

In situ колебательная спектроскопия – I: органические адсорбаты

- принципы регистрации колебательных спектров адсорбатов
- выявление разных форм адсорбатов
- адсорбированные интермедиаты в электрокатализе
- ориентационные эффекты
- возможности для исследования кинетики
- (сольватация в органических растворителях)

In situ колебательная спектроскопия

Для получения сигнала адсорбата:

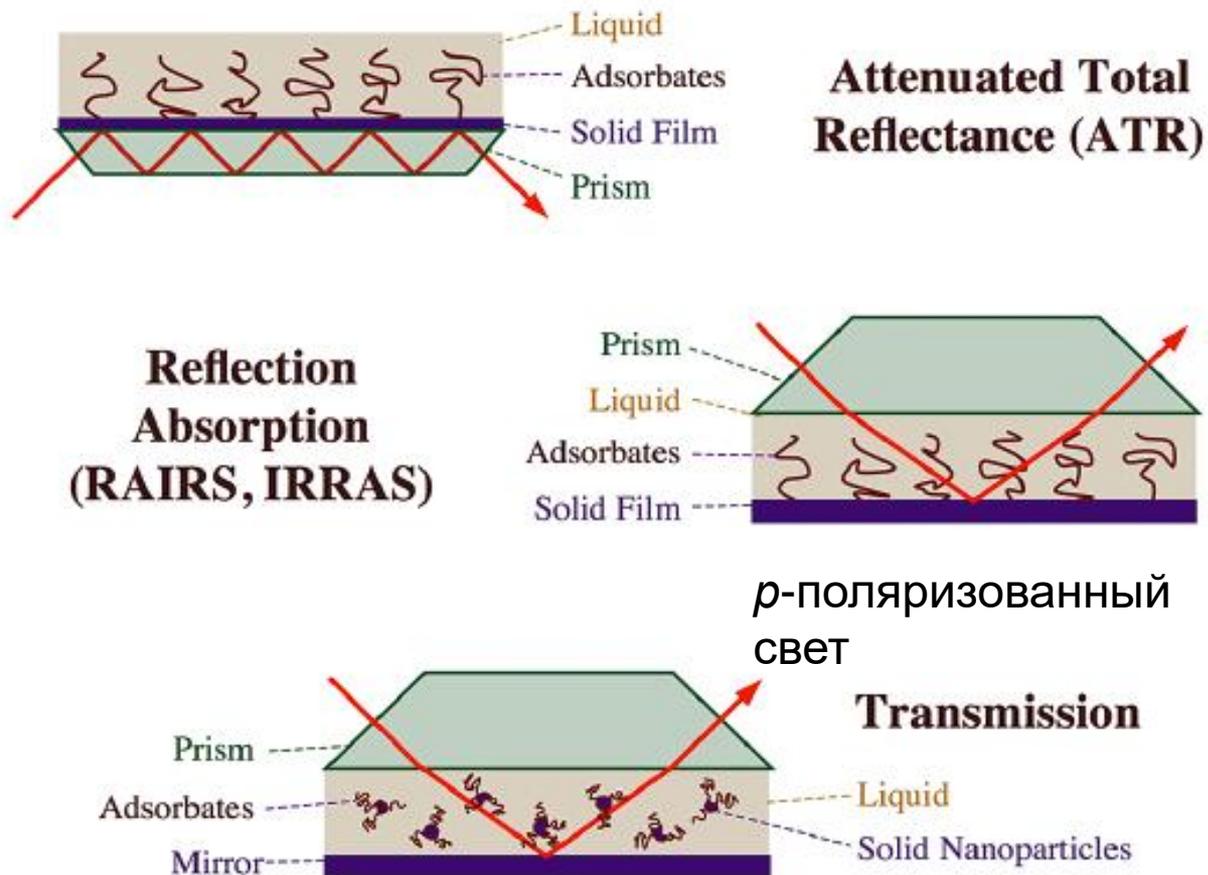
Для получения зависимостей от потенциала:

Electromodulation infrared spectroscopy (EMIRS) – с модуляцией потенциала

Subtraction normalized infrared spectroscopy (SNIFTIRS) – с нормализацией вычитанием

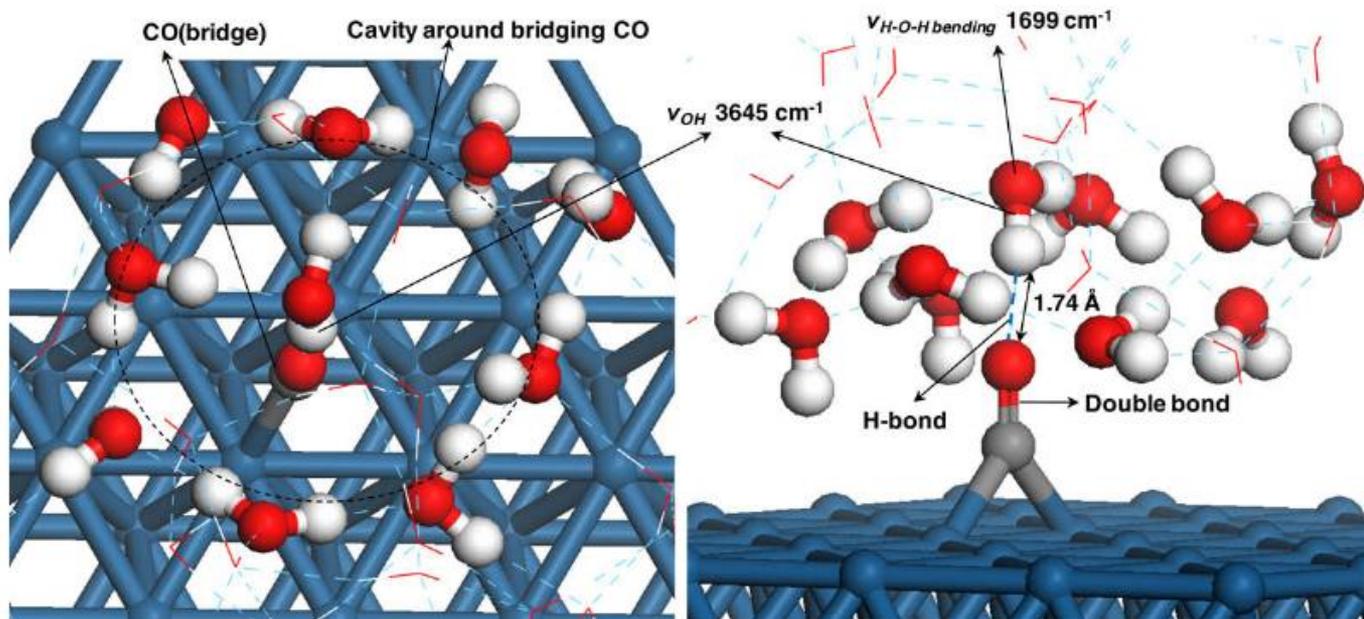
Surface enhanced infrared absorption spectroscopy (SEIRAS)

Surface enhanced Raman spectroscopy (SERS)

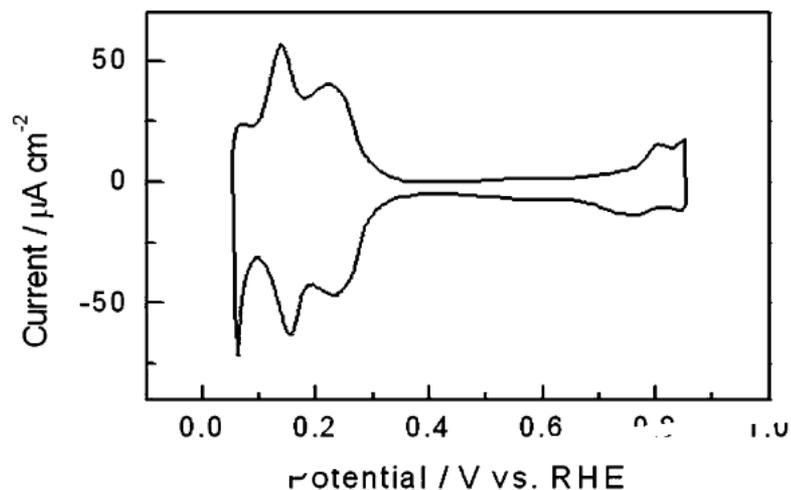


Chem. Rev. **2012**, 112, 2920–2986
Rep. Prog. Phys. **2005**, 68, 1095–1127
Progr. Surface Sci, **1997**, 55, 271–340

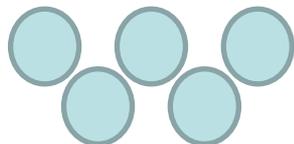
ИК-спектроскопия адсорбированного CO – разные формы



