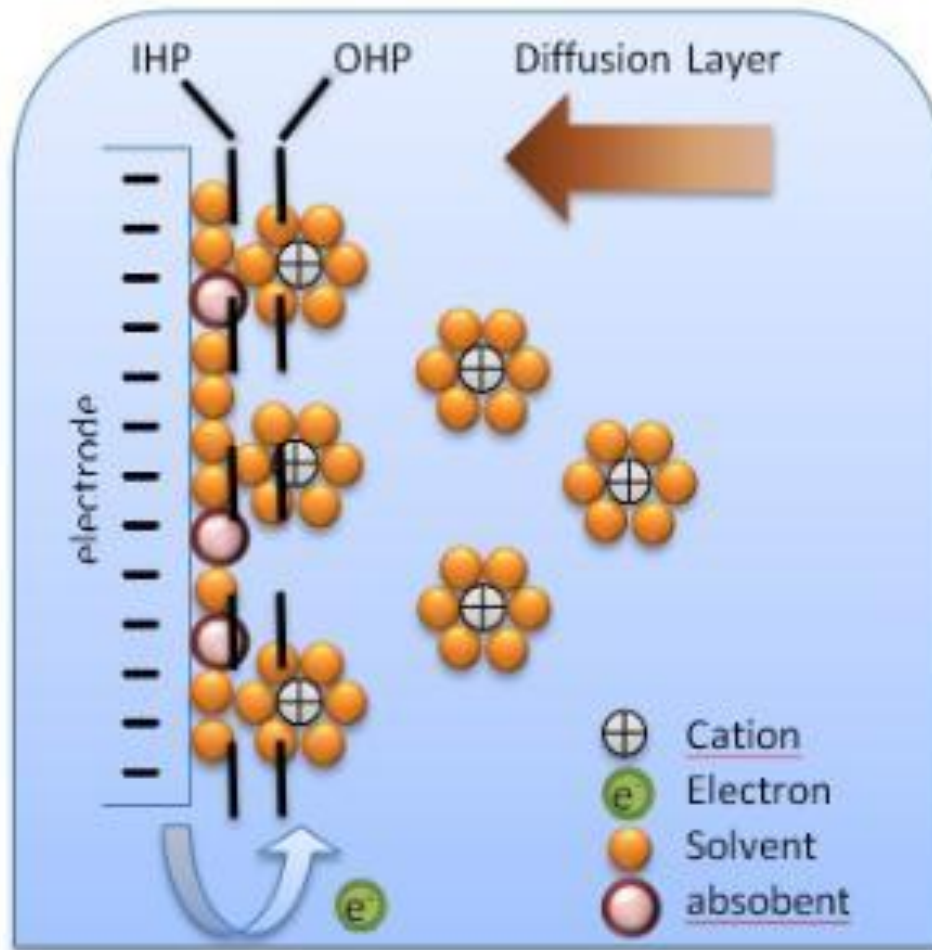


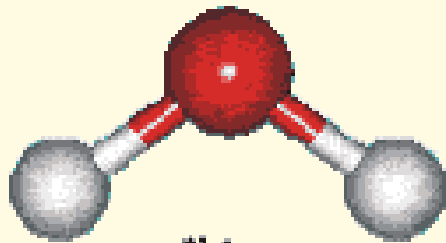
Kombinovane metode ispitivanja granice metal/elektrolit

***In-situ* refleksijska infracrvena
spektroskopija sa Furijeovom
transformacijom (RFTIRS -
Reflectance Fourier Transform
InfraRed Spectrometry).**

