

Different Analysis of b2 Peaks in SERS Spectra of 4-aminobenzenethiol

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The SERS spectra of 4-aminobenzenethiol (ABT) have served as the "probe" molecule, which have helped spectroscopists to build up the electromagnetic (EM) and chemical (CHEM) enhancement mechanisms. In particular, the b2-peaks (9b, 3, and 19b) of the SERS spectra of ABT have been attributed to arise from the vibronic charge-transfer (CT) between Au or Ag surface and the ABT. Quite recently, however, Tian and co-workers [1] claimed that the b2-peaks are not the CT-enhanced spectra of ABT. Instead, these peaks arise from the 4,4'-dimercaptoazobenzenes (DMABs) that are produced by the oxidative coupling of two ABTs. Their claim is under intense debate currently. Herein, we studied spatially and temporally resolved SERS spectra of ABTs on Ag thin film (thickness of 10 nm), to investigate such claim. Herein, we present a series of additional evidences that strongly support that the b2 intensities of ABTs do not arise from the CT-enhancement: (1) the b2-peaks can be locally "activated" (i. e. turned on) irreversibly with focused laser radiation; (2) the TOF-SIM spectrometry on the activated region show depletion of ABT-Ag⁺ ions; and finally (3) the spatially resolved FT-IR spectra of the activated region show two pronounced peaks at 1377 cm⁻¹ and 1460 cm⁻¹, both of which can be assigned to the stretching mode of N=N bond. While the result does not disprove the existence of CT or CHEM enhancement in general, the results do show that previous interpretations of the spectra of ABTs should be re-interpreted.

Reference

1. Yi-Fan Huang, Hong-Ping Zhu, Guo-Kun Liu, De-Yin Wu,* Bin Ren,* and Zhong-Qun Tian, J. AM. CHEM. SOC. 2010, 132, 9244-9246

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