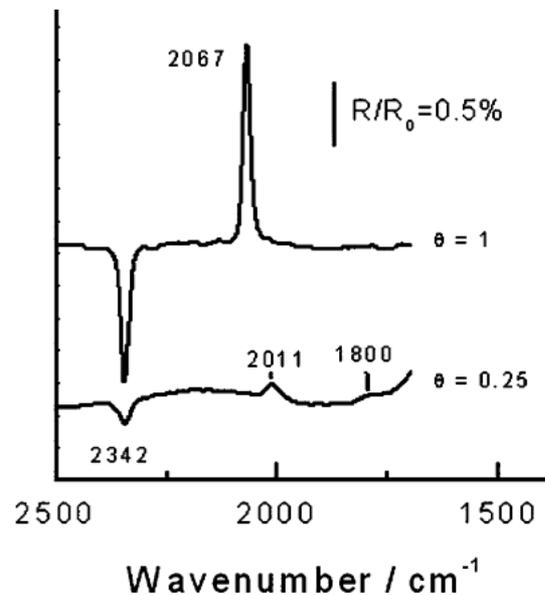
	CO _(atop)	CO _(bridge)	CO _(fcc hollow)
B.E. (kcal/mol)	34.9	25.0	25.8
C-O bond length (Å)	1.15	1.18	1.20
<i>Vibrational frequency (cm⁻¹)</i>			
Theory	2039	1840	1728
Experiment	2040 ^a 2066 ^b	1865 ^a 1851 ^c	1788 ^b



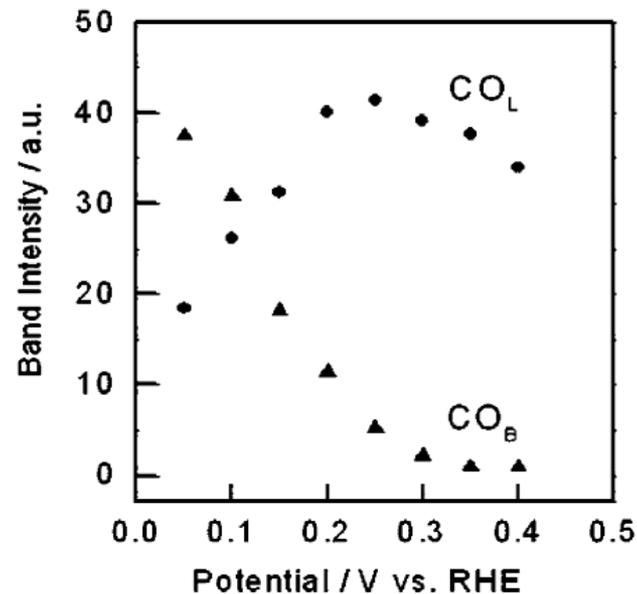
Cyclic voltammogram for Pt(110) obtained in 0.1 M HClO₄, immediately after the flame annealing and cooling in H₂/Ar. Sweep rate, 50 mV/s.



Линейная и мостиковая (сильнее связанная) формы адсорбированного CO

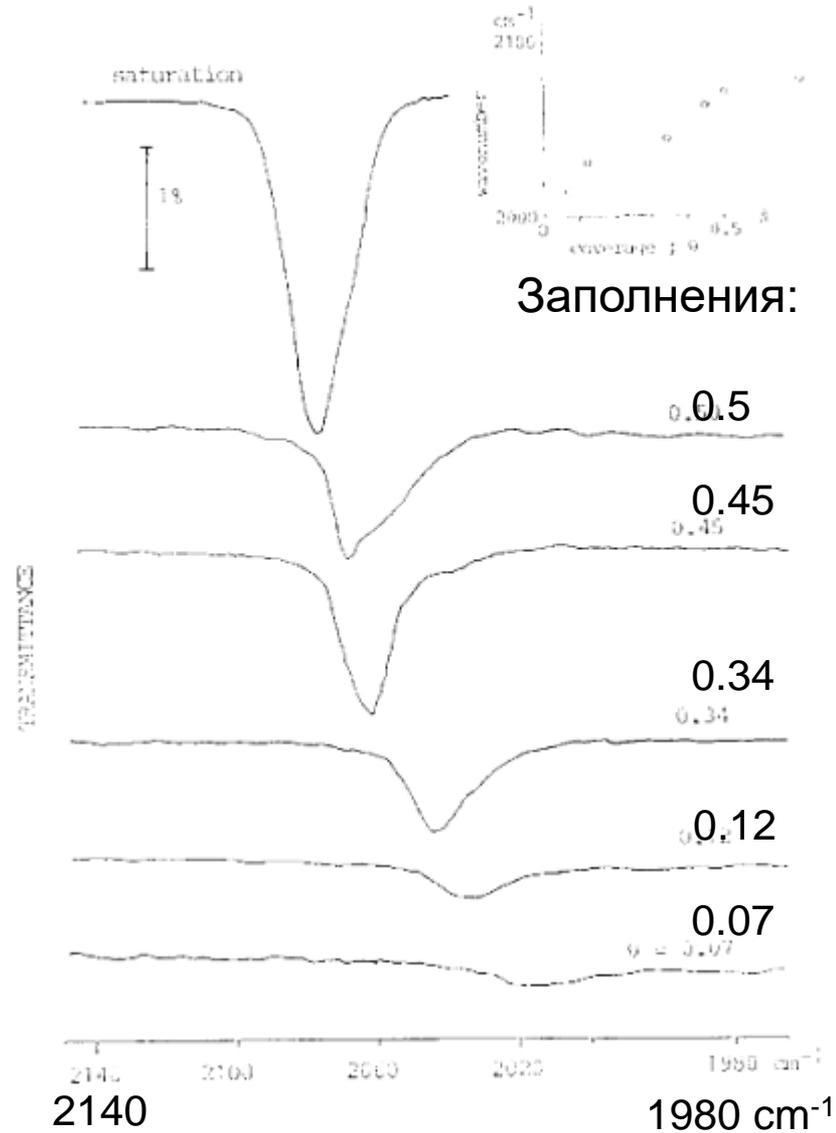
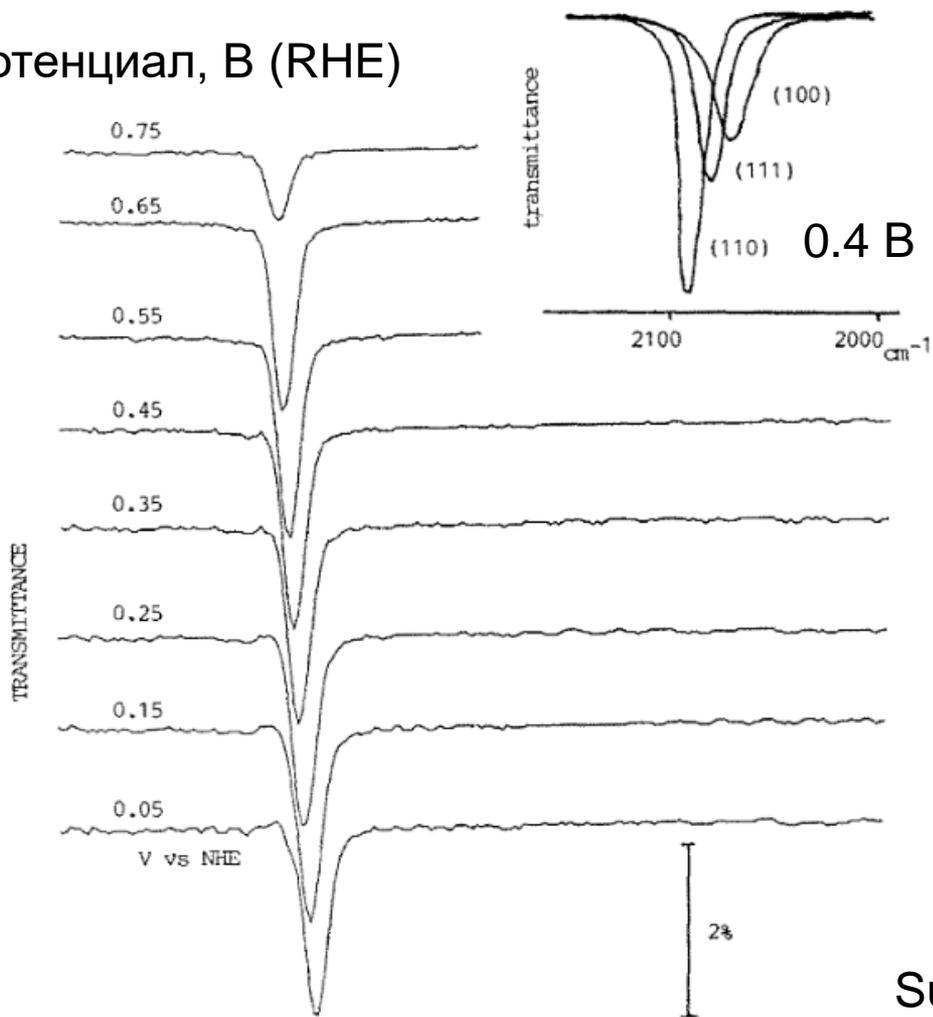


IR spectra (100 scans, 8 cm⁻¹ resolution) of CO adsorbed at 0.20 V on a Pt(110) in 0.1 M HClO₄ solution at two different coverages as indicated. Sample potential: 0.85 V; reference potential: 0.20 V.

