

From the Properties of Long-lived Intermediates in Mass Spectrometry to Applied Plasma Chemistry

Prof. Dr. Roman M. Balabin

East China University of Technology (ECUT)

Bond Street Holdings, Nevis

Outline

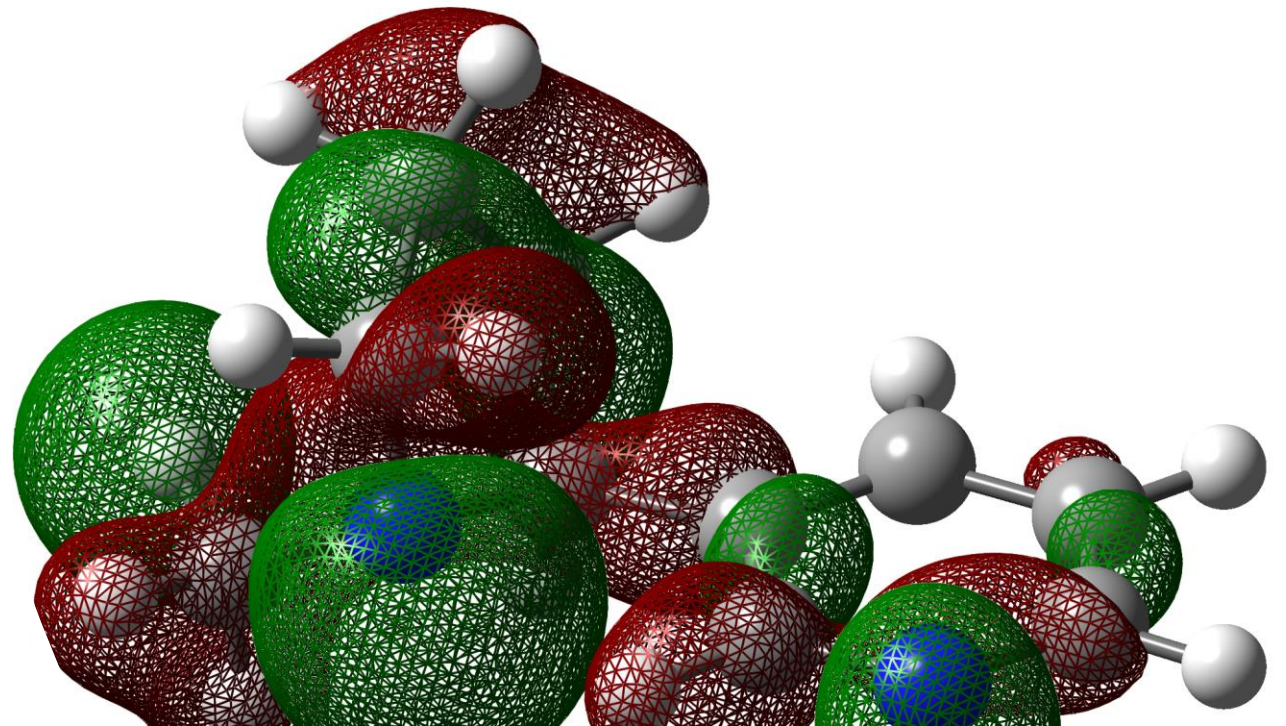
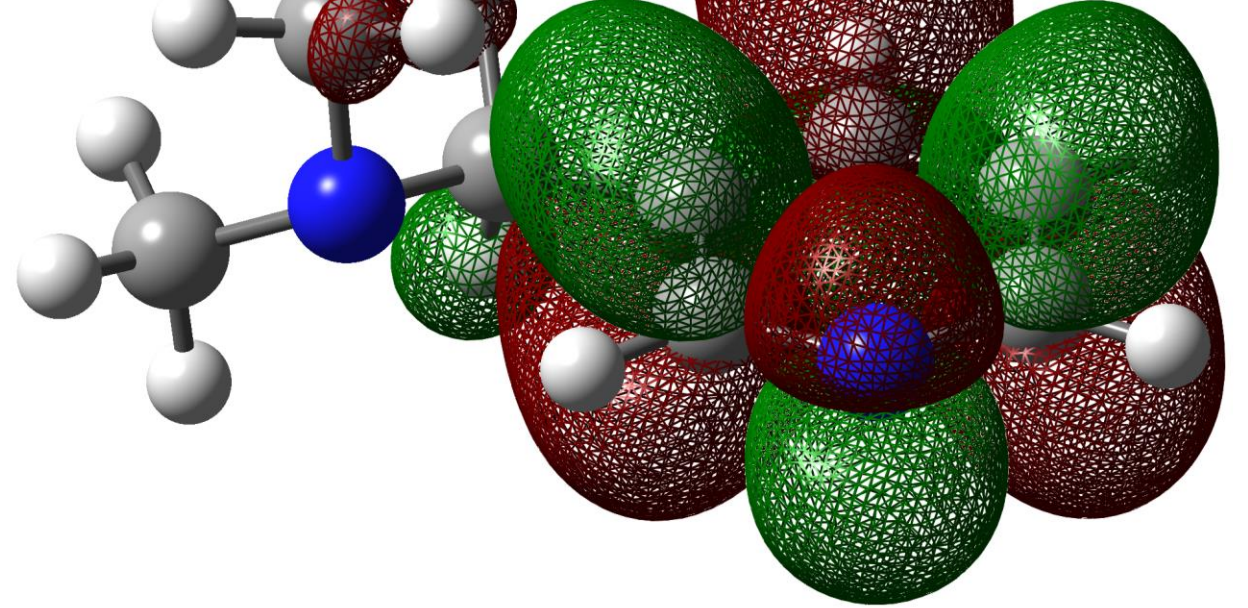
Part I. CV / Bio

Part II. Brainware Analytics

Part III. The HyDRA Challenge

Part IV. Nitrogen Fixation by
Ambient Plasma

Part V. Project Timeline



Part I. CV / Bio

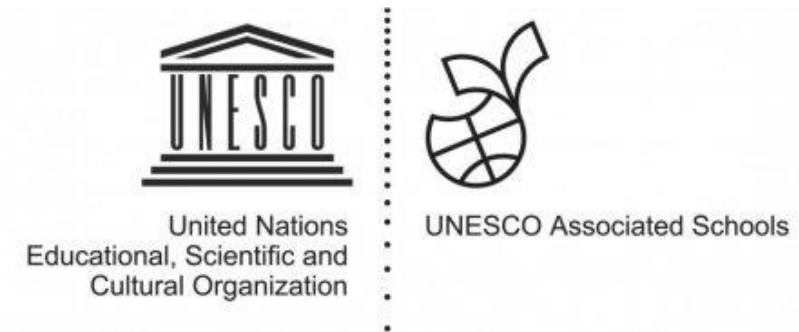
Early Years: 1985–2002

- Lived on Khersonskaya and Volgina str. (Moscow)
- Summer vacations in **Spassk** (Bednodemyanovsk) of Penza Oblast, especially in 1992–1994
- Shortly lived in **Anapa** (Kuban, 1988–1989), **Pyatigorsk** (Stavropolye, 1990), **Sochi** (1991) and **Tallin** (1990–1991)
- First travel to Western Europe, **Rome**, in Aug 1995
- Moved to **Blaibach** (Oberpfalz, Bayern, Germany) in 1996–1997
- Lived in **Zandt** (Oberpfalz, Bayern) in 1998



