A Photoinduced Kinetic Model for Size-dependent Effects in SERS of Bioinorganic Hybrid Systems

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The observation of surface-enhanced Raman scattering (SERS) on semiconductors confirms the existence of the chemical effect in a system where a plasmon resonance is not present. Our group studies dopamine-TiO_2 complexes, where the resonance is attributed to excitation between the HOMO of dopamine (DA) and the conduction band of TiO_2. Measurements on DA-TiO_2 on nanoparticles with 2- and 5-nm diameters reveal a stark behavior as a function of adsorbate coverage. While the 2-nm nanoparticles exhibit a saturation effect, a broad maximum is measured for the case of 5 nm. We rule out adsorbate-adsorbate direct interactions since the vibrational frequencies remain constant with coverage. Instead, we favor adsorbate-adsorbate indirect interactions through the conduction band. We present a theoretical model of a low density electron gas formed in the conduction band of TiO_2 upon irradiation, which modifies the dielectric properties of the complex and provides a competition mechanism for Raman scattering. The behavior in the case of 5 nm is extremely well described by this model; deviations for the case of a 2-nm nanoparticle are attributed to quantum confinement present in TiO_2 nanoparticles below 3-nm diameter. These are expected in our model, which requires a fully formed conduction band. The fit parameters extracted from the model give reasonable values for the properties of the electron gas.