ELEKTRODA I ELEKTROLIT

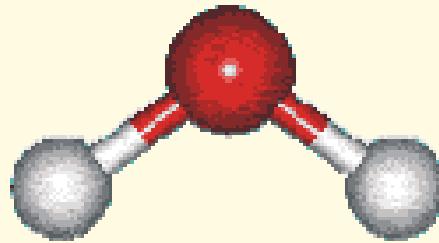


Molekul vode i IR spektar



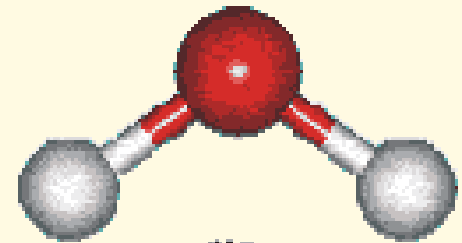
ν_1

symmetric stretch



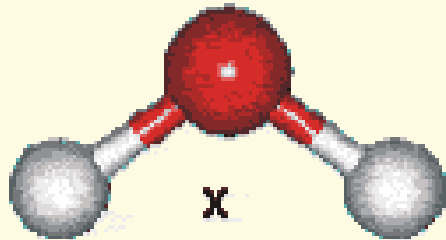
ν_3

asymmetric stretch

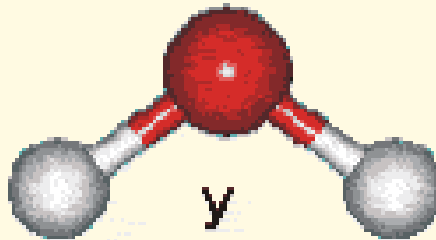


ν_2

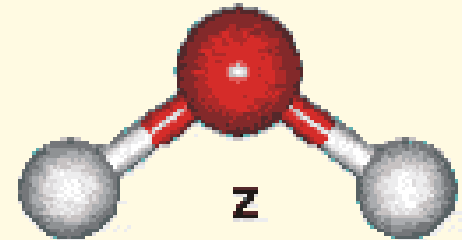
bend



x



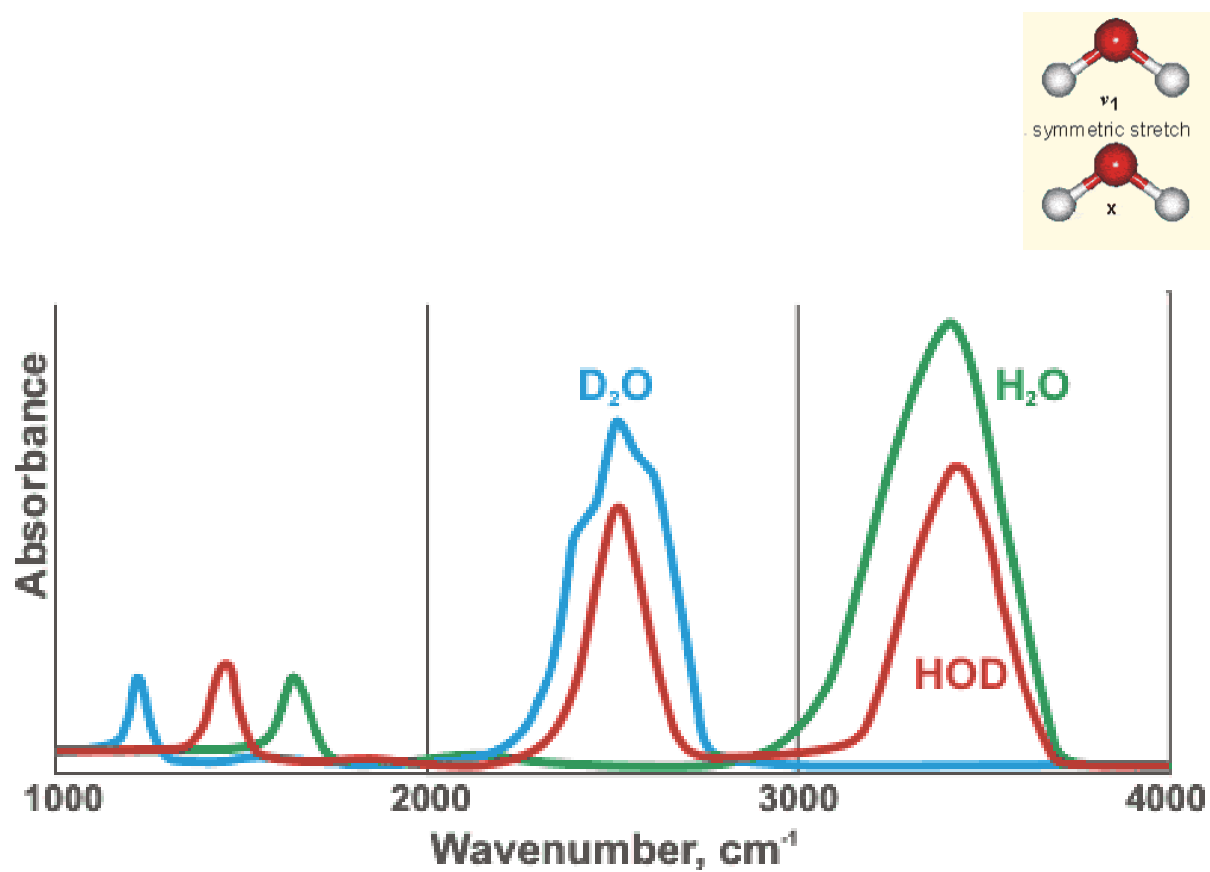
y



z

librations

IR spektar vode



Vazi i za druge rastvarace koji se koriste u elektrohemiji

FTIRS

- Brza tehnika
- Prevazidjen problem modulacije potencijala (snimanje na, prakticno, konstantnom potencijalu)
- Povecanje broja snimaka za povecanje odnosa S/N



RFTIRS u Elektrohemiji

Elektricno polje može biti samo paralelno u odnosu na površinu elektronskog provodnika

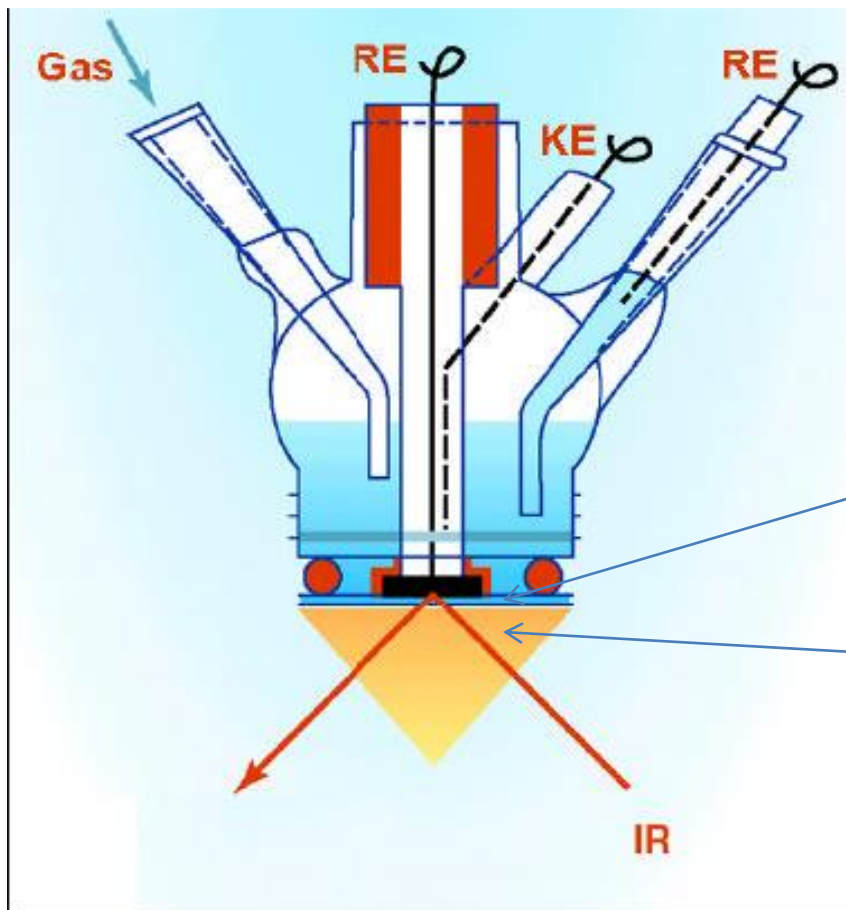
SELEKCIONO PRAVILO:

AKTIVNI MODOVİ NORMALNI NA POVRŠINU!

