

In situ колебательная спектроскопия – II: неорганические адсорбаты

Модельные ИК-спектроскопические эксперименты по коадсорбции воды и ионов

ИК-спектроскопия адсорбированного водорода

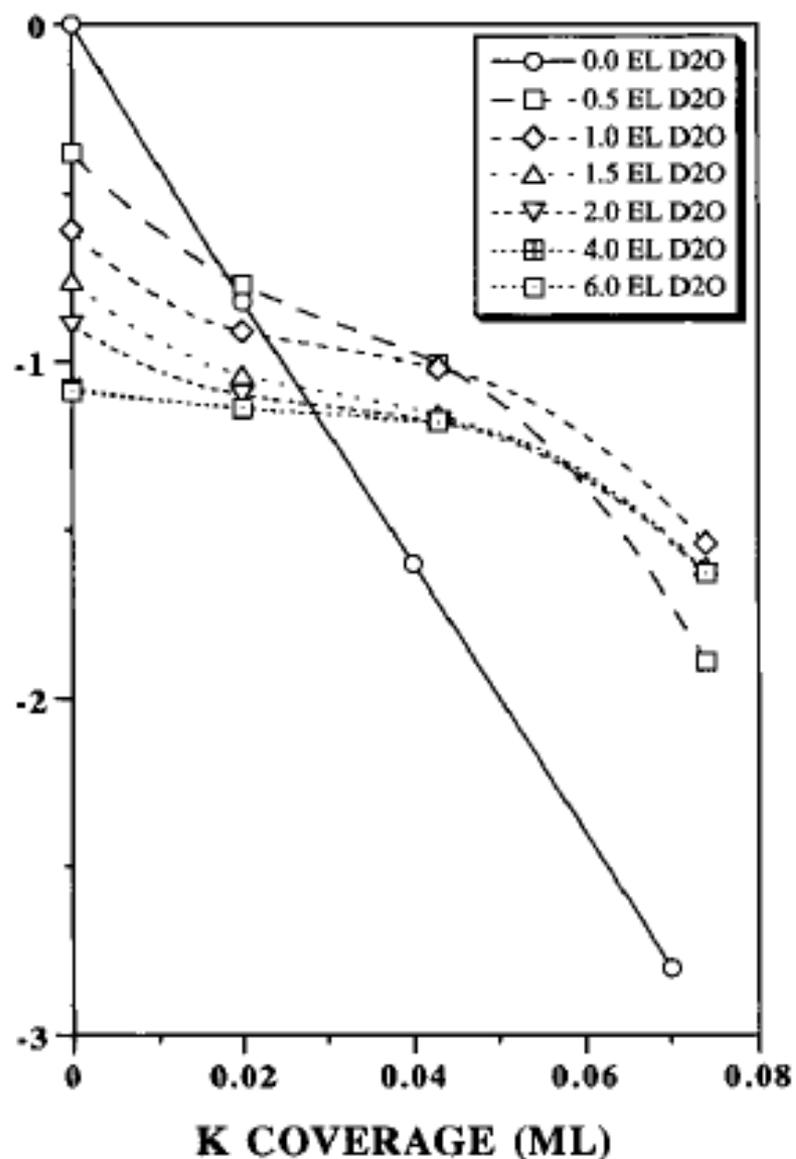
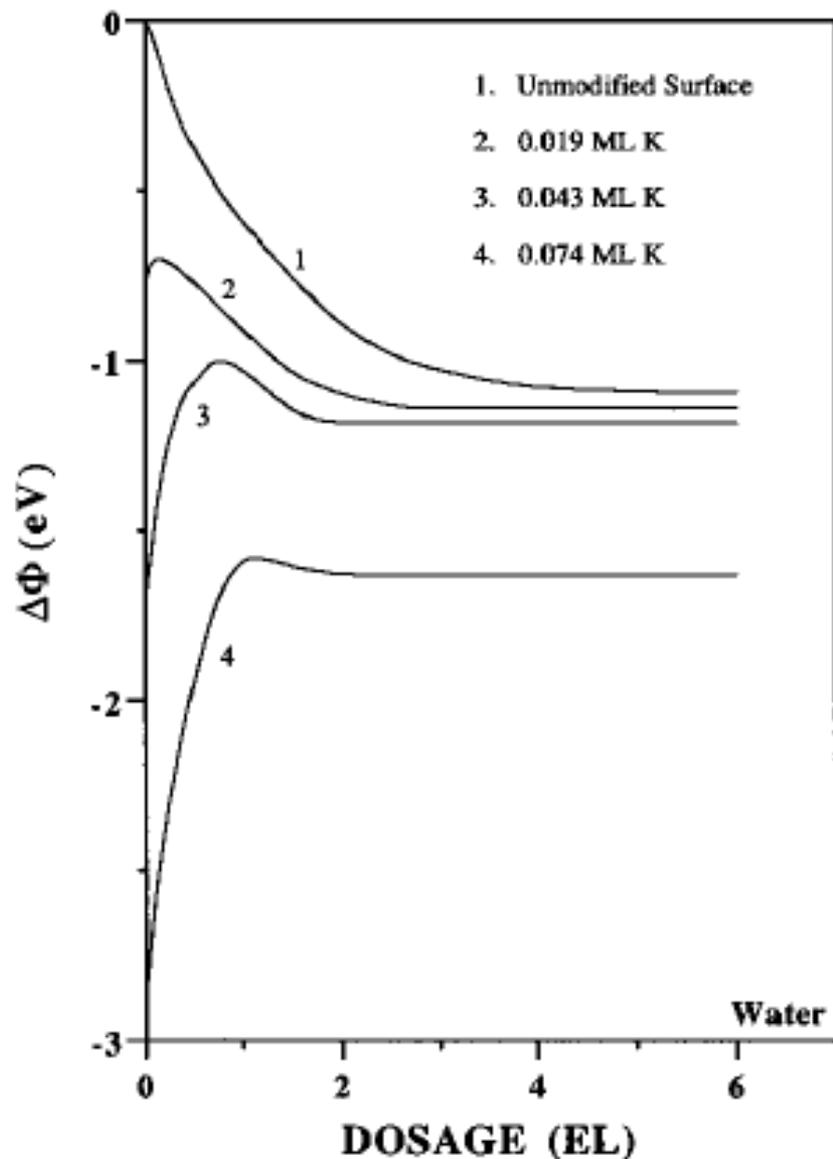
Адсорбированный сульфат

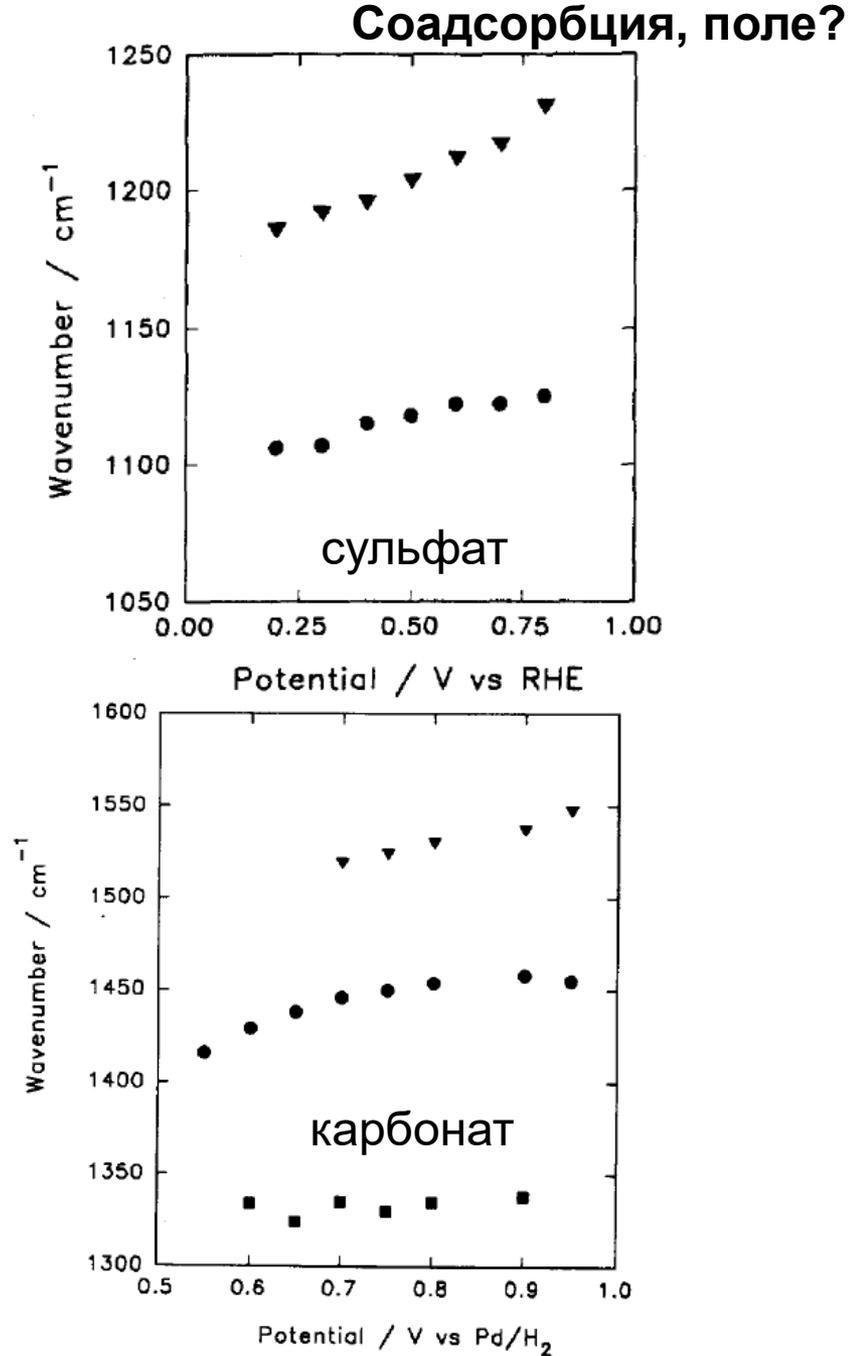
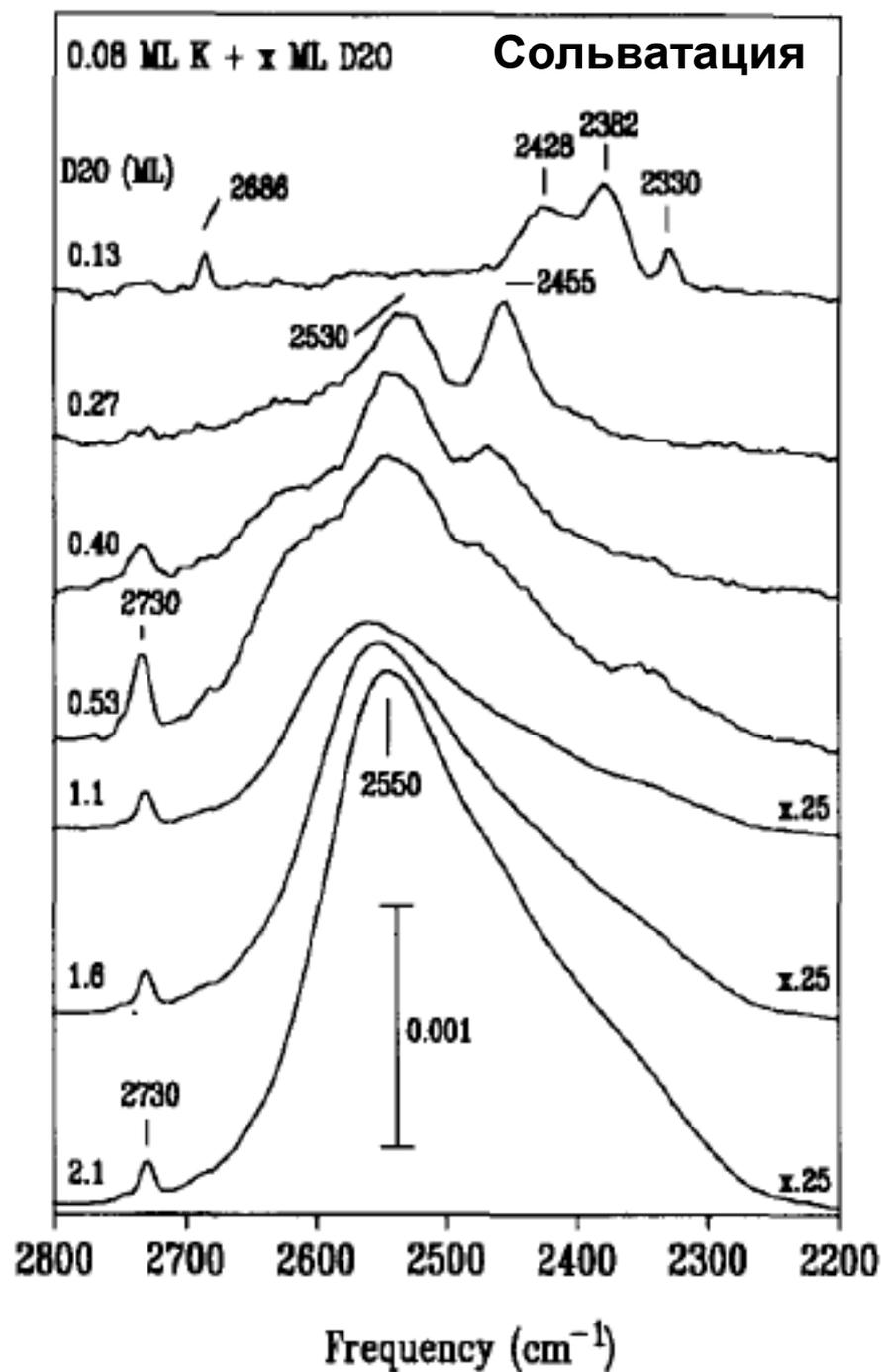
Электрокатализ – интермедиаты

