QUANTUM CHEMICAL STUDY OF RAMAN SPECTROSCOPY OF SUBSTITUTED BENZENE DERIVATIVES ADSORBED ON METAL SURFACES[a]

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Surface-enhanced Raman spectroscopy (SERS) can be applied to obtain the information of molecules at the noble metal surfaces. But there are a number of difficulties to clearly correlate Raman spectra with microscopic molecular structures on metal surfaces. The main reason is that it is difficult to characterize unambiguously the metal surface structures and the influence of the binding interaction on SERS signals of the probe molecules. According to the surface selection rule of SERS, the electromagnetic enhancement will not change relative Raman intensities of vibrational modes with the same irreducible representation. Therefore, the change of the relative Raman intensities of the total symmetric modes may only originate from the chemical enhancement. In order to understand how the chemical interaction modulates the Raman intensity of individual modes, it is necessary to systematically investigate the Raman spectra of probe molecules themselves and the dependence of SERS signals on the binding interaction, adsorption sites, excitation wavelengths and metal property. Some probe molecules, including aniline, 1,4-benzenediamine, p-aminothiophenol, benzyl chlorine, and 4,4′-bipyridine are investigated based on quantum chemical calculations. Raman spectra of these molecules and their adsorbed species were predicted and compared with experimentally measured spectra. The metal surfaces were mimicked using the metallic cluster model, where the silver or gold surfaces were replaced by silver or gold clusters, respectively. The density functional theory approach was employed to obtain the optimized structures and vibrational spectra by combining all-electron basis sets of 6-311+G** for atoms in the molecules and the poseudopotential basis set of LANL2DZ for metal atoms. The vibrational frequency shift and the relative Raman intensity are related to the adsorption configuration of the probe molecules. For all these molecules, the ring breathing mode and the C-C stretching mode show the strongest SERS signals and are sensitive to the binding interaction. They play an important role in obtaining the adsorption structure of molecules on metal surfaces.

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