Individual Molecules on Surfaces: From Chemical Reactions to Ultra-Short Timescales

D. Peller, F. Albrecht, L. Patera, N. Pavliček, N. Kocić, T. L. Cocker, R. Huber and J. Repp

Department of Physics, University of Regensburg, 93040 Regensburg, Germany
E-mail: Jascha.Repp@ur.de

We investigated different kind of π–conjugated molecules in a combined scanning tunnelling (STM) and atomic force microscope (AFM). Whereas both measurement channels show features with sub-molecular resolution, the information they can provide is truly complementary. For example, STM allows the direct imaging of the unperturbed molecular orbitals [1], whereas the AFM channel directly reveals the molecular geometry [2, 3]. When applied to STM-based single-molecule synthesis and on-surface chemistry, the combination of these techniques enables a direct quantification of the interplay of geometry and electronic coupling in real space [3, 4]. In particular, in many cases only the AFM channel enables discriminating different binding sites inside a single molecule, which is a prerequisite to obtain a full atomistic description of regioselectivity in on-surface chemistry [4]. Similarly, in the case of hydrogen-bonded molecular assembly the AFM provides direct insight into the bond rearrangement upon crystallization in two dimensions [5], which is elusive for STM.

The possibility of tailoring optical waveforms has allowed scientists to steer ultrafast electronic motion directly via the oscillating carrier wave of light – a principle dubbed “lightwave electronics” [6]. Terahertz (THz) scanning tunnelling microscopy [7] (THz-STM) has introduced a new paradigm by combining STM with lightwave electronics. In THz-STM, the electric field of a phase-stable single-cycle THz waveform acts as a transient bias voltage across an STM junction. In analogy to the all-electronic pump-probe scheme introduced recently in STM [8] these voltage transients may result in a net current that can be detected by time-integrating electronics.

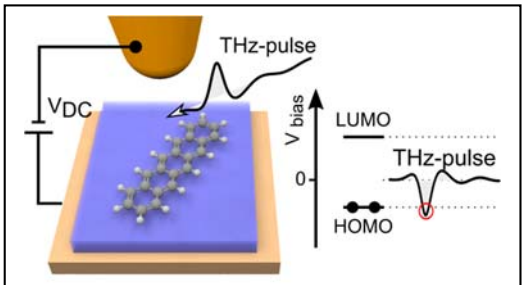

Figure 1: Schematic representation of the lightwave-STM setup, in which the THz-pulse acts as a bias transient.

By means of a low-noise low-temperature lightwave-STM we entered an unprecedented tunnelling regime, where the peak of a terahertz electric-field waveform opens an otherwise forbidden tunnelling channel through a single molecular orbital. In this way, the terahertz peak removes a single electron from an individual pentacene molecule’s highest occupied molecular orbital within a time window of ~100 fs – faster than an oscillation cycle of the terahertz wave. This quantum process allowed us to capture a microscopic real-space snapshot of the molecular orbital on a sub-cycle time scale. By correlating two successive state-selective tunnelling events, we directly tracked coherent THz vibrations of a single molecule in the time domain [9].

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