Адсорбция полиоксометаллатов

ИК-спектроскопия в исследованиях интеркаляции (берлинская лазурь)

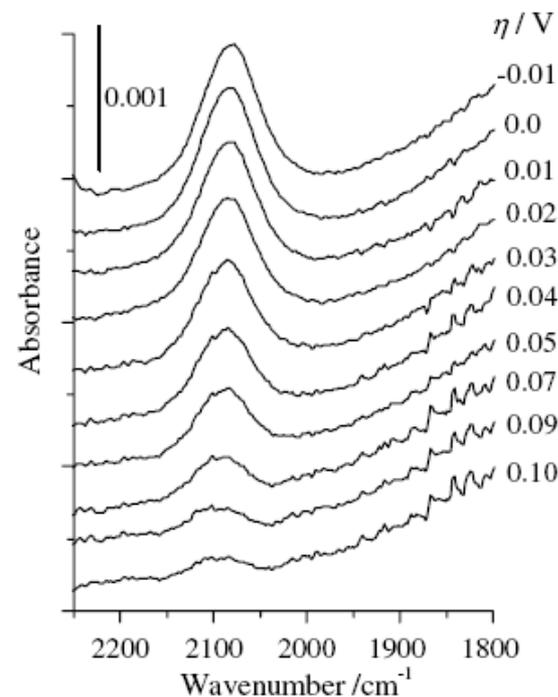
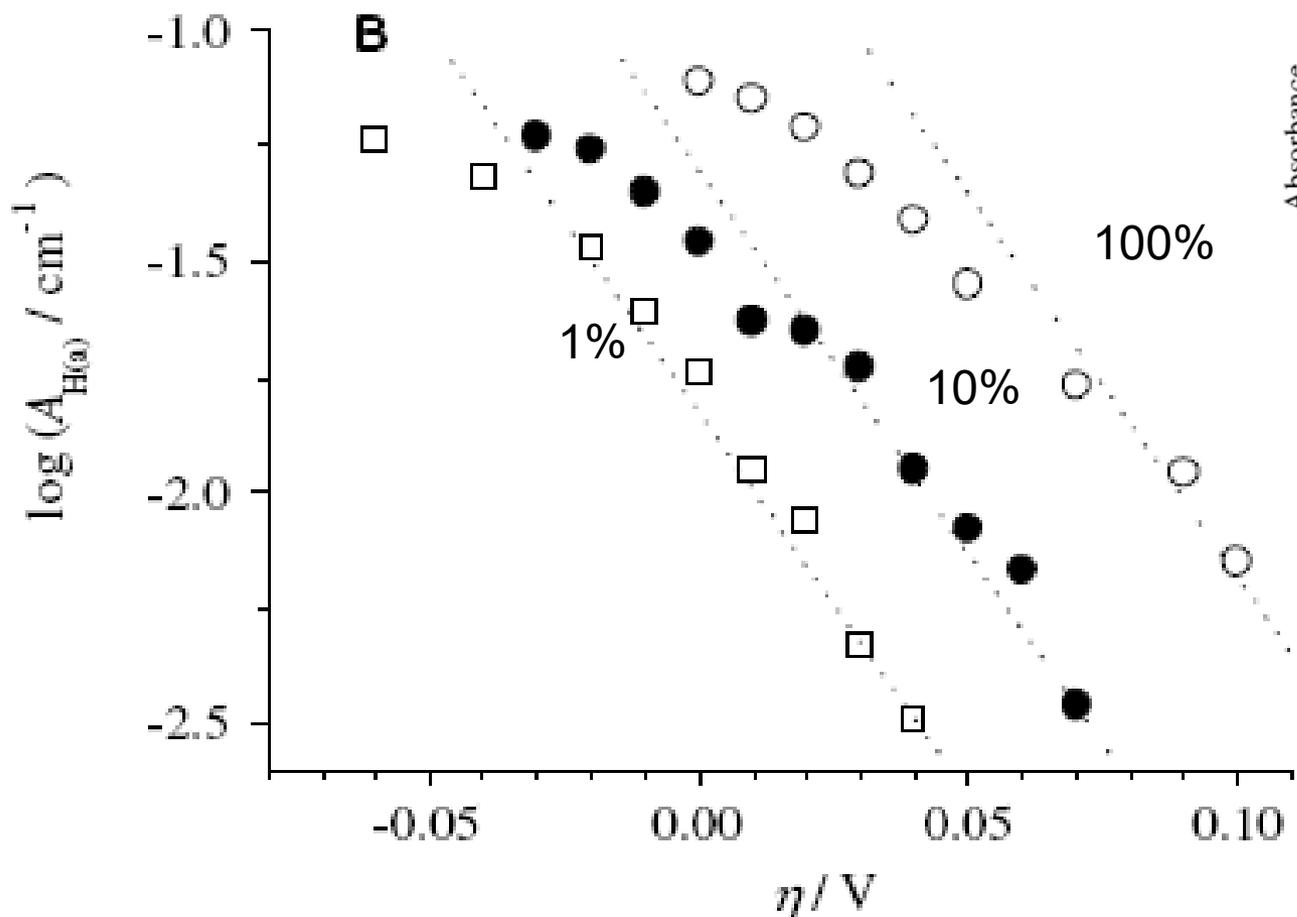
Имитация соадсорбции воды и ионов в вакуумных экспериментах (изменения работы выхода электрона)





