

POTENTIAL-DEPENDENT SERS INVESTIGATION ON THE ADSORPTION OF PYRIDINE CARBOXYLIC ACIDS ON SILVER

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Abstract: The potential-dependent SER spectra of the three pyridinecarboxylic acids on polycrystalline silver electrodes are studied in this paper. Their surface geometries may be detected from the high quality potential-dependent surface Raman signal. It is indicated that picolinic acid may keep the adsorbed Pattern perpendicularly with both N-atom and carboxylate group with the varying of potential, while the adsorption Pattern of isonicotinic acid and nicotinic acid may change. The probable reasons are given.

Fig.1 shows the potential-dependent SERS of picolinic acid on Ag electrode from KCl solution. It is shown that the 1011 cm^{-1} (ring breathing), 1055 cm^{-1} (CN bending), 1577 cm^{-1} (CC stretching), 1476 cm^{-1} (CC, CN stretching) and 1378 cm^{-1} (COO^- symmetric stretching) all are enhanced greatly. However, the band assigned to $\nu(\text{C-COO}^-)$ at 1295 cm^{-1} only as a very weak peak. According to the SERS selection rules, picolinic acid may be adsorbed on Ag electrode perpendicularly with both N-atom of the heteroaromatic ring and carboxylate group. And the adsorption Pattern of picolinic acid on Ag doesn't change with the varying of potential due to the dependent-SER spectra having no great change in the relative intensities and band positions, as shown in Fig.2. From the Fig.3, however, the potential-dependent SER spectra of isonicotinic acid vary regularly with negative shifting of potential. For instance, the 850 cm^{-1} (out-of-plane ring vibration) and 1225 cm^{-1} (C-Sub stretching) are enhanced gradually; on the contrary, the 1007 cm^{-1} (In-plane ring vibration), 1202 cm^{-1} and 1093 cm^{-1} (In-plane C-H bending) are weakened greatly. It is interesting that the 419 cm^{-1} and 1225 cm^{-1} are respectively shifted to 433 cm^{-1} and 1218 cm^{-1} from -0.1 V to -0.4 V . It is indicated that the adsorption behavior of isonicotinic acid on Ag is varied drastically with the shifting of potential. As above, with regards to the variation of some important surface Raman bands of isonicotinic acid and nicotinic acid respectively in Fig.3 and Fig.5, the variation of adsorption behavior of them on Ag can be analyzed. At higher potential values, isonicotinic acid and nicotinic acid both perpendicularly adsorbed via carboxylate group; at low potential values, the former flatly adsorbed via ring plane and the later adsorbed via oxygen lone pair electrons. The probable reasons are given in this paper. The surface Raman signal disappears on Ag surfaces at about -0.8 V due to the potential-driven desorption or the occurrence of hydrogen evolution at the surface. Table 1 lists the frequencies and the intensities of Raman bands in above cases. The assignments are acquired by referencing [1,2,3].

References:

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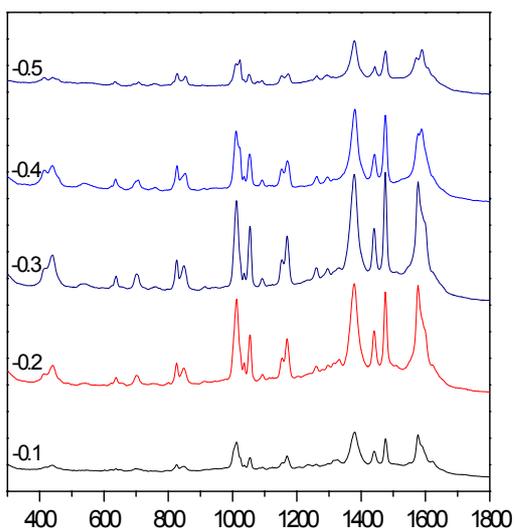


Fig.1 the potential-dependent SERS of picolinic acid adsorbed on Ag

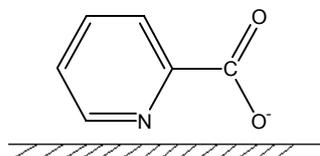


Fig.2. the orientation of picolinic acid on Ag electrode

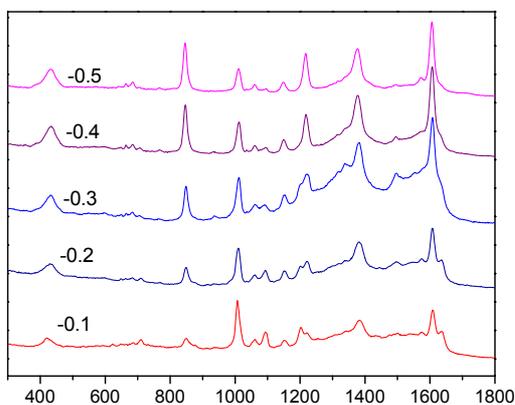


Fig.3 the potential-dependent SERS of isonicotinic acid adsorbed on Ag

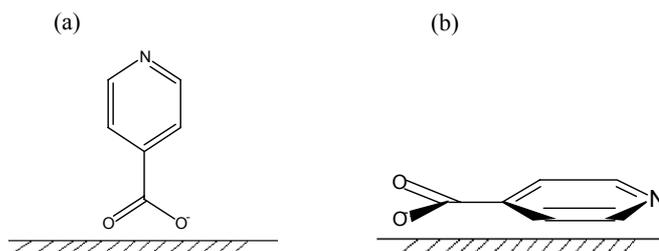


Fig.4. the orientation of isonicotinic acid on Ag electrode at -0.1V • a • and -0.4V • b •

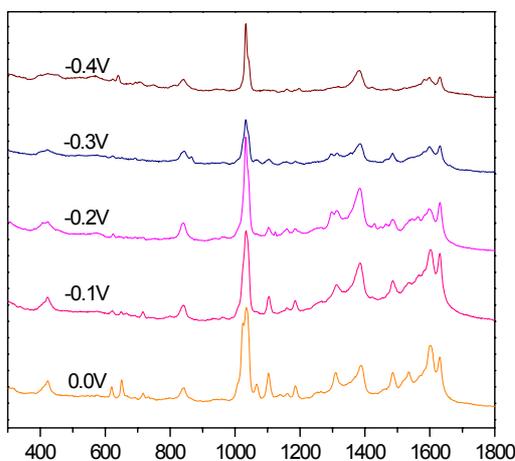


Fig.5. the potential-dependent SERS of nicotinic acid adsorbed on Ag

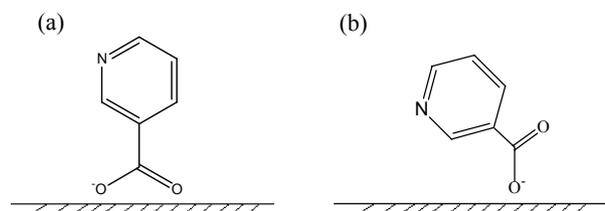


Fig.6. the orientation of nicotinic acid on Ag electrode at 0.0V • a • and -0.2V • b •