

On the chemical bonding effects in the Raman response: Benzenethiol adsorbed on silver clusters

Saikin S., Olivares-Amaya R., Rappoport D., Stopa M., Aspuru-Guzik A.
Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

We study the effects of chemical bonding on Raman scattering from benzenethiol chemisorbed on silver clusters using time-dependent density functional theory (TDDFT). Raman scattering cross sections are computed using a formalism that employs analytical derivatives of frequency-dependent electronic polarizabilities, which treats both off-resonant and resonant enhancement within the same scheme. In the off-resonant regime, Raman scattering into molecular vibrational modes is enhanced by one order of magnitude and shows pronounced dependence on the orientation and the local symmetry of the molecule. Additional strong enhancement of the order of 10^2 arises from resonant transitions to mixed metal-molecular electronic states. The Raman enhancement is analyzed using Raman excitation profiles (REPs) for the range of excitation energies 1.6-3.0 eV, in which isolated benzenethiol does not have electronic transitions. The computed vibrational frequency shifts and relative Raman scattering cross sections of the metal-molecular complexes are in good agreement with experimental data on surface enhanced Raman scattering (SERS) from benzenethiol adsorbed on silver surfaces. Characterization and understanding of these effects, associated with chemical enhancement mechanism, may be used to improve the detection sensitivity in molecular Raman scattering. © 2009 the Owner Societies.

<http://dx.doi.org/10.1039/b906885f>
