

# ULTRAVIOLET LASER EXCITED SURFACE RAMAN SCATTERING OF P-HYDROXYBENZOIC ACID ON THE Au ELECTRODE

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**Abstract:** The surface Raman spectra of adsorbed P-Hydroxybenzoic Acid (PHBA) on the roughened Au electrode have been measured with ultraviolet (UV) excitation at 325 nm in present work. The surface Raman spectra of PHBA are changed sensitively and regularly to the negative shifting of potential, which indicates that the PHBA molecules are chemisorbed on Au surface. The charge transfer effect between the adsorbed PHBA and Au electrode is proposed in the present work. The probable reasons are given.

The sensitive surface Raman spectra of PHBA adsorbed on the rough Au electrode over a wide potential region are observed as shown in Fig.1. It can be observed that with the potential negative shifting from  $-0.1\text{V}$  to  $-0.9\text{V}$ , most bands' relative intensities change obviously, especially in the high wave-number region, and partial vibration frequencies are shifted about  $3\text{-}10\text{ cm}^{-1}$ , indicating the surface Raman spectra are very sensitive to the electrode potential. The intensities of the major Raman modes as a function of potential are given in Fig. 2. The important consideration to keep in mind is that the potential at which resonance (potential of maximum intensity) occurs varies with vibrational mode. Several intensity reversals occur, and maxima in the intensity vs. potential plot are not observed to be coincident. With respect to the phenomena, it may imply that PHBA molecules are chemisorbed on Au surface and the applied potential could influence the metal-PHBA interaction. The surface Raman signal disappears on Au surfaces at about  $-1.1\text{V}$  due to the potential-driven desorption or the occurrence of hydrogen evolution at the surface.

As known that the charge transfer (CT) mechanism is particularly effective when an electron is transferred from surface to the adsorbed molecule in the negative ion state (perturbed affinity level of chemisorbed molecule)[1]. On the basis of molecule-surface model where the charge-transfer band is due to electron excitation from the metal to the adsorbed molecule, the transition energy from the top of the 0 K Fermi distribution of the metal to the acceptor orbital of the molecule ( $E_e$ ) may be estimated [2] as

$$E_{CT}(\bullet_F) = W_M - E_A - E_C; \quad E_C = (\bullet_M - \bullet)e^2 / [2 \bullet (\bullet + \bullet_M)R], \quad (*)$$

Thus,  $E_{CT}(\bullet_F) = 2.33$  to  $3.33\text{ eV}$  is the estimated transition energy from the Au surface to adsorbed PHBA molecule. According to the charge-transfer transition model, it can be analyzed that the charge-transfer from the gold to the adsorbed PHBA molecule could be induced by UV excitation at  $325\text{nm}$  although it has relative high photon energy. According to theoretical analyse with these finding, it may be reasonable to assume that charge transfer occurs between the metal and adsorbed molecule with UV excitation. This study may be helpful for the theoretical investigation of SERS in UV region.

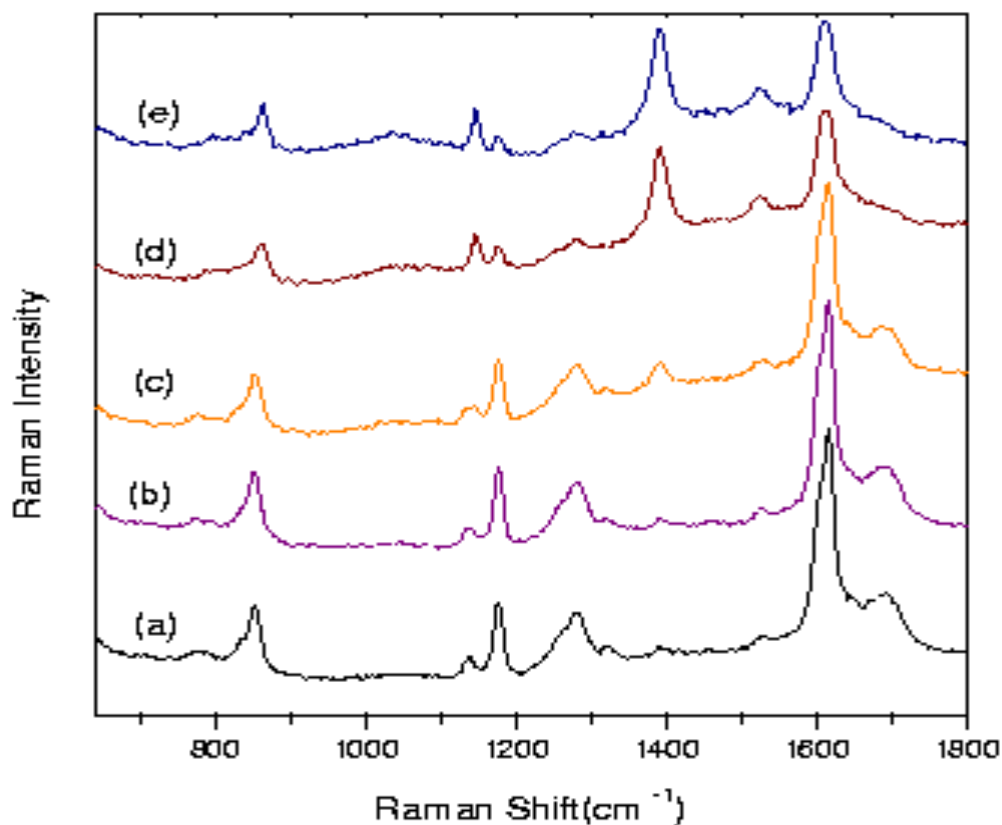


Fig.1. The potential-dependent surface spectra of PHBA adsorbed on the Au electrode with ultraviolet 325nm excitation. The solution was 0.02M PHBA+0.1M KCl. (a)-0.1V;(b)-0.3V;(c) -0.5V;(d) -0.7V;(e)-0.9V.

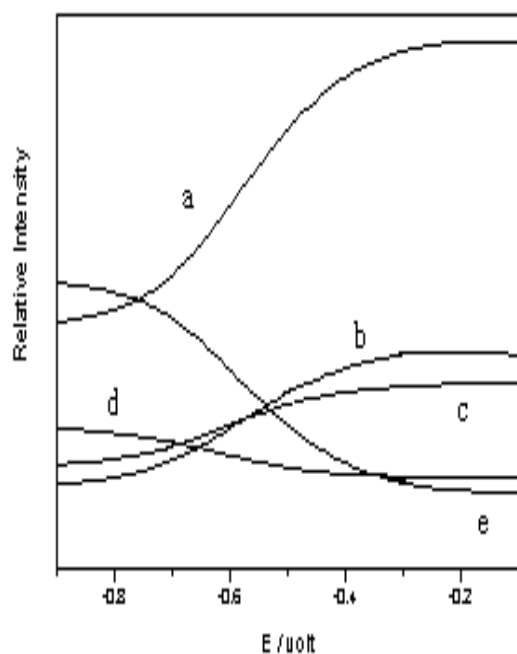


Fig.2. Raman intensity dependence due to adsorbed PHBA as a function of electrode potential.

(a)1613  $\text{cm}^{-1}$ ; (b)1177  $\text{cm}^{-1}$ ; (c)1280  $\text{cm}^{-1}$ ;  
(d)1145  $\text{cm}^{-1}$ ; e)1390  $\text{cm}^{-1}$

#### References:

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