

Electrochemical SERS study of the pesticide Methyl Parathion on gold nanostructures

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Highlights

Surface Enhanced Raman Spectra of pesticide molecule Methyl Parathion were obtained on Au NPs using different radiations; Electrochemical potential influence on molecular cleavage and plasmonic catalysis.

Resumo/Abstract

Surface Enhanced Raman Scattering (SERS) has been explored for detecting trace amounts of pesticides in food due to its high sensitivity, given the necessity of adequate inspection when it comes to the illegal use of these substances.^{1, 2} Given these compounds' high reactivity, molecule-metal interactions can trigger chemical reaction or fragmentation, highlighting that a detailed spectral analysis from the pesticide's SERS signal is essential, rather than just focusing exclusively on analytical techniques for detection. In this work, SERS studies of the prohibited insecticide, Methyl Parathion, were performed on a gold nanostructured surface using different radiations, 633 and 785 nm. The Au SERS spectrum obtained at 785 nm suggests that the pesticide's interaction with gold nanostructures most likely induces molecular cleavage, given the appearance of new bands at 1235 and 1330 cm^{-1} , attributed to p-nitrophenolate's -NO₂ and CO stretchings, respectively, which could be related to the formation of the pesticide's fragments. When 633 nm radiation is used, azo bond formation through plasmonic catalysis can be observed, given the appearance of new bands at 1140, 1410 and 1460 cm^{-1} , attributed to N=N modes, from 4-hydroxyazobenzene (4-HAB).³ The occurrence of this photo-induced reaction can also be an indicator of the pesticide's fragmentation, since the 4-HAB formation is a result of p-nitrophenol dimerization. An electrochemical SERS study further revealed potential-dependent molecular transformations at specific voltages, including the energy modulation of the photochemical reaction reaching optimal dimerization conditions around -0.2 V and the formation of p-aminophenol as a result of the electrochemical reduction of the pesticide's nitrophenolate fragment starting approximately at -0.6 V. When the system returned to initial conditions at 0.0 V, p-aminophenol was catalyzed into its dimer, 4-HAB. However, the pesticide was not restored to its intact form, since Methyl Parathion's SERS signals were not detected in the final acquisition.

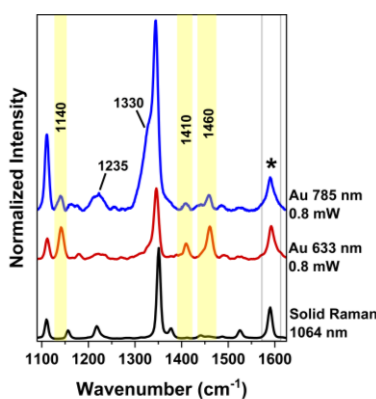


Figure 1: Au SERS spectra of Methyl Parathion in 633 and 785 nm radiation and solid Raman in 1064 nm.

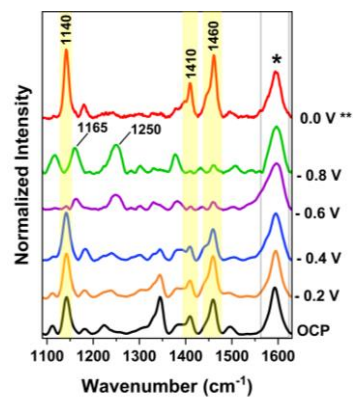


Figure 2: SERS spectra of MP obtained at 633 nm and different electrode potentials.

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