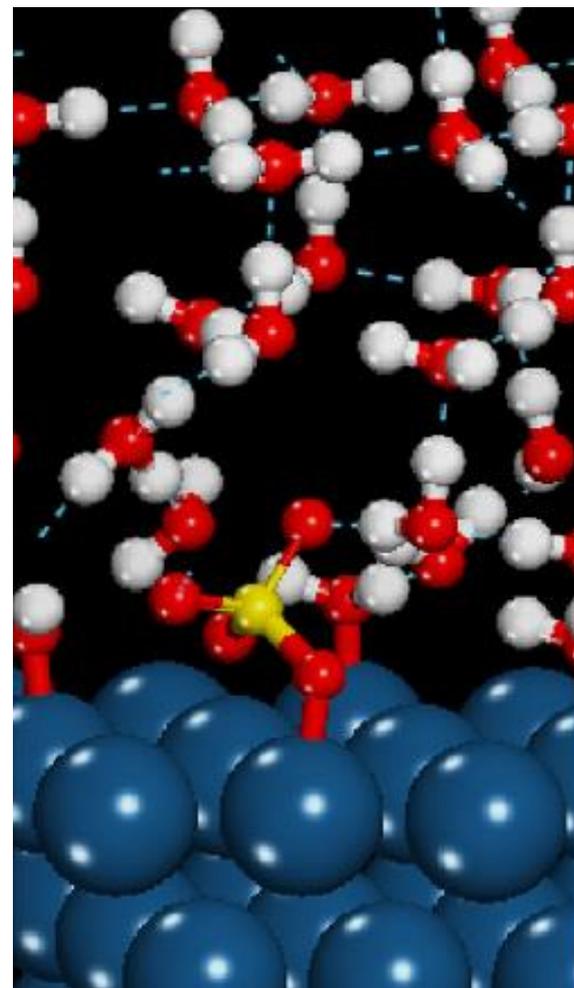
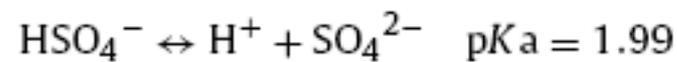
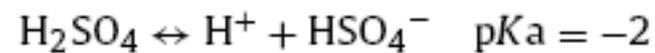
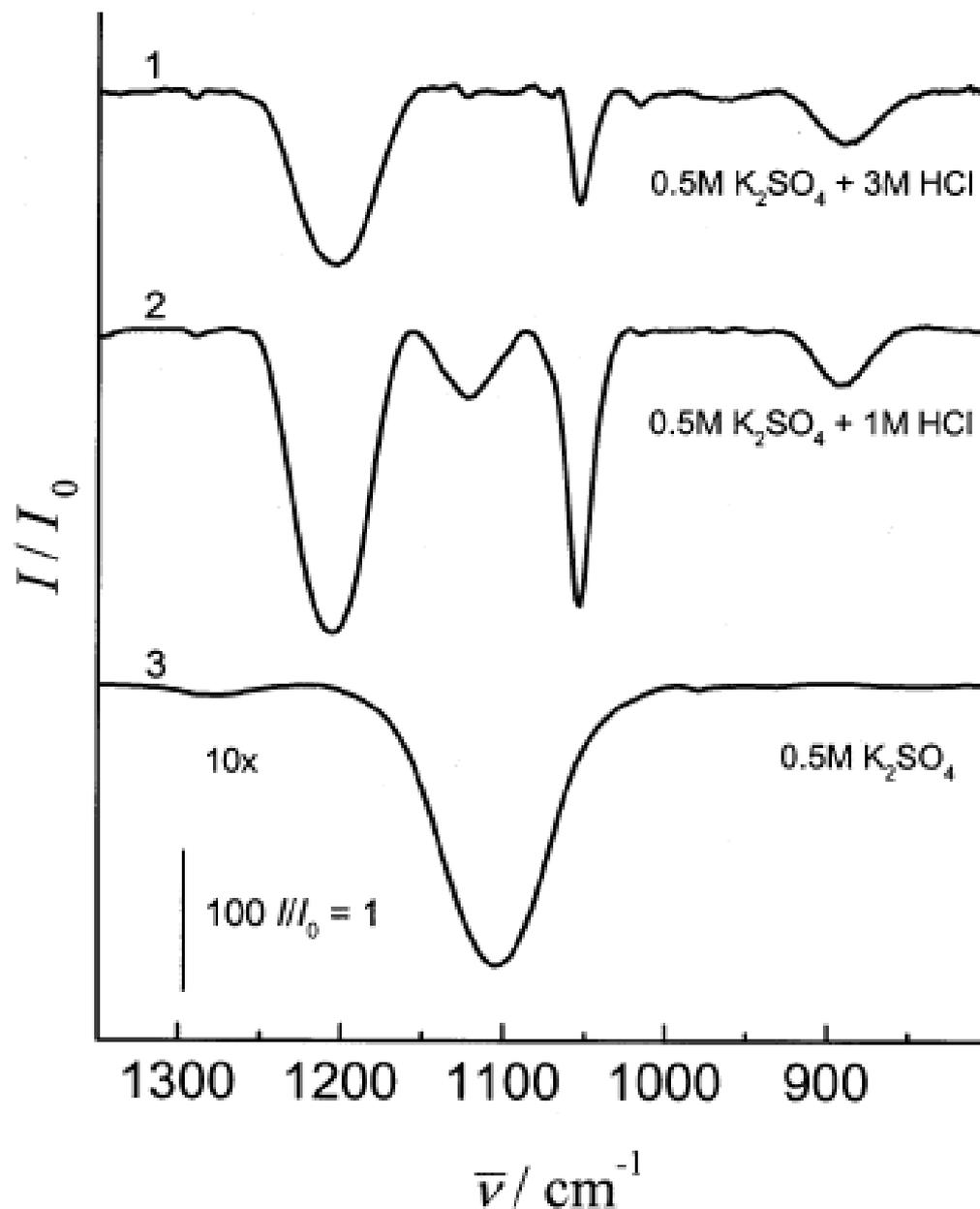
$$a_{\text{H(a)}} = \theta_{\text{H(a)}} / (1 - \theta_{\text{H(a)}}), \quad \text{Langmuir}$$

$$a_{\text{H(a)}} = \left\{ \theta_{\text{H(a)}} / (1 - \theta_{\text{H(a)}}) \right\} \exp(g\theta_{\text{H(a)}}), \quad \text{Frumkin}$$



Определение
заполнения атомами
Н при разных
содержаниях H_2 в
газовой фазе

Сульфат/бисульфат на Pt (протонирование на поверхности – не как в объеме)



Сульфат на высокоиндексных гранях Pd: [*n*(111) (111)]

Pd(111)

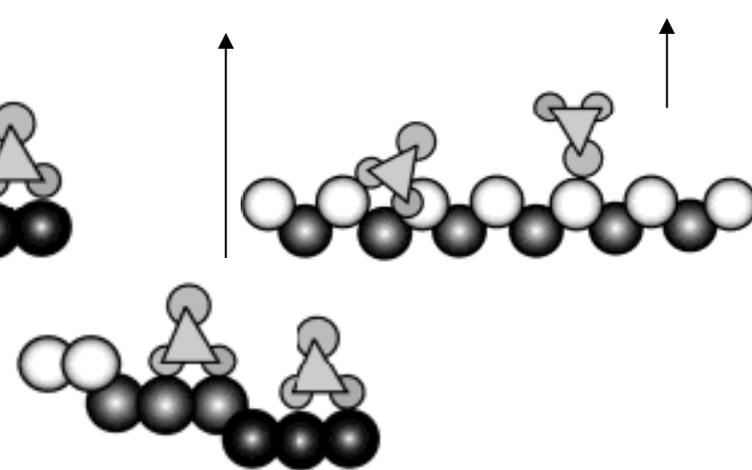
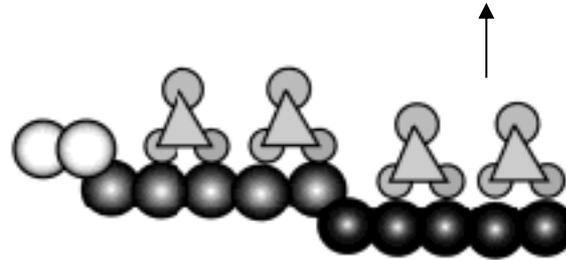
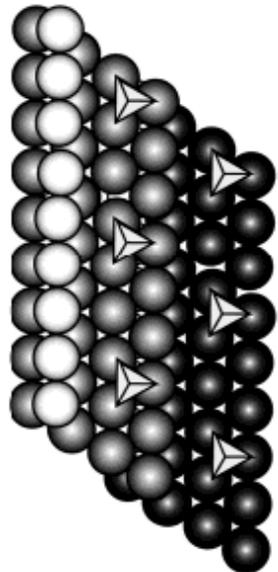
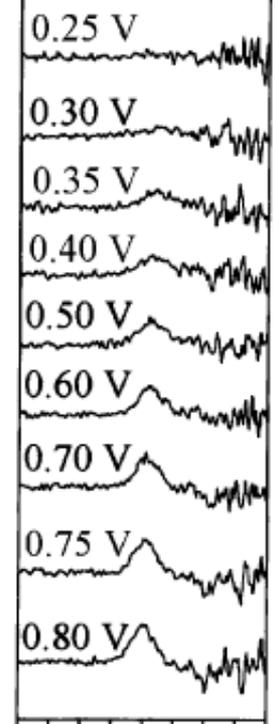
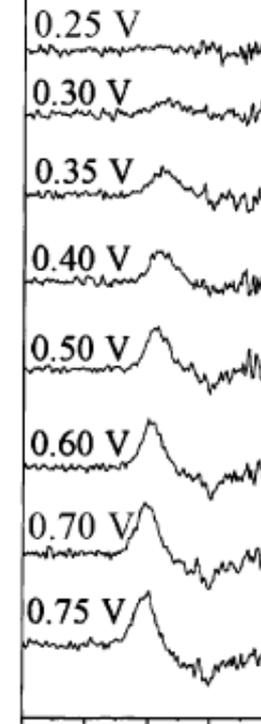
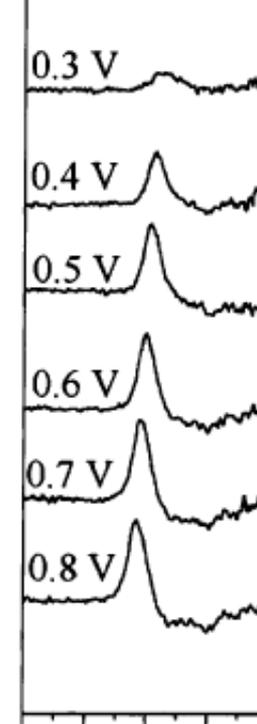
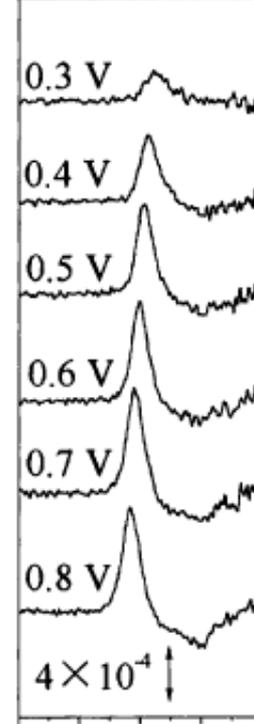
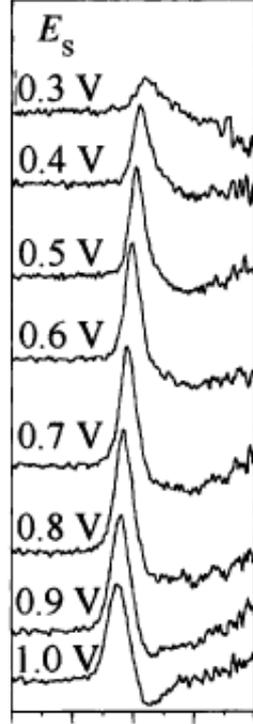
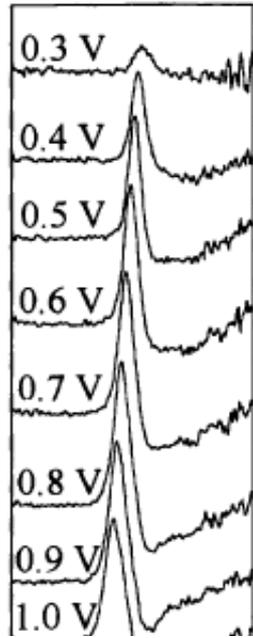
Pd(10 10 9) (*n* = 20)

Pd(997) (*n* = 9)