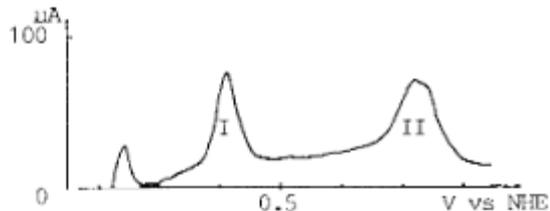


CO на грани Pt (110)

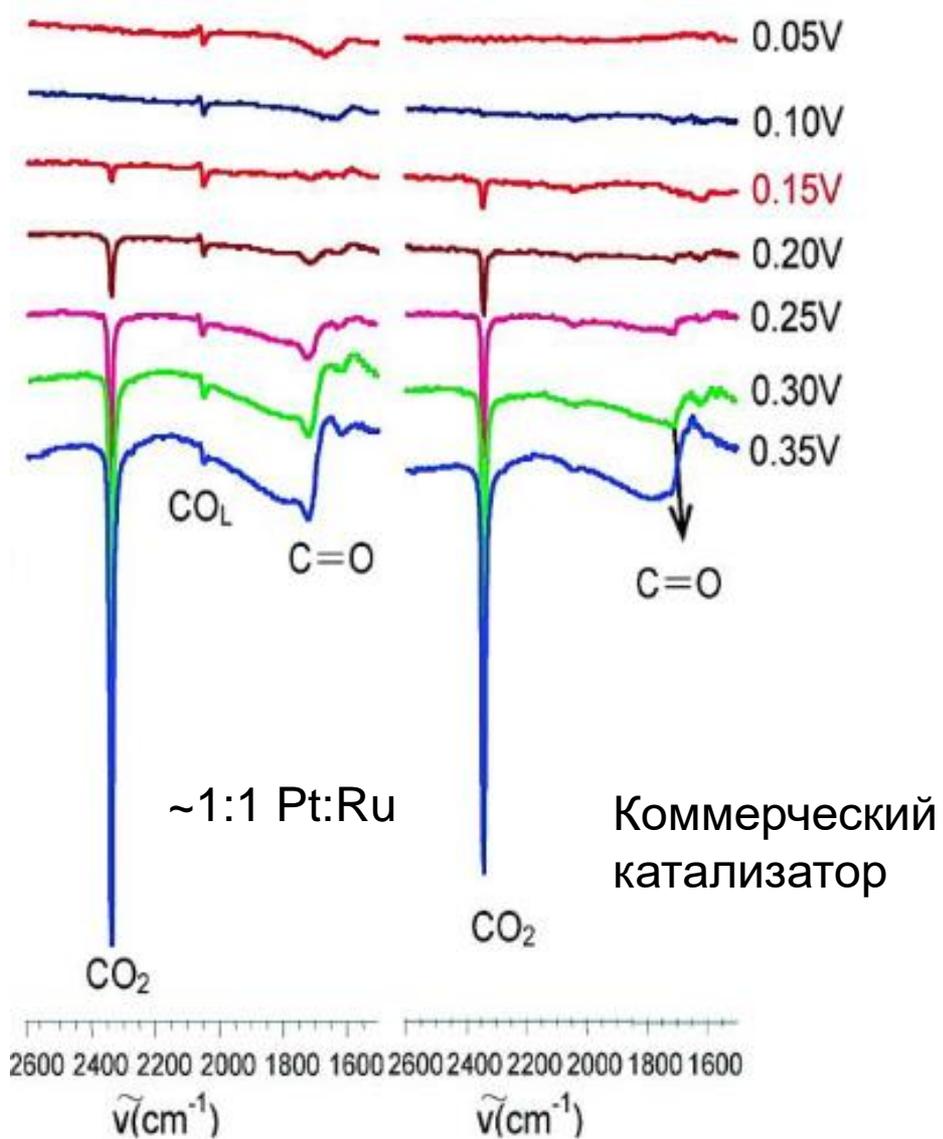
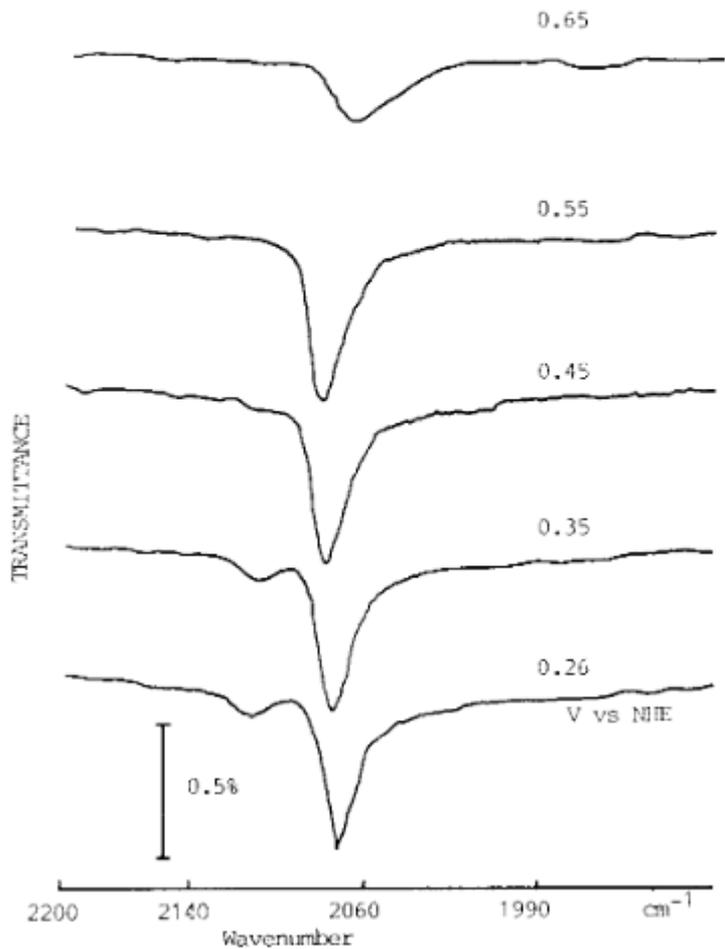
Потенциал, В (RHE)



Заполнения:

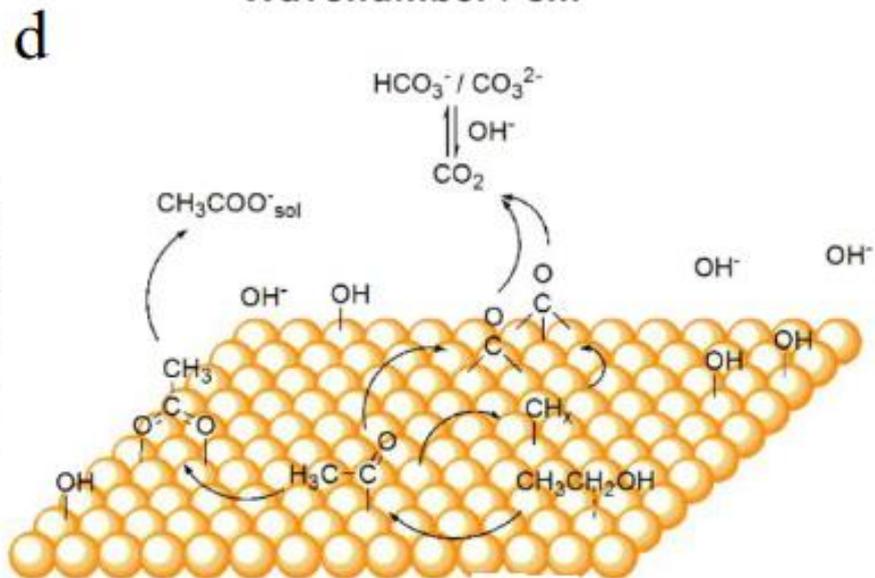
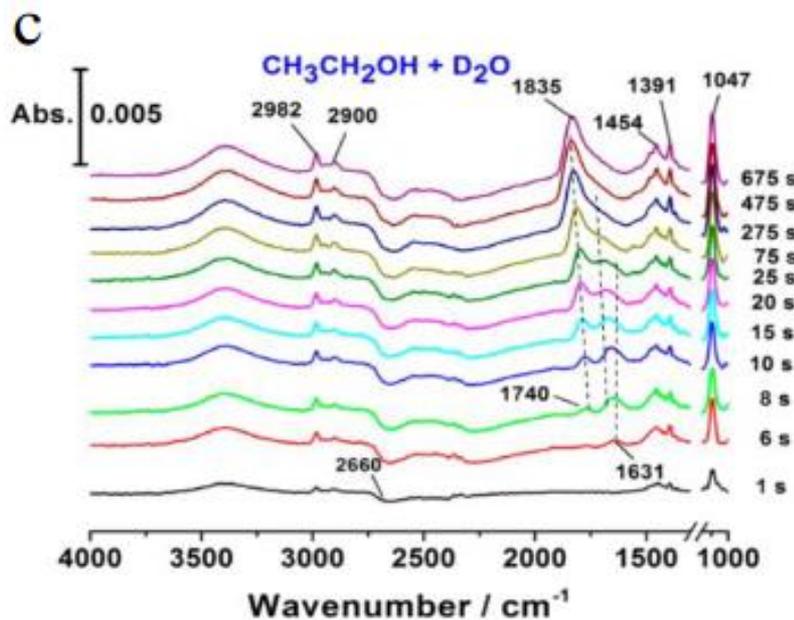
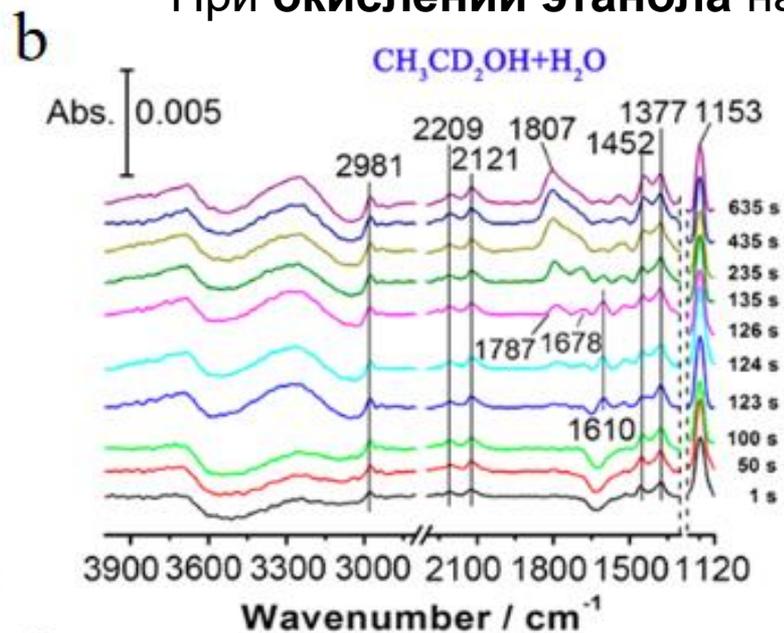
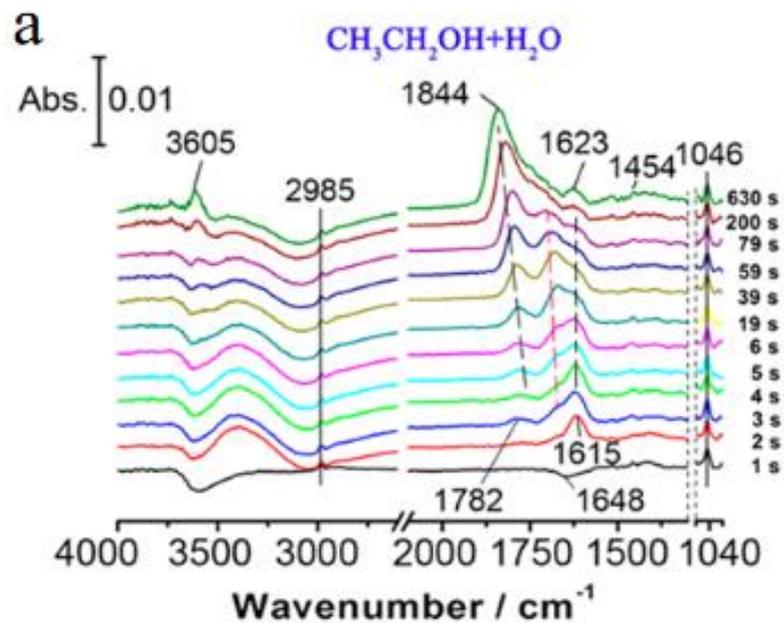


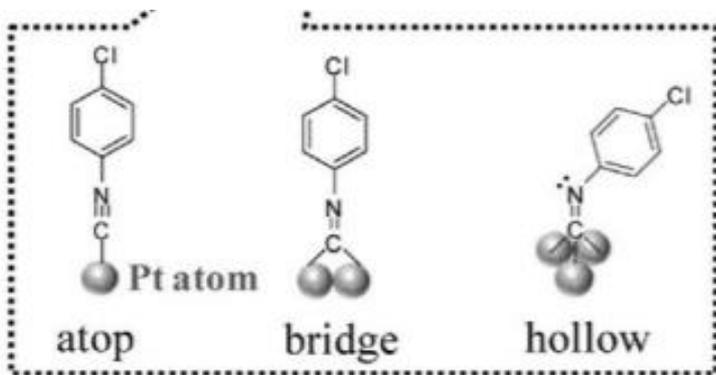
CO на адатомах Cu на Pt(110)



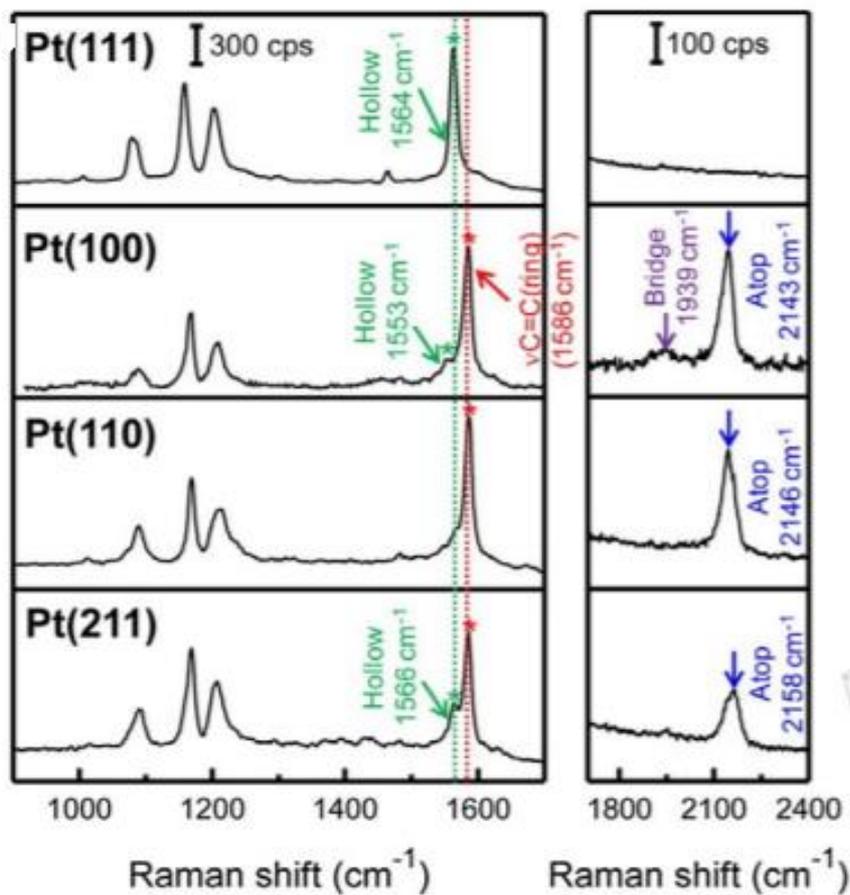
Адсорбаты при **окислении метанола** на Pt-Ru