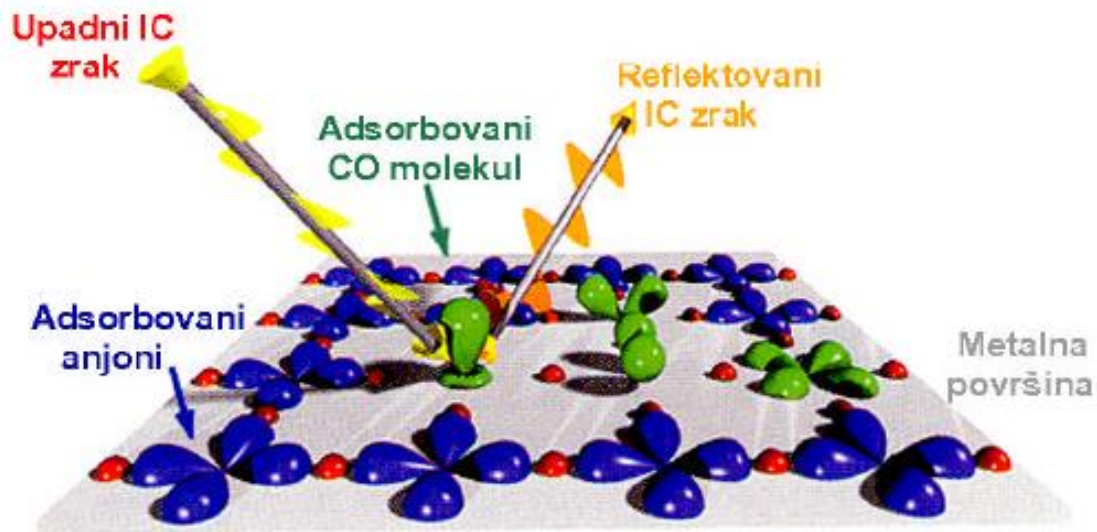
Debljina sloja elektrolita
delovi mm

Konfiguracija “tankog sloja”

CaF₂ prizma (ogranicen izbor
zbog korozivne sredine)



