THEORETICAL STUDY ON SERS OF WAGGING VIBRATIONS OF BENZYL RADICAL ADSORBED ON SILVER ELECTRODES

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Electrochemical surface-enhanced Raman spectroscopy (EC-SERS) has been used to characterize adsorbed species widely but reaction intermediates rarely on electrodes. In previous studies, the observed SERS signals were proposed from surface benzyl species due to the electrochemical reduction of benzyl chloride on silver electrode surfaces. In this work, we reinvestigated the vibrational assignments of benzyl chloride and benzyl radical as the reaction intermediate. On the basis of density functional theoretical (DFT) calculations and normal mode analysis, our systematical results provide more reasonable new assignments for both surface species. Further, we investigated adsorption configurations, binding energies, and vibrational frequency shifts of benzyl radical interacting with silver. Our calculated results show that the wagging vibration displays significant vibrational frequency shift, strong coupling with some intramolecular modes in the phenyl ring, and significant changes in intensity of Raman signals. The study also provides absolute Raman intensity in benzyl halides and discuss the enhancement effect mainly due to the binding interaction with respect to free benzyl radical.

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