Molecular modelling of heterogeneous electron transfer reactions: where do we stand ?

Renat R. Nazmutdinov

Kazan National Research State Technological University

Moscow, October, 25 2012

Первые работы – предвестники «квантовой электрохимии»

ing these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $8.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1191.

Contribution from the Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822

Quantum Mechanical Description of Electrode Reactions. I. Extended Huckel Molecular Orbital Treatment of the Halide-Bridged Electrode Reactions of Platinum Complexes

CHIU-NAN LAI and ARTHUR T. HUBBARD*

Received July 27, 1973 AIC305631

The extended Huckel molecular orbital method has been employed to calculate the activation energies of the halide bridged electrochemical interconversion of typical Pt(IV) and Pt(II) complexes. Conventional spectroscopic values of the mo parameters were employed. When combined with the theory of absolute rates for adiabatic reactions, the calculated activation energies led to theoretical rates in qualitative agreement with experimental values based upon the Tafel equation and the Gouy-Chapman-Stern theory of electrode processes. Covalent interaction between the reactants and the electrode surface, although important in establishing the reaction pathway, was neglected in these calculations and will be introduced at a later stage. The procedure described here appears to allow unequivocal identification of the electronic states primarily

Расширенный метод Хюккеля

M.A. Leban, A.T. Hubbard, J. Electroanal. Chem. 74 (1976) 253.

(кластерная модель плотности части ДЭС)

М.Ш. Шапник, В.Н Галеев, Электрохимия, 15 (1979) 827.

(теоретико-групповой анализ элементарного акта)

meth

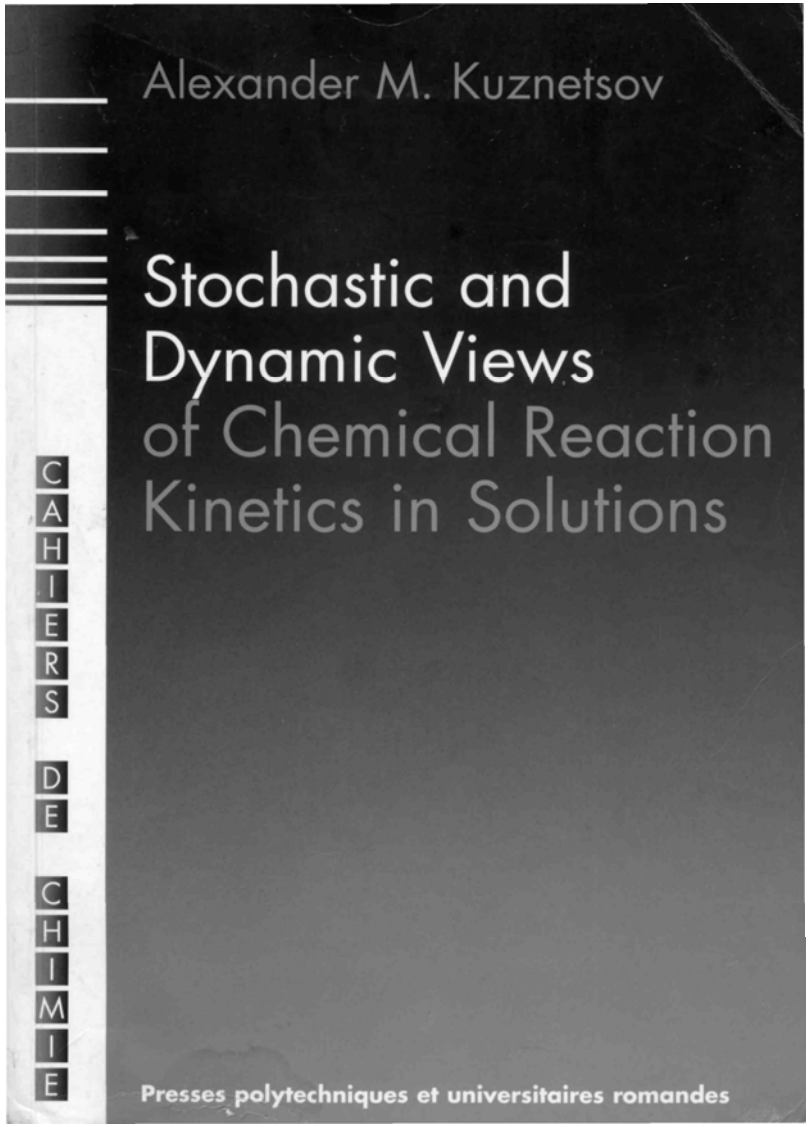
Как моделировать элементарный акт переноса заряда ?

Современная теория переноса заряда

Квантовая химия, Методы молекулярной динамики и Монте-Карло

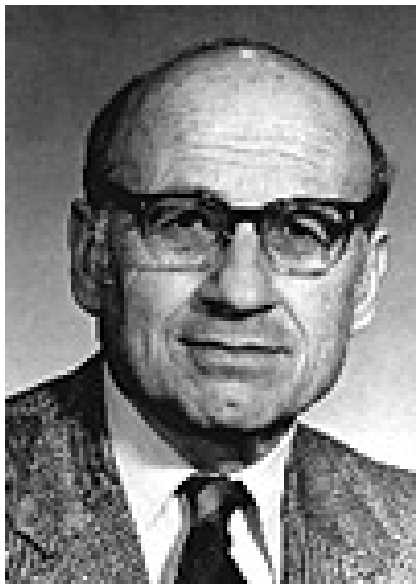
Эксперимент

В настоящее время физические основы реакций переноса заряда в конденсированных средах в целом понятны



В микроскопическом моделировании элементарного акта именно теория играет первую скрипку…

С помощью современных методов квантовой химии сегодня можно «рассчитать всё» :)

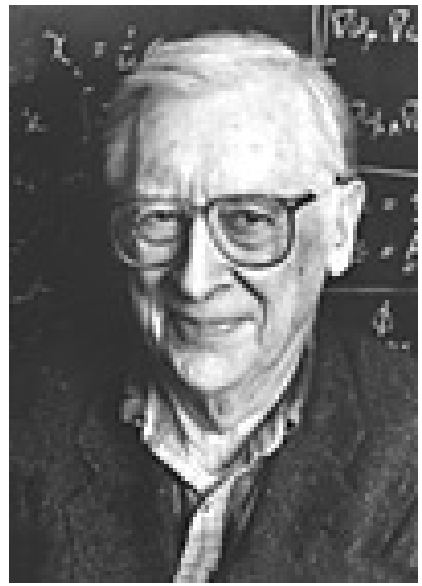


The Nobel Prize in Chemistry 1998

"for his development of the density-functional theory"

Walter Kohn

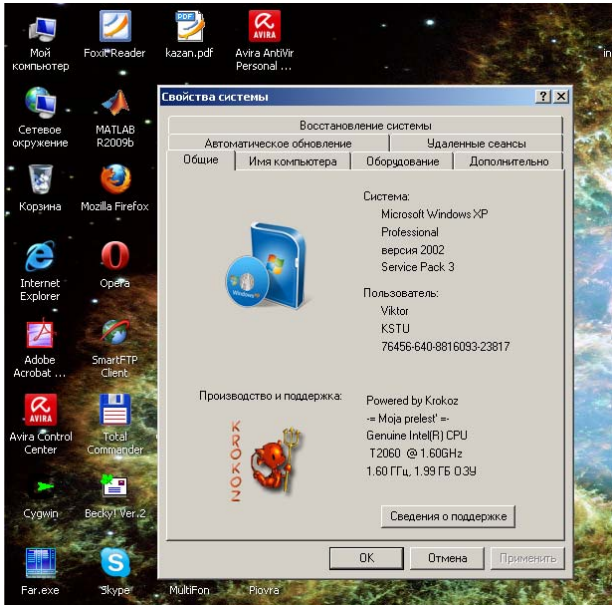
"for his development of computational methods in quantum chemistry"



John Pople

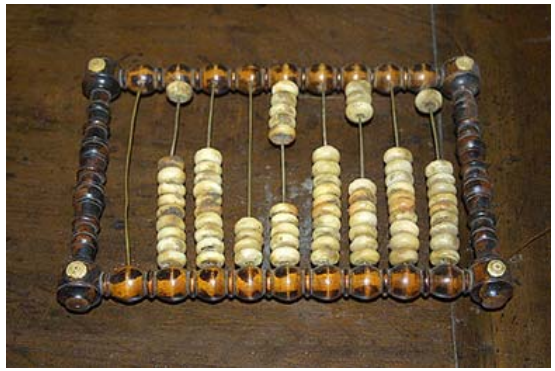
ec

Сегодня



Laptop

Позавчера

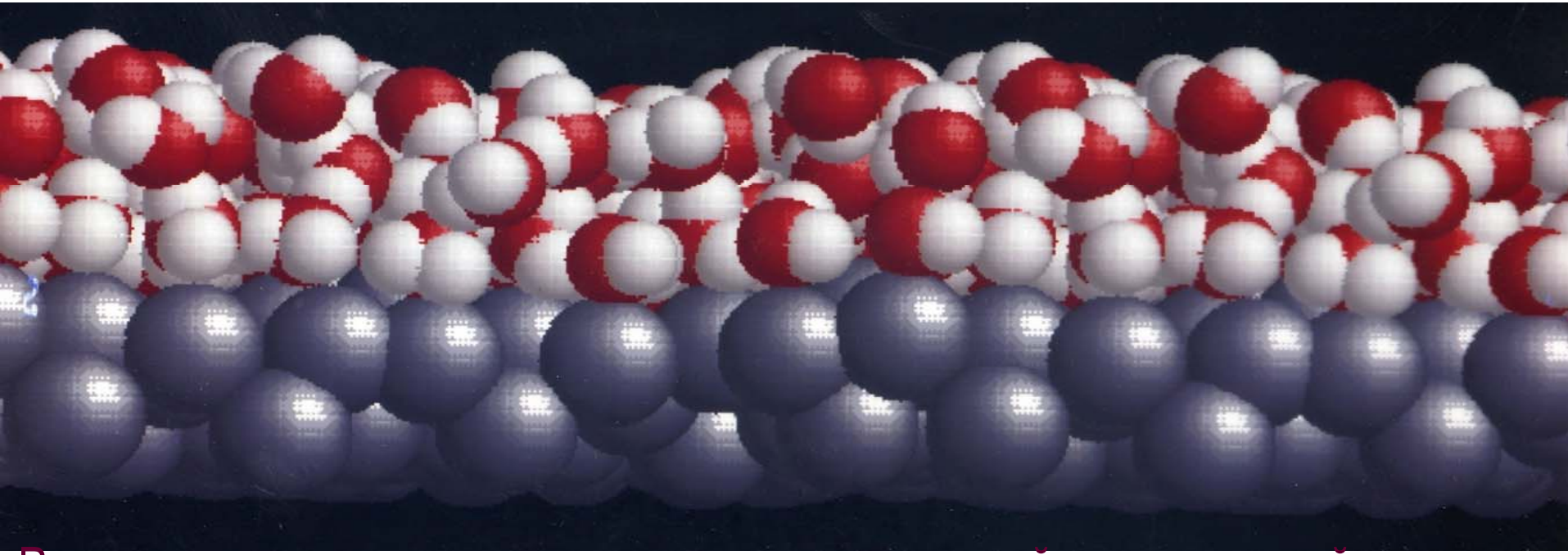


Вчера

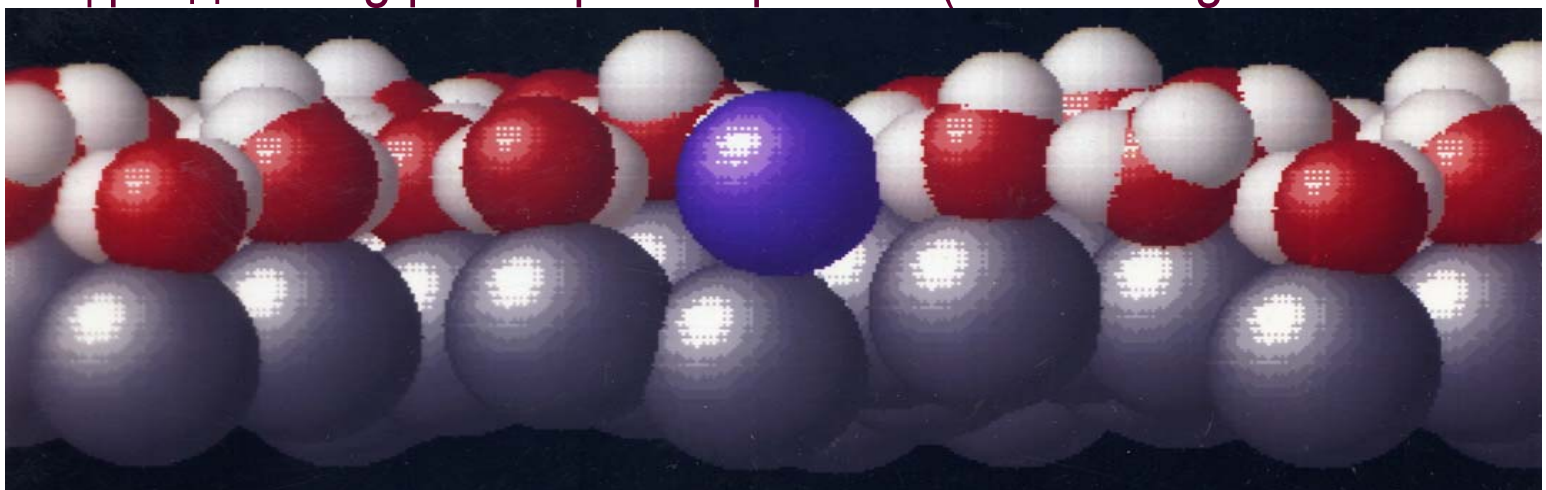
EC-1033 RAM - 0.5M, $2*10^2$ кГц.
EC-1045 RAM- 1M, $8*10^2$ кГц.
Площадь – 200 $м^2$

Завтра ?

