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Optical properties of copper clusters in zeolite 4A with surface enhanced Raman spectroscopy applications

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Abstract
In this study, we used the ion exchange properties of zeolite 4A to stabilize copper ionic species. These species showed absorption bands in the ultraviolet region between 210 and 320 nm. Complementarily, DFT (Density-Functional Theory) at different levels of approximation was employed in combination with the LANL2DZ (Los Alamos National Laboratory 2 double zeta) and SDD (Stuttgart/Dresden) basis sets to find hints of optical absorption behavior associated with electronic transitions. The copper clusters in ZA were evaluated as SERS (Surface-Enhanced Raman Spectroscopy) substrate using pyridine (Py) and methylene blue (MB) molecules. Additionally, molecular descriptors as electron transfer factor, electronegativity and global hardness were considered to study the charge transfer between the molecular systems and the ionic copper species. The DFT calculations suggest that the Cu_3^+ cluster manifests optically. The molecular descriptors allowed to identify the effect of charge transfer from the analyte to the cluster, specifically toward the LUMO or higher energy orbitals, and the systems obtained showed capacity as SERS substrates, evaluated on Py and MB.

Keywords Copper ions · Chemical enhancement mechanism · Zeolite 4A · Theoretical and experimental analysis

1 Introduction

Zeolites are hydrated aluminosilicates and they feature the characteristic to exchange cations [1]. In addition, they can host different structures in their matrix, and it makes them attractive for different applications [2]. Zeolite 4A (ZA) has Na^+ as the only exchange ion, which facilitates its study [3]. The different active sites in ZA provide conditions for the ion exchange or structure hosting [4].

Surface-enhanced Raman scattering (SERS) is used for its high sensitivity, selectivity and reliability in the traces detection of chemical molecules [5–7]. When a molecule interacts with the SERS substrate, it amplifies the Raman signal by several orders of magnitude. This effect is associated with two mechanisms: (1) electromagnetic effect (EM), which consists of an intensification of the Raman spectrum caused by the scattered radiation due to the metal surface and (2) chemical effect (CE), based on charge transfer and/or complex formation between the absorbed molecules and the substrate surface [8]. SERS substrates are made of Ag, Au or Cu and they incorporate metallic elements [9–13]. Additionally, there are reports of oxides such as: ZnO, Ag_xMo_yOz, Fe_2O_3 and carbon composites with SERS applications [14–18]. There are currently few theoretical and experimental results in the literature on the SERS response of ionic species. However, the presence of ionic systems has been analyzed in some matrices, finding a promising increase in SERS activity [19]. Ag^+ ions have allowed the formation of complexes in molecules providing SERS active sites that contribute an enhancement factor reaching up to 10^7 [20]. Recently, Lancu et al. analyzed the increase in the SERS effect due to the interaction of Ag^+, Ca^{2+}, Pb^{2+} and

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