Scale Effects in Plasmon-Enhanced Raman Spectroscopy

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Plasmon-enhanced Raman measurements are inherently scale-dependent, i.e. the apparent chemical information is determined by the spatial extent over which electromagnetic confinement, chemical coupling, and structural heterogeneity are sampled. In SERS, spectra are typically representative of an average over a multitude of molecules and multiple nonequivalent hotspots. Consequently, band positions and intensities reflect ensemble behaviour rather than a uniquely local configuration [1]. In TERS, the interaction volume is compressed to a single tip-sample junction, and in the highest-resolution regime, the signal becomes sensitive to the atomic structure of the apex itself [2, 3]. In such conditions, atomic-scale fluctuations in the apex geometry are not merely a secondary perturbation, but rather an integral component of the signal-forming mechanism. This is due to the fact that minor alterations in the apex geometry result in changes to the local field gradient, the effective Raman selection rules, and the degree of chemically specific tip-molecule coupling [2, 3]. This phenomenon elucidates the capability of TERS to approach base-to-base contrast in single-stranded DNA and to facilitate a sequencing-like readout along a quasi-one-dimensional molecular scaffold [4]. Concurrently, the same extreme confinement limits on transferability are evident: a spectrum acquired from a structurally heterogeneous object such as a single virus is expected to reflect localised nanoscale variation rather than a molecular fingerprint which is globally representative [5]. Consequently, scale effects in plasmon-enhanced Raman spectroscopy should be understood as a transition from ensemble averaging to atomically modulated local probing, where the experimental resolution defines both the information content and the interpretability of the spectrum [1-5].

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