Модель реакционного слоя

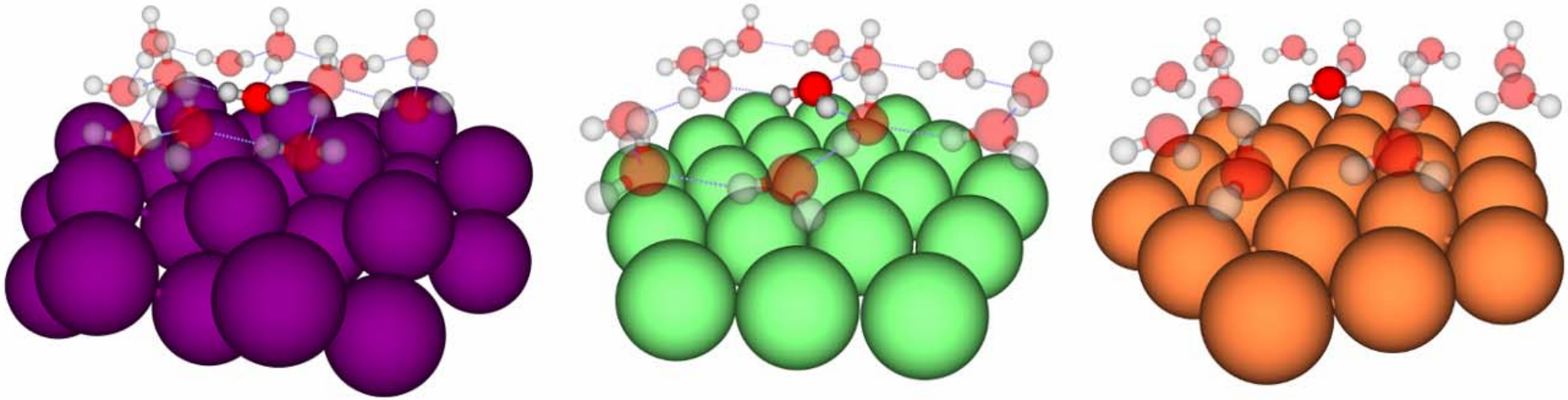


Результаты моделирования методом классической молекулярной динамики границ раздела Hg/раствор электролита (K. Heinzinger and co-workers)



Изучение взаимодействия поверхности электродов с водой – важнейшая задача квантово-химического моделирования

Hydrophilicity row: Ga > Hg ≥ Bi(111)



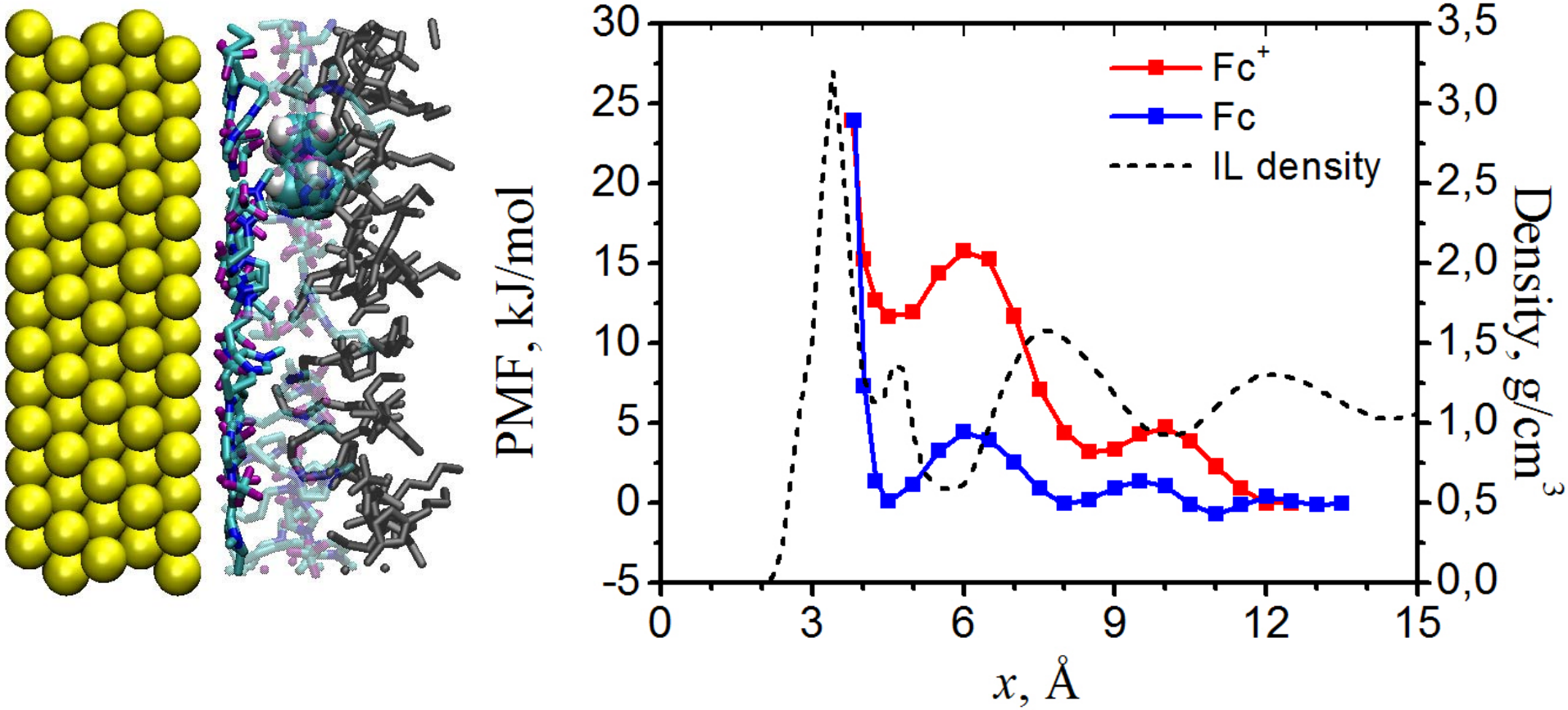
bismuth gallium mercury

Cluster model/DFT

Эффект упрочнения водородных связей в слое адсорбированных молекул воды играет важную роль.

Пример более сложного реакционного слоя

Fc/Fc⁺, Au(111)



MD simulations (S. Kislenko)

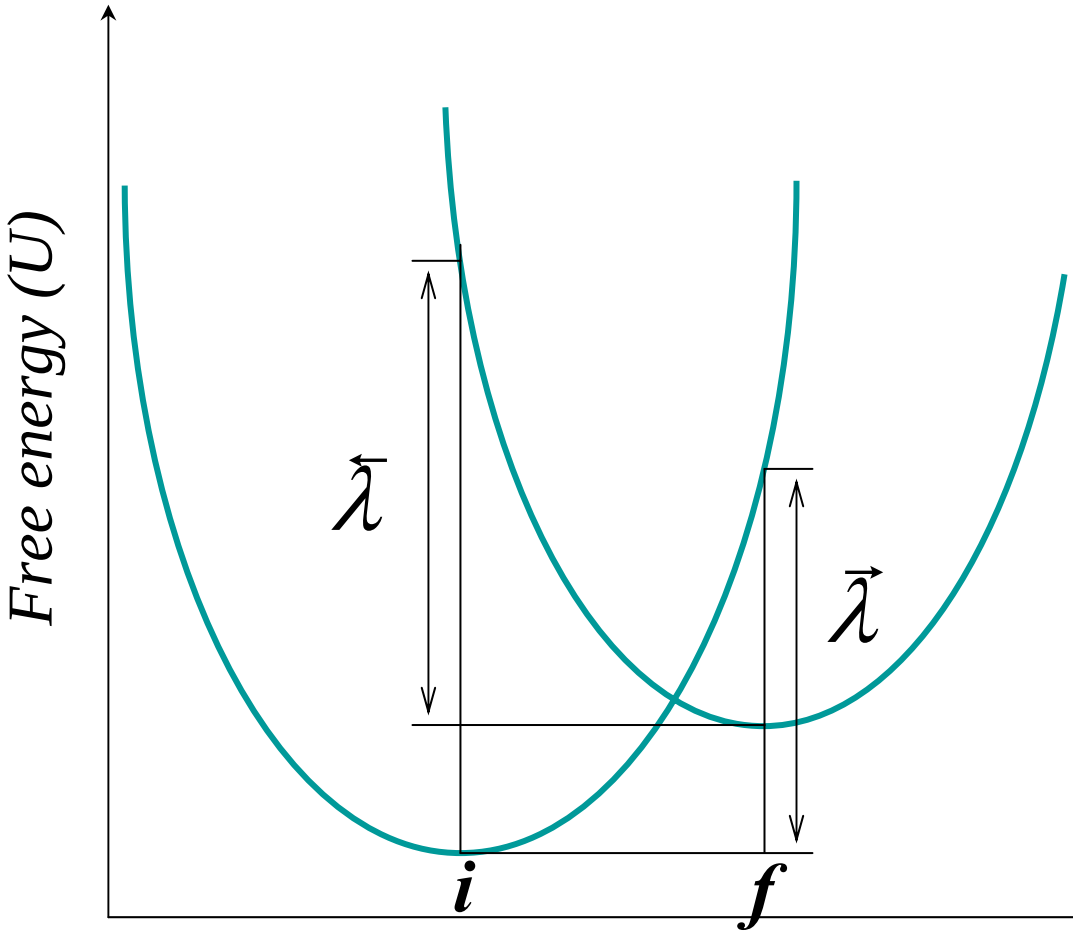
Transition state theory (TST)

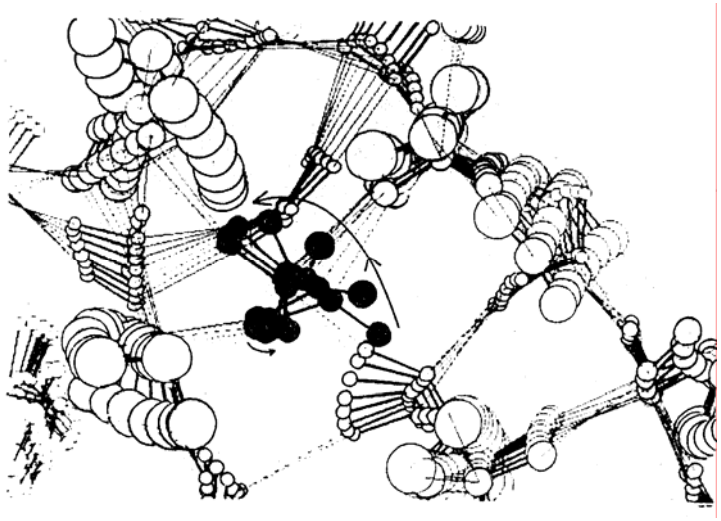
Three-dimensional reaction energy surface (solvent and intramolecular coordinates)

A simple way to define the solvent coordinate

(Marcus theory)

λ is the solvent reorganization energy





(Ohmine, 1992)

$$U_i(q) = \lambda q^2$$

$$U_f(q) = \lambda(q-1)^2 + \Delta I$$

$$\Delta E_a = \frac{(\lambda + \Delta I)^2}{4\lambda}$$

Stochastic theory

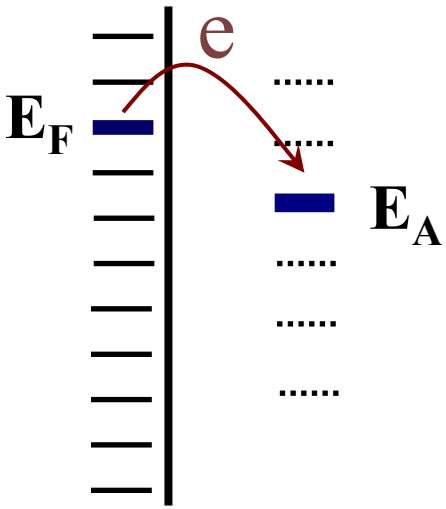
Hendrik A. Kramers
/pioneered a stochastic
appoach in chemical kinetics/

Leonid D. Zusman
/extended Kramers theory
to electron transfer reactions/

Reaction rate depends on dynamical solvent properties as well (*friction, viscosity*)

In terms of stochastic theory an overcoming of the activation barrier more resembles "climbing" (diffusion)

Solvent correlation function



$$K(\tau)=\left\langle E_A(0), E_A(\tau)\right\rangle$$

$$K(\tau) = 2k_B T \lambda_s \frac{Q(\tau)}{Q(0)}$$

$$Q(\tau) = \frac{i}{2\pi}\int_{-\infty}^{\infty} \exp(-i\omega\tau)\left[\frac{1}{\varepsilon(\omega)} - \frac{1}{\varepsilon_\infty}\right]\frac{d\omega}{\omega}$$

S. Mukamel et al.

dielectric spectrum

N solvent modes (exact expansion)

Solvent reorganization energy

correlation times

$$K(\tau) = 2k_B T \lambda \sum_{i=1}^{N} \delta_i \exp(-\tau / \tau_i^*)$$

Solvent correlation function

$$\sum_{i=1}^{N} \delta_i = 1$$

Динамика элементарного акта напоминает игру оркестра

δ_i is the contribution of *i*-th mode to the solvent reorganization energy

The solvent reorganization energy is “distributed” among N solvent coordinates.

