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Review

Action spectroscopy for single-molecule reactions – Experiments and theory

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Butene
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ABSTRACT

We review several representative experimental results of action spectroscopy (AS) of single molecules on metal surfaces using a scanning tunneling microscope (STM) by M. Kawai's group over last decade. The experimental procedures to observe STM-AS are described. A brief description of a low-temperature STM and experimental setup are followed by key experimental techniques of how to determine an onset bias voltage of a reaction and how to measure a current change associated with reactions and finally how to observe AS for single molecule reactions. The experimental results are presented for vibrationally mediated chemical transformation of *trans*-2-butene to 1.3-butadiene molecule and rotational motion of a single *cis*-2-butene molecule among four equivalent orientations on Pd(1 1 0). The AS obtained from the motion clearly detects more vibrational modes than inelastic electron tunneling spectroscopy with an STM. AS is demonstrated as a useful and novel single molecule vibrational spectroscopy. The AS for a lateral hopping of water dimer on Pt(1 1 1) is presented as an example of novelty. Several distinct vibrational modes are detected as the thresholds in the AS. The assignment of the vibrational modes determined from the analysis of the AS is made from a view of the adsorption geometry of hydrogen-bond donor or acceptor molecules in water dimer.

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A generic theory of STM-AS, i.e., a reaction rate or yield as a function of bias voltage, is presented using a single adsorbate resonance model for single molecule reactions induced by the inelastic tunneling current. Formulas for the reaction rate $R(V)$ and $Y(V)$, i.e., reaction yield per electron $Y(V) = eR(V)/I$ are derived. It provides a versatile framework to analyze any vibrationally mediated reactions of single adsorbates on metal surfaces. Numerical examples are presented to demonstrate generic features of the vibrational generation rate and $Y(V)$ at different levels of approximations and to show how the effective broadening of the vibrational density of states (as described by Gaussian or Lorentzian functions) manifest themselves in $Y(V)$ near the threshold bias voltage corresponding to a vibrational excitation responsible for reactions. A prefactor of $Y(V)$ is explicitly derived for various types of elementary processes. Our generic formula of $Y(V)$ also underlines the need to observe $Y(V)$ at both bias voltage polarities, which can provide additional insight into the adsorbate projected density of states near the Fermi level within a span of the vibrational energy.

The theory is applied to analysis of some highlights of the experimental results: Xe transfer, hopping of a single CO molecule on Pd(1 1 0), a dissociation of a single dimethyl disulfide $(CH_3S)_2$ and a hopping of a dissociated product, i.e., single methyl thiolate CH_3S on Cu(1 1 1). It underlines that an observation of $Y(V)$ at both bias polarities permits us to certain insight into the molecular alignment with respect to the Fermi level.

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