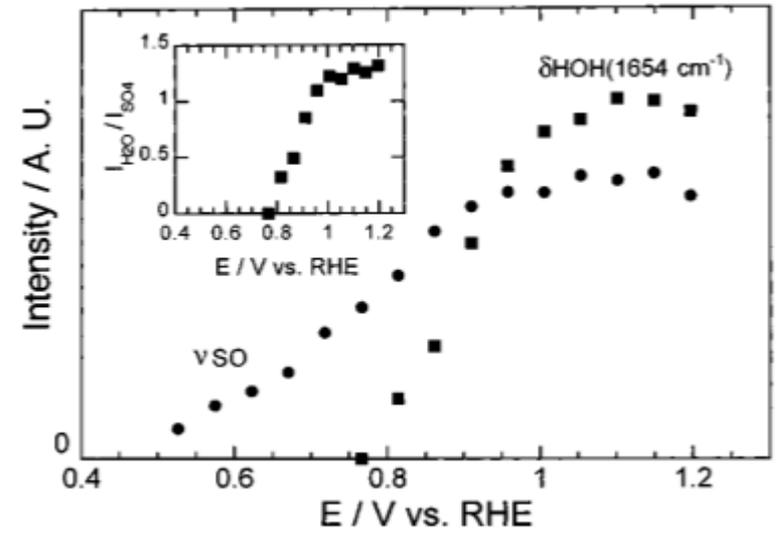
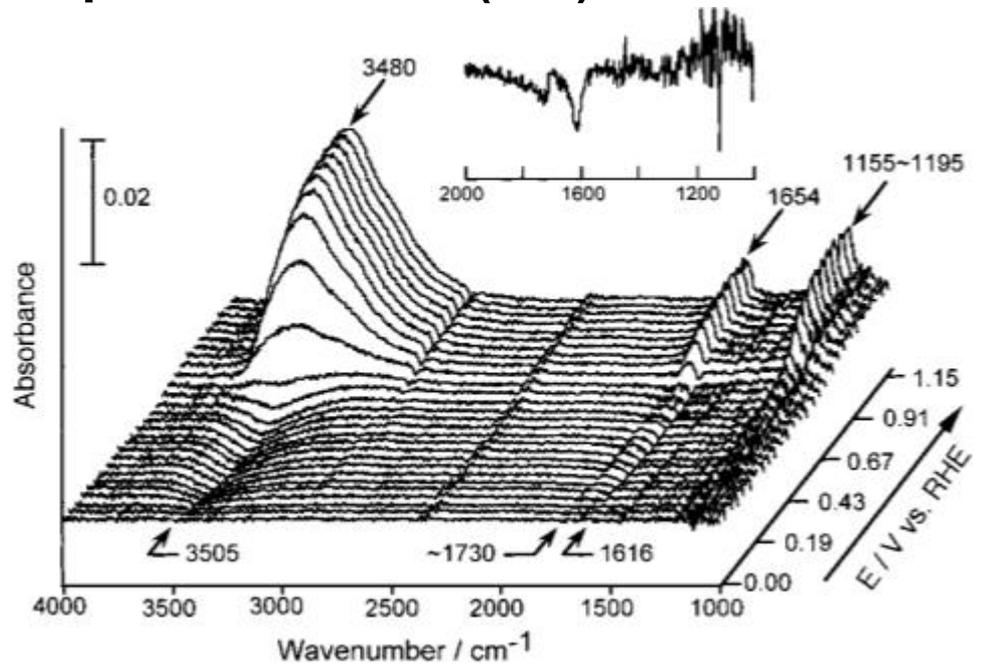
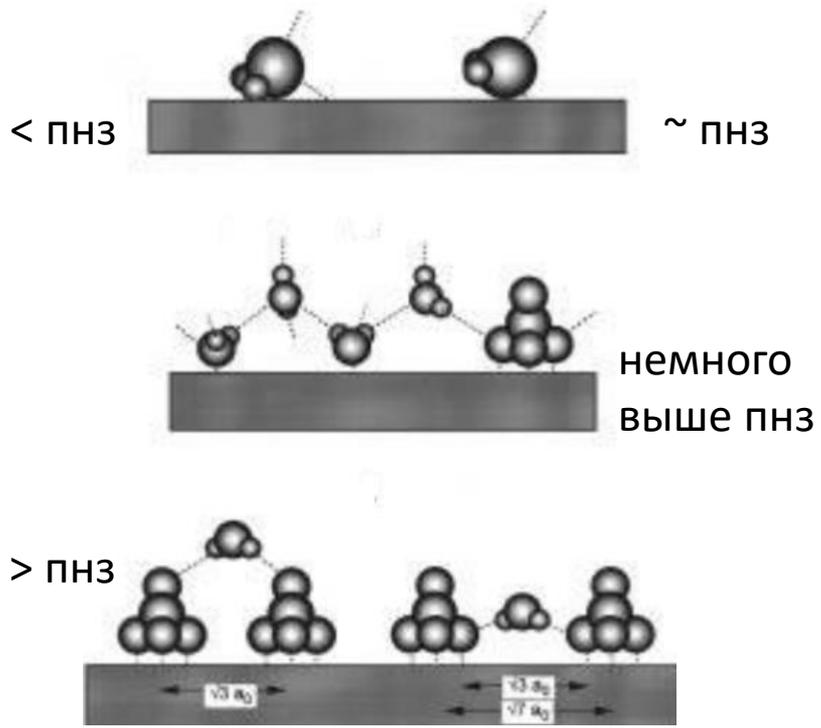
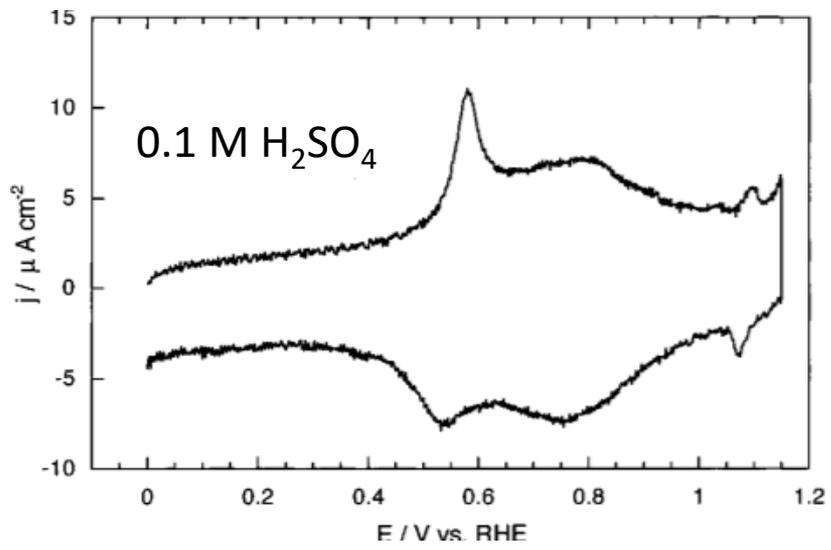
Pd(553) (*n* = 5)

Pd(331) (*n* = 3)

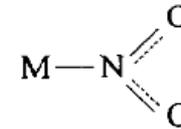
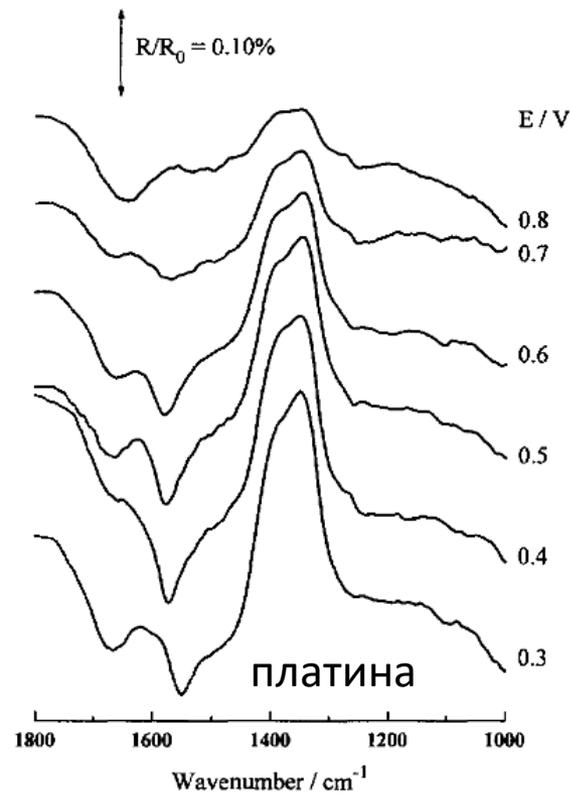
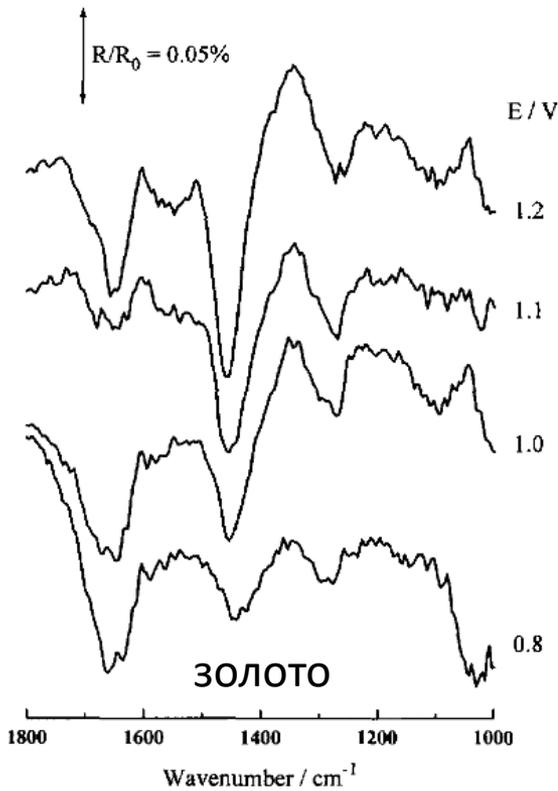
Pd(110) (*n* = 2)



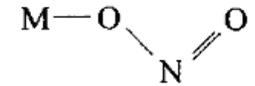
Сульфат/вода на Au(111)



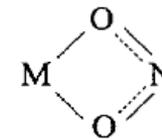
Нитрат и его восстановление до нитрита



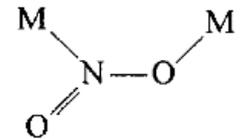
Nitro complex (I)
 $\nu_s(\text{NO}_2)$ 1306 - 1365 cm⁻¹
 $\nu_a(\text{NO}_2)$ 1340 - 1490 cm⁻¹
 C_{2v}



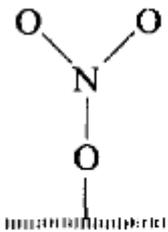
Nitrito complex (II)
 $\nu(\text{N=O})$ 1400 - 1485 cm⁻¹
 $\nu(\text{NO})$ 1050 - 1110 cm⁻¹
 C_s



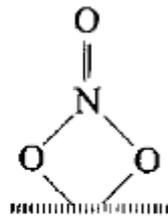
Chelating nitro complex (III)
 $\nu_s(\text{NO}_2)$ 1170 - 1225 cm⁻¹
 $\nu_a(\text{NO}_2)$ 1266 - 1390 cm⁻¹
 C_{2v}



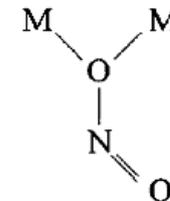
Bridging nitro complex (IV)
 $\nu(\text{NO}_2)$ 1412 and 1236 cm⁻¹
 C_s



