The role of the electrolyte on the SERS spectra of pyridine

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SERS spectra of pyridine has been recorded on a silver electrode in a potential range from 0.0 to -1.20 V with a saline solution, pyridine / KCl (0.1M / 0.1M), by using the 514.5 nm exciting line by us [1]. Under these experimental conditions, the maximum intensity of the enhanced 8a and 9a bands is reached at -0.75 V and -1.20 V, respectively, being the 9a band what dominates the spectrum at negative electrode potential. Although this behavior has been explained under a resonant charge transfer mechanism, the nature of the electronic resonance processes involved in the enhancement of each band is different. The 8a band is enhanced due to an electronic excitation between the ground and excited charge transfer electronic state of the metal-adsorbate surface complex, while the activity of the 9a band is due to a plasmon-like excitation taking into account an overall electronic structure of small metal clusters [2] which is able to selectively modify the relative intensities of specific SERS band.
We intend now to record pyridine SERS spectra under the same experimental conditions but varying only the type of electrolyte in order to check how it affects the relative intensities and vibrational wavenumbers of the bands as well as the electrode potential to which the enhanced bands reach the maximum intensity. Different electrolytes like KCl, NaCl, KBr, NaBr and Na_2SO_4, have been selected in such way that allows us to compare SERS spectra in which changes only the cation or the anion of the electrolyte. From the analysis of all these SERS spectra, it can be concluded that no significant wavenumbers shifts have been detected, while the relative intensities of the bands and the electrode potential to which the maximum intensity is reached are slightly modified. NaBr electrolyte requieres more negative electrode potential in order to enhance the 8a and 9a bands and to resolve the 12 and 1 pair.

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References
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