Extreme Optical Forces and Catalysis through Plasmonics Confinement to the Atom scale

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We show how plasmonically-enhanced light-induced van-der-Waals forces pull single adatoms from metal facets, to create picocavities which confine light to volumes < $1nm^3$. The thousand-fold stronger optical forces depend on nearby molecules as well as temperature and local optical field, and offer a route to single-molecule optical tweezers.

Our ability to trap light into extreme nanoscale gaps between coinage metals using plasmonics has enabled routine vibrational measurements of molecular monolayers, even within active molecular electronics devices [1]. We recently showed that single metal atoms can be pulled out of the interface by light [2] (or electric fields), and that coordination bonds with individual molecules can be tracked in real time [3-6], or their redox state observed [7]. We discuss new observations for the thousand-fold enhanced optical forces in such nanogaps.

Such spectroscopy reveals a wealth of information: from how applying voltages can twist the conducting molecules in a gap [8], to how solvated charge is able to penetrate self-assembled monolayers [9]. The robust and precise self-assembly of the nanoparticle-on-mirror geometry is ideal for tunnelling photocurrent devices [10], and shows that asymmetry is created in the junction, likely by such picocavities. We also discuss the dynamics of the picocavity formation [11], and how this may be now controlled.

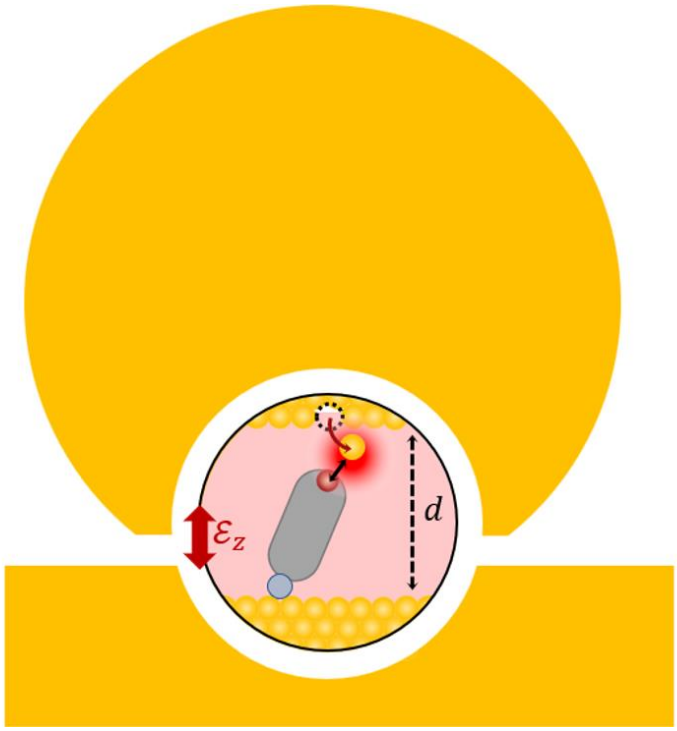

Fig. 1 Inside plasmonic nanogaps, the optical forces on individual metal atoms are magnified x1000, driving new photochemistries.

References

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