Unidentate nitrate
 $\nu_s(\text{NO}_2)$ 1305 cm⁻¹
 $\nu(\text{NO})$ 1008 cm⁻¹

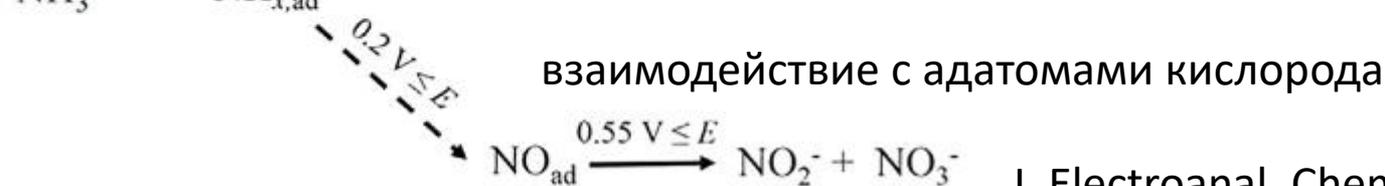
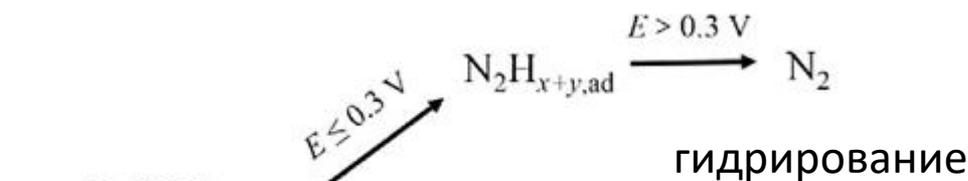
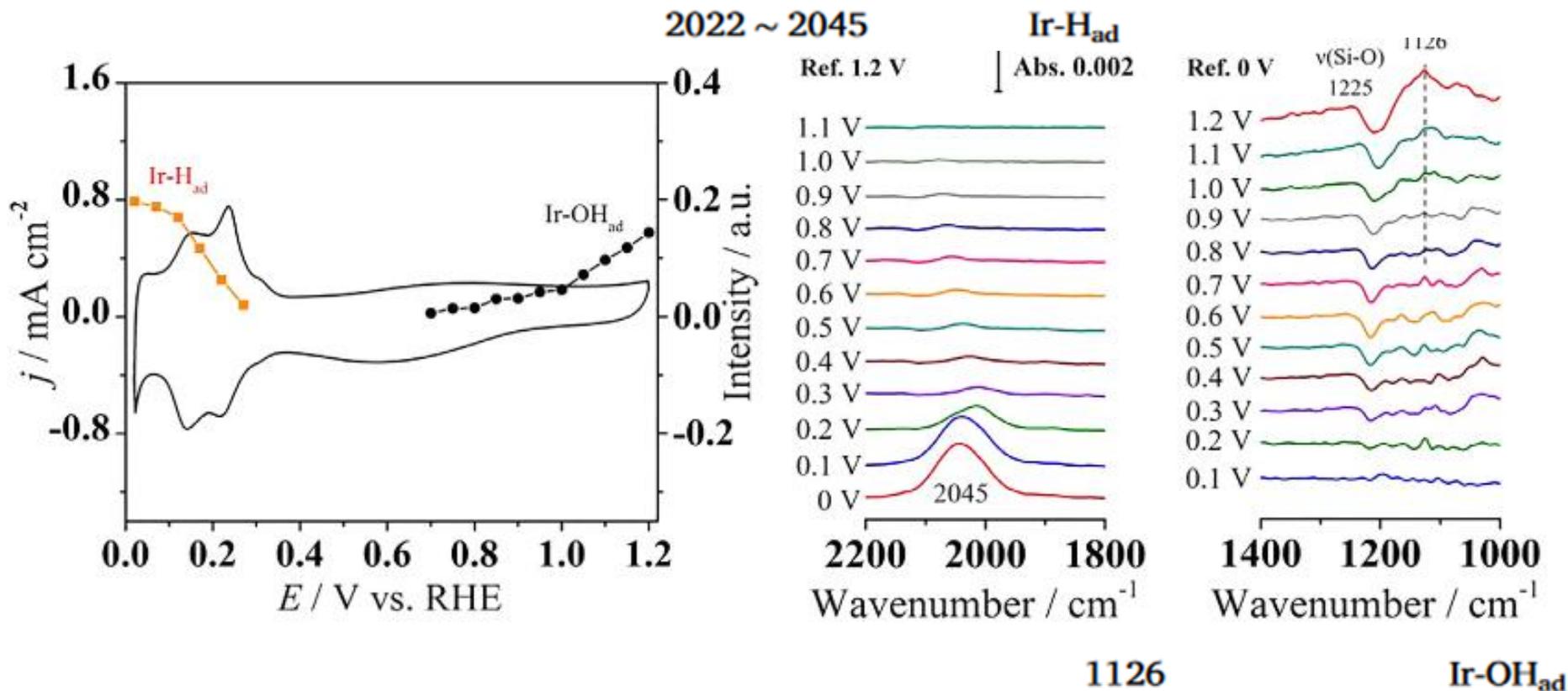


Chelating bidentate nitrate
 $\nu(\text{N=O})$ 1476 cm⁻¹
 $\nu_s(\text{NO}_2)$ 1025 cm⁻¹



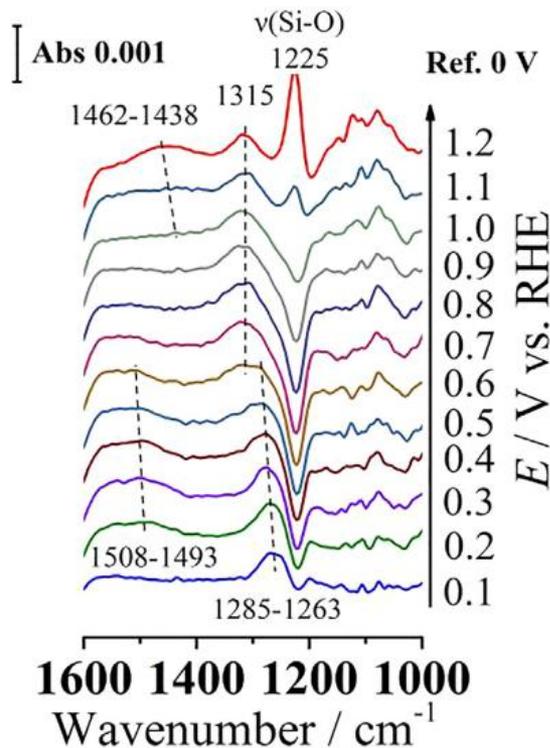
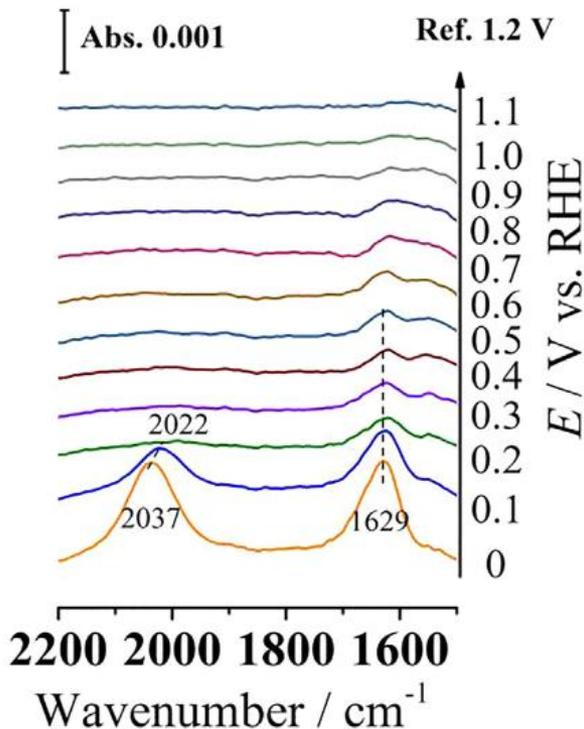
Bridging nitro complex (V)
 $\nu(\text{NO}_2)$ 1460 and 1019 cm⁻¹
 C_s

Адсорбция водорода и кислорода на иридии в щелочной среде

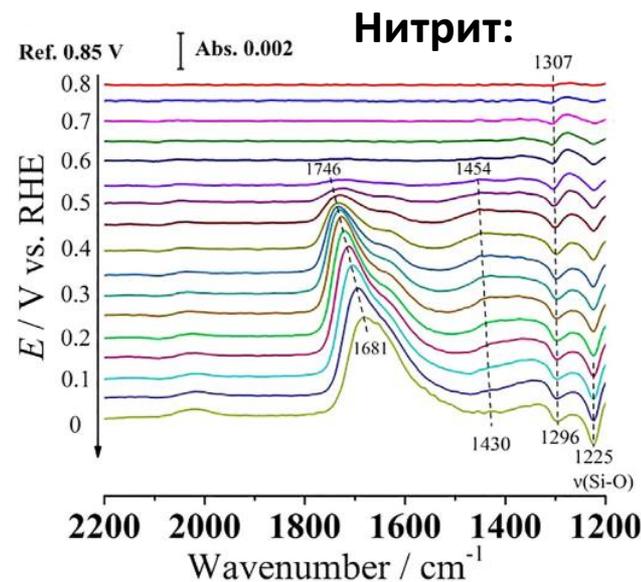


Электрокатализ превращений соединений азота на иридии

Аммиак:

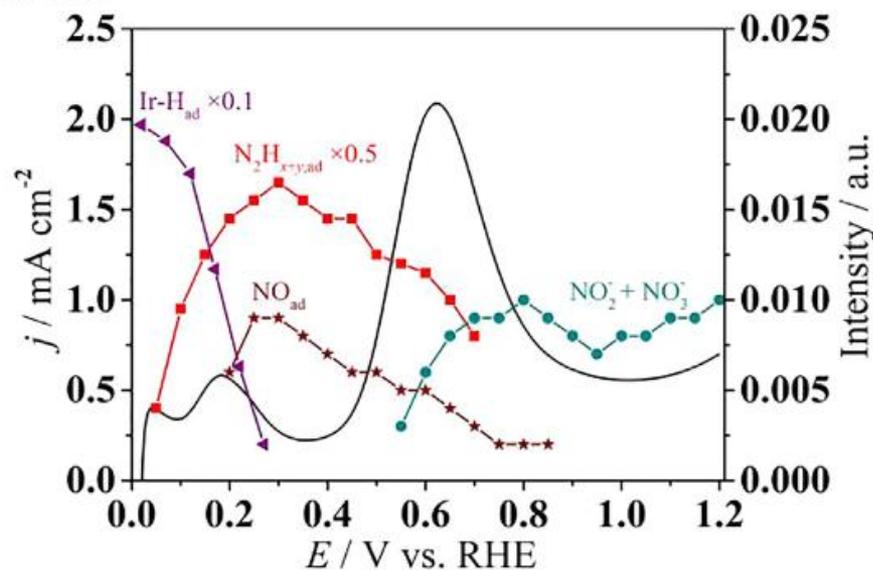


азота на иридии

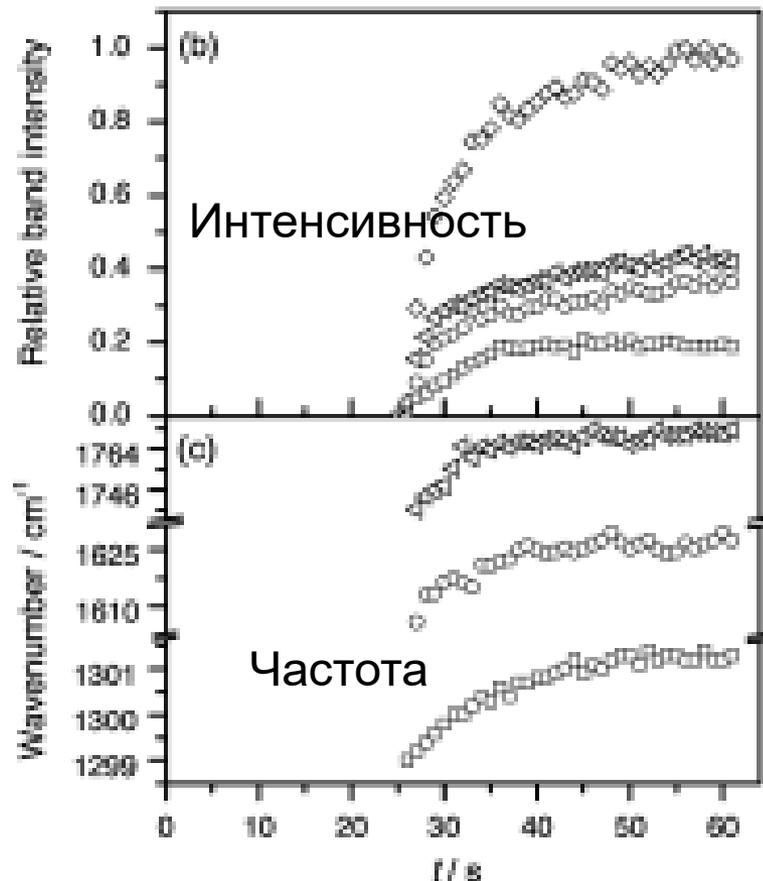
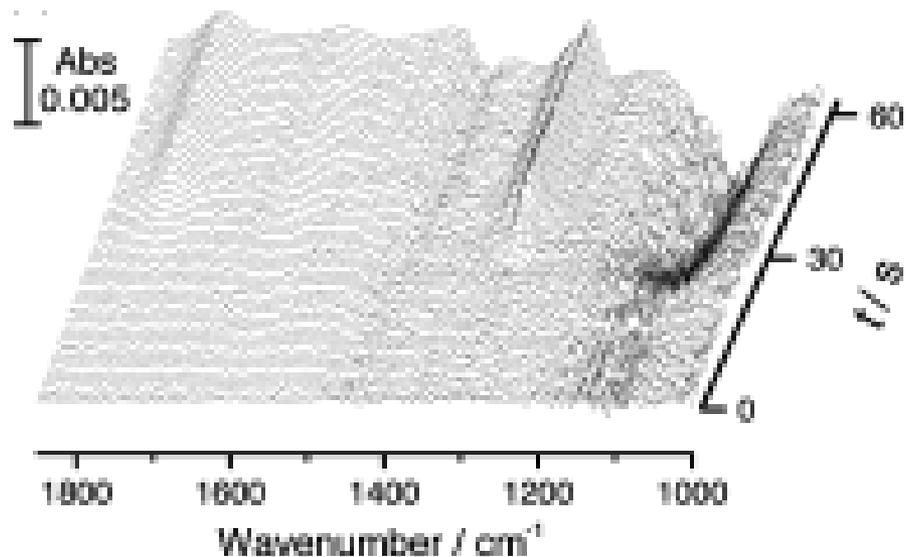


Нитрит:

1681 ~ 1746	$\nu(\text{N}-\text{O})$ of NO (linearly)
1629	$\delta(\text{H}-\text{O}-\text{H})$ of H_2O and $\delta(\text{H}-\text{N}-\text{H})$ of NH_3
1493 ~ 1508	$\nu(\text{N}-\text{O})$ of NO (bridged)
1438 ~ 1462	$\nu(\text{N}-\text{O})$ of NO_3^-
1430 ~ 1454	$\nu(\text{N}-\text{O})$ of NO (hollow)
1296 ~ 1315	$\nu(\text{N}-\text{O})$ of NO_2^- (bridged)
1263 ~ 1285	NH_2 wagging mode of N_2H_4

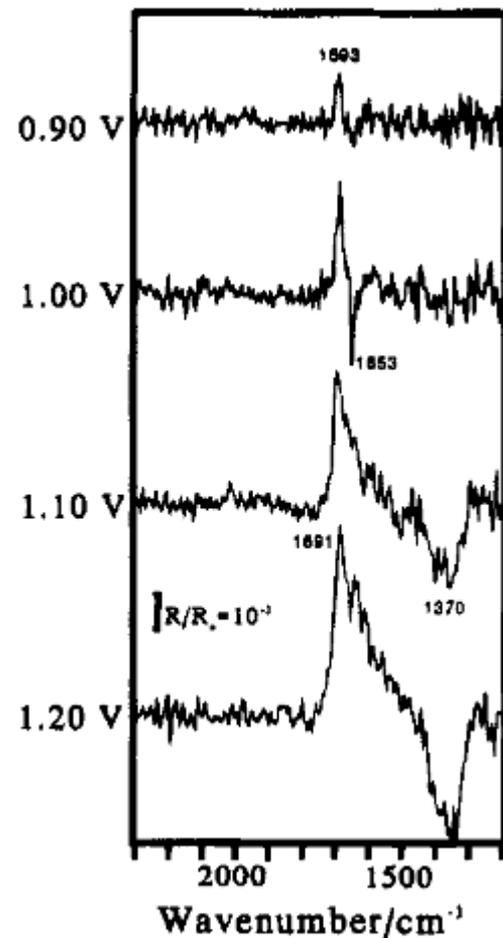
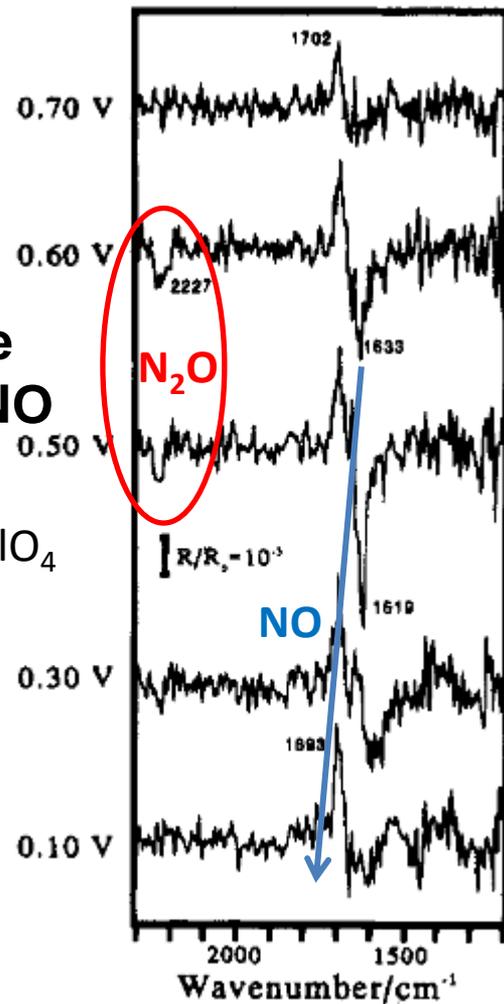
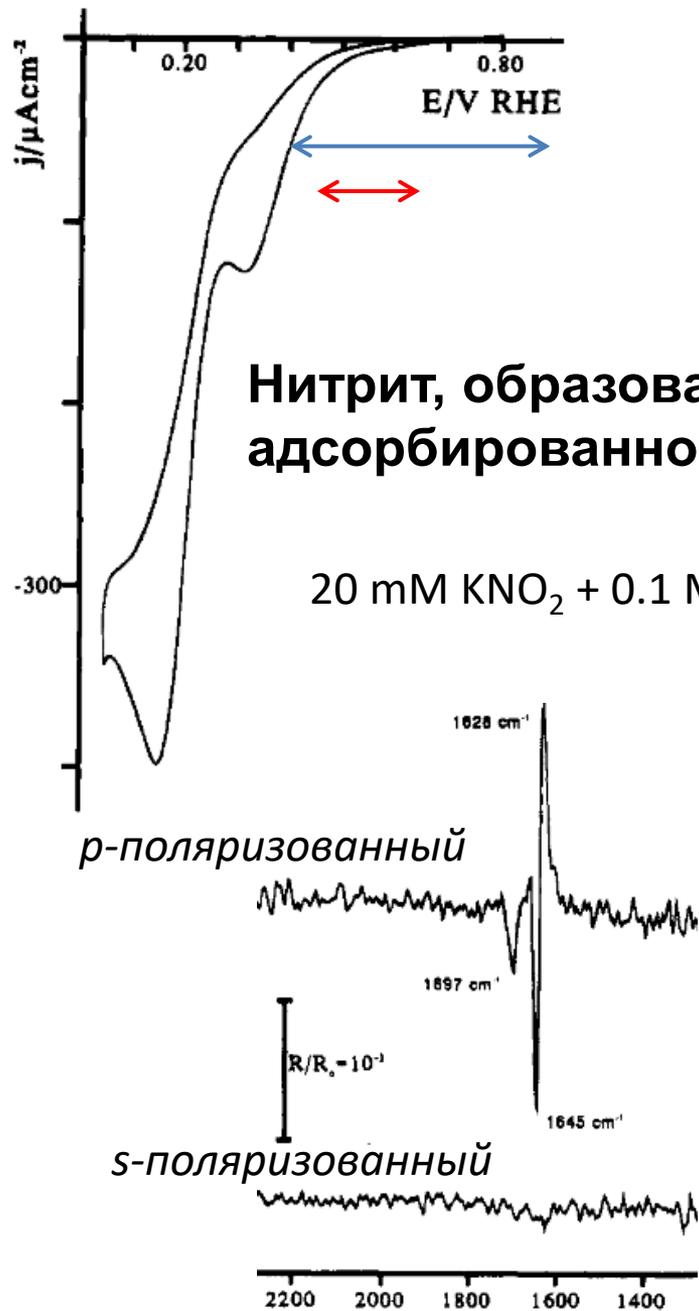