RFTIRS u Elektrohemiji

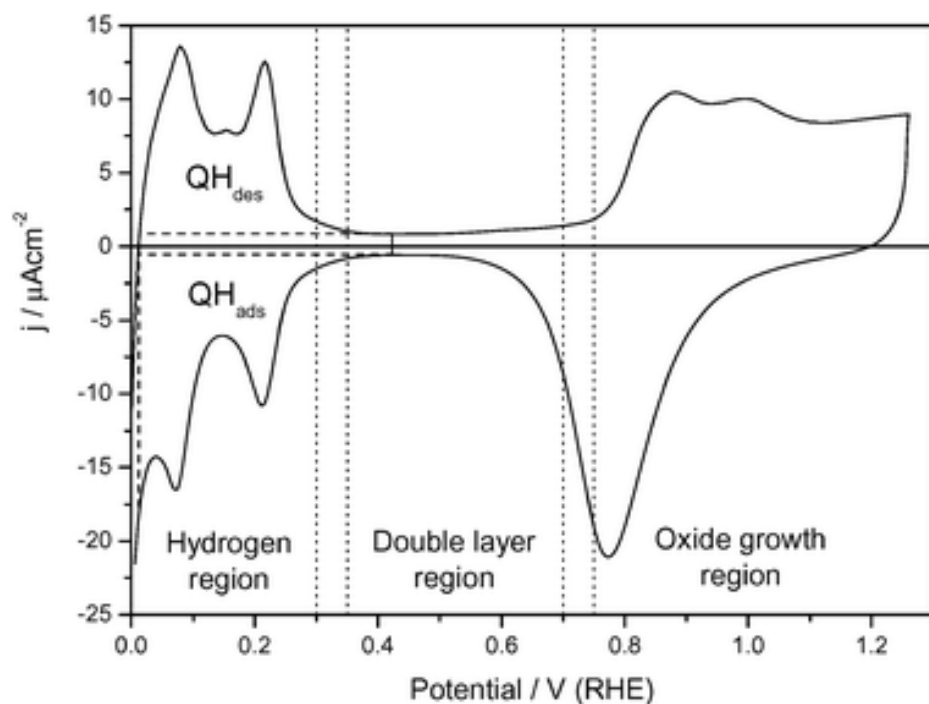


SIGNAL = R/R_0 NA DATOM POTENCIJALU

SIGNAL ZAVISI OD R I R_0

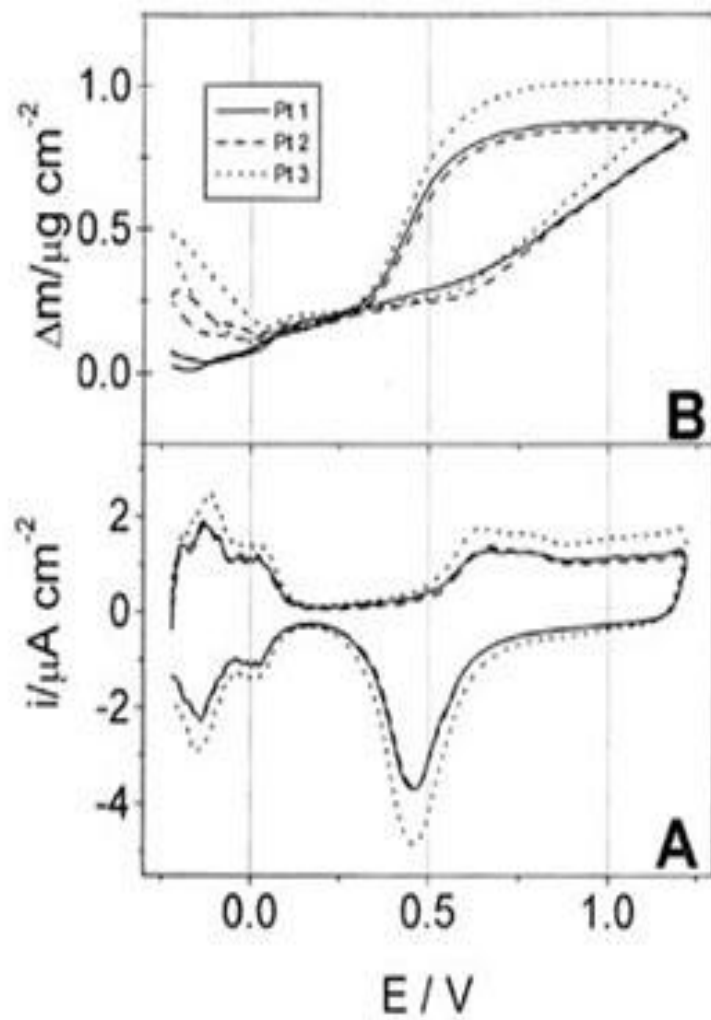
KONFIGURACIJA TANKOG SLOJA

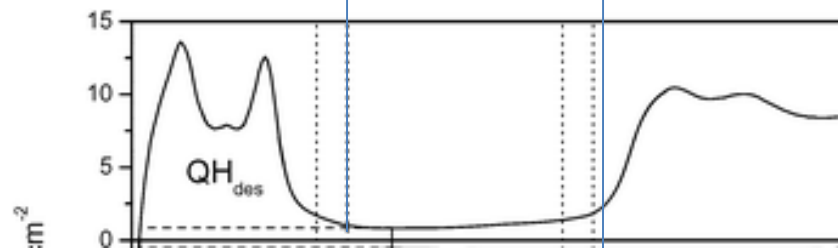
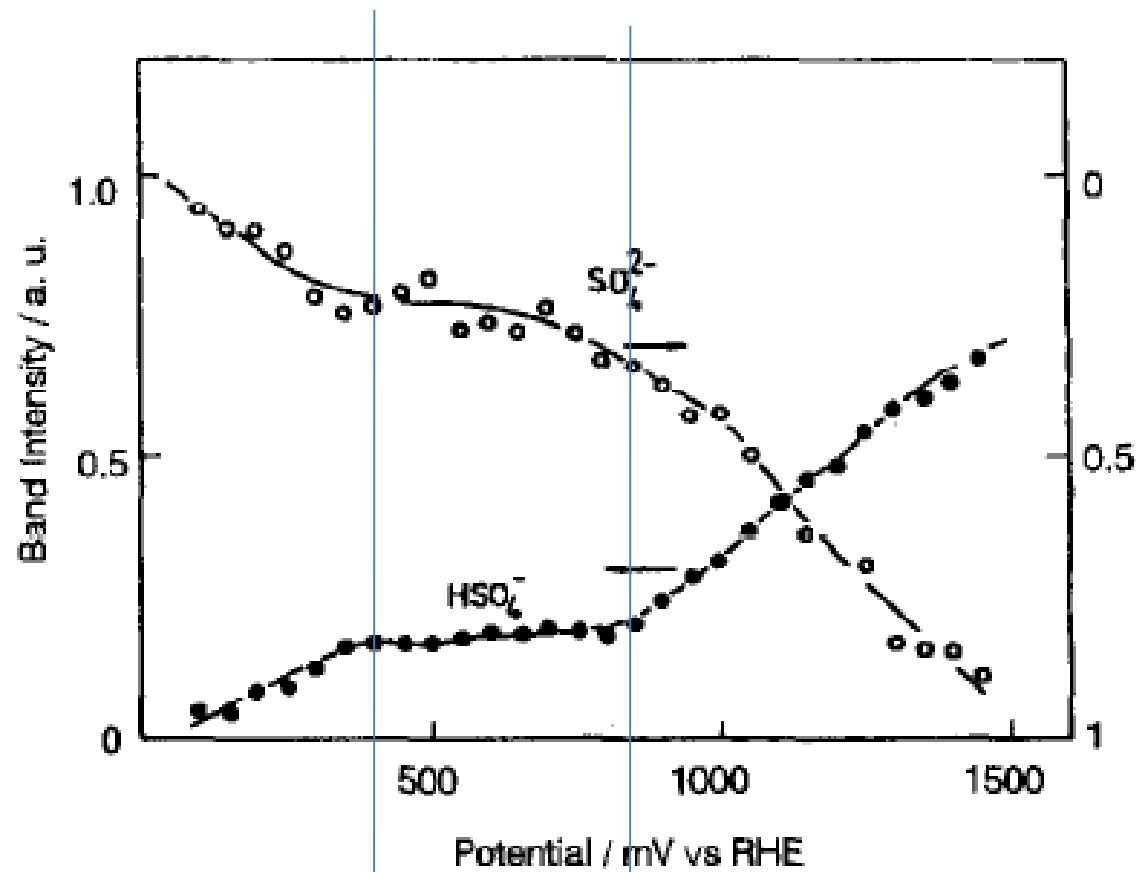
- Tanki sloj je difuziono dekuplovan od ostatka rastvora
- (Pseudo)faradejska reakcija površine može da naruši ravnotežu u elektrolitu i zakomplikuje interpretaciju rezultata



