Optical Suppression of Energy Barriers in Single Molecule-Metal Binding

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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 \textit{picocavities} \cite{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 \cite{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 \cite{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 $\propto \exp\left(-U_f(I)/k_B T\right)$ where intensity $I$ suppresses the barrier, scaling as $U_f(I) \propto U_f^0/I$.

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure1.png}
\caption{a, Plasmonic nano-cavity 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.}
\end{figure}

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
\begin{enumerate}
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