Кинетика адсорбции



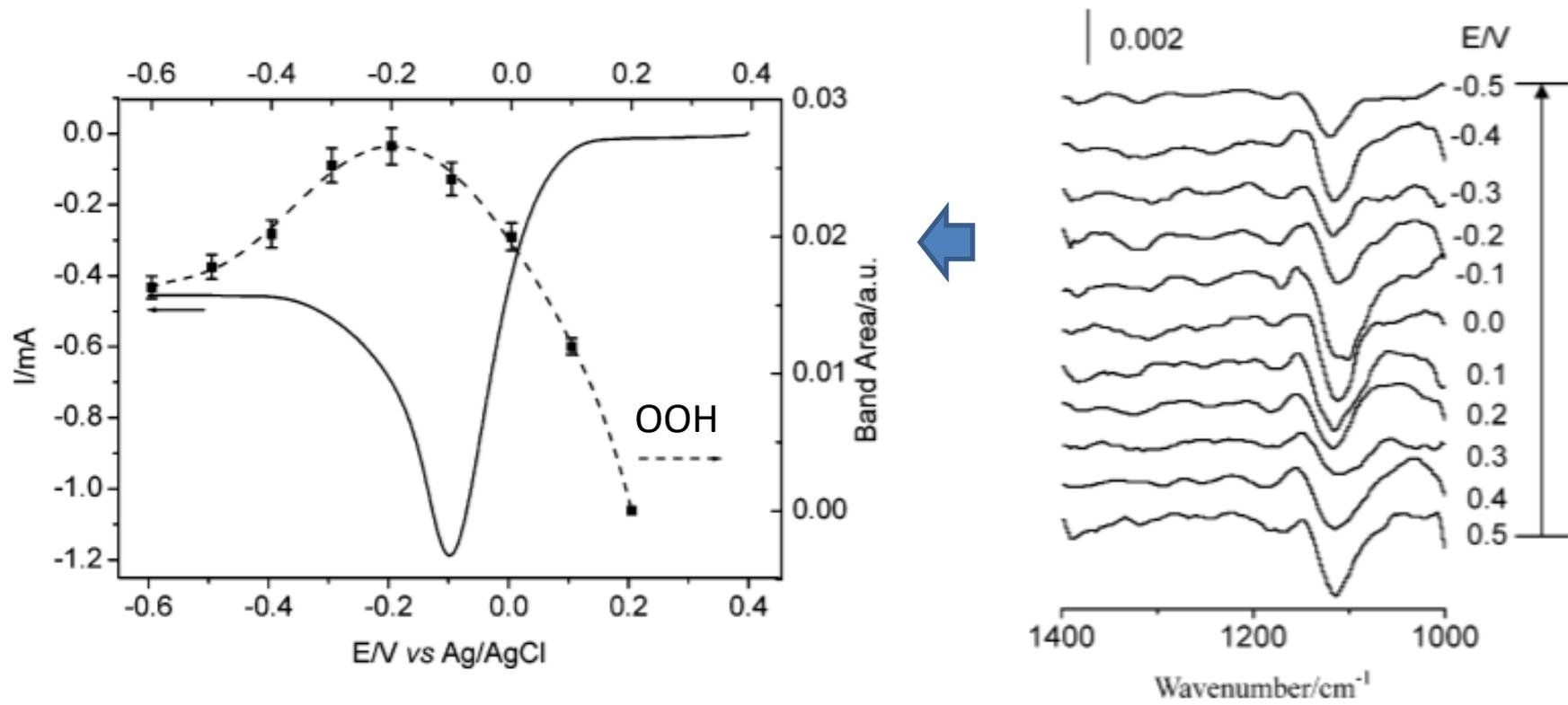
Nitro		
<chem>M-N(=O)=O</chem>	$\nu_2(\text{NO}_2)$ (1343-1488 cm^{-1}) *	$\nu_3(\text{NO}_2)$ (1306-1364 cm^{-1})
Nitrito		
<chem>M-O-N=O</chem>	$\nu(\text{N=O})$ (1393-1485 cm^{-1})	$\nu(\text{N-O})$ (1048-1114 cm^{-1})
Chelating Nitrito		
<chem>M-O-N-O</chem>	$\nu_2(\text{NO}_2)$ (1241-1390 cm^{-1}) *	$\nu_3(\text{NO}_2)$ (1160-1230 cm^{-1})

Нитрит-анион на платине

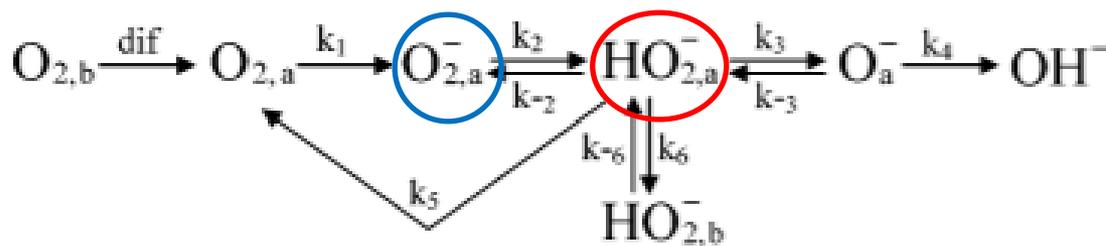


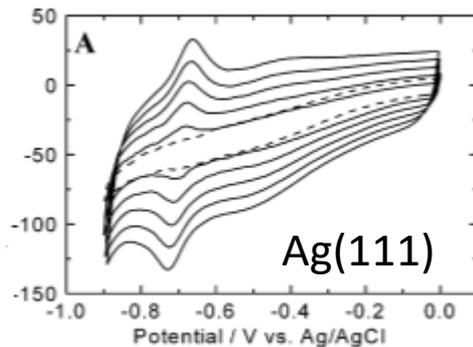
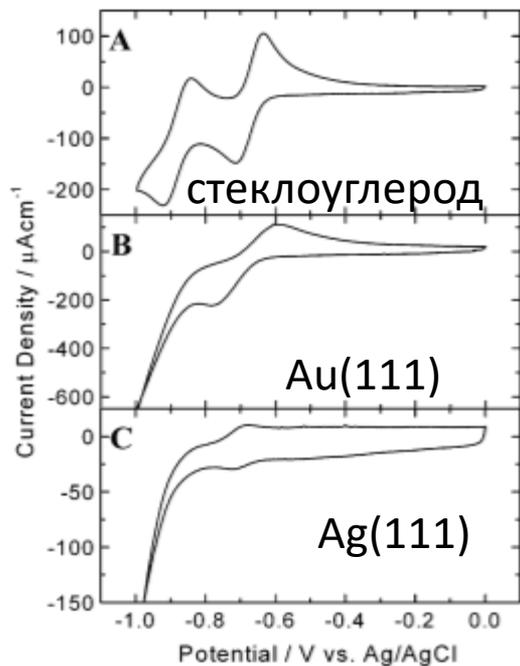
Pt(100), разные потенциалы \rightarrow 0.8 V

Пероксид на золоте (интермедиат восстановления кислорода)



в тяжелой воде

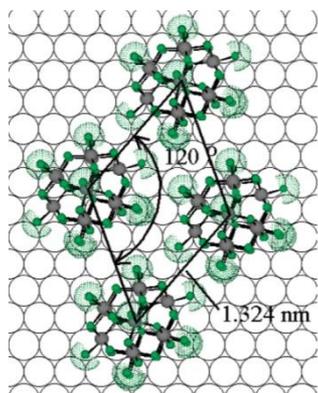
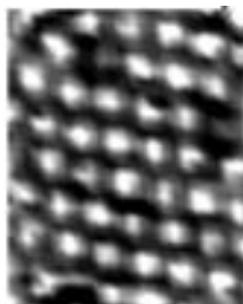
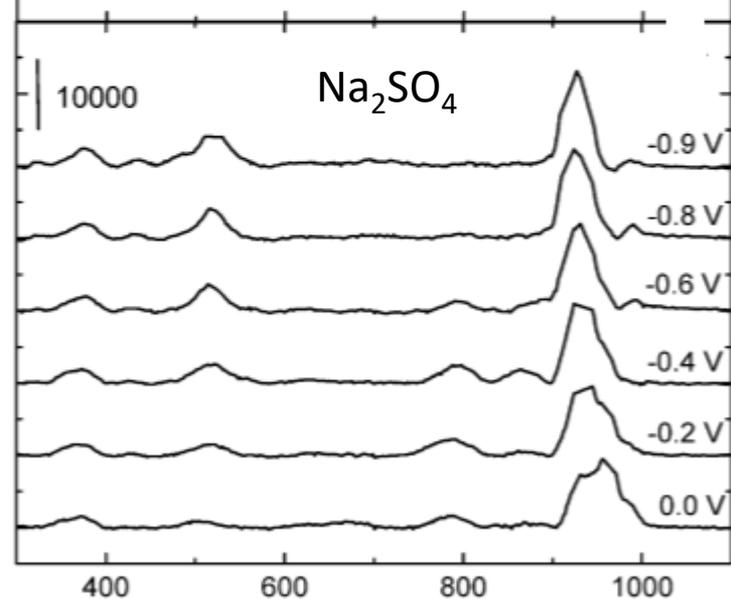
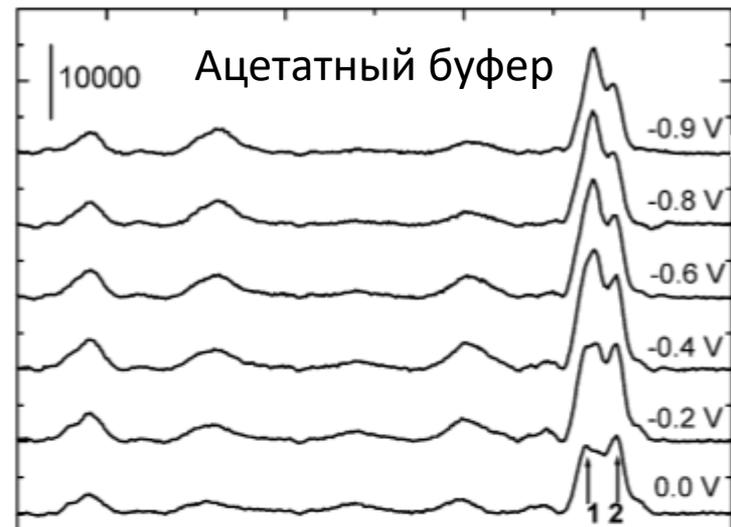




