Vibrational Excitation of Molecules in STM-IETS - A Theoretical Approach

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Tunneling electrons can be used to excite vibrations in molecules. By combining the high spatial resolution of scanning electron microscopy (STM) with the chemical selectivity of Inelastic Electron Tunneling Spectroscopy (IETS) it is now possible to obtain vibrational spectra of single molecules adsorbed on a surface. This way identification and selective removal of isotopes in molecules can be done (e.g. H and D in acetylene).

Interestingly in large molecules, the vibrational spectrum obtained by STM-IETS seems to depend on the impact point of the electrons on the molecular surface. Selective excitation of vibrational modes by the STM tip has been proposed to explain these experimental findings (so-called 'excitation of local vibrations' model [1]).

Therefore, we want to simulate the dynamical response of acetylene and phtalocyanine (NPc) induced by the impact of tunneling electrons. To this end, we perform molecular dynamics simulations based on time-dependent density functional theory (TDDFT) in which tunneling electrons are modeled by means of Gaussian wave packets. Vibrational spectra are then obtained by Fourier analysis of the velocity autocorrelation function. This way, we study the relative strength of the excited molecular vibrations in dependence of the impact point of the tunneling electrons. Finally, a comparison between numerical results and experimental findings is attempted and the validity of the 'excitation of local vibrations' model is discussed.

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[1] N. Ogawa, G. Mikaelian and W. Ho, Phys. Rev. Lett. **98**, 166103 (2007).