Reaction free energy surface can be described using N solvent coordinate (q_1, … q_N) and (probably) one intramolecular degree of freedom (r):

$$E_i(q_1,\ldots,q_N;r) = \sum_{j=1}^{N} \delta_j \lambda_j q_j^2 + U_i(r)$$

reactant

$$E_f(q_1,\ldots,q_N;r) = \sum_{j=1}^{N} \delta_j \lambda_j (q_j - 1)^2 + U_f(r) + \Delta I$$

product

Usually N = 2 (e.g., dimethylacetamide), 3 (EG, alcohols etc)

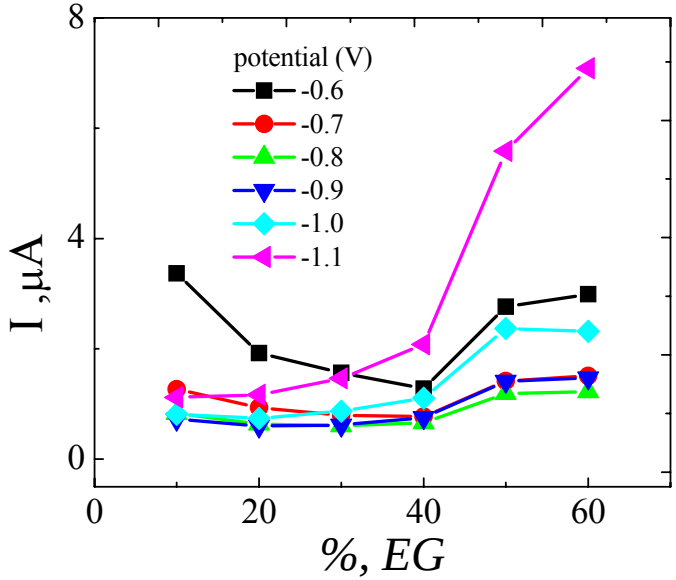
$S_2O_8^{2-}$ reduction at a mercury electrode from water-EG mixtures

$$S_2O_8^{2-} + e = SO_4^{2-} + SO_4^{-}$$

The first ET is rate limiting

- reaction is <u>adiabatic</u>

- <u>BBET</u> reaction proceeds at large overvoltages, in the vicinity of activationless discharge, i.e. at <u>small</u> activation barriers



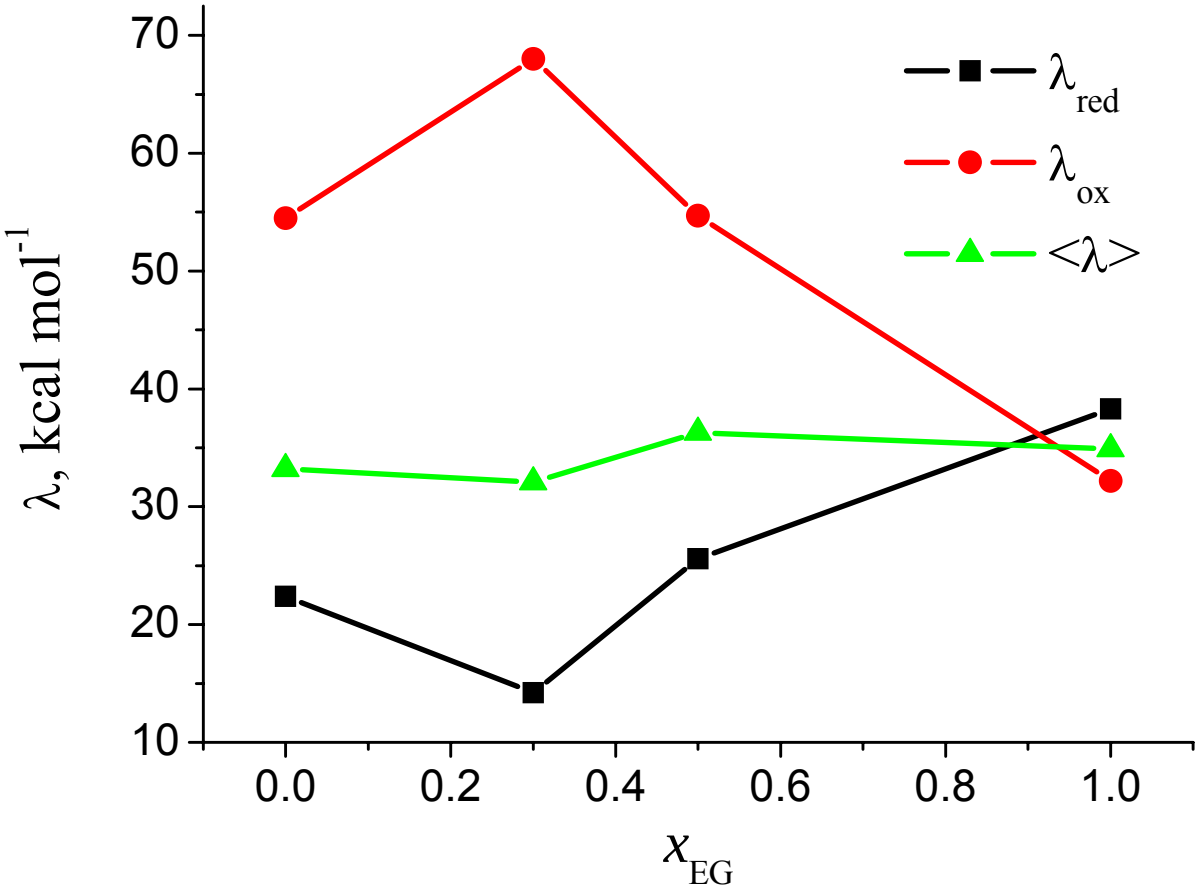
- reaction reveals an <u>anomalous solvent viscosity effect</u>

Exp. data (P.A. Zagrebin et al)

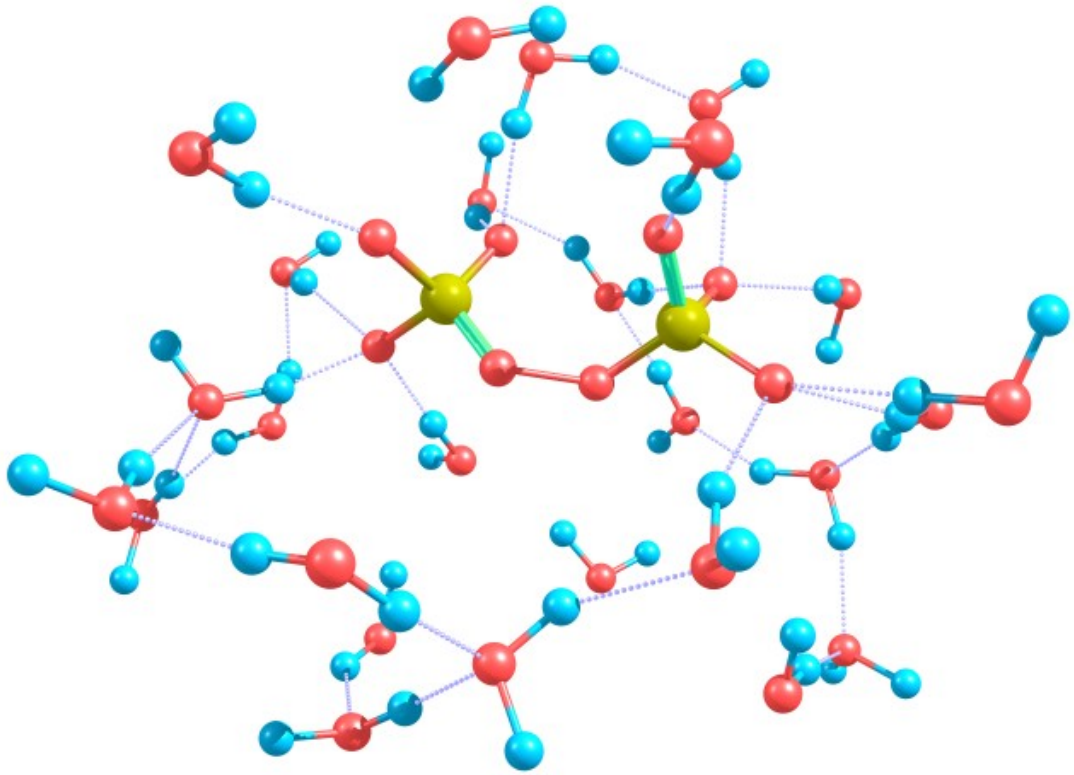
- Pekar factor in the solvent reorganization energy is nearly constant

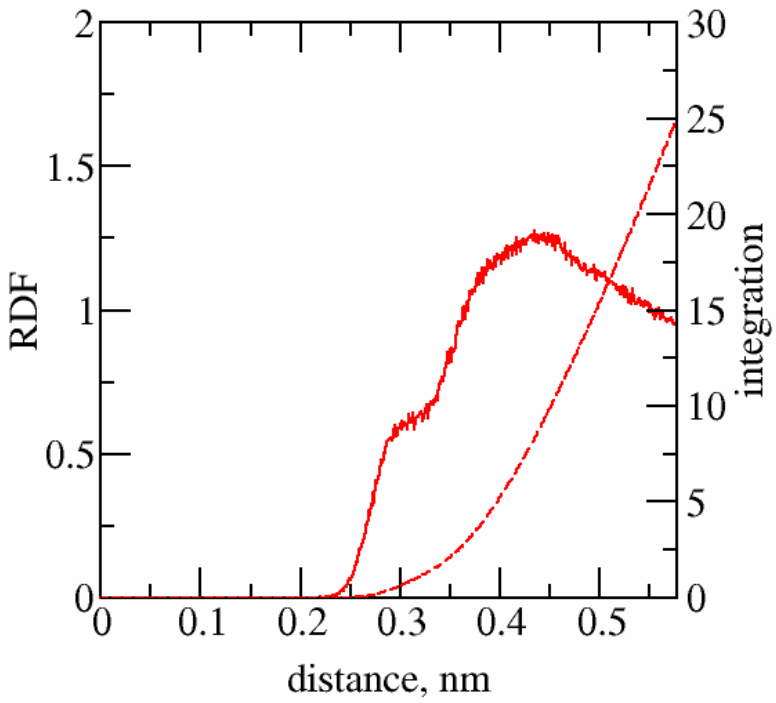
- MD simulations predict even a slight increase of $\langle\lambda\rangle$

Bulk contribution to the solvent reorganization energy as computed form molecular dynamics (O. Ismailova, M. Probst et al)