При окислении этанола на Pd

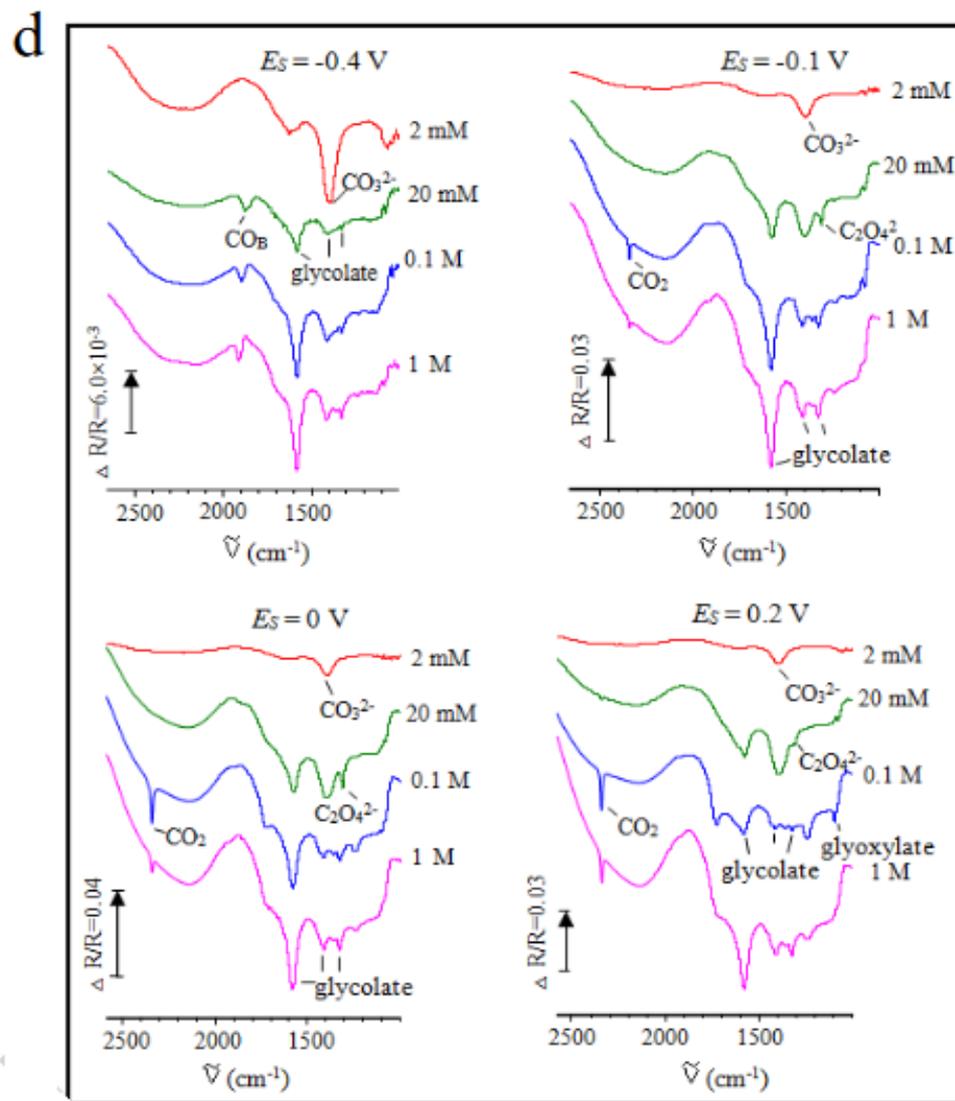
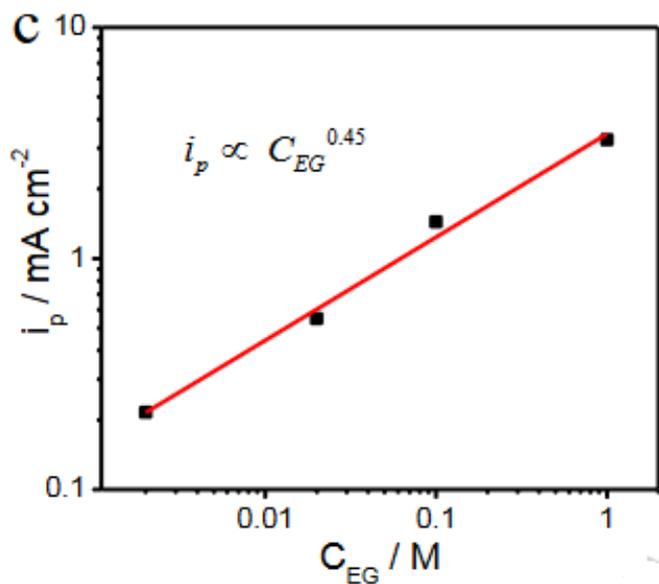
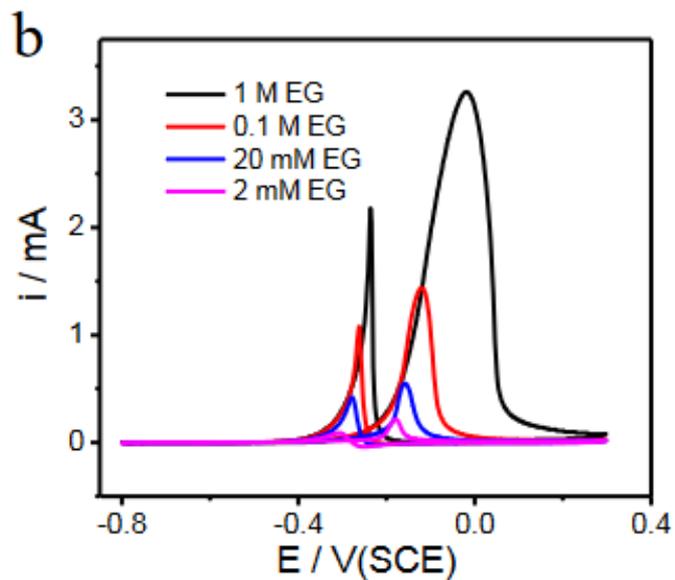




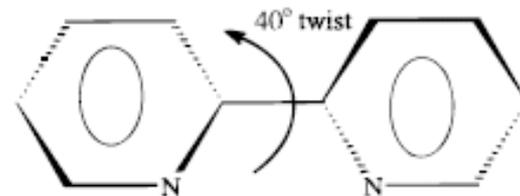
Analyst 145 (2020) 2482–2509



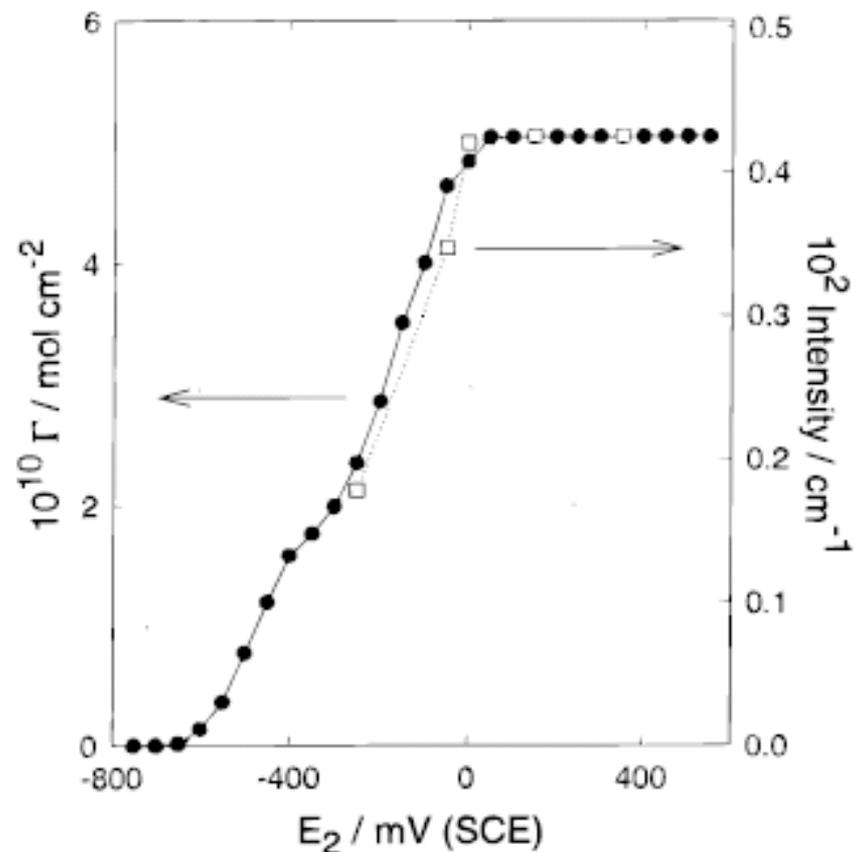
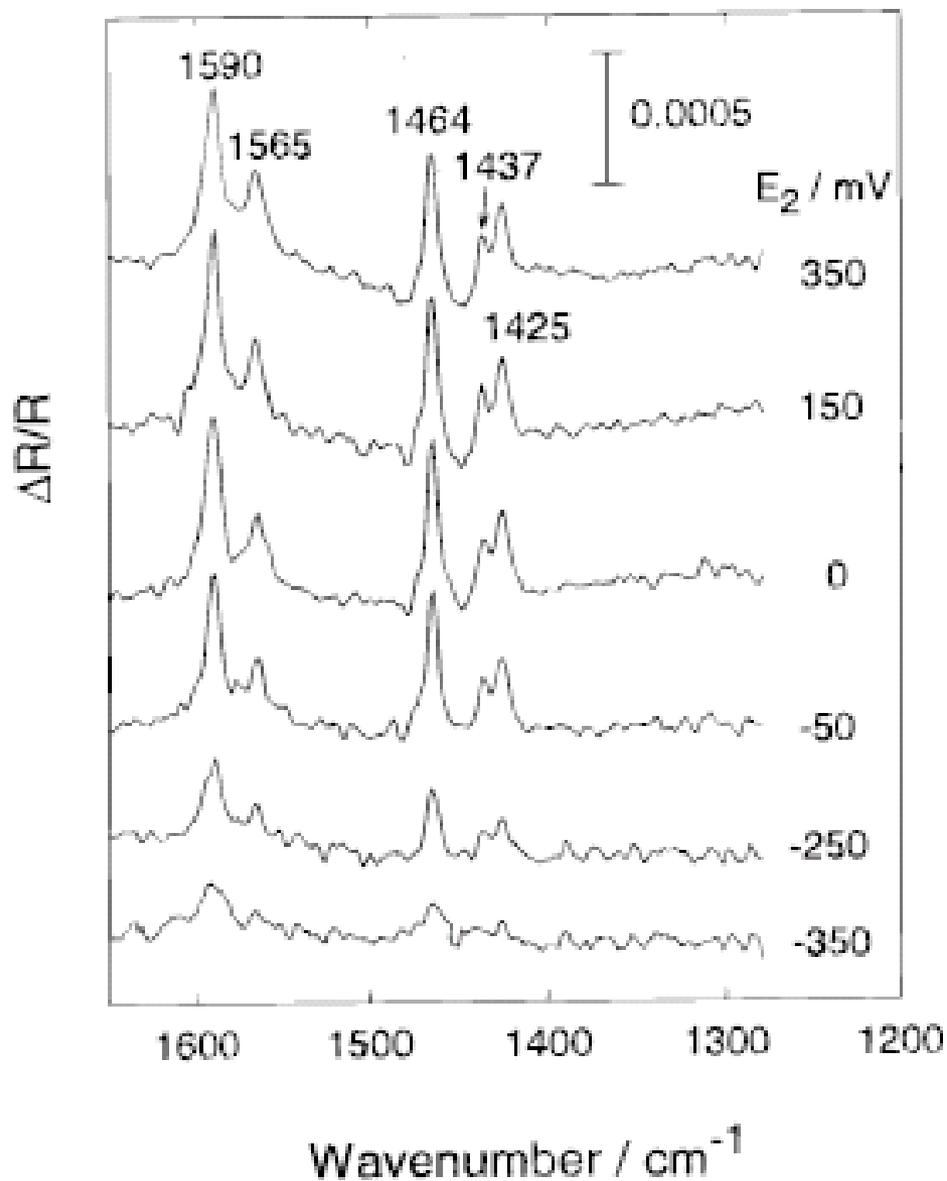
При окислении этиленгликоля на Pd



