

Important impact of the experimental platform on the efficient simultaneous control of electronic and vibrational properties of molecular junctions

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A recent work [1] reported on simultaneous surface enhanced Raman scattering (SERS) and transport current-voltage I-V measurements in electromigrated molecular junctions based on fullerene C₆₀. In molecular junctions, the SERS is observable because of the enormous electromagnetic enhancement near sharp metallic electrodes (tips), which act as highly efficient plasmonic antennas [2]. Vibrational frequencies measured in Ref. 1 were found to be slightly but significantly shifted by the applied bias V. Companion DFT calculations indicated that these V-driven shifts cannot be due to a simple vibrational Stark effect but are compatible to a partial reduction of the C₆₀ molecule, whose lowest unoccupied molecular orbital (LUMO) becomes partially occupied under bias. The V-values used in experiment turned out to be far less than needed for adding an entire electron to the molecule.

In this context, one of the questions addressed here is whether the experimental platform of Ref. 1 represents the most favorable setup to achieve a(n almost) complete bias-driven reduction [3]. The answer [3] is that (i) no matter how high the voltage is, reduction cannot exceed 50% in an experimental setup (like that of Ref. 1) where the molecule is symmetrically coupled to the (source and drain) electrodes, (ii) reduction can be almost complete in cases of highly asymmetric molecule-electrode couplings, but in this case (iii) biases corresponding to current plateaus are required, which common junctions cannot withstand.

We next discuss that, much more than in two-terminal setups, the molecular charge, orbital energies, and vibrational properties can be efficiently controlled in case of (redox) molecules embedded in scanning tunneling microscope (STM) junctions in electrochemical (EC) environment [4]. The electrochemical setup provides a unique chance to control the molecular properties. The key role in the unprecedented efficiency of this control is played by the electrolyte gating, which enables a continuous change in the molecular charge by up to an entire electron (complete redox process). To exemplify, we consider EC-STM experimental transport data for the redox unit (viologen) [5], whose essential constituent is 4,4'-bipyridine (44BPY), a molecule of special interest for the charge transport at the nanoscale, on which we focused in a series of recent studies [6,7,8,9,10]. The relevant redox process is between the oxidized (44BPY²⁺) and the reduced (44BPY^{•+}) species.

Obviously, to observe changes in vibrational properties of the kind mentioned above, the vibrational properties of the oxidized and reduced species must significantly differ. Fig. 1 depicts that this is indeed the case for the EC-STM junctions considered here.

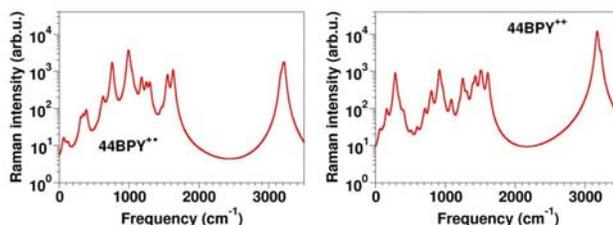


Fig. 1 Raman spectra of the dicationic and cationic species of bipyridine exhibit substantial differences. Notice the logarithmic scale on the ordinate axis.

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