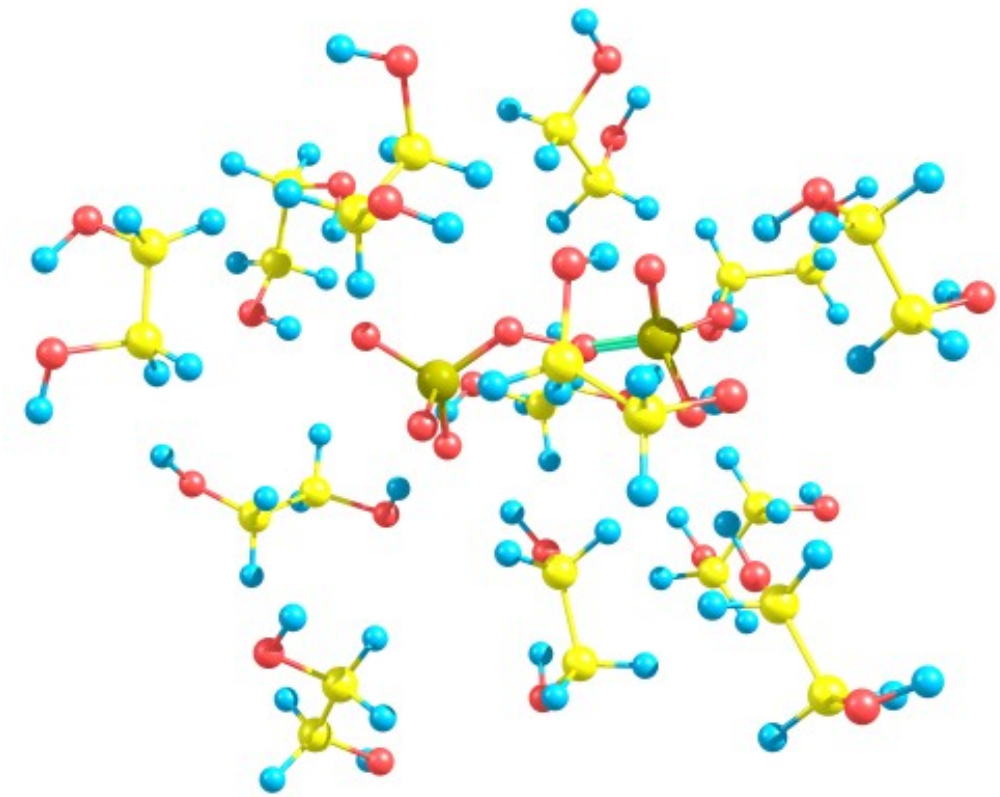
Результаты моделирования методом МД

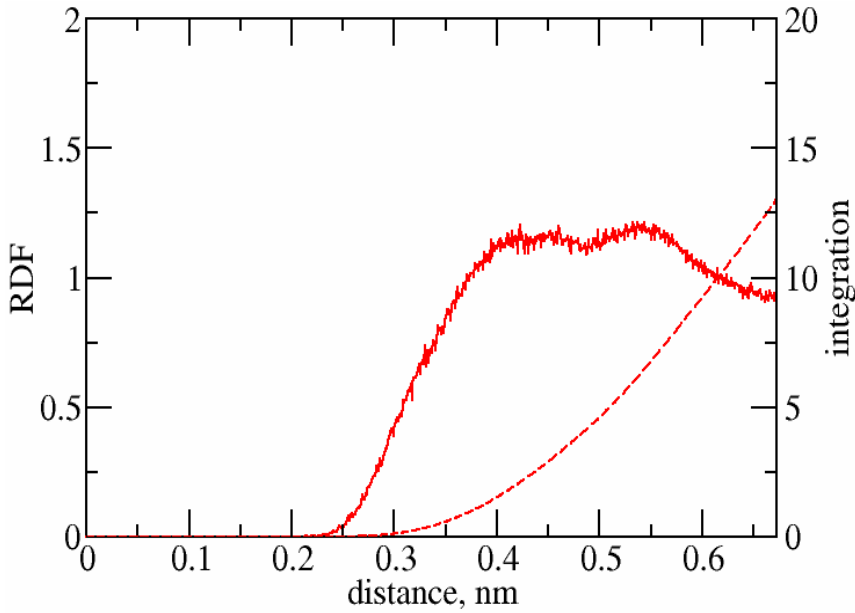




$S_2O_8^{2-}$/water

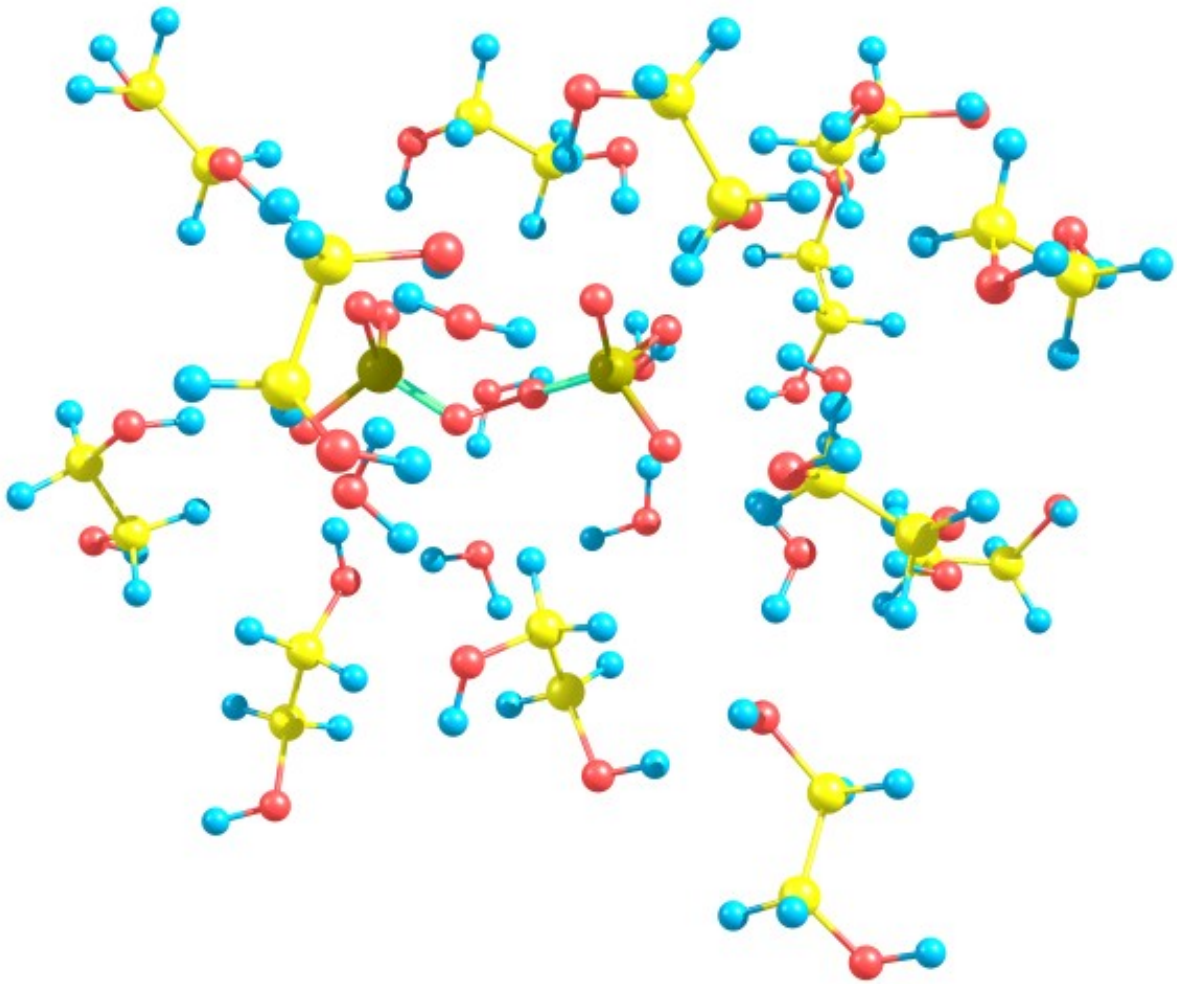
Результаты моделирования методом МД





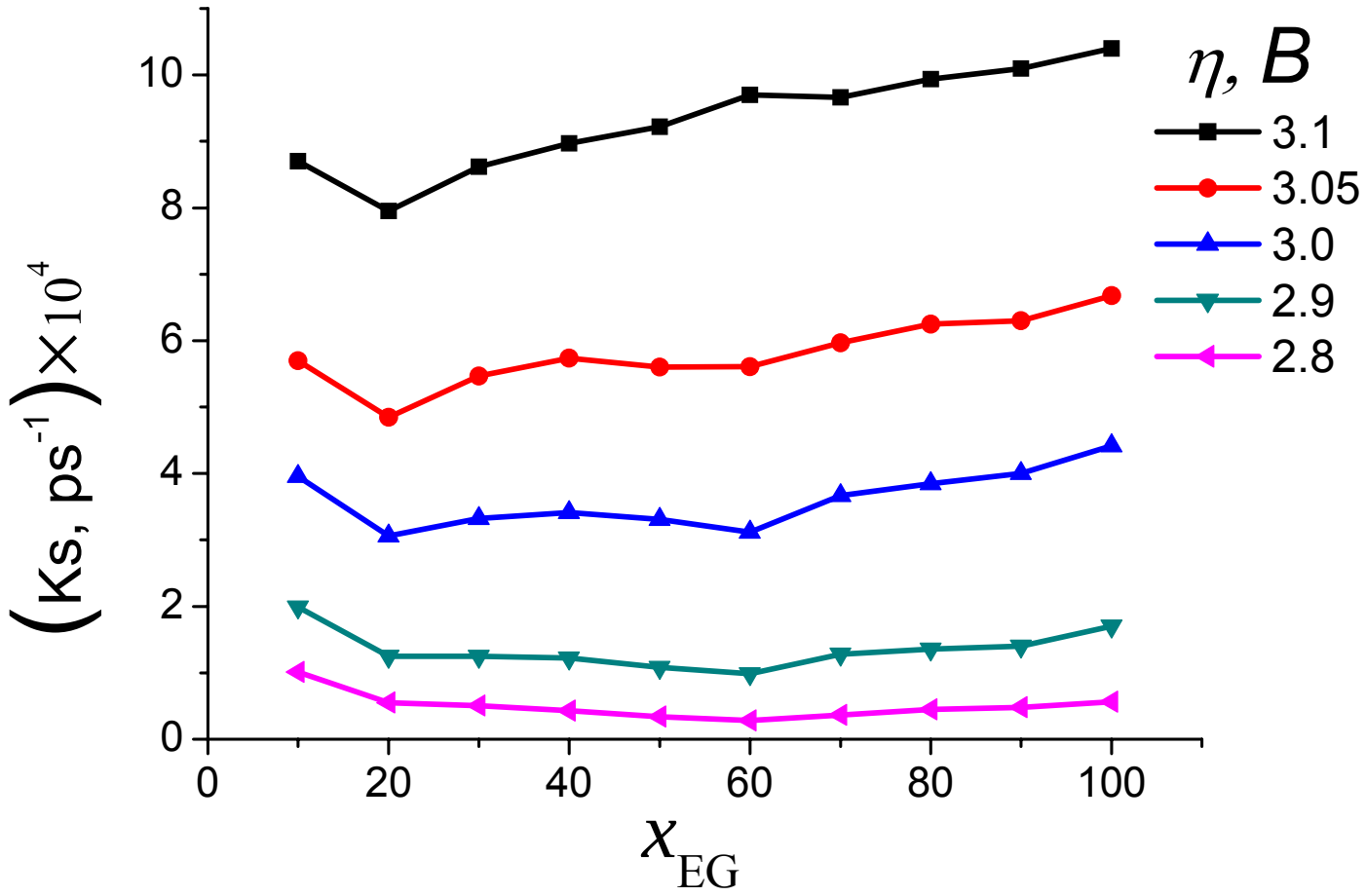
$S_2O_8^{2-}$/EG

Результаты моделирования методом МД (смешанная система, 50%-вода, 50% - этиленгликоль)



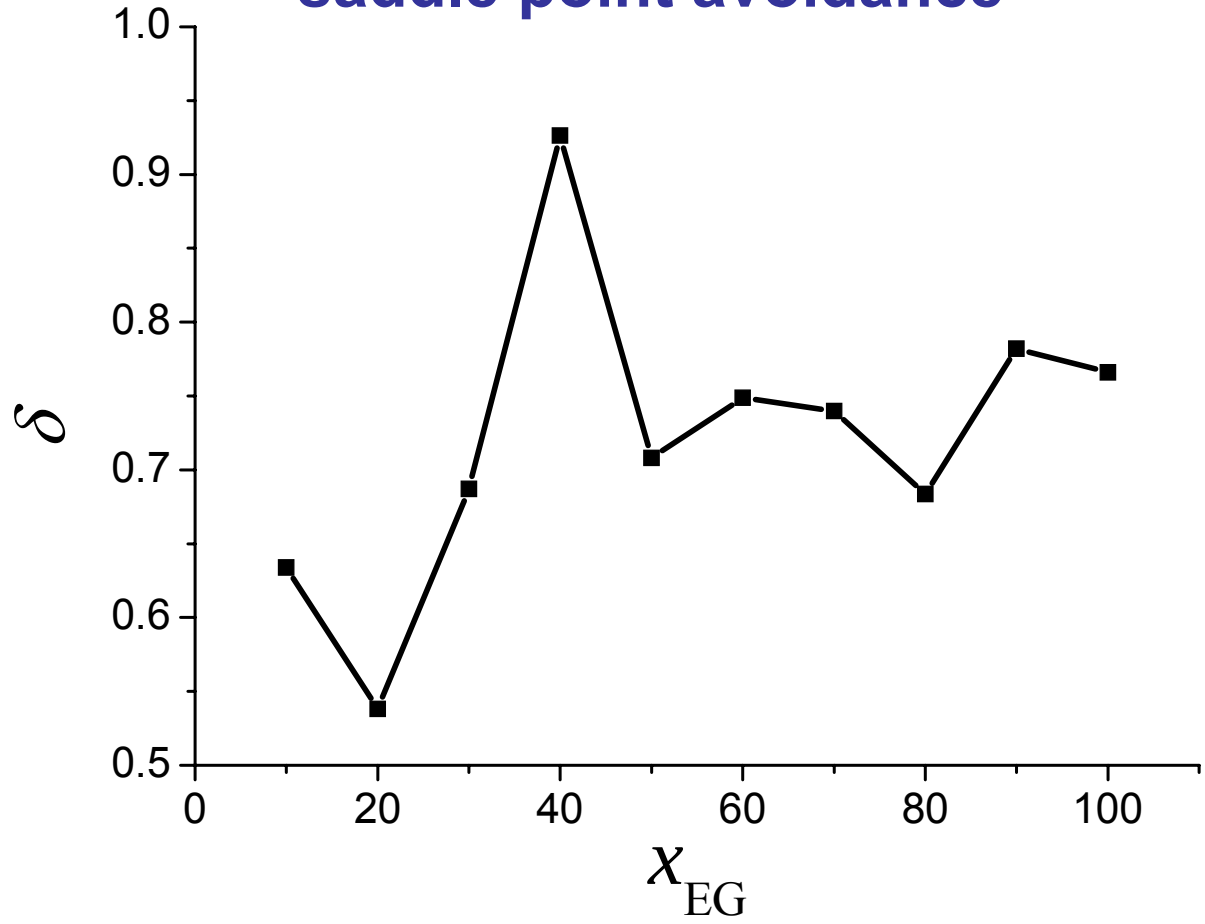
$S_2O_8^{2-}/EG/H_2O$

Results of Langevin molecular dynamics simulations



avoid

An attempt to explain:
saddle point avoidance

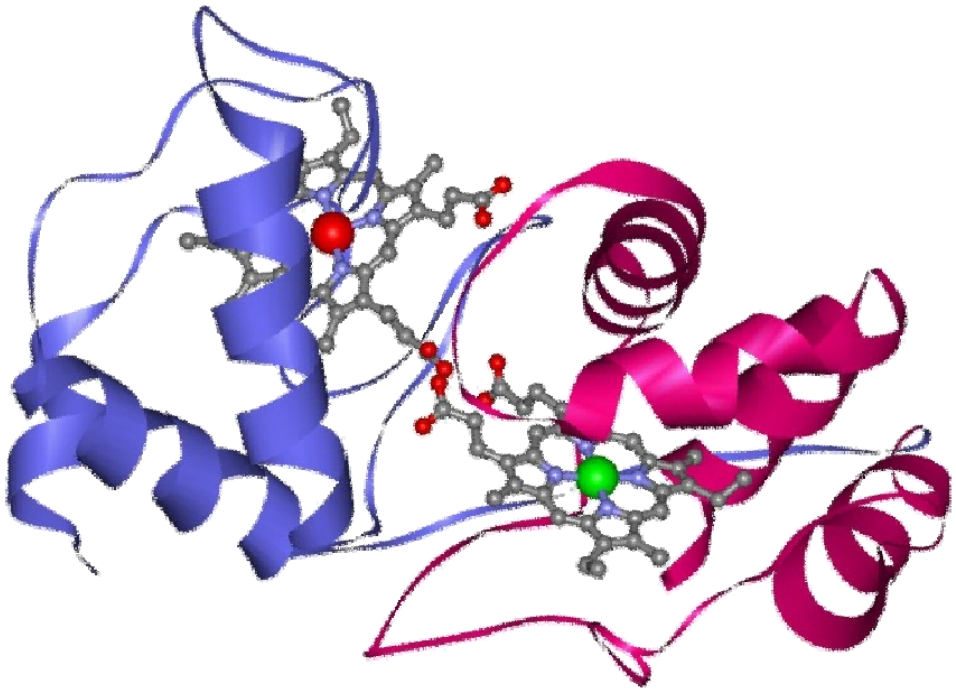


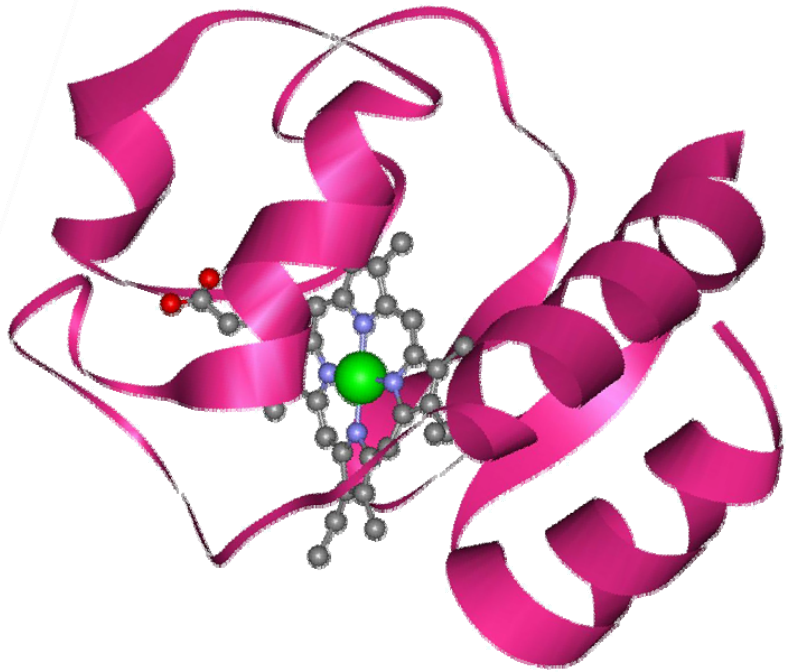
Эффекты отклонения маршрута реакции от седловой точки играют важную роль в интерпретации результатов моделирования.