SNIFTIRS



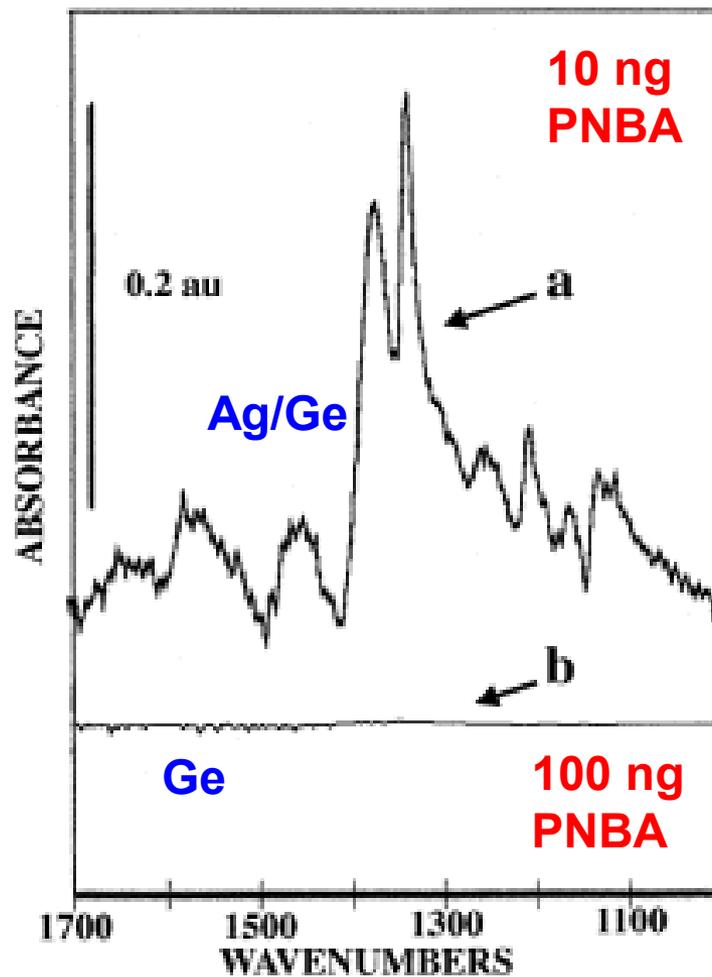
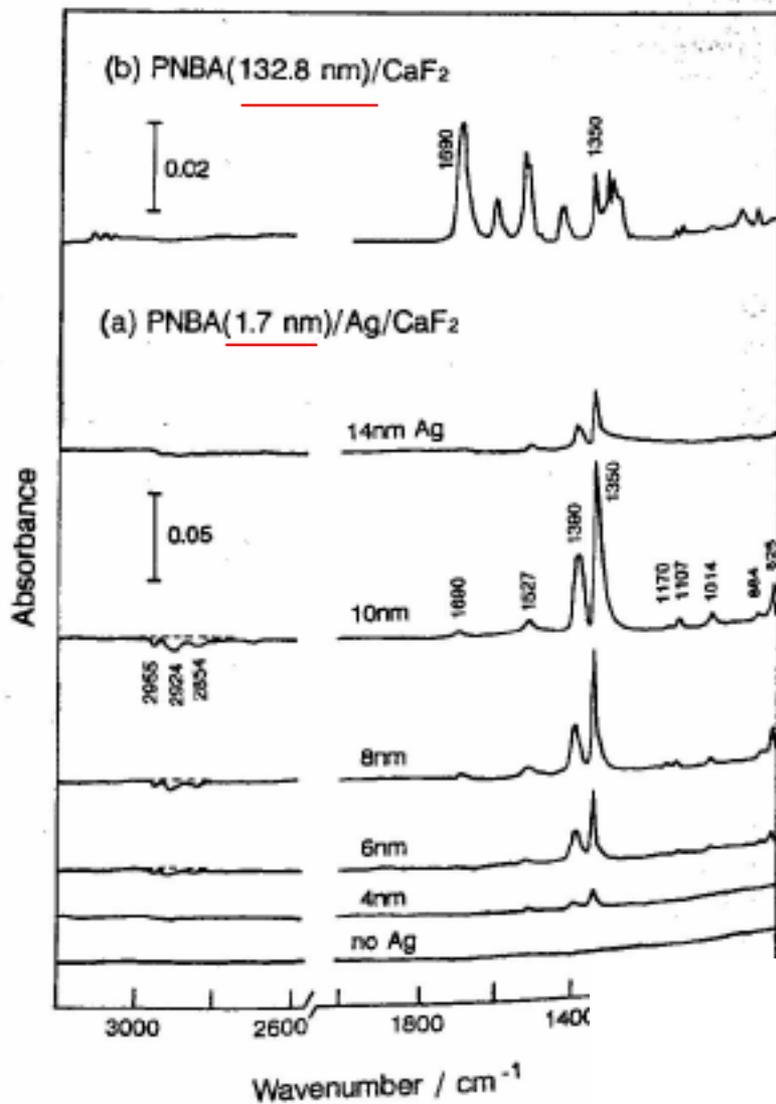
(адсорбция на золоте)



Переориентация – два Γ_{max}

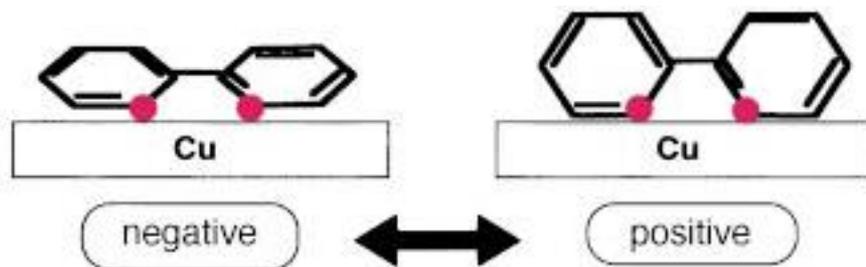
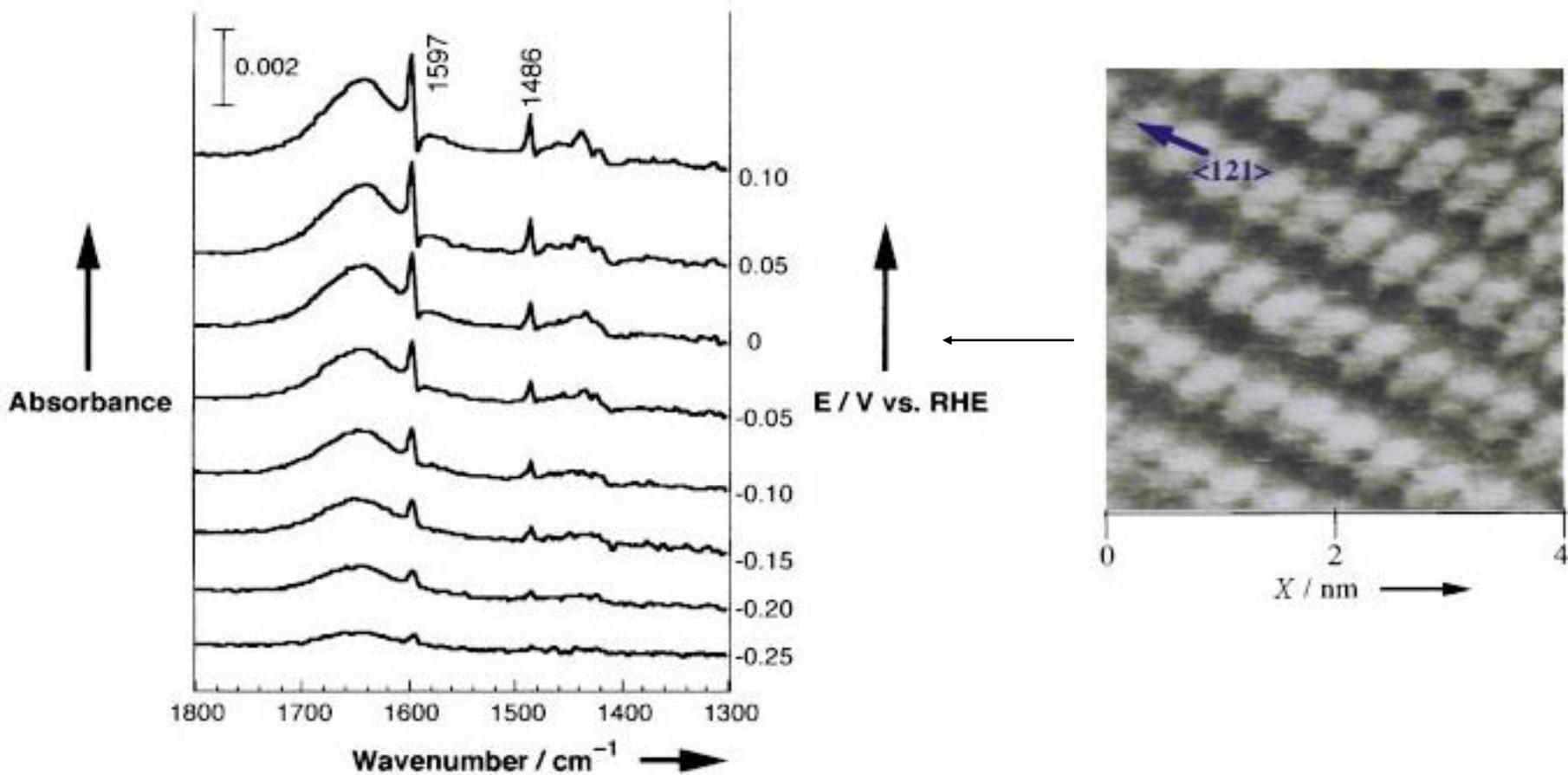
п-нитробензойная кислота (PNBA)

