DFT study of the Effect of the electrode potential on anchoring of metal-molecule hybrids

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The impact of the molecular adsorption process on the electronic structure is the key in phenomena involved in electrochemistry, catalysis, molecular electronics, SERS, photoelectric conversion, etc. The effect of the electrode potential on a collection of relevant systems, comonly used as SERS adsorbates,[1-3] has been investigated. These molecules has been clasified in groups (*Gi*) based on their charge transfer (CT) exctited state behaviour *vs* the electrode as follows: pyridine and pirazine (*G1*), adenine and protonated adenine (*G2*), benzoate and isonicotinate (*G3*) and finally chloride and cyanide (*G4*). The effect of electrode potential[3] were modeled with Molecule-Ag_n^q charged hybrid systems, were $q=0,\pm1$ and n=2, 3, 5 and 7, through the charge per metallic atom $q_{eff}=q/n$. As a conclusion, we have found diferenciated correlations for the charge injection on the metal, the molecule-metal afinity and the excited CT states energies.

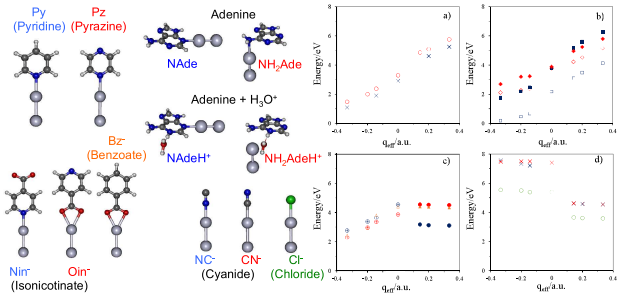

Figure 1. Systems (left), and CT_0 vertical energies (right), *vs* q_{eff} of: (a) Py (hollow red circles), Pz (blue X). (b) NAde (blue filled squares), NH_2Ade (red filled diamonds). Hollow marks add hydronium to the system. (c) $NIni^-$ (blue circled +), $OIni^-$ (red circled +), Bz^- (hollow orange triangles). Filled marks belong to the A→M transition. (d) Cl^- (green circles), CN^- (red X), NC^- (blue X). These energies belong to the A-M transition.

References

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