunnelling devices** (Fig.4a): Connecting symmetrical molecules across electrically-contacted nanogaps reveals asymmetry in zero-bias photocurrents. DC currents can flow either way, slowly varying in time and with irradiation, randomly directed in each device. Picocavities explain the geometrical rectification seen in recent experiments,²¹ from tunnelling conductance driven by 50mV ‘optical’ bias ($>k_B T/e$) at 100 μ W illumination. This suggests molecular (opto)electronic devices which can clock charge through at 100THz optical frequencies.

(ii) **In-situ single-site photocatalysis** (Fig.4b) can track at the single-molecule level how reactants and products favourably combine at single metal adatoms. Being able to watch the influence of coordination bonds, and how this triggers photo-reactions greatly aids a nanoscale view of catalytic mechanisms.²⁵

(iii) **Pico-tweezers** (Fig.4c): Light-enhanced VdW forces open the way to all-optical atomic force microscopies, using multiple colours to excite and laterally translate individual atoms, or sheets. Moving adatoms change electrical paths, giving optical memristive elements.²⁶ Single-atom switching delivers low-energy IT devices that can be controlled in ambient conditions.

(v) **Quantum optical devices** (Fig.4d) are in prospect based on addressing single atoms, bonds, electrons, or molecules in the picocavity field. Only a few quantum states are thermally excited in the picocavity potential formed by a Au-N coordination bond, with fast optical addressing capable of driving entangled states. Single spins and charges are accessible through spin-orbit coupling.²⁷ Electronic dipoles of dye molecules or semiconductors (perovskites, TMDs, etc) coupling to picocavities may give extreme Purcell factors with ultrastrong coupling or pico-lasing, but break present light-matter formalisms.

(v) **Pico-chemistry** (Fig.4e) gives access to alternative optical-driven reactions. The extreme optomechanical coupling reported¹ (exceeding room temperature), selectively injects energy into molecules without allowing thermalization, exciting up vibrational ladders. Stimulated Raman scattering selects particular bonds, going beyond coherent control techniques to sculpt reaction coordinates. Despite the

confined gap, diffusive access to reactants and products has already been proven. Picocavities also influence vibrational strong-coupling, potentially explaining adatom catalytic reactivities.

(vi) **Single-molecule electrochemical processes** (Fig.4f) can be tracked in real time at picocavities. Single-molecule redox has been observed to influence picocavity formation and decay,²⁸ and even single (de)protonation events can be tracked in real time to reveal the local electrochemical and pH landscape.²⁹ Complex questions tackled include the solvation of ions at metal surfaces, organisation of water and solvents, and light-induced electrocatalysis.

(vii) **Optically-controlled hot-spot sensing** through the light-induced VdW interactions, can sift through trace molecules and optically attract those of highest tip polarizability. This suggests unusual light-controlled chromatography, where binding-unbinding rates (and hence elution rates) are influenced by light intensity and colour.

Remaining challenges for picocavity science

Many fundamental questions remain. One is the role of charge transfer. While DFT claims adatom coordination bonds are partly ionic, it is unclear how lifting Au adatoms off a surface can locally polarise the surrounding free charges, and what oxidation state all atoms are in. This is especially pertinent for the thiol bond typically used to anchor molecules on the lower Au mirror. It is believed that thiol binding plucks Au atoms out of the substrate as Au^(I) 'staples' (so not observed as picocavities).³⁰ The influence of this partially-charged mixed S/Au^(I)/vacancy atomic layer has unknown influence on the optics of metallic Au (but cannot affect bonds on the other end, eg. C≡N-Au). Picocavities do form on the lower mirror,³¹ suggesting that picocavity-staple geometries give similarly strong coordination bonds. Experiments using non-thiol binding systems such as Ru[bpy]₃ give similar picocavities. It thus appears that the molecular tips play a crucial role in picocavity formation and decay rates. Generally redox-active molecules give a profusion of picocavities unless chemically stabilised,^{28,32} which likely reflects interactions of picocavities with electron transport and transfer.

The influence of self-assembled monolayer molecular packing is similarly not known, nor how this rearranges to allow Au adatoms to penetrate the molecular layer. In the (stable) NC-BPT system, every picocavity has a different vibrational spectrum, despite the unique energetic minimum from DFT calculations. Formation times of picocavities are <50μs,³³ but records only when the adatom is within 3Å thus amplifying SERS hundred-fold. On the other hand, picocavities show two decay rates;²² the fast rate matches picocavity formation rates, while the slower one may arise from atomic reorganisation of the vacated surface pit that prevents adatoms dropping back in without many surface rearrangements. Picocavities might suppress their subsequent local creation, although analysis suggests not.²²

Note, fluctuations from picocavities are important in *every* SERS measurement (although ignored), because their dynamics leads to broadened lines hiding a profusion of different processes, especially when employing long integration times. Picocavity generation clearly resculpts facets, but is suppressed for adatoms of higher energy, for instance using (100) facets on nanocubes.²⁴

Different dynamics controls the wandering of picocavity SERS lines of ~4 cm⁻¹/s. The optically-measured adatom diffusion rate $D \sim 0.5 \text{ \AA}^2/\text{s}$ can be used (assuming constrained damped Brownian motion) with the coordination-bond potential (spring constant $k \sim 5 \text{ eV/\AA}^2$) to extract a relaxation time $\tau = k_B T /$

(kD) \sim 50ms which is extremely slow compared to formation times or vibrational frequencies.¹⁸ Changes in pH or redox landscape occur on the same timescale. This suggests Au adatoms couple to a frictional viscous reservoir, possibly through intermolecular interactions in the SAM, surface waves on the metal facets, or screening electrons in the metal. It is also unclear how Landau damping of electrons can be applied to picocavities.¹¹

A challenge for the theory community is to develop rigorous models. Despite observing $<100\text{cm}^{-1}$ picocavity lines delocalised over the entire molecule, picocavity fields reach only $<0.2\text{nm}$ into the molecule (Fig.2d). Picocavity SERS intensities and correlations cannot yet be matched by DFT theories and are so far overlooked. Nanogap optical fields of GV/m can be reached ($EF_{\text{nano}}>300$), capable of breaking bonds and field ionizing. A confluence of different effects must thus be fully connected in picocavities. From deep understanding, will come remarkable progress in this successor field to nano-optics.

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Author Contributions

The author wrote the full manuscript.

Conflicts of interest

The author declares no conflicts of interest.

Corresponding author

Correspondence to J.J.B. (jjb12@cam.ac.uk)

Supplementary Information

This contains the definition of ellipsoidal structure parameters and ellipsoidal dipolar field on-axis. This material is available free of charge via the internet at <https://doi.org/10.1039/C6CS00919K>. Data for all the figures can be found at DOI: (will be in Cambridge open data archive, at proof stage)

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