SEIRAS

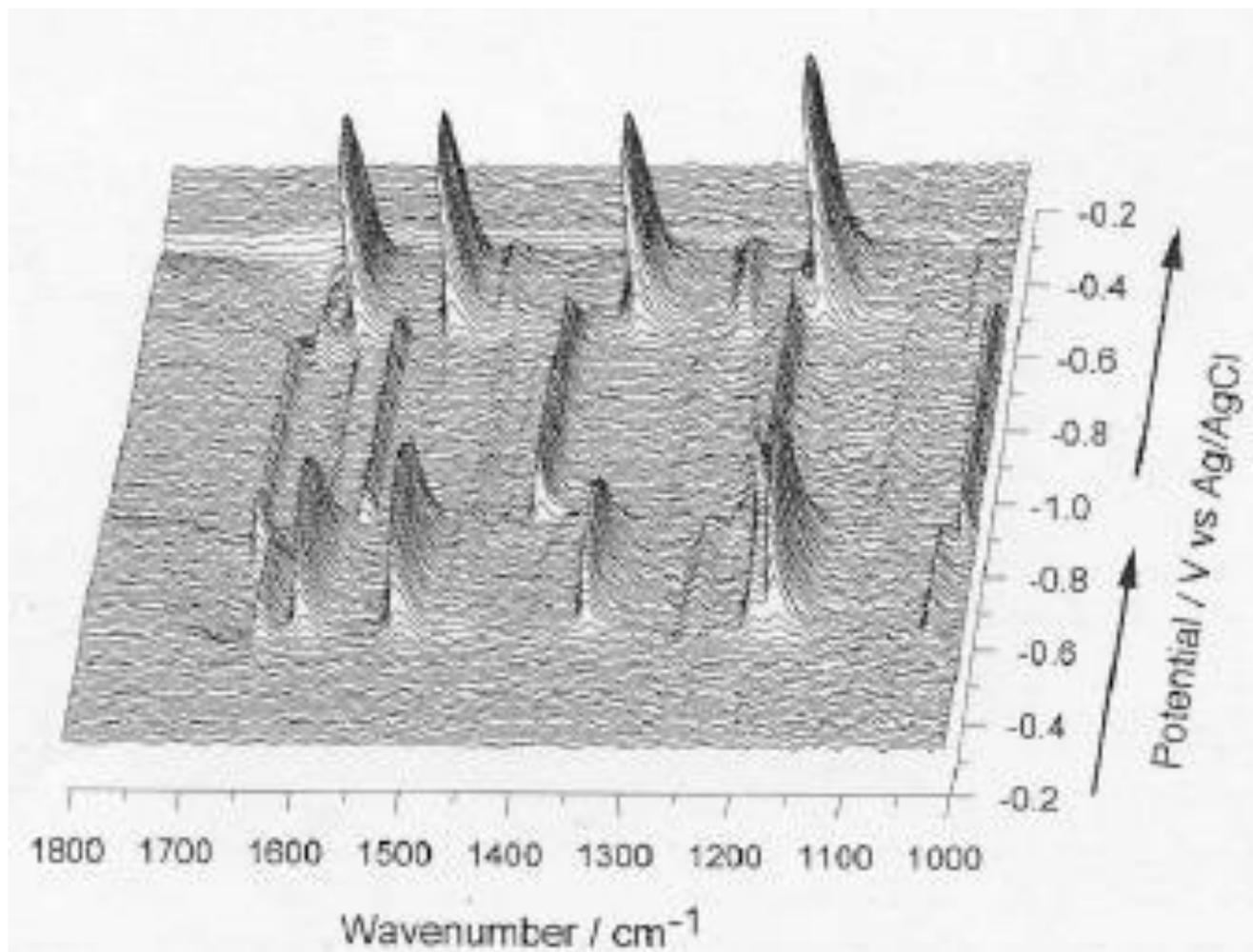


25 mm × 5 mm

SEIRAS



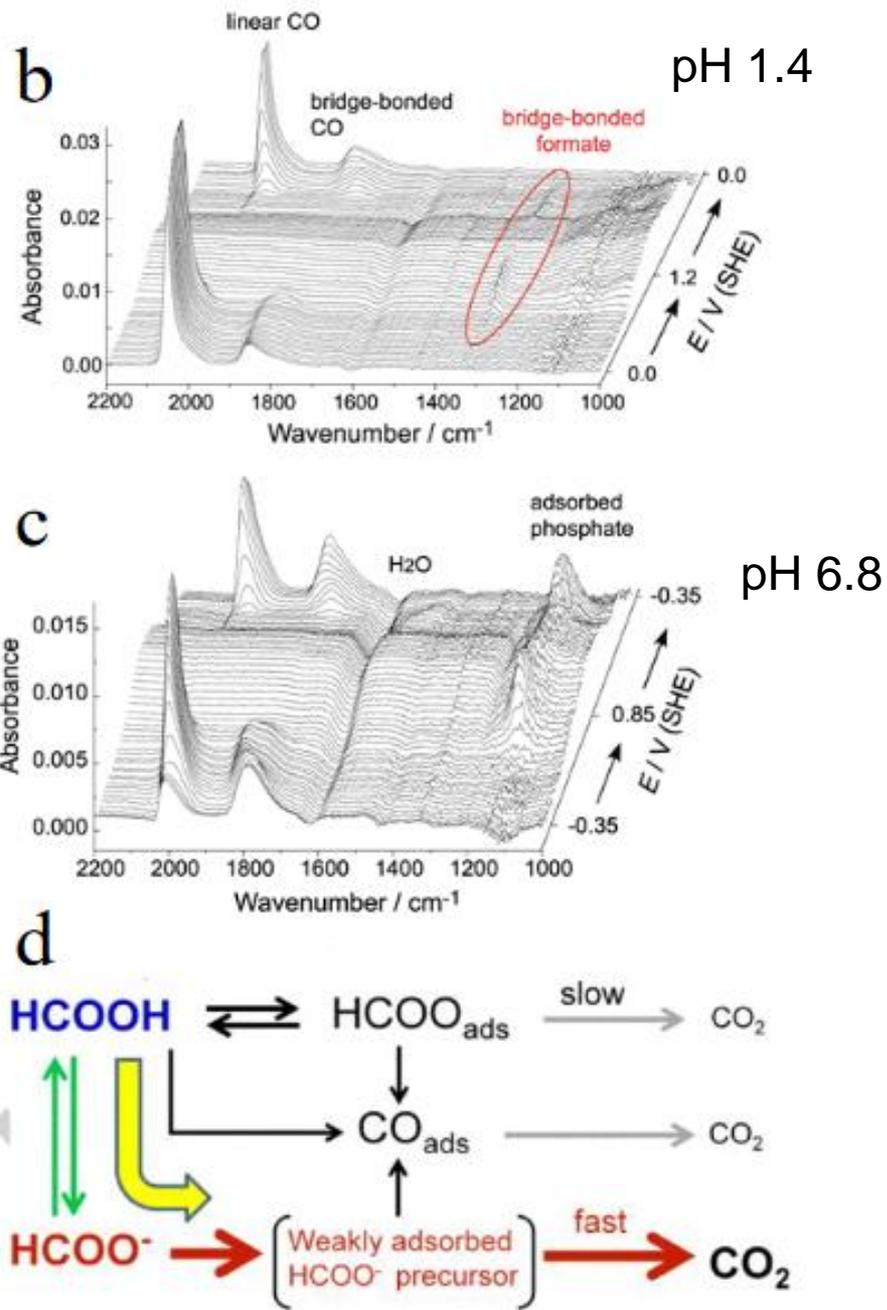
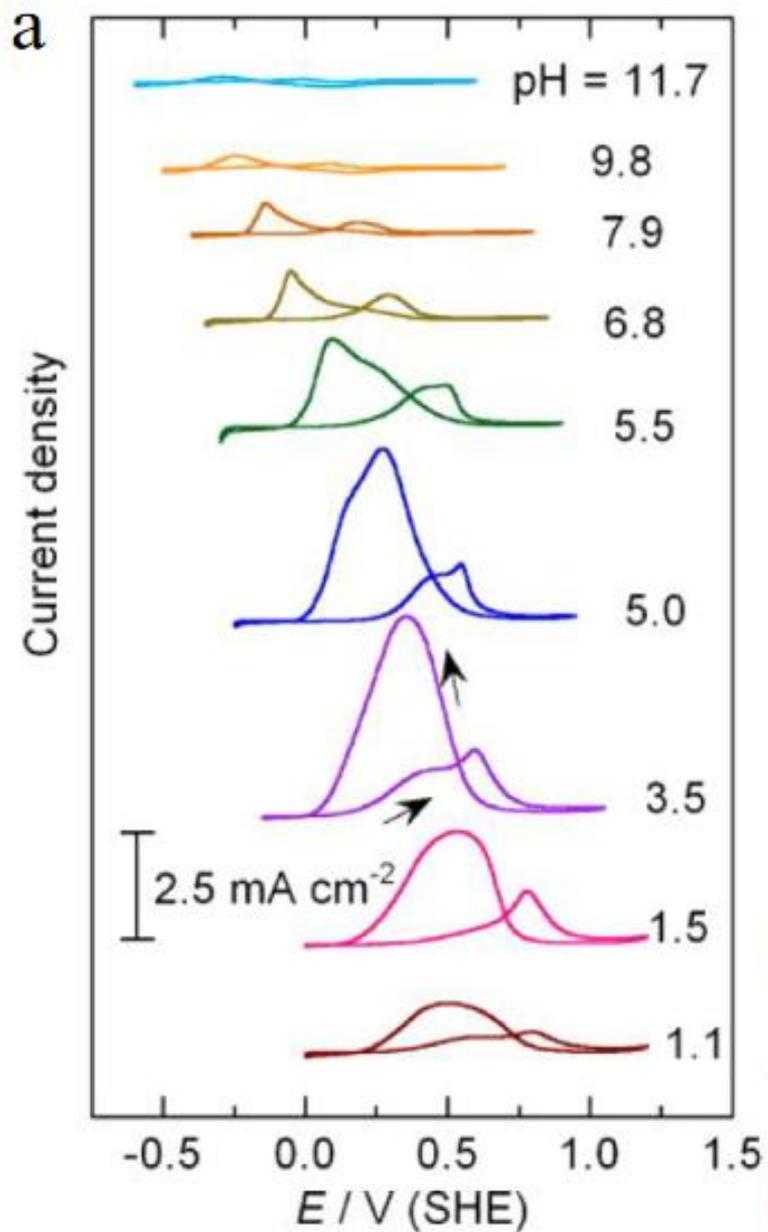
Виологен, окисление и восстановление на серебре (один спектр за 0.6 с)

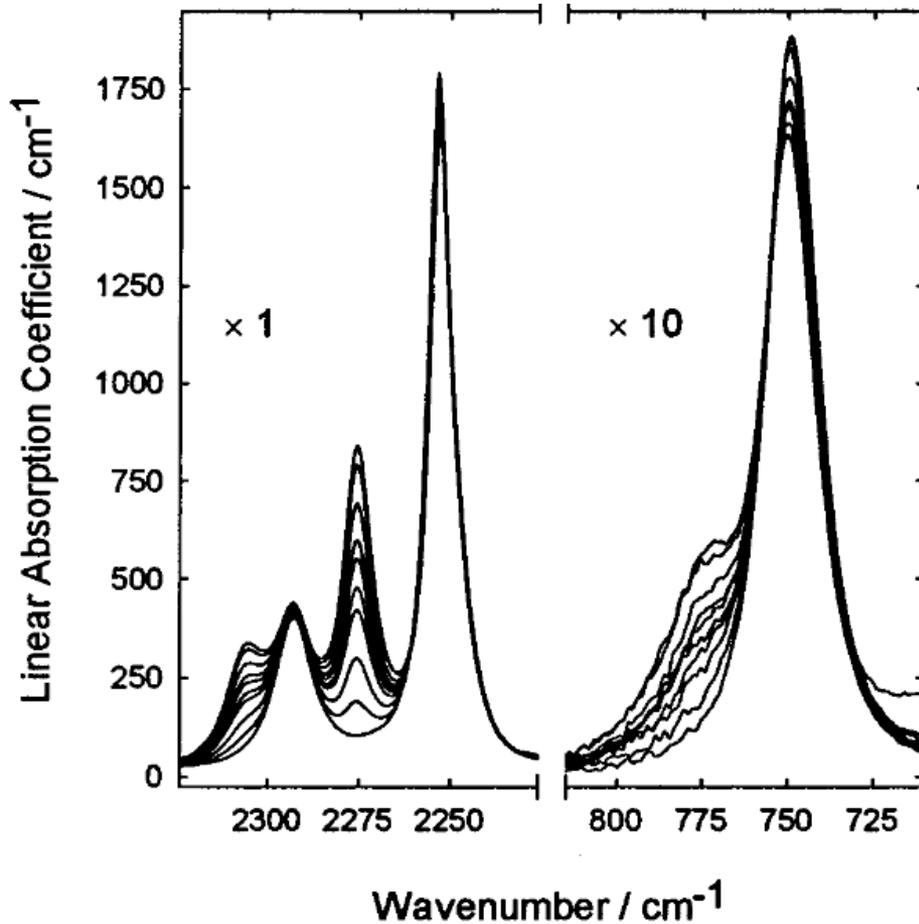


Окисленная форма

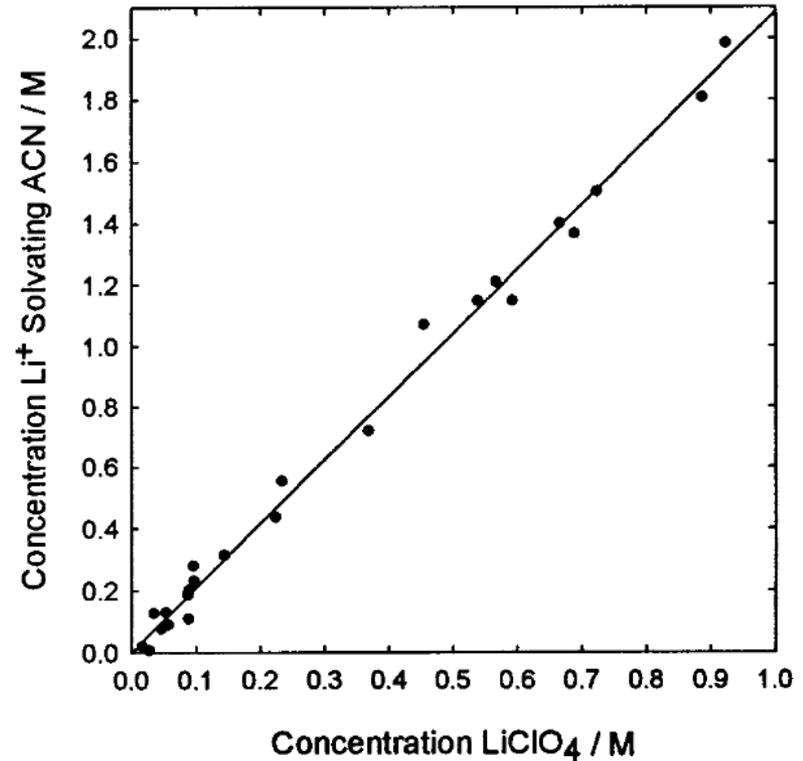
Восстановленная форма

Окисленная форма





ACN ν_2 and $2\nu_8$ spectral regions of LiClO_4 -ACN solutions of various concentrations, 0.000 (pure ACN), 0.098, 0.224, 0.368, 0.455, 0.538, 0.592, 0.723, 0.887, and 0.923 M.



ИК-спектроскопия для исследования сольватации: молекулы ацетонитрила в сольватных оболочках дают сдвинутые полосы.