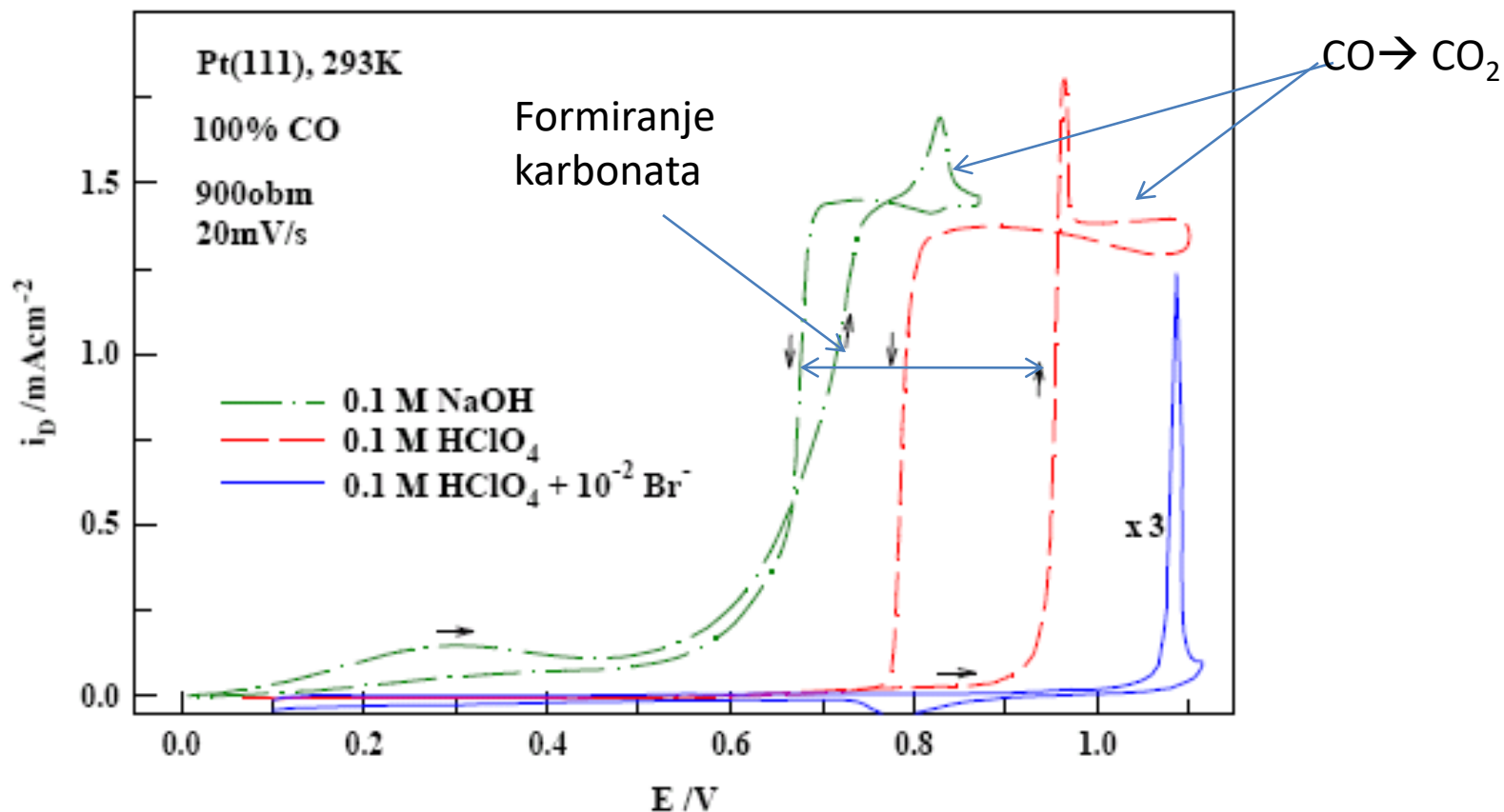
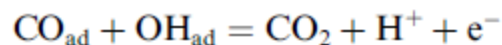
Gde se sta desava?

QMB + CV

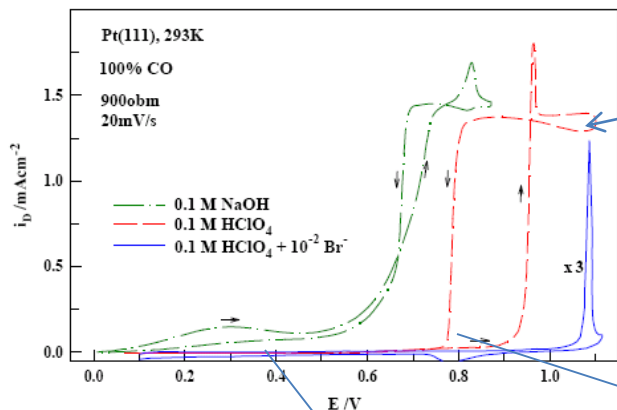




Primer: CO_{ads}@Pt(111)