Построение реакционных поверхностей свободной энергии: проблемы на послезавтра:

Non-Gaussian fluctuations

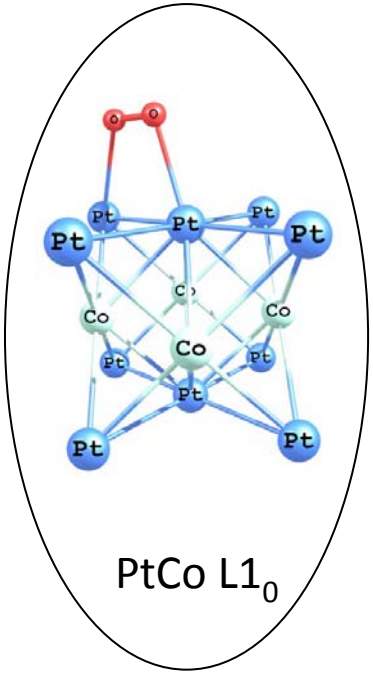
- ferroelectric domains at a protein/water interface
  D.N. LeBard, D.V. Matyushov, PCCP, 12 (2010) 15335





Non-linear response ?

ordered structure



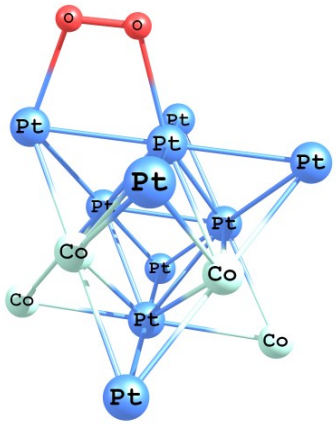
PtCo $L1_0$

Orbital overlap effects (strong coupling)

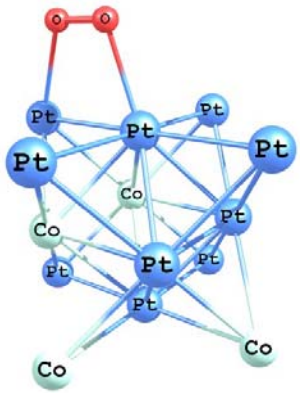
News-Anderson Hamiltonian, narrow band approximation

Ordered PtCo alloys are catalytically more active in the elecroreduction of O_2 (E.R. Savinova et al., exp)

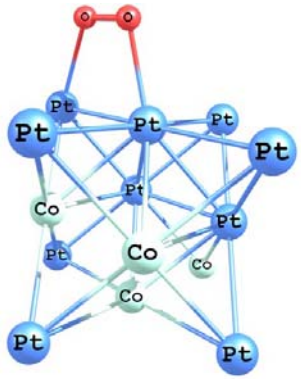
disordered model structures



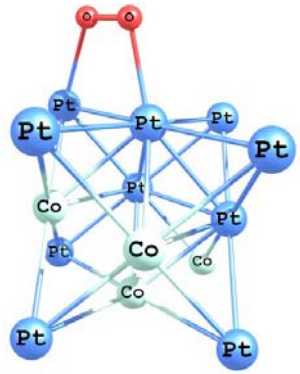
PtCo A1 (i)



PtCo A1 (ii)

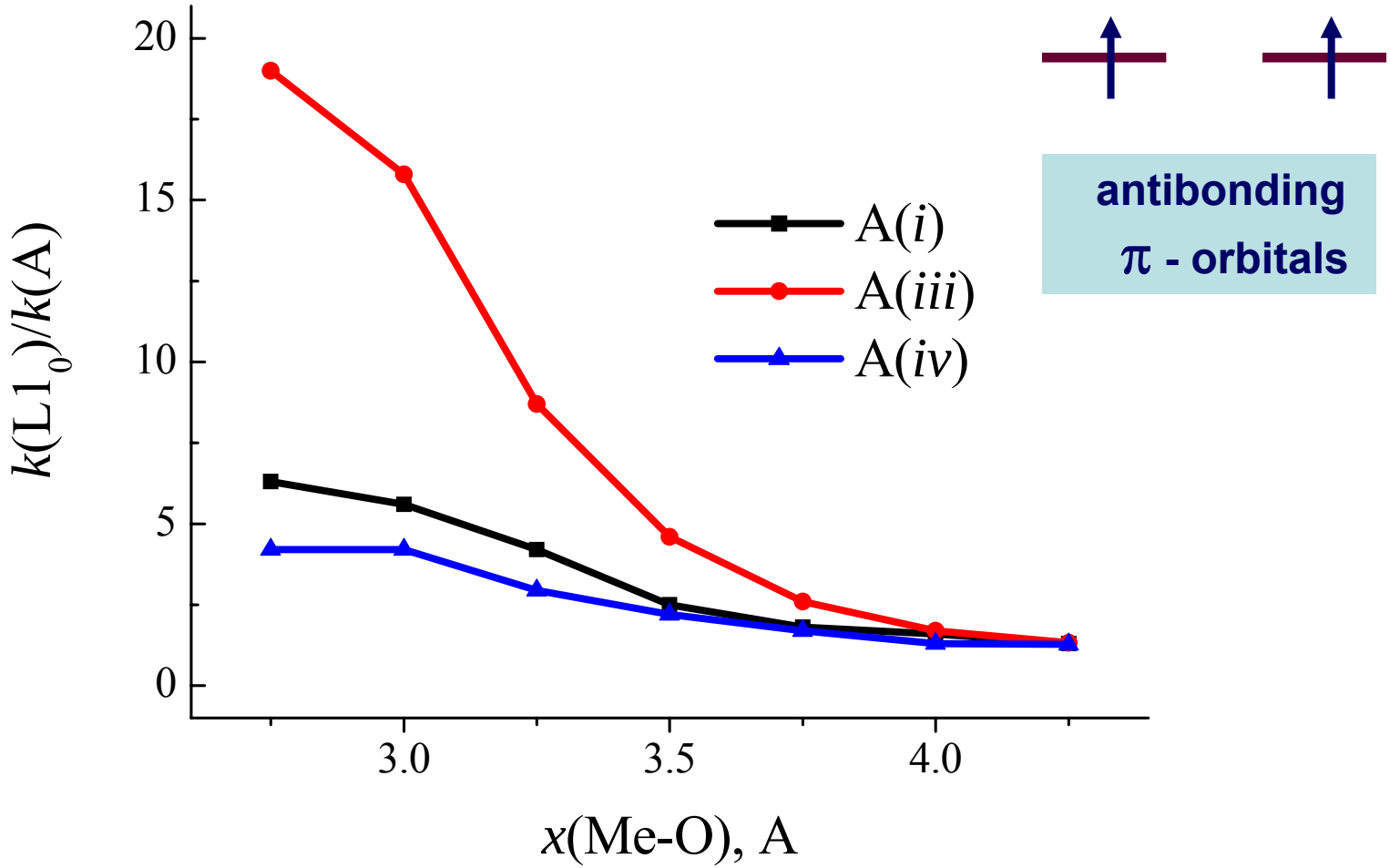


PtCo A1 (iii)



PtCo A1 (iv)

Predicted ratio of rate constants



Ordered PtCo structure is catalytically more active

Electronic transmission coefficient

$$\kappa_e = \frac{1-\exp(-2\pi\gamma_e)}{1-(1/2)\exp(-2\pi\gamma_e)}$$

Landau-Zener factor

half of resonance splitting

$$\gamma_e = \frac{\left(\frac{\Delta E_e}{2}\right)^2}{\hbar\omega_{eff}}\sqrt{\frac{\pi}{(\lambda_s+\lambda_{in})\cdot k_B T}}$$

effective frequency

Two important limiting cases:

$\gamma_e << 1 \Rightarrow \kappa_e \approx \gamma_e$ **(non-adiabatic)**

$\gamma_e >> 1 \Rightarrow \kappa_e \approx 1$ **(adiabatic)**

It is reasonable to employ the perturbation theory for large molecular systems

$$\frac{\Delta E_e}{2} \approx \int \Psi_i \hat{V} \Psi_f dV - \int \Psi_i \hat{V} \Psi_i dV \cdot \int \Psi_i \Psi_f dV$$

Perturbation (molecular electrostatic potential)

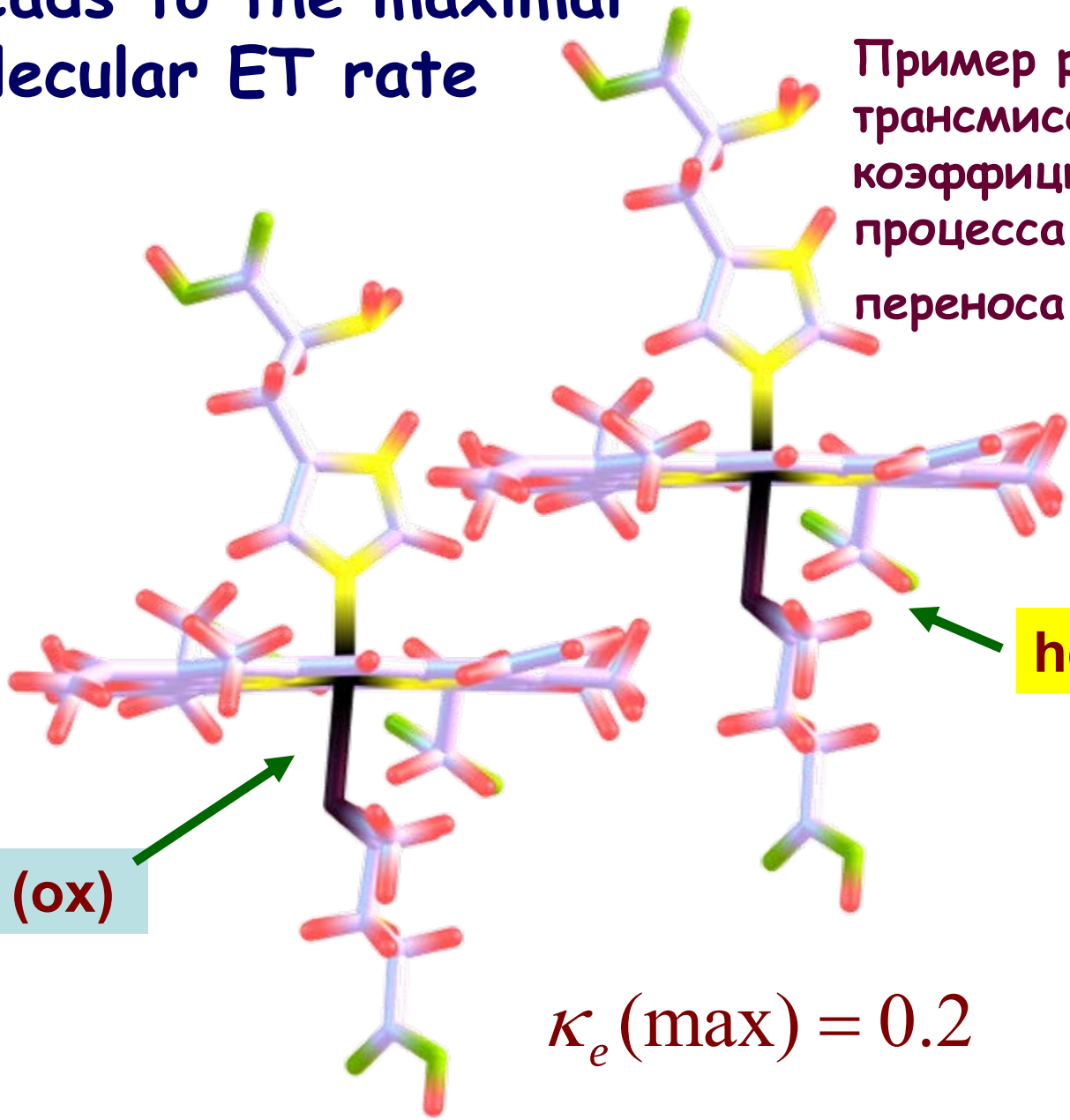
$$V(\vec{r}) = -\sum_i \frac{Z_i}{\left|\vec{R}_i - \vec{r}\right|} + \sum_j \int \frac{\left|\psi_j\left(\vec{r}^{\,\prime}\right)\right|^2 d\Omega^{\prime}}{\left|\vec{r}^{\,\prime} - \vec{r}\right|}$$

$$V(\vec{r}) \approx \sum_i \frac{q_i^*}{\left|\vec{R}_i - \vec{r}\right|}$$

ChelpG atomic charges

Orientation of the cyt c_4 heme groups which leads to the maximal intramolecular ET rate

Пример расчёта трансмиссионного коэффициента для процесса гомогенного переноса электрона

