SURFACE CHEMISTRY

Reorganization takes energy

Atomic force microscopy is used to measure reorganization energies upon charging individual molecules adsorbed on insulators.

Alexander L. Shluger and Peter Grutter

Many processes in biology, nanotechnology, photocatalysis and electronics involve transfer of electrons between different agents: molecules, defects or nanoparticles. In the molecular world, electron transfer reactions are associated with geometric modifications (such as a change in bond length or bond angle) of the species involved; this energy cost is called the inner reorganization energy. Since molecules are often dissolved in a solvent or adsorbed on a substrate, there is also an energy cost associated to a change in the environment (such as solvation energy); this is called the outer reorganization energy. Reorganization energy is one of the key concepts introduced in the theory of electron transfer by Rudolph Marcus (1992 Nobel Prize in Chemistry) to describe the rate of electron transfer between molecular species and thus the kinetics of chemical reactions. Reorganization energy controls charge mobility in organic electronics, efficiency of organic photovoltaic devices and the reliability of electronic devices. Typical reorganization energies of rigid organic molecules are 0.1–0.2 eV and decrease as the size of the molecule increases. Reorganization energy can be measured using photoelectron spectroscopy on a large ensemble of molecules, but direct experimental determinations are still rare. In most cases, in fact, it is easier to measure rates of electron transfer and then deduce the reorganization energy using Marcus theory.

Writing in *Nature Nanotechnology*, Fatayer et al. now show direct measurements of the reorganization energy of an individual molecule adsorbed on an insulating substrate upon trapping and releasing a single electron using atomic force microscopy (AFM)[1]. This energy reflects the response of the whole system to changes of molecular charge. Using an AFM tip as a source of electrons and operating at low temperature, Fatayer et al. address single molecules in a statistically meaningful way, and investigate how the reorganization energy depends on the character of
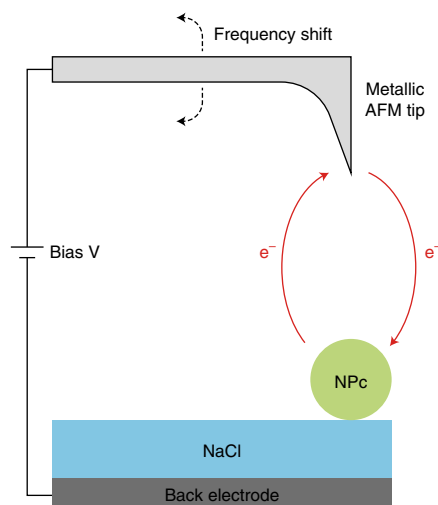

Fig. 1 | An atomic force microscope is used to detect the energy dependence for a single electron to tunnel on or off a single molecule. The frequency shift experienced by the AFM tip is proportional to the electrostatic force experienced in the interaction with the molecule, which in turn depends on the molecular charge. NPc, naphthalocyanine.

the molecule–surface interaction. This knowledge is vital for a molecular-level understanding of the mechanisms of electro- and photocatalysis, solar cells and molecular electronics.

The feasibility of controlling the molecular dynamics of a single molecule through the localization of the electronic excitation inside the molecule has been demonstrated by scanning tunnelling microscopy[2,3]. Using AFM, Fatayer et al. can take advantage of the single-charge sensitivity offered by this technique to measure single-molecule excitations on insulators[4] (Fig. 1). The AFM tip is attached to a cantilever and serves both as an electrode and as a sensor. By carefully tracking the resonance frequency of the cantilever, small changes in tip–sample force can be detected due to a single molecular charging event. Insulating a single molecule from a back electrode

with a thick, insulating layer (NaCl) prevents the charge on the molecule from leaking away. The rate for electrons to tunnel between the tip and the sample can be controlled by changing the tip–sample distance as well as the bias applied between the tip and the back electrode. An increased tunnelling probability for an electron between the tip and the sample is observed if the tip–sample bias is tuned to a value where electronic states of the tip and the sample are aligned. A careful statistical analysis of the tunnelling probability as a function of tip–sample bias allowed Fatayer et al. to determine the molecular energy levels. They found that the maximum probability for tunnelling into the molecule is not at the same energy as that for tunnelling out of the molecule; this difference is directly related to the reorganization energy, which, for a rigid naphthalocyanine molecule on NaCl, turns out to be ~0.8 eV. Theoretical modelling corroborates this value and shows that ~97% of this energy is outer reorganization energy due to polarization of the NaCl layer and metal substrate by the positively charged naphthalocyanine.

The combination of such ultra-sensitive experiments and accurate theory can lead to the investigation of different factors affecting reorganization energies of molecule/substrate systems; for example, the investigation of how the reorganization energy of individual molecules depends on the adsorption site, an impossible task using spectroscopic methods. If adsorbed molecules are mobile, they diffuse from terraces to steps, dislocations and kinks and adsorb there; in other cases, molecules remain adsorbed on point defects (missing atoms or pairs of atoms). Other interesting effects include changes in the character of the molecule–surface interaction and mobility due to charging. However, such measurements face many challenges: electron attachment may lead to dissociation of the molecule[5] as well as enhancing its mobility; the molecule can react with the insulator and defects in the insulator can leak the charge. A further challenge

is to understand what determines the substantial width of the orbital resonance peaks extracted from the energy-dependent tunnelling probability in the work of Fatayer et al. Nevertheless, this work marks an important transition from observation[6] of charge-induced molecular processes at insulating surfaces to quantitative characterization at the atomic scale. ❑

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