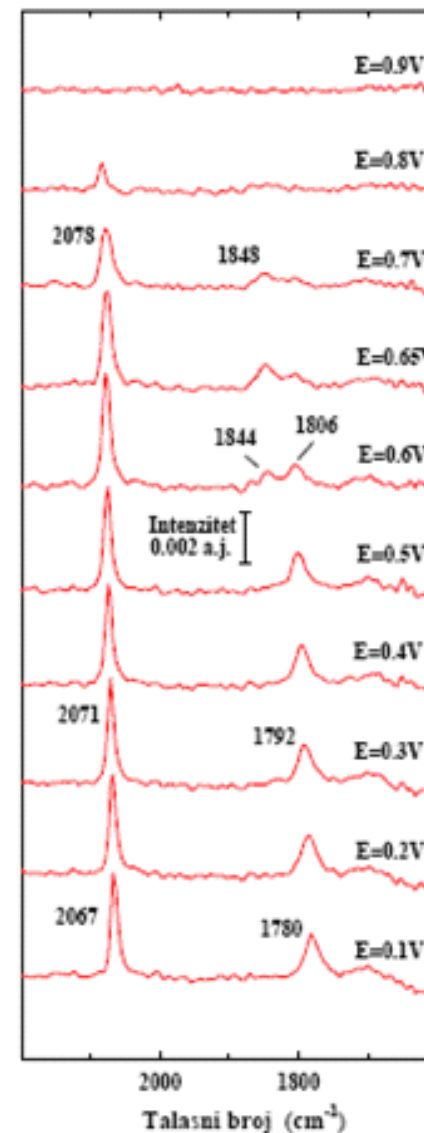
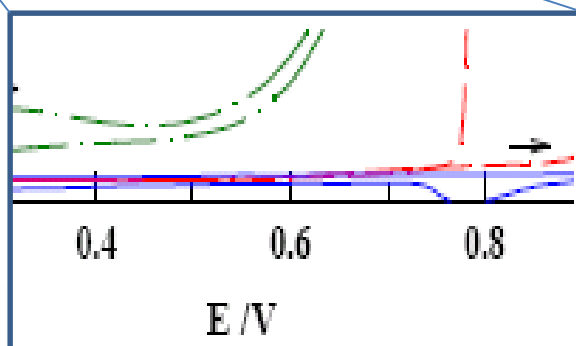


Struja - potencijal krive za monokristalnu elektrodu Pt(111)u : 0,1M NaOH, 0,1M HClO₄ i 0,1M HClO₄ + 10⁻² M Br⁻, zasićene sa CO, pri brzini promene potencijala od 20mV/s, i 900 obrtaja radne elektrode u minuti na 293K. Potencijali su izraženi u odnosu na zasićenu kalomelsku elektrodu (ZKE)



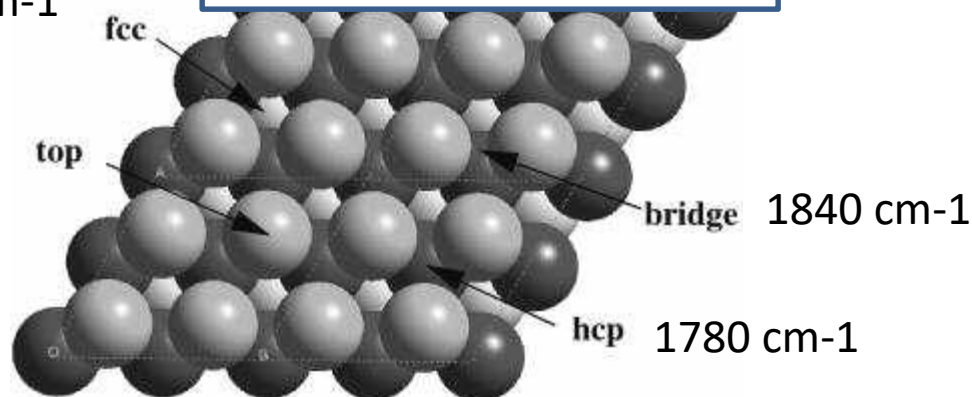
Bulk elektroliza

Površinski procesi



1780 cm^{-1}

2078 cm^{-1}



FTIR *in situ* merenja oksidacije CO u 0,1M rastvoru HClO₄ zasićenom sa CO na površini Pt(111) pri različitim elektrodnim potencijalima. Spektar je stabilan do 0,5V, posle čega se pojavljuje nova istežuća C-O traka na 1840 cm^{-1} usled nastanka CO_{ad} u koordinaciji mosta.

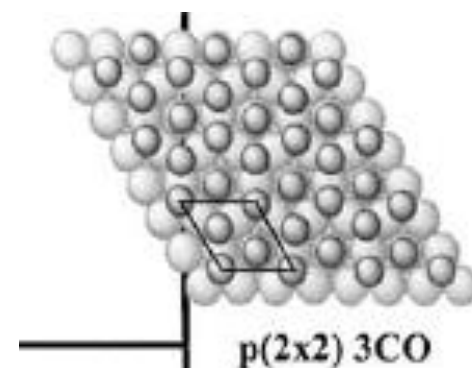
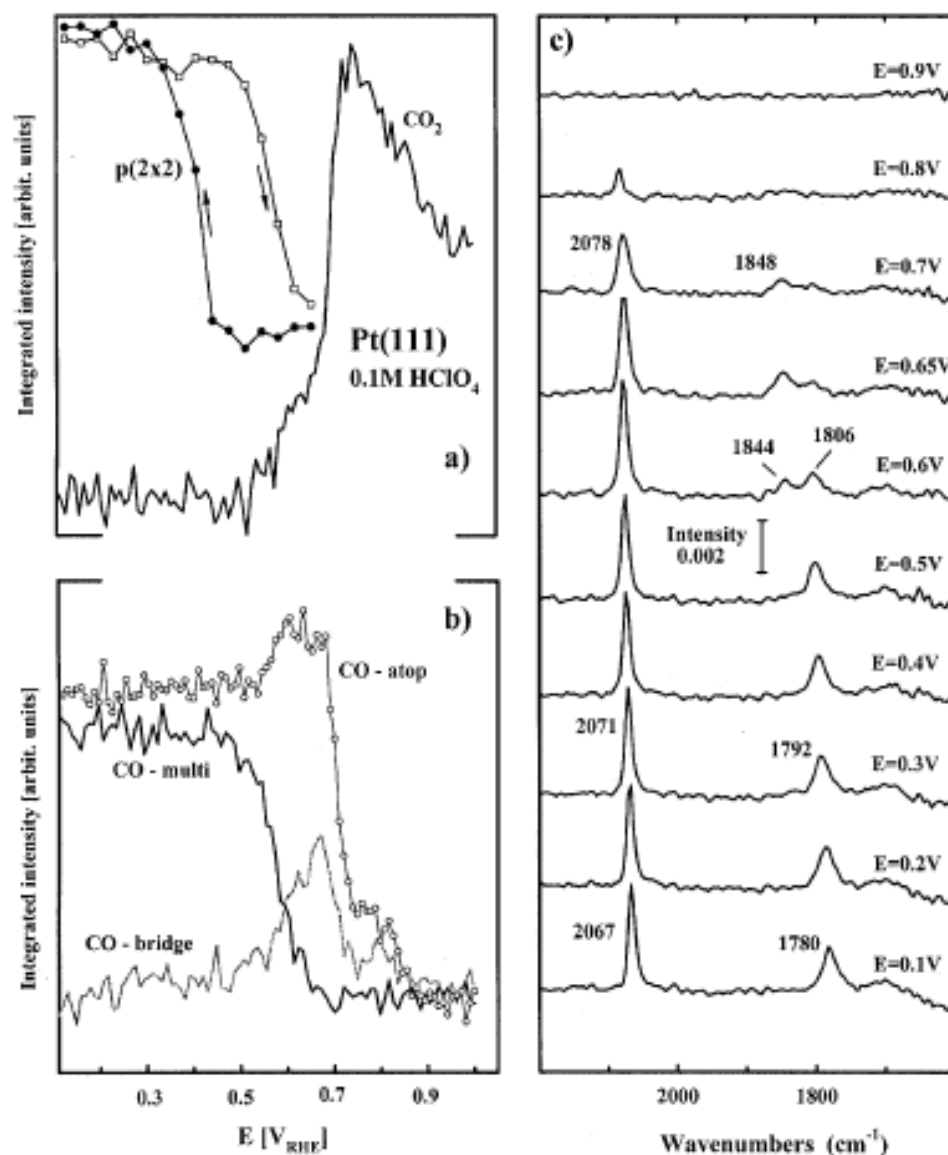


