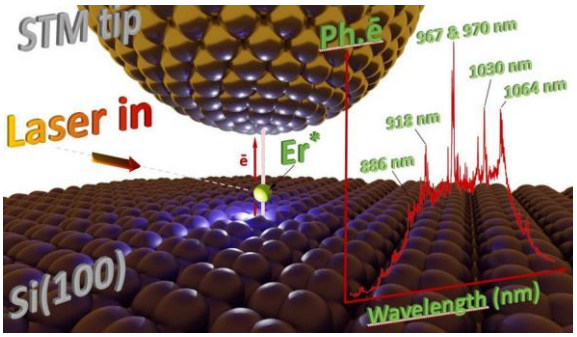
Optical Spectroscopy at the Atomic Scale: Readout of a Single-Atom Electronic States

Damien RIEDEL, Eric Duverger

Institut des Sciences Moléculaires d'Orsay (ISMO), CNRS, Univ. Paris Sud, Université Paris-Saclay, F-91405 Orsay, France.

Abstract:

Understanding how light interacts with matter at the atomic scale is a major challenge in nanoscience, as many key optoelectronic and quantum processes occur locally at defects, molecules, or individual atoms adsorbed on surfaces or embedded in solid-state environments. Conventional far-field optical spectroscopies, however, are limited by diffraction and often rely on ensembles of emitters [1]. Scanning probe techniques such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM) offer atomic spatial resolution but, in their conventional implementations, provide limited direct access to optically excited electronic states. Moreover, their conventional detection bandwidth is insufficient to directly resolve the ultrafast electronic dynamics of atomic and molecular adsorbates.



In this work, I explore a novel approach using a tunable supercontinuum laser to probe the excited states of individual erbium (Er) atoms adsorbed on semiconductor surfaces through optoelectronic readout [2]. For Er adatoms on bare Si(100) at cryogenic temperatures, laser-driven STM photocurrent spectroscopy reveals distinct signatures associated with intra-atomic optical transitions and exciton-mediated relaxation processes.

The photocurrent spectra exhibit distinct contributions from both the silicon substrate and the Er adatoms, enabling the identification of several optically driven processes at the single-atom level. In particular, additional photocurrent peaks are attributed to relaxation pathways of the Er adatom followed by the dissociation of nearby trapped excitons. Density functional theory calculations incorporating spin–orbit coupling support the assignment of these features to specific intra-atomic transitions involving 4f ⟶ 4f and 4f ⟶ 5d electronic excitations.

These findings open new avenues for investigating quantum emitters and excitonic processes at the atomic scale, and for exploring atomically precise optoelectronic functionalities relevant to nanoscale photonics and quantum information technologies.

[1] Nano Lett. 2010, **10**, 10, 3857–3862
[2] ACS Nano 2024, **18**, 13, 9656–9669