

# Optical Suppression of Energy Barriers in Single Molecule-Metal Binding

Qianqi Lin<sup>1</sup>, Shu Hu<sup>1</sup>, Tamás Földes<sup>2,3</sup>, Junyang Huang<sup>1</sup>, Demelza Wright<sup>1</sup>, Jack Griffiths<sup>1</sup>, Bart de Nijs<sup>1</sup>, Edina Rosta<sup>2,3</sup>, Jeremy J. Baumberg<sup>1\*</sup>

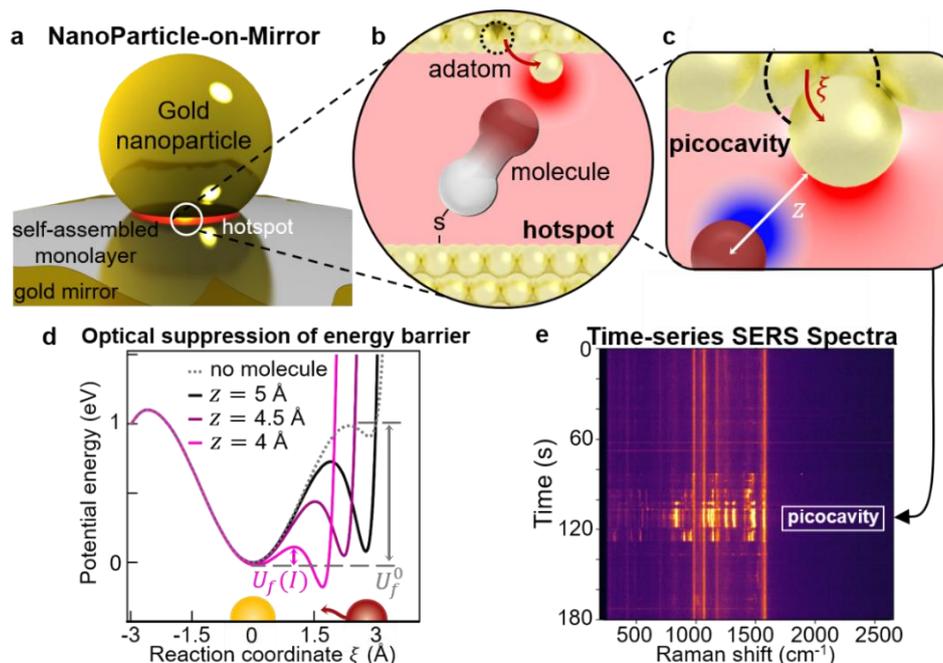
1. Nanophotonics Centre, Department of Physics, Cavendish Laboratory, University of Cambridge, Cambridge, CB3 0HE, England, U.K.

2. Department of Chemistry, King's College London, 7 Trinity Street, London, SE1 1DB, U.K.

3. Department of Physics and Astronomy, University College London, London, WC1E 6BT, U.K.

Understanding the interactions between molecules and metal surfaces is of widespread importance in electrochemistry, sensing, medical imaging/targeting, molecular electronics and spintronics. Although many techniques have characterized the molecule-metal transient bonds, conflicting conclusions arise from their buried location and heterogeneity, while single-molecule probes are scarce. Confinement of optical fields to picometre length-scales around adatoms (termed *picocavities* [1], Fig.1a,b) has enabled tip-enhanced and surface-enhanced Raman spectroscopies (TERS and SERS, Fig.1e) of single-molecules. However how adatoms change with molecule-metal interactions, with light (both key ingredients in photocatalysis), and how they link to picocavity formation in metal nanogaps is not understood.

In this work [2], we demonstrate how the molecule-metal opto-chemical interaction influences the formation and stabilisation of adatoms yielding picocavities, as well as adlayers resulting in *flares* [3]. Through statistics from different molecules across a range of laser powers and modelling by density functional theory (DFT), **we show how the local polarisation of molecule-metal electrons is amplified by illumination, gradually eliminating the energy barrier for adatom extraction and subsequently binding molecule-to-metal, instead of photothermal heating at the surface** (Fig.1c,d). We find rates  $\propto \exp\{-U_f(I)/k_B T\}$  where intensity  $I$  suppresses the barrier, scaling as  $U_f(I) \propto U_f^0/I$ .



**Fig. 1** a, Plasmonic nanocavity assembly, with optical field trapped in the hotspot. b,c, Scheme of a picocavity, with optical field (red) localised around adatom attracting the molecule tip.  $\xi$  is reaction coordinate of adatom from initial site in facet,  $z$  is molecule tip-adatom separation. d, Energy for picocavities when  $z$  decreases by light (solid) vs without molecule (dashed).  $U_f^0$  is barrier for adatom formation when laser is off,  $U_f(I)$  is same barrier but at laser intensity  $I$ . e, Example of surface-enhanced Raman scattering (SERS) spectra for a picocavity.

Interactions between a polarizable atom and metallic atom create extremely powerful optical forces ( $>nN$ ) capable of rearranging the material interface. This work provides not only a vital intuition for utilising light-molecule-metal systems to control single-atom optical switches and semiconductor-metal optoelectronic devices, but also a strong spur to develop new theories capable of combining electromagnetism with quantum mechanics.

## References

[1] F. Benz et al., “Single-molecule optomechanics in ‘picocavities’”, *Science* **354**, 726 (2016).

[2] Q. Lin et al., “Optical Suppression of Energy Barriers in Single Molecule-Metal Binding”, under review (2021).

[3] C. Carnegie et al., “Flickering nanometre-scale disorder in a crystal lattice tracked by plasmonic flare light emission”, *Nat. Commun.* **11**, 682 (2020).