Fig. 2. (a) Potential-dependent stability of the $p(2 \times 2)\text{-}3\text{CO}_{\text{ad}}$ structure on Pt(111) in 0.1 M HClO_4 in CO-saturated solution, and CO_2 production as a function of electrode potential (data extracted from FTIR measurements) during the oxidation of CO_{ad} . (b) Integrated intensities for CO_{ad} -atop, CO_{ad} -multi and CO_{ad} -bridge on Pt(111) as a function of electrode potential in CO-saturated 0.1 M HClO_4 solution. (c) FTIR spectra obtained during progressive oxidation of CO_{ad} on Pt(111) in 0.1 M HClO_4 from the initial potential, $\approx E = 0.1$ V. Each spectrum, displayed as absorbance spectra $-\log(R/R_0)$, was acquired from 100 interferometer scans at the range potential indicated, rationed to the corresponding spectrum obtained at the final potential, $\approx E = 1.0$ V.

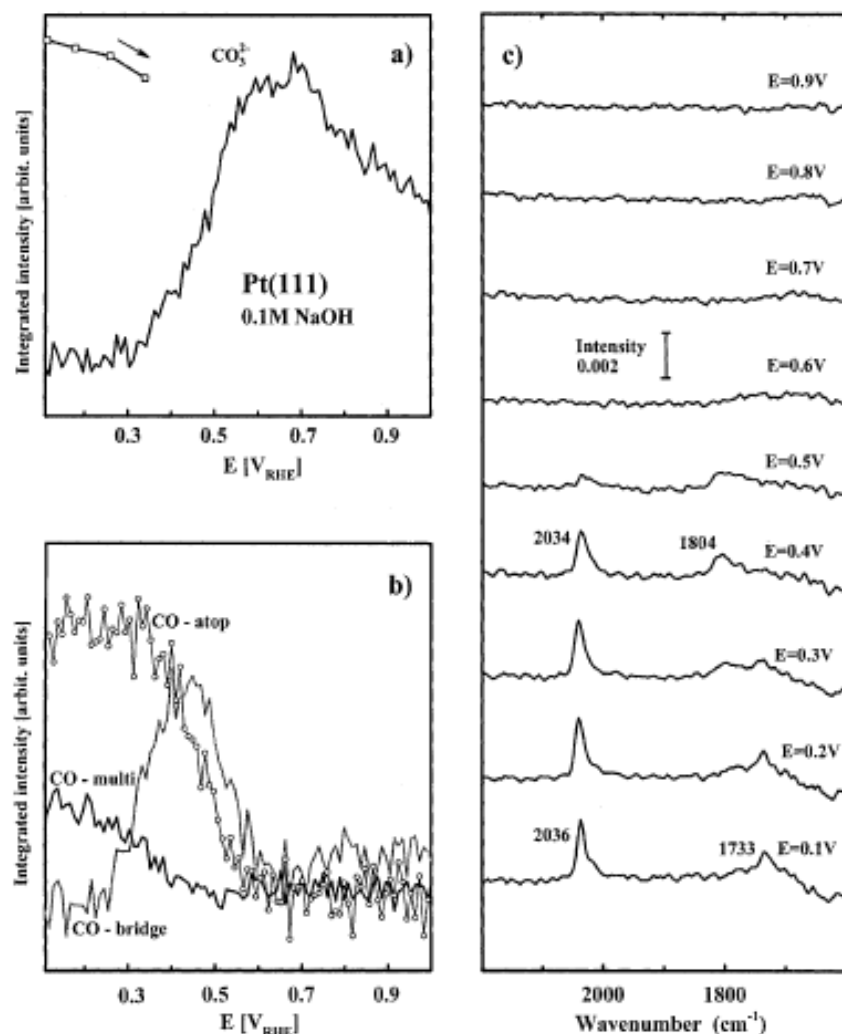


Fig. 4. (a) Potential-dependent stability of the $p(2 \times 2)\text{-}3\text{CO}_{\text{ad}}$ structure on Pt(111) in 0.1 M NaOH in CO-saturated solution, and CO_3^{2-} production as a function of electrode potential (data extracted from FTIR measurements) during the oxidation of CO_{ad} . (b) Integrated intensities for CO_{ad} -atop, CO_{ad} -multi and CO_{ad} -bridge on Pt(111) as a function of electrode potential in CO-saturated 0.1 M NaOH solution. (c) FTIR spectra obtained during progressive oxidation of CO_{ad} on Pt(111) in 0.1 M NaOH from the initial potential, $\approx E = 0.1$ V. Each spectrum, displayed as absorbance spectra $-\log(R/R_0)$, was acquired from 100 interferometer scans at the range potential indicated, rationed to the corresponding spectrum obtained at the final potential, $\approx E = 1.0$ V.