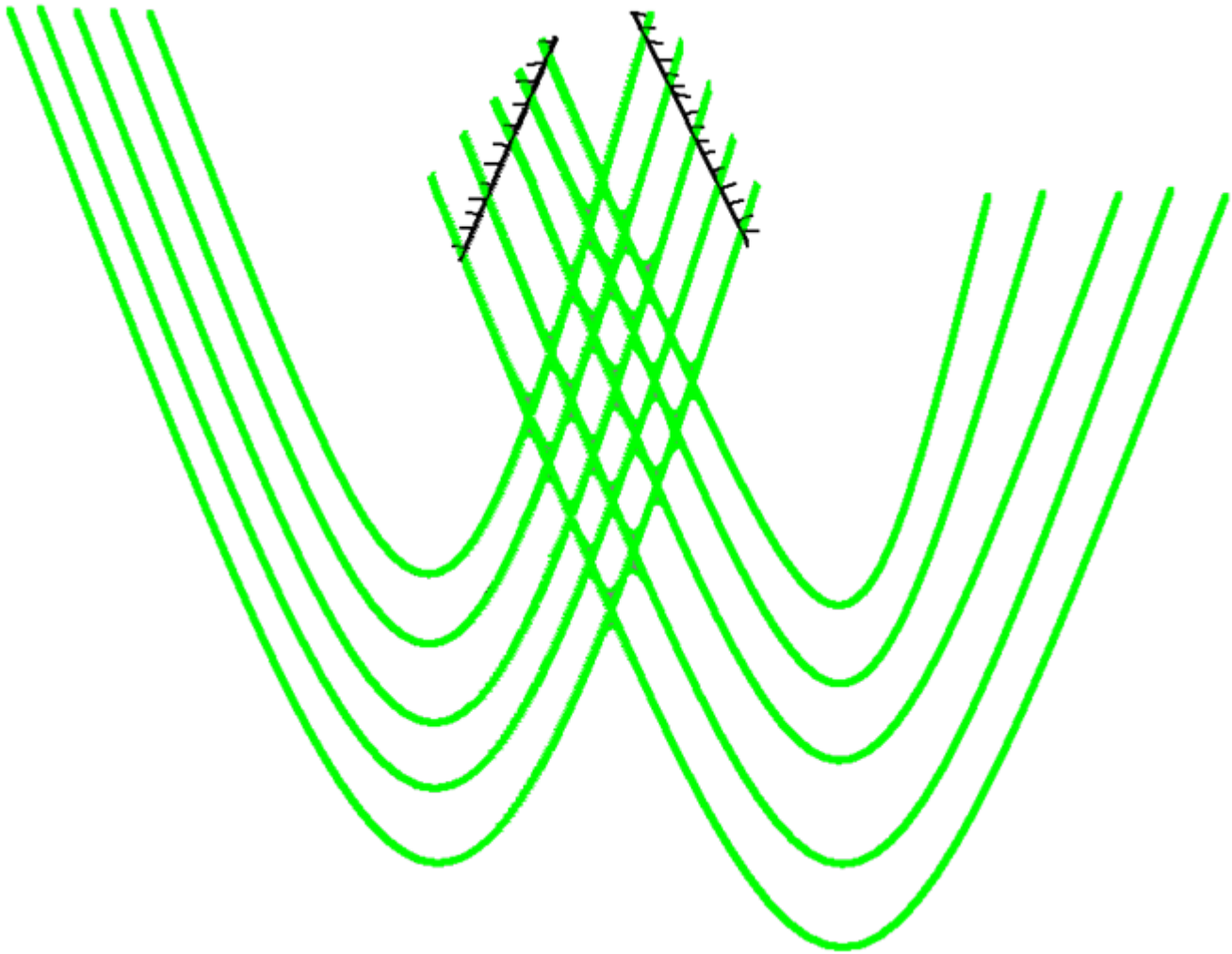


heme B (red)

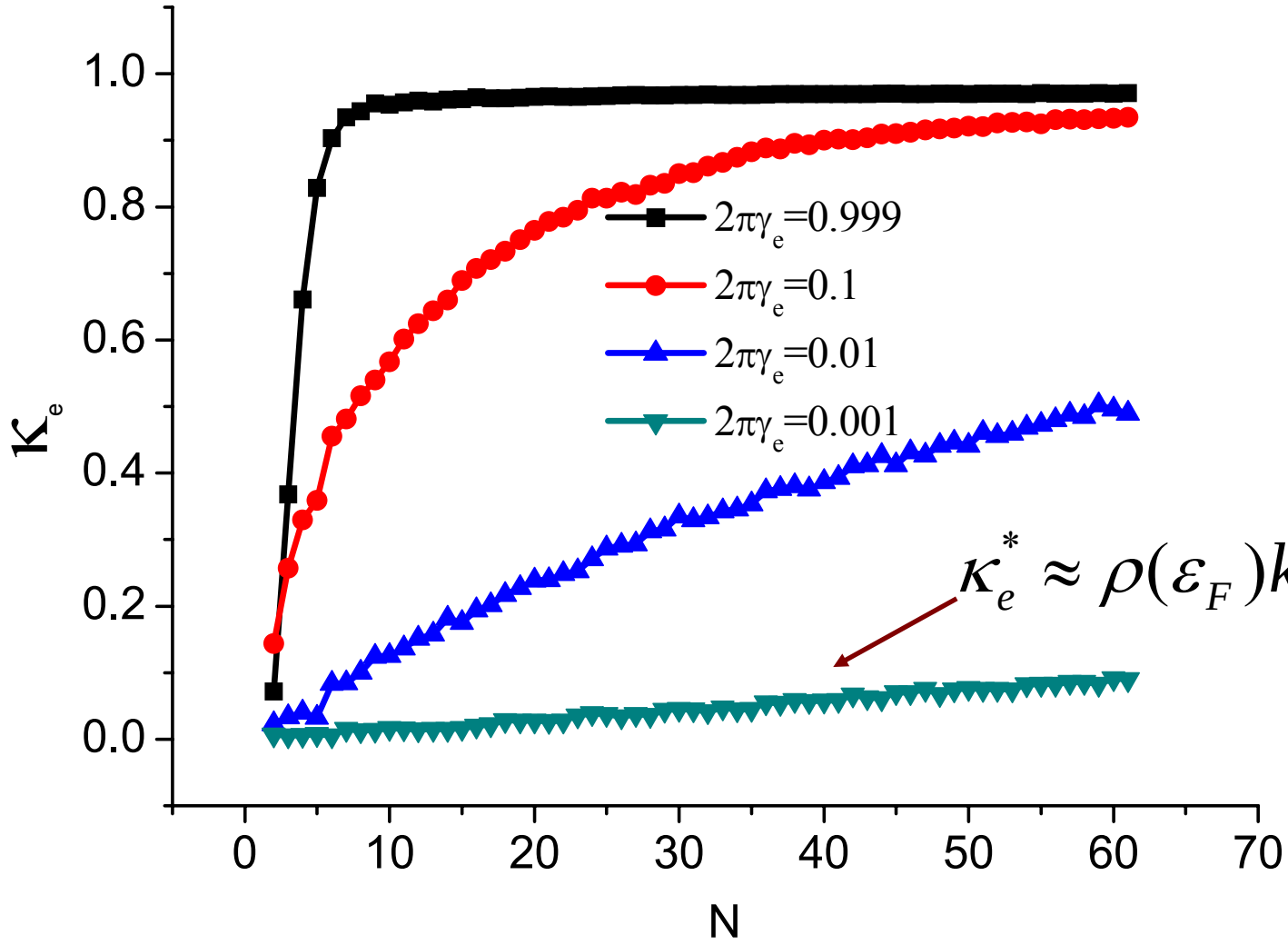
heme A (ox)

$$\kappa_e(\max) = 0.2$$

Моделирование методом Монте-Карло
(случайное блуждание по узлам двумерной решётки)



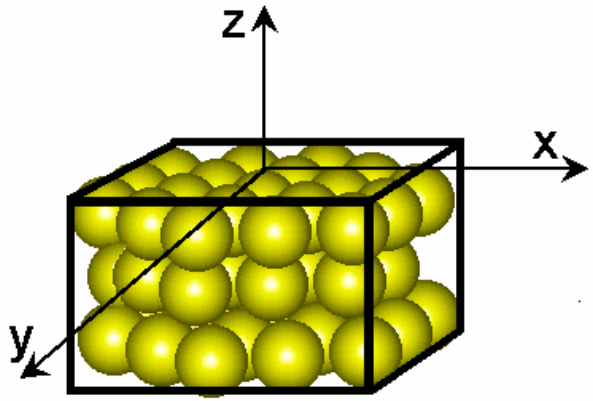
Electronic transmission coefficient vs density of electronic states calculated with the help of MC simulations at different values of γ_e

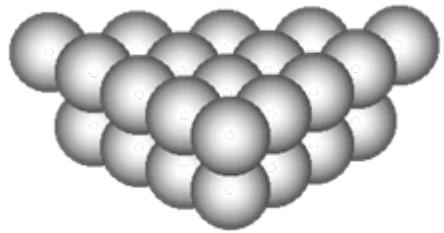


density of electronic states

Model calculation of electronic transmission coefficient for interfacial reactions: some challenges.

1. Model of a charged metal surface (cluster, slabs, "jellium", etc)





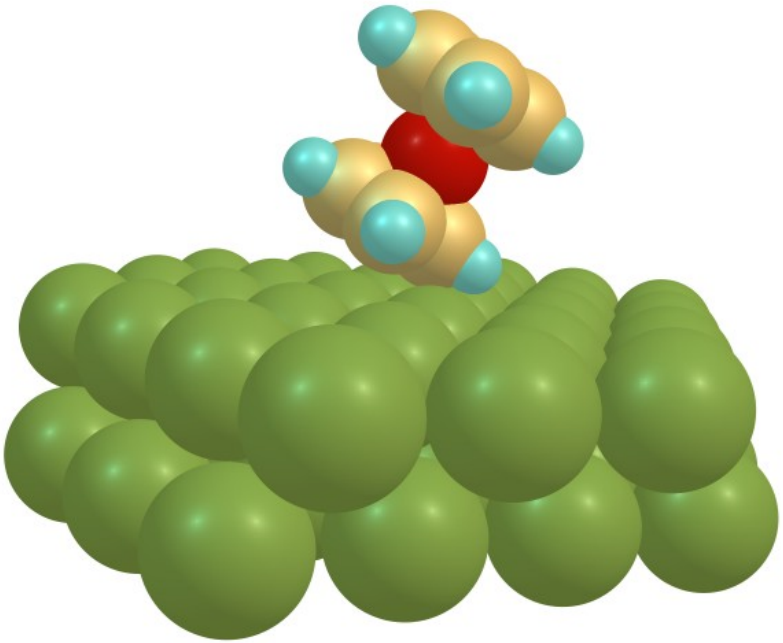
2. Solvent effect on the wave functions and perturbation

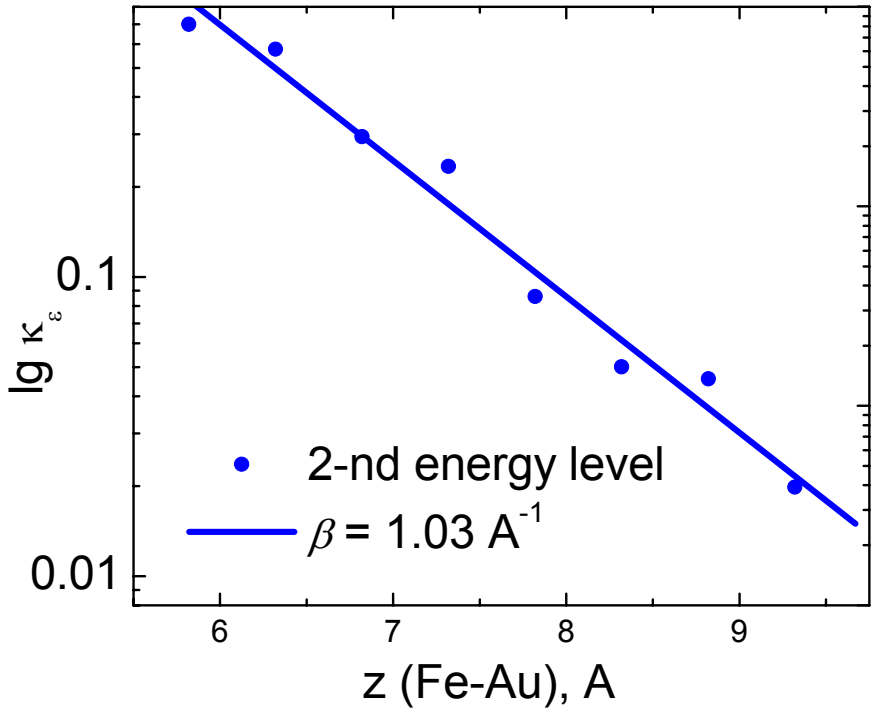
3. Asymptotic behaviour of wave functions

