

Abstract to

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**Energy alignment at the molecule – electrode interface:  
A balance of ionization potential or electrochemical potential**

**Ayelet Vilan**, Chemical and Biological Physics, Weizmann Institute of Science.

A major aspect of hetero-interfaces is the relative position the energy levels / bands of two adjacent phases, shortly known as the ‘injection barrier’. From inorganic semiconductors to thin organic films, interfacial energy alignment is accompanied by charge redistribution and therefore, a build-up of potential profile across the interface. There are two extreme scenarios for predicting the energy alignment. One extreme is ‘vacuum level alignment’ (also known as Schottky limit); it assumes an inert interface where the energy to extract an electron (work-function, WF or ionization-potential) is constant before and after contacting (adsorption for molecules). Namely, there is no induced interface dipole and the injection barrier is directly the difference between the frontier energies of the isolated phases. The opposite extreme is ‘Fermi-level alignment’ (Bardeen limit) where the injection barrier is fixed regardless of changes in WF, which is compensated by a significant induced dipole. These fundamental considerations hold also for molecules (isolated or within a monolayer) adsorbed onto electrodes, though they represent an extreme state of matter. First, any interface-induced potential drop must be confined into merely one molecule, which translates into immense electric fields. Second, the mechanism of such charging or polarization obviously differs from thin films as there are no free carriers and the frontier molecular levels are normally  $> 1\text{eV}$  away from the electrode’s Fermi level. This explains the prevailing concept that adsorbed molecules follow vacuum level alignment. However, evidence is growing for the opposite: variation in electrode’s work-function induces large alteration in molecular dipole with a negligible change in injection barrier. Namely, it is as if the molecules are “Fermi-level-pinned”, but molecules have no Fermi level! Instead the electrochemical potential of the molecule is a well-defined thermodynamic quantity. I will describe how electrochemical balance combined with the chemical “hardness / softness” (electronic polarizability) considerations provide a qualitative guiding rule for both energy alignment and polarization (dipole) of adsorbed molecules. This concept will be demonstrated on our own work with molecular monolayers on Si(111) and by reference to literature works on thiol-bonded monolayers on Au.