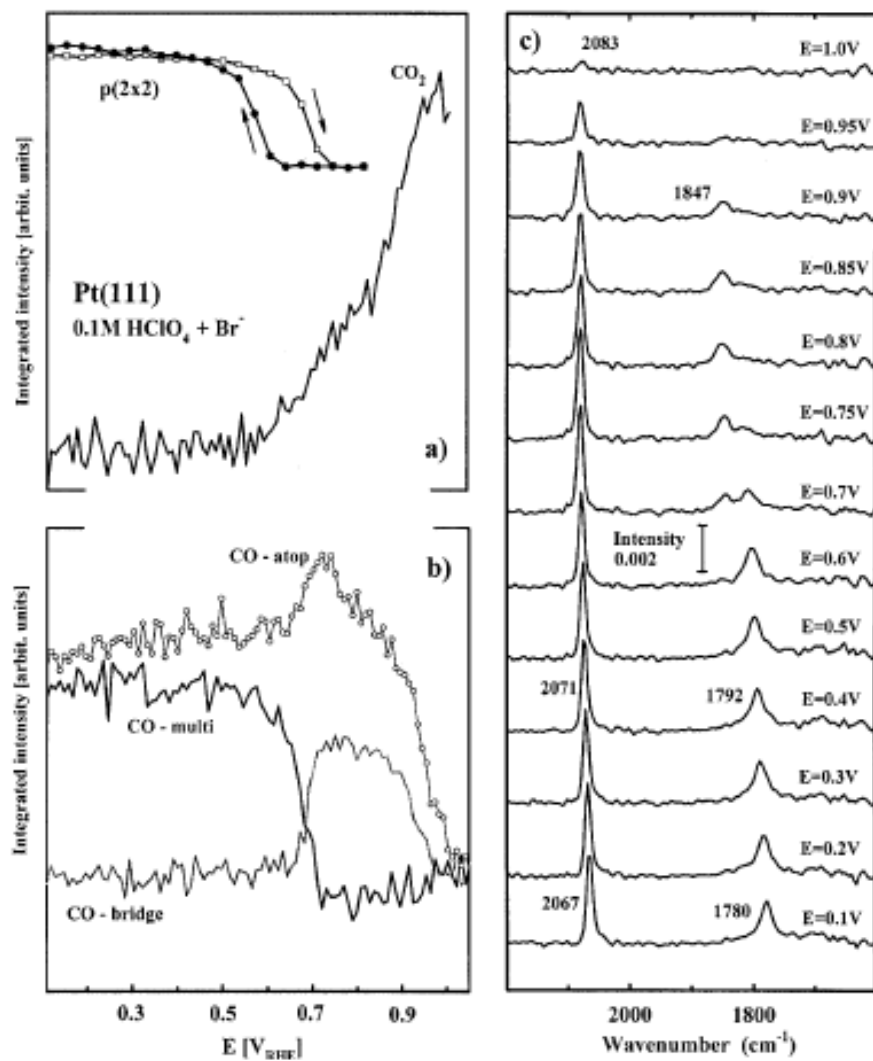


Fig. 5. (a) Potential-dependent stability of the $p(2 \times 2)$ - 3CO_{ad} structure in $0.1\text{ M HClO}_4 + 10^{-2}\text{ M Br}^-$ in CO -saturated solution, and CO_2 production as a function of electrode potential (data extracted from FTIR measurements) during the oxidation of CO_{ad} . (b) Integrated intensities for CO_{ad} -atop, CO_{ad} -multi and CO_{ad} -bridge on $\text{Pt}(111)$ as a function of electrode potential in CO -saturated solution. (c) FTIR spectra obtained during progressive oxidation of CO_{ad} on $\text{Pt}(111)$ in $0.1\text{ M HClO}_4 + 10^{-2}\text{ M Br}^-$ from the initial potential, $\approx E = 0.1\text{ V}$. Each spectrum, displayed as absorbance spectra $-\log(R/R_0)$, was acquired from 100 interferometer scans at the range potential indicated, rationed to the corresponding spectrum obtained at the final potential, $\approx E = 1.0\text{ V}$.

Glavna uloga: identifikacija adsorbovanih reaktivnih vrsta i intermedijera u cilju razjasnjenja mehanizma

Wavenumber (cm ⁻¹)	mode	Functional group or chemical species
2980-2850	ν (CH) [74]	CH ₃ , CH ₂
2632 (broad)	ν (OH) str. [74]	COOH, acetic acid
2341	ν (OCO) [74]	asym. str. CO ₂
2055-2060	ν (CO) [51]	adsorbed CO (on top)
1713	ν (CO) [74]	carbonyl, acetic acid, acetaldehyde
1404-1412	ν OCO [75]	sym. str. adsorbed acetate
ca.1370	δ (CH ₃) [74]	sym. def. acetaldehyde, acetic acid
1286/1360	ν C-OH + δ OH [72]	COOH
1258	ν C-OH [51]	adsorbed residue
1100	ν Cl-O	ClO ₄ ⁻