4. $V(\vec{r}) = ?$

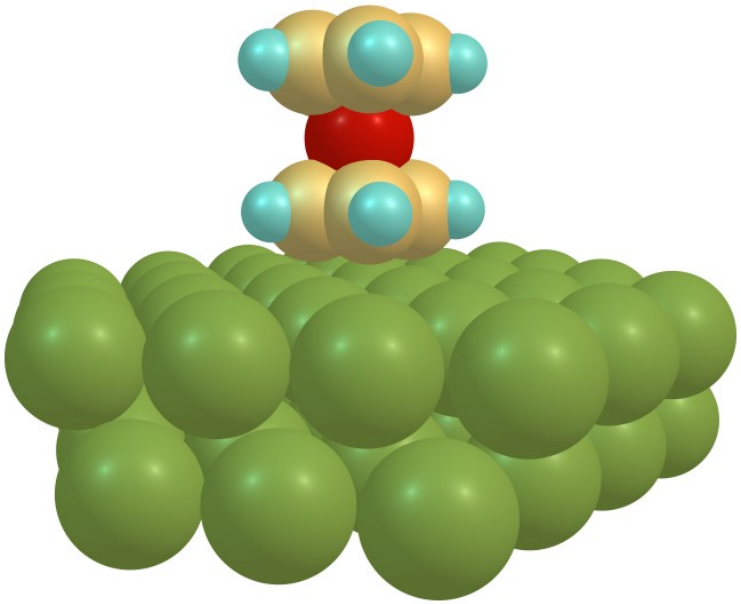
$$Fc^{+} + e \rightleftarrows Fc$$

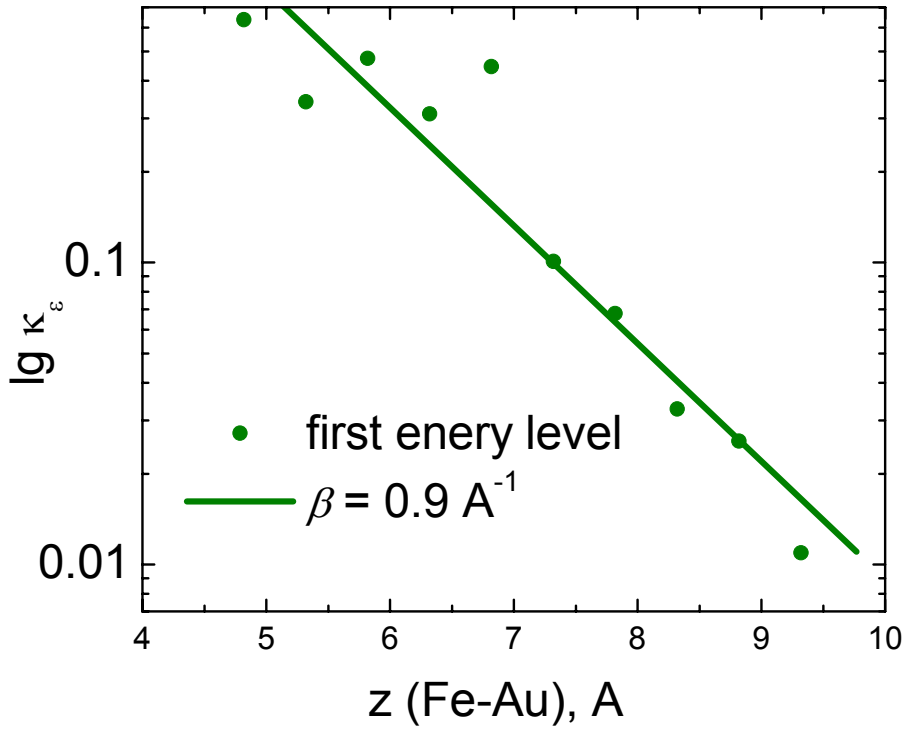
$$\kappa = \kappa_0 \exp(-\beta z)$$





Au_{54} cluster

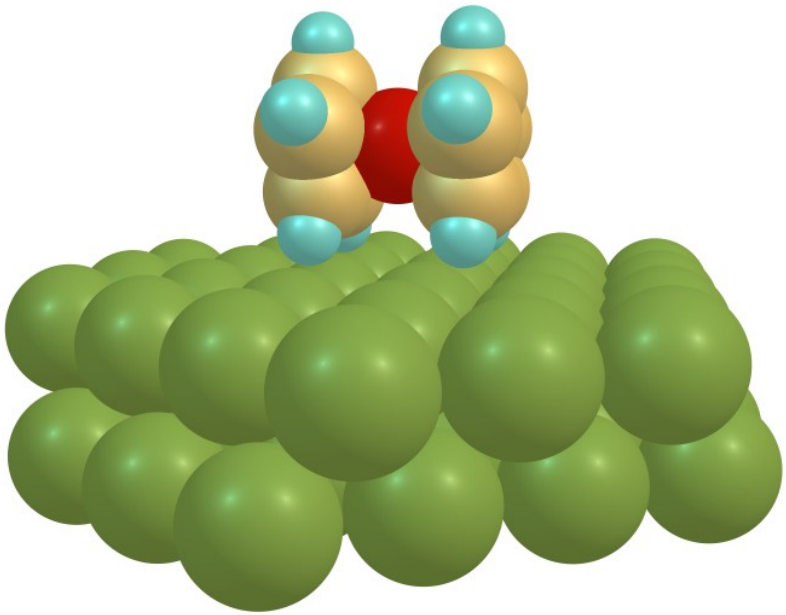


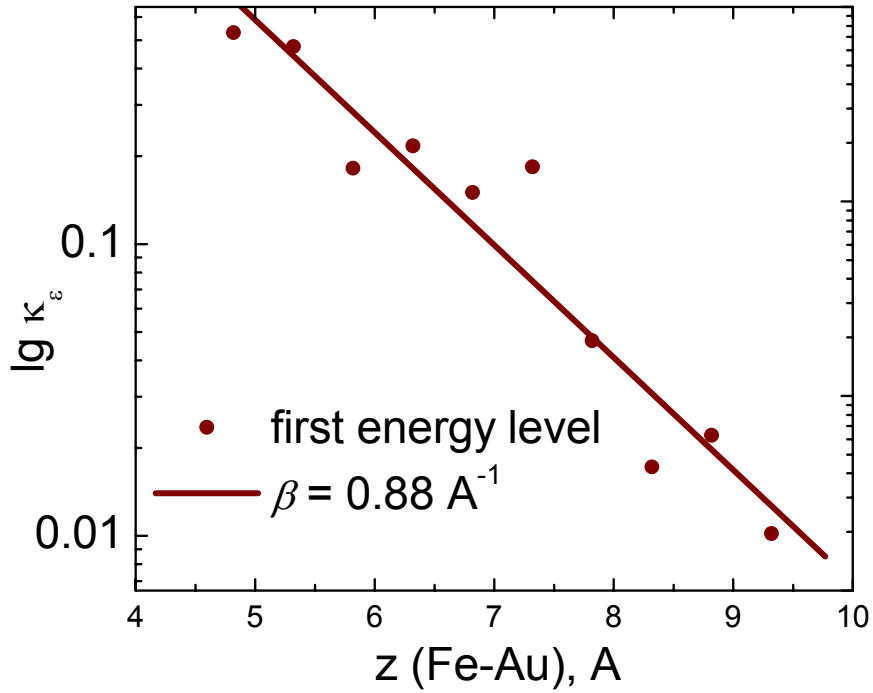


vertical orientation

Fc

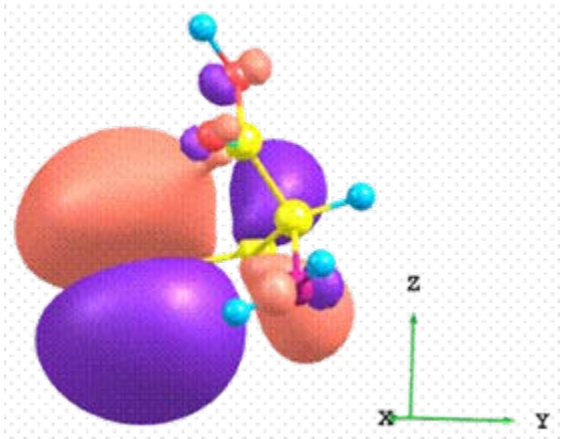
Наклоны расчётных зависимостей находятся
в хорошем согласии с экспериментальными оценками



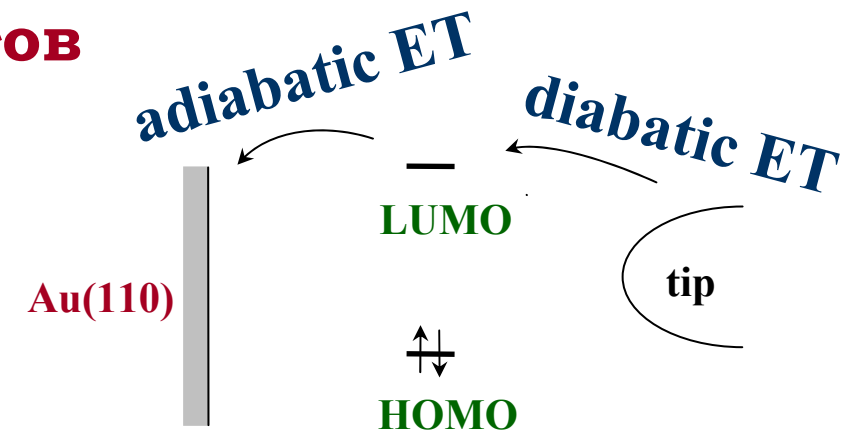


horizontal orientation

Квантово-химическое моделирование туннельных контрастов



STM configuration



resonance integral

bias potential

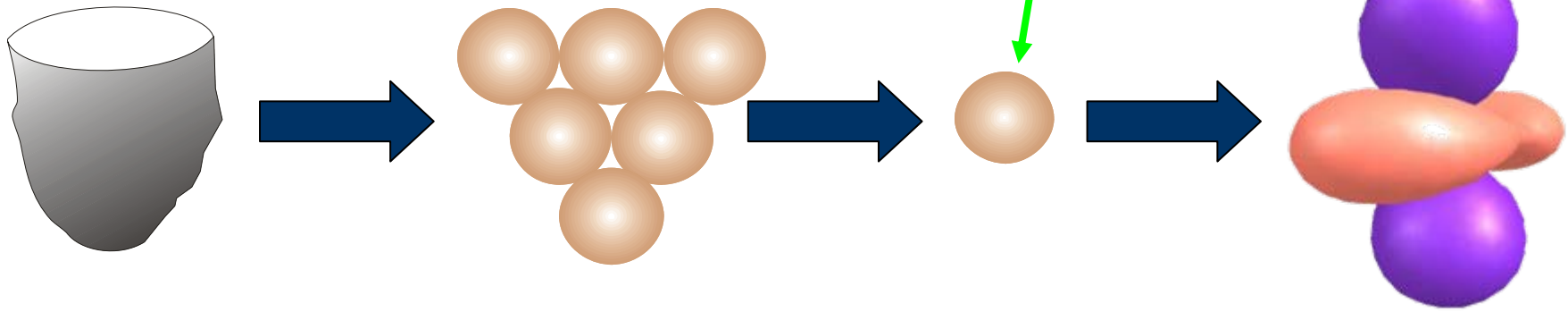
$$I \approx \frac{e_o}{\hbar} \rho(\varepsilon_F) H_{if}^2 \int_0^{\psi_{bias}} d\varepsilon \rho_{ads}(\varepsilon)$$

