ON THE USEFULNESS OF ELECTRON PROPAGATOR METHODS FOR A RELIABLE COMPUTATION OF EXPERIMENTAL OBSERVABLES

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Electron propagator methods (EPMs) are well known in the physical-chemical community as a useful tool for the identification of signals observed in ultraviolet photoelectron spectra (UPS) of isolated organic molecules. However, to completely reproduce an experimental UPS the vibrational signature associated to each electronic signal of interest should be computed.

In the first part of this contribution, the implementation of a simple protocol for the simulation of vibrationally resolved UPS is briefly described and its application to the calculation of the spectra of seven semi-rigid organic molecules is proposed.[a,b]

Chemical community is particularly interested in processes that occur in solutions, and therefore the energy which is needed to remove (or to add) an electron from a molecular system is often measured by means of electrochemical techniques. As a consequence, in this case the experimental observables of interest are oxidation and reduction potentials, which differ from the ionization potentials and the electron affinities computed with EPMs.

In the second part of this contribution, experimental redox potentials of 12 organic dyes are compared with ionization potentials and electron affinities computed through EPMs. Differences between computed and observed values are rationalised in terms of polarization and solvation effects, and the estimation of redox potentials through the employment of suitable corrections to the values calculated with EPMs is discussed.

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[a] A. Baiardi, L. Paoloni, V. Barone, V. G. Zakrzewski, J. V. Ortiz, *J. Chem. Theory Comput.*, **2017**, 13, 3120-3135.

[b] L. Paoloni, M. Fusè, A. Baiardi, V. Barone, *J. Chem. Theory Comput.*, **2020**, 16, 5218-5226.