Vibronic and Resonance Raman Spectra of Extended Viologens Modelled by Multireference Approaches

Julia Romanova[1], Vincent Liégeois[1], Lubomír Pospíšil[2,3], Thomas Magnera[4], Josef Michl[4] and Benoît Champagne[1]

[1] Laboratoire de Chimie Théorique, Unité de Chimie Physique Théorique et Structurale (UCPTS), University of Namur, Rue de Bruxelles 61, 5000 Namur, Belgium

[2] J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3,18223 Prague, Czech Republic

[3] Department of Organic Chemistry, Charles University, Albertov 2030, Prague 2, Czech Republic

[4] Department of Organic Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215, USA

Due to the unique combination of electronic, optical, and magnetic properties, extended viologens are regarded as very promising materials with potential applications in electrochromic devices and field-effect transistors [1,2]. These compounds can undergo two consecutive one-electron reductions to form a stable radical cation in the first step and then a neutral state with multireference character. The redox behavior is even more complex because a dimerization of the radical cations may compete with the second reduction step. The product of the side reaction has similar absorption properties as the neutral state. Therefore, a reliable structural identification of the neutral state is required.

The experimental characterization of electrogenerated species in solution can be done by in-situ absorption and resonance Raman spectroscopy. However, the interpretation of the experimental spectra and the unraveling of the photophysical properties can be hampered by the complexity of the vibrational structures, which call therefore for the use of well-designed theoretical models and of accurate first principles calculations. In this study, multireference approaches are employed to simulate and interpret the absorption and resonance Raman spectra of extended viologens. The structures of the ground and the brightest excited state were obtained by state-specific and state-averaged complete active space self-consistent field theory (CASSCF). Multiconfigurational second-order perturbation theory (CASPT2) was applied to take into account the remaining dynamic correlation effects on the electronic transition energies. The quantum-chemical calculations were performed by the MOLPRO package, while the vibronic and resonance Raman spectra were simulated by a program developed locally.

[1] (a) Takahashi, K.; Nihira, T.; Akiyama, K.; Ikegami, Y.; Fukuyo, E. *J. Chem. Soc. Comm.* **1992**, 620; (b) Funston, A.; Kirby, J. P.; Miller, J. R.; Pospíšil, L.; Fiedler, J.; Hromadová, M.; Gál, M.; Pecka, J.; Valášek, M.; Zawada, Z.; Rempala, P.; Michl, J., *J. Phys. Chem. A* **2005**, 109, 10862; (c) Pospíšil, L.; Fiedler, J.; Hromadová, M.; Gál, M.; Valášek, M.; Pecka, J.; Michl, J. *J. Electrochem. Soc.* **2006**, *153* (11), E179.

[2] (a) Grätzel, M. *Nature* **2001**, 409, 575; (b) Kolivoška, V.; Gál, M.; Pospíšil, L.; Valášek, M.; Hromadová, M. *Phys. Chem. Chem. Phys.* **2011**, 13, 11422; (c) Kolivoška, V.; Valášek, M.; Gál, M.; Sokolová, R.; Bulíčková, J.; Pospíšil, L.; Mészáros, G.; Hromadová, M. *J. Phys. Chem. Lett.* **2013**, 4, 589.

[3] MOLPRO, version 2012.1, a package of ab initio programs, Werner, H.-J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M. and others.