tunneling current

density of electronic states of the tip

density of electronic states of a molecule adsorbed

Model of the tip



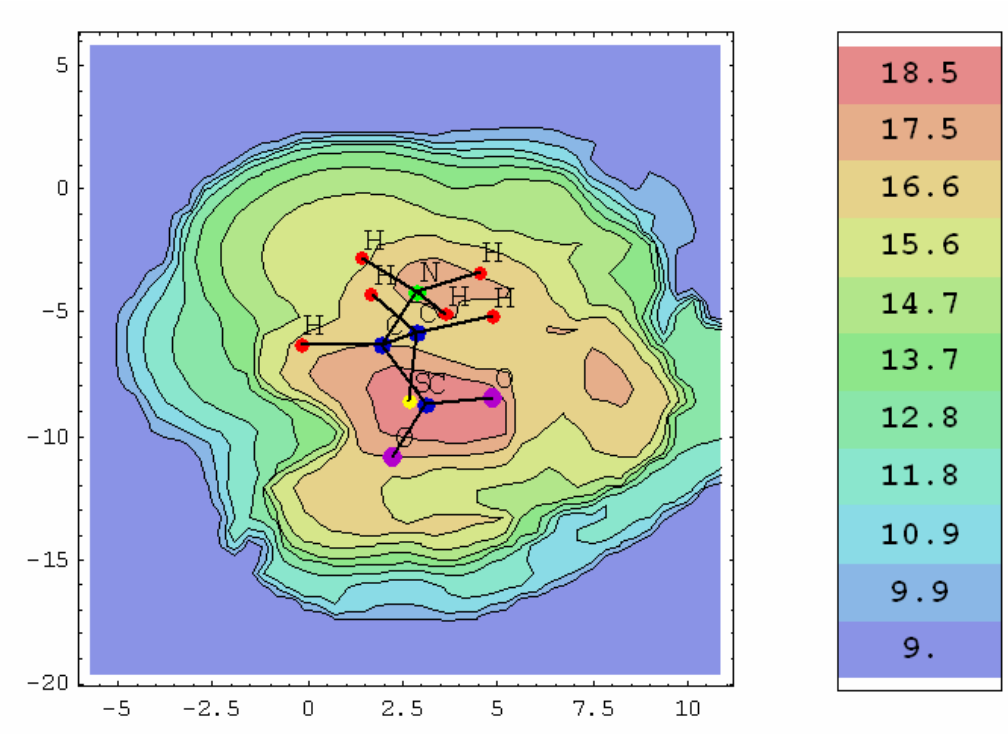
A real STM tip

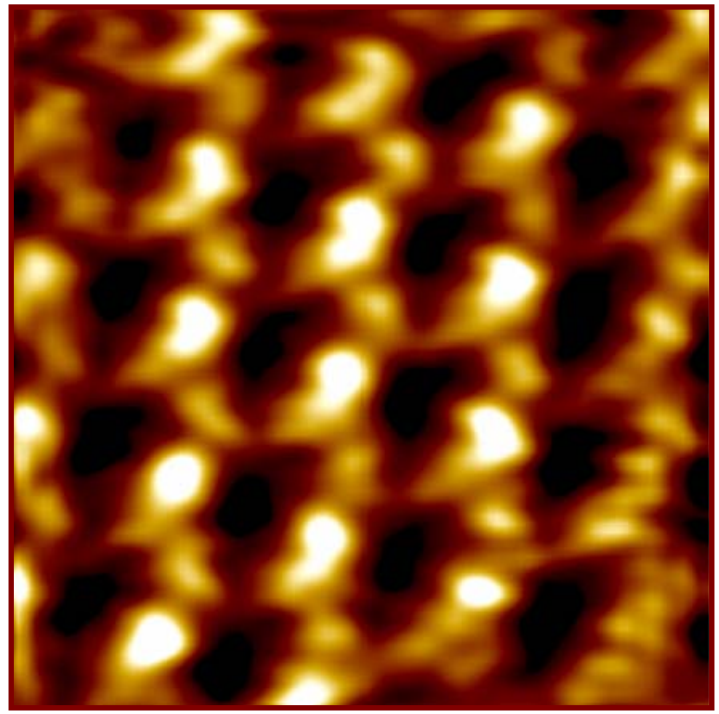
W cluster,
W-H_2O cluster

$5dz^2$ orbital of a tungsten atom plays a crucial role in constructing images

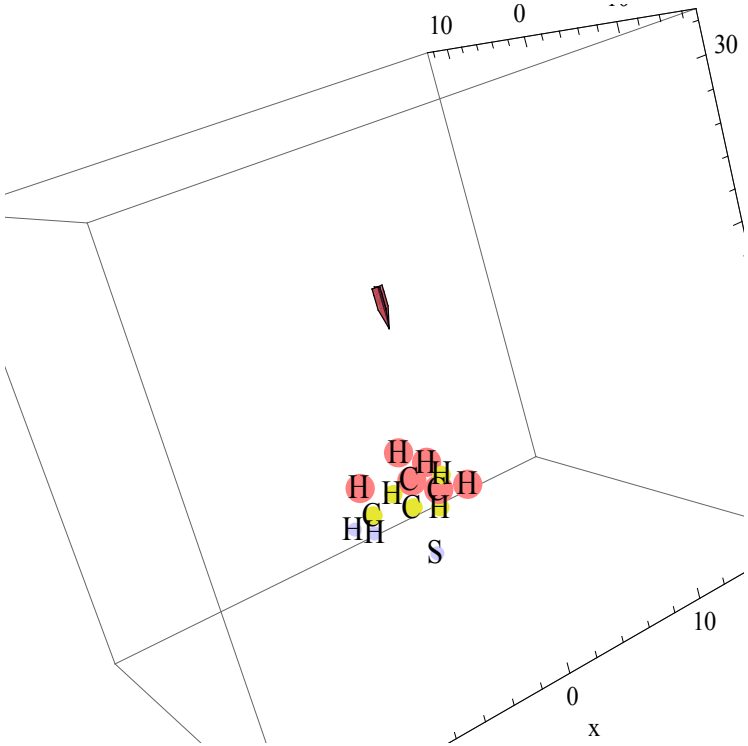
Model STM contrast

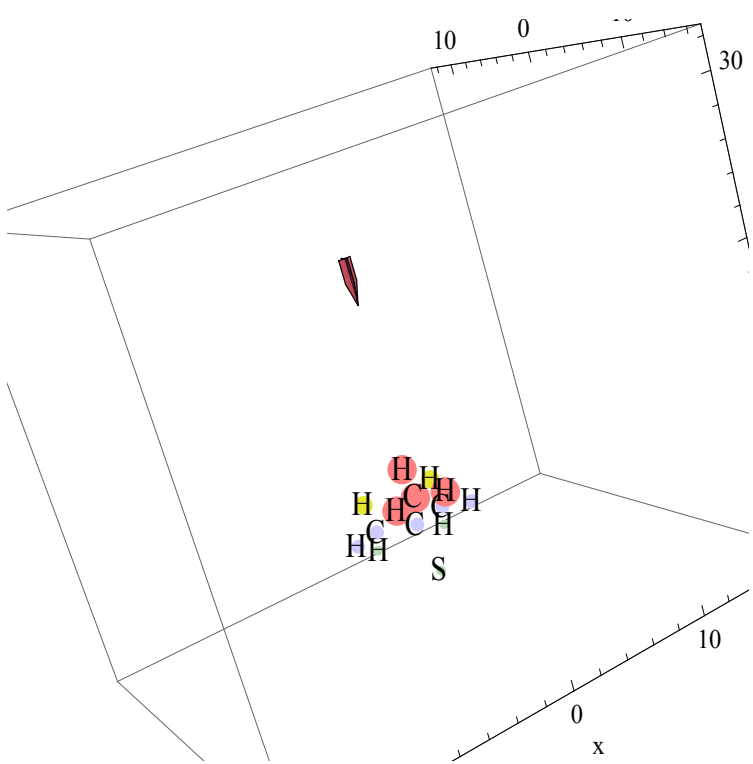
Cysteine adsorption on Au(110) elecrode (in situ STM images)



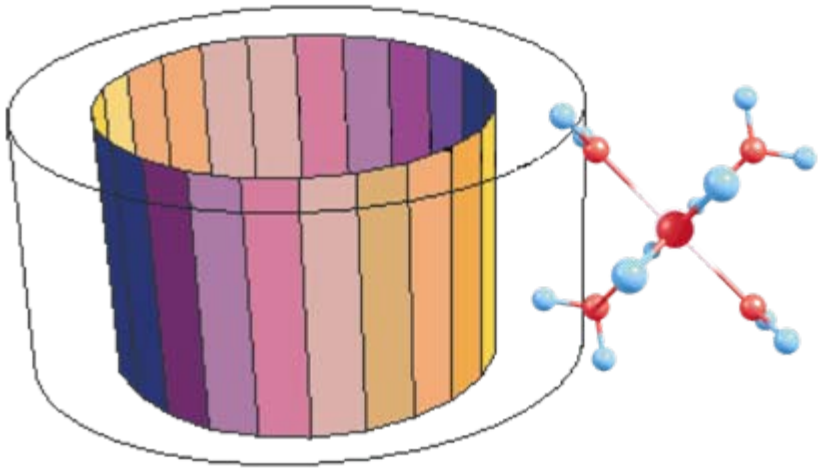


Модельный контраст качественно описывает экспериментальные данные



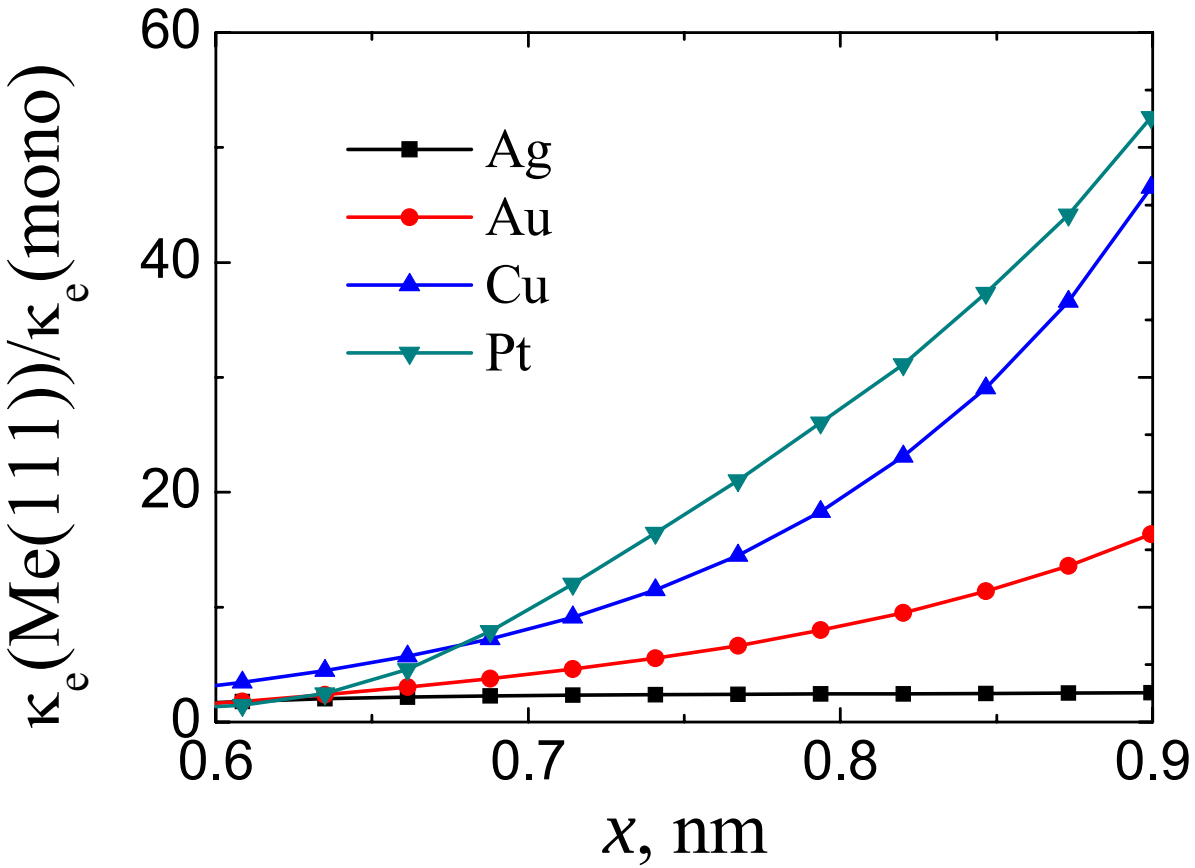


Contributions of different atoms to the STM image



Эффекты ингибирования реакций переноса электрона на металлических нанопроволоках (модельный прогноз)

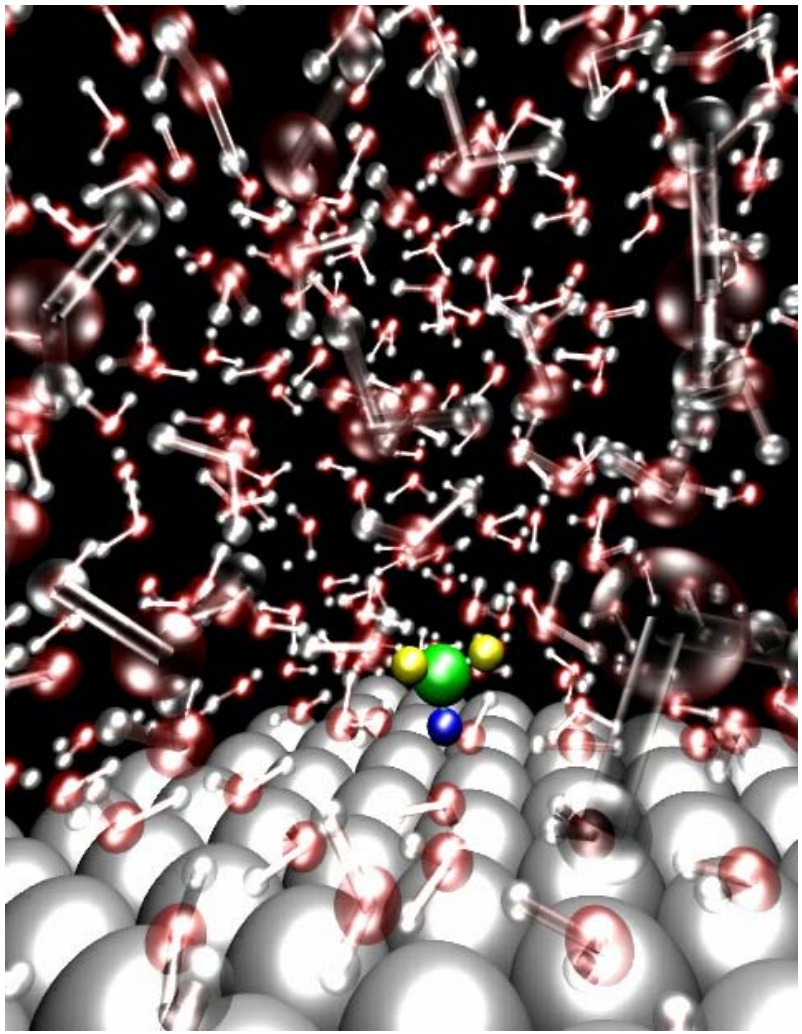
Me(111) vs monoatomic wires Fe(III)/Fe(II)



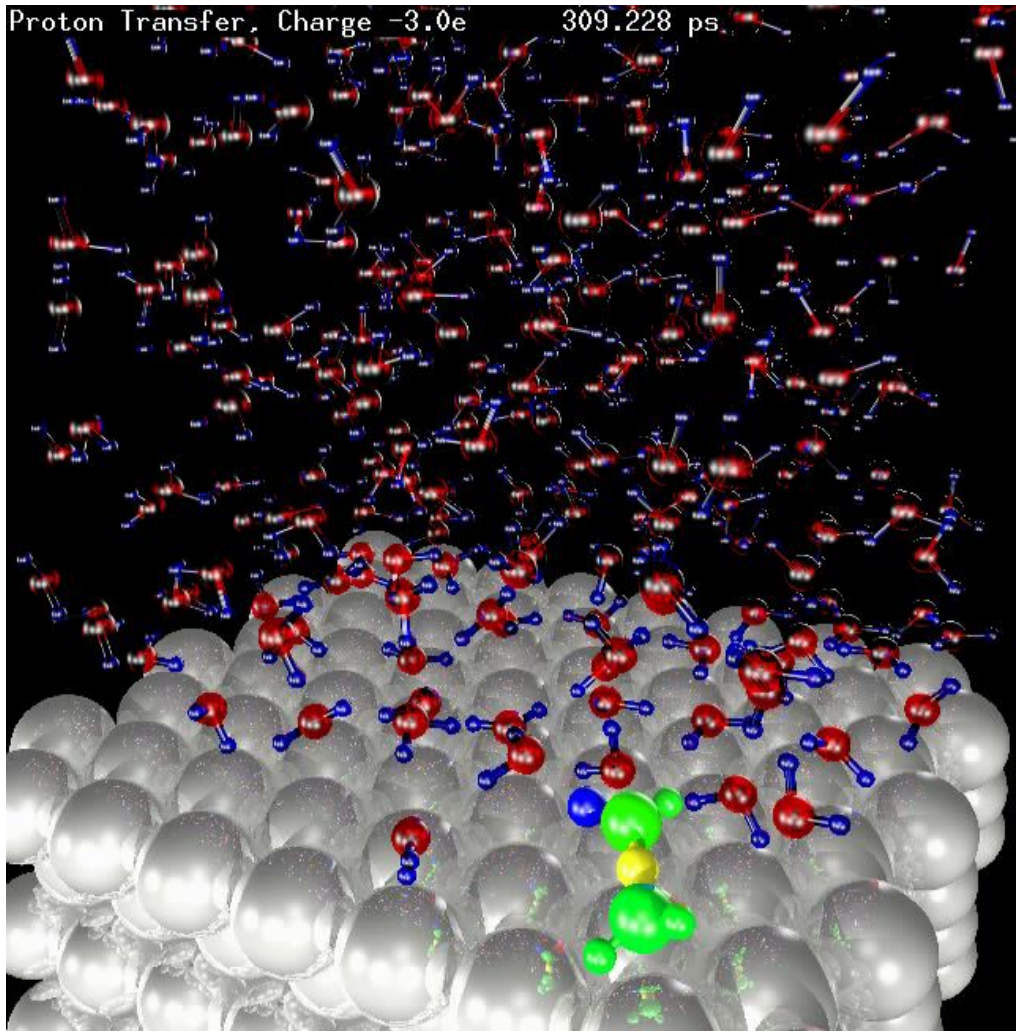
Электрохимическое выделение водорода

$2H^+ + 2\bar{e} = H_2$

Результаты моделирования методом МД



Hg/H_2O



Pt/H_2O

Теория замедленного разряда

$$\ln j + \frac{n_i F \psi'}{RT} = \ln(k_s[c]) - \frac{\theta(\eta - \psi')F}{RT}$$

θ - коэффициент симметрии

k_s - гетерогенная константа скорости

n_i - заряд реагирующей частицы

Фрумкин А.Н.

Одна из задач теории и молекулярного моделирования –предложить простой и физически прозрачный способ обработки экспериментальных данных

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