Адсорбированный,
в растворе фона

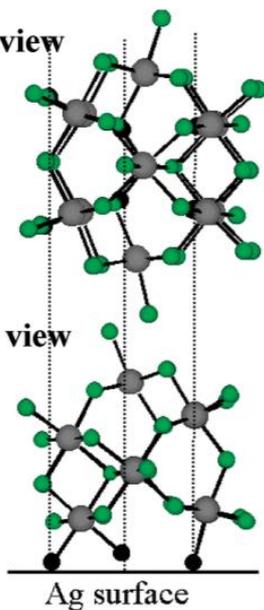
Реагент в
растворе

Лакунарный Кеггинский анион $[\text{SiW}_{11}\text{O}_{39}]^{8-}$



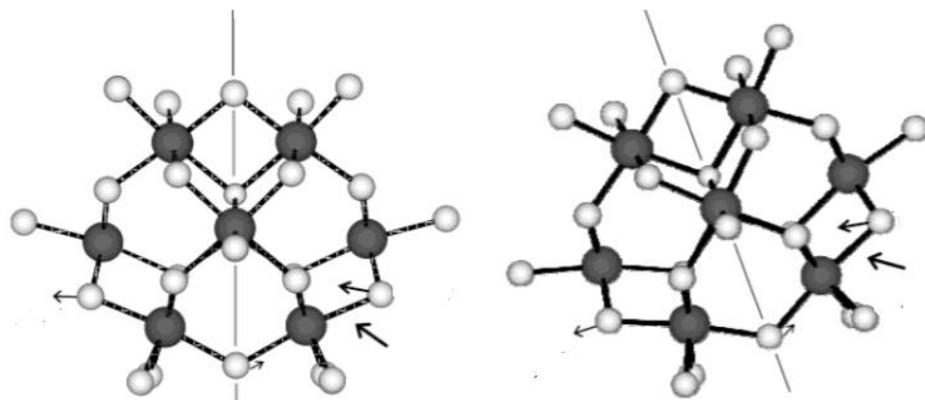
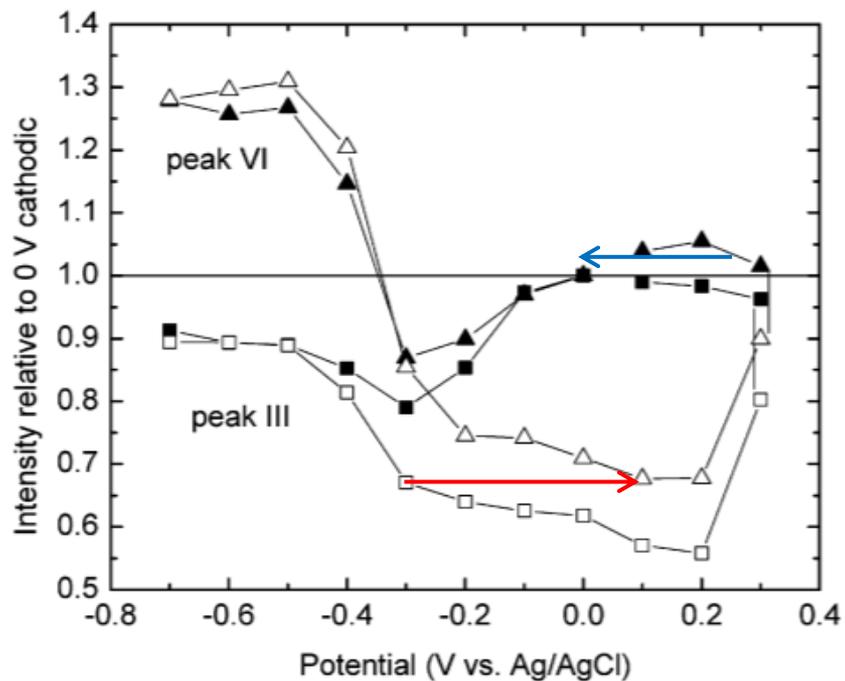
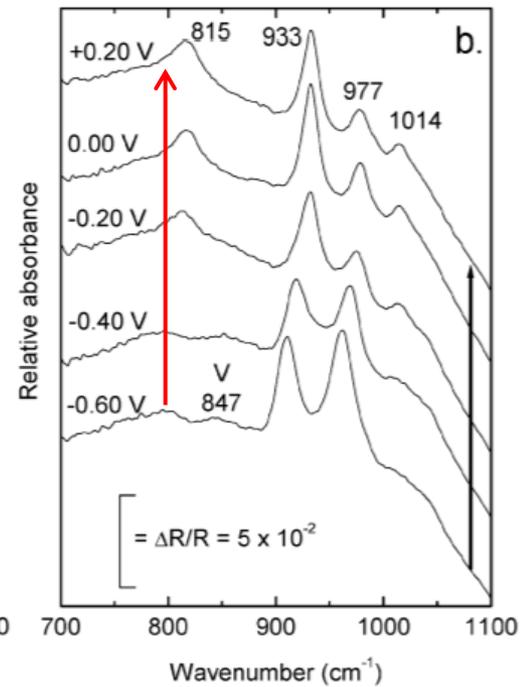
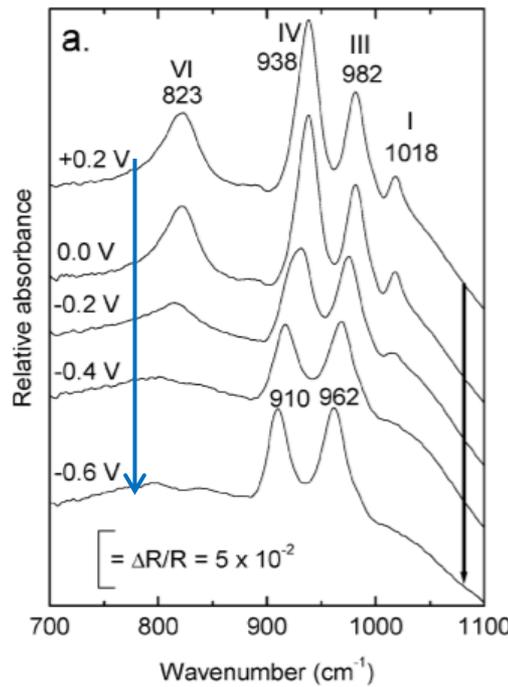
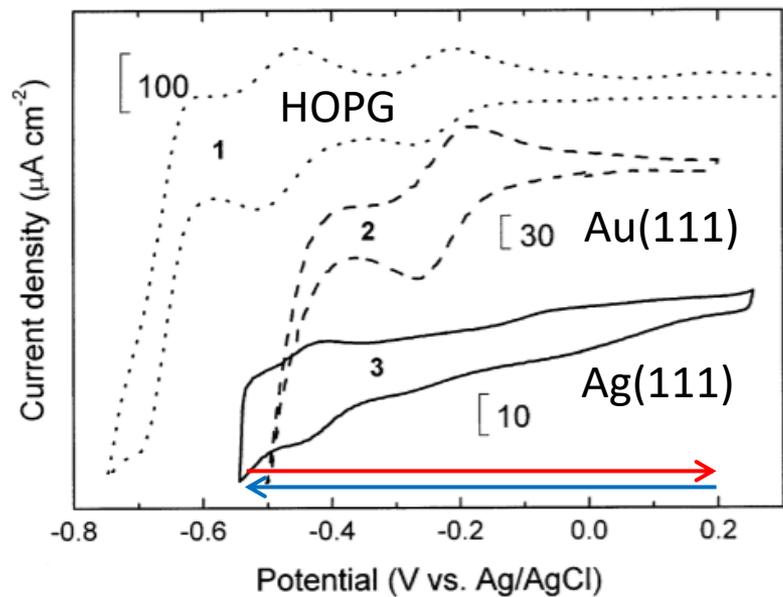
Top view

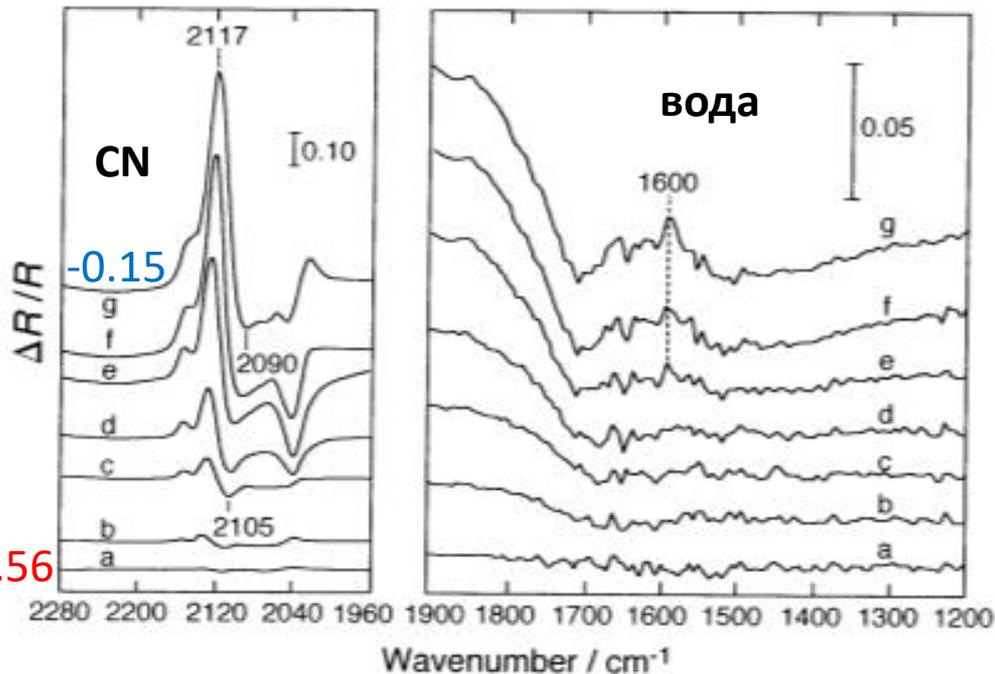
Side view



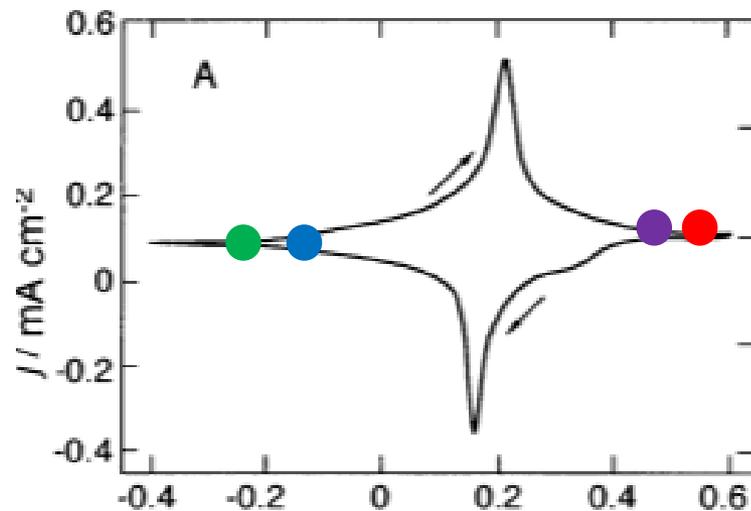
995	$\nu_s \text{ W-O}_t$
971	$\nu_s \text{ W-O}_t$
936	$\nu_s \text{ W-O}_t$
	$\nu_s \text{ W-O}_t$
~887	$\nu_{as} \text{ W-O}_{2c1}-\text{W}$
795	$\nu_{as} \text{ W-O}_{2c2}-\text{W}$
512	$\delta \text{ W-O}_{2c1}-\text{W}; \delta \text{ W-O}_{2c2}-\text{W}$
381	$\delta \text{ W-O}_{2c1}-\text{W}; \delta \text{ W-O}_{2c2}-\text{W};$ $\delta \text{ O-Si-O}$

Кеггинский анион $[\text{SiW}_{12}\text{O}_{40}]^{4-}$





Берлинская лазурь



+0.56

-0.25

