Área: FIS

Theoretical study on the absorption spectrum of para-halobenzonitriles and their respective radical anions using multiconfigurational calculations

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Highlights

Theoretical vertical absorption spectra were obtained using multiconfigurational methods. Investigation of photodegradation of molecules in SERS experiments. Calculations of radical species.

Resumo/Abstract

When analyzing resonant SERS spectra obtained for para-halobenzonitriles, the presence of a vibrational mode around 2000 cm^{-1} suggested the formation of a radical[1] anion through a metal-ligand charge transfer. To further investigate it, a computational study was performed considering the neutral and the respective radical anions species. DFT calculations were used for geometry optimization and theoretical vibrational frequencies on the theory level M062X-D3(0)//Def2-TZVPP[2] and multiconfigurational calculations (CASSCF/NEVPT2) alongside the same atomic basis were used to obtain the theoretical vertical absorption spectra.

The geometry optimization shows that the CN bond length is aproximately 0,2Å larger for the radical anions, suggesting that the ciano group carbon's character shifts from sp to sp^2. The formation of the nitrile radical anion is also enforced by the occupation of ciano bond's antiligand orbital, observed in the NEVPT2 calculations for the radical species. When comparing the theoretical vibrational spectra, the energy shift is also observed for the ν(CN) band, with an average shift of 200 cm^{-1} to a lower wavenumbers for the radical species relative to neutral molecules. The theoretical vertical absorption spectra, obtained with multiconfigurational calculations for the IBnzCN molecule, suggests that the molecule degrades eliminating the halogen, due to the low energy excited states with compostion of the σ* orbital of the carbon-halogen bond. This state is relevant for both the neutral and radical anion species and agrees with the experimental results obtained, which shows a different behaviour for IBnzCN when compared to the other molecules of the para-halobenzonitrile group.

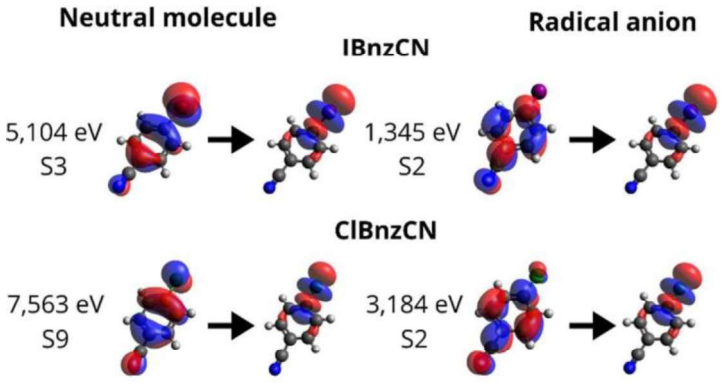

Figure 1: Characterization of the degradation states for the molecules IBnzCN and ClBnzCN generated by a NEVPT2 calculation.

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