Quantum Coherence of Molecules and Atoms: Pump-probe techniques in STM

Normally, the electronics of STM cannot capture the underlying dynamics faster than a few kHz. M. Garg et al. circumvented this difficulty by measuring the photon-induce current by two orthogonally polarized near-infrared laser pulses with slightly different carrier frequencies (*1*). It should be noted that the photon-induced current from a broadband laser they used (~ 0.4 eV) directly reflects the LDOS of the underlying object, the dI/dV signal in IETS, not the rectified current of d2I/dV2 (*2-4*). In this way, the photon-induced current will vary with the beating generated by the two beams and changing the delay between the two pulses allows them to observe the coherence of two dipole-coupled states from the PTCDA molecules with sub-femtosecond temporal resolution. For PTCDA molecules directly absorbed on Au(111), the coherence is between the surface state and the LUMO, which will decay in less than 10 fs where the two laser pulses are still overlapped. The direct coherence between HOMO and LUMO, induced by two-photon absorption, is also shown on the PTCDA molecules that are well-isolated by three PTCDA molecules layers (*1*).

Similar techniques were firstly applied to the nanoscale probing of spin dynamics with temporal resolution corresponding to the optical pulse width in principle (*5*). Instead of on-off modulation, S. Yoshida et al. modulated the circularized polarization of laser pulses (90 MHz, ~130 fs) at slightly different frequencies (1 MHz and 1.001MHz) for pump and probe train and thus avoided introducing thermal expansion. Through the lock-in amplifier, difference of tunneling current between the cases when both pump and probe pulses have synchronized polarization and when they have asynchronous polarization could be measured. With this technique, Spin relaxation in a single quantum well with a width of 6 nm was observed with a spatial resolution of ∼1 nm, the temperature dependence of which implies the underlying decoherence mechanism. In addition to spin relaxation (~ 10 ns), spin precession at different magnetic field at 2.5 K, which provides an estimation of the g factor, was observed successfully.

Another extension of STM toolbox is the integration of THz pulses in a pump-probe scheme. Lightwave-driven tunnelling can be used as an atomically localized pump in a pump–probe scheme incorporating two terahertz-driven tunnelling processes. This has been shown in single-molecule THz-STM experiments performed at 10 K in ultrahigh vacuum (*6*), where one terahertz-driven tunnelling event transiently charge the molecule and coherently launched the oscillation of the molecule above the substrate and a second read out the motion of the molecule with ultrafast time resolution. More recently, THz-STM has been combined with action spectroscopy of single molecules, where a terahertz pump pulse exerted a local force and modified the potential landscape of a magnesium phthalocyanine molecule, inducing a coherent hindered rotation (*7, 8*). A subsequent terahertz probe pulse stimulated tunnelling through one of the molecular orbitals, thereby destabilizing the molecule’s adsorption position on the substrate, which rests in one of two orientations when unexcited. By reading out the orientation of the molecular switch after each terahertz-induced tunnelling event, the terahertz-pump-induced hindered rotation of the molecule was shown to affect its switching probability (*8*)

The integration of pump-probe spectroscopy with STM has also allowed studies of spin relaxation in magnetic atoms on the nanosecond time scale. By aligning the Zeeman splitting of the two spins through the effective magnetic field emanated from the tip, Veldman et al were able to tune the level of entanglement between the two TiH, spin ½ objects, reflected by the avoided crossing of ESR spectrum (*9*). Under the entangled condition, they used DC pump-probe techniques to only flip the spin of atom underneath the tip while preserving the coherence of the system (from 60 ns to 130 ns, benefited from the localized 3d orbital who holds the spin). The coherent oscillation of the magnetization of the atom underneath the tip (~10 ns period) is the product of the coherent evolution mediated by flip-flop interaction of the two spin ½ system. The enhanced quantum coherence of the entangled spin system is another bonus originating from.the two-level system that consists of the singlet and triplet states having magnetic quantum number m = 0, and thus, it is not sensitive to magnetic field fluctuations to first order (*10*). This gives a spin coherence time that is more than one order of magnitude longer compared with other states in this system of coupled atoms and with individual Ti atoms. The similar coherent evolution of spin systems is inaugurally demonstrated by K. Yang et al. who combined ESR-STM with microwave AC pulsing schemes (*11*). The initialization process of creating superposition states of the spin is accomplished by a Rabi flop process rather than a DC pulse. By performing Ramsey fringe and spin echo measurements, the decoherence time T2\* (~40 ns) and T2 (~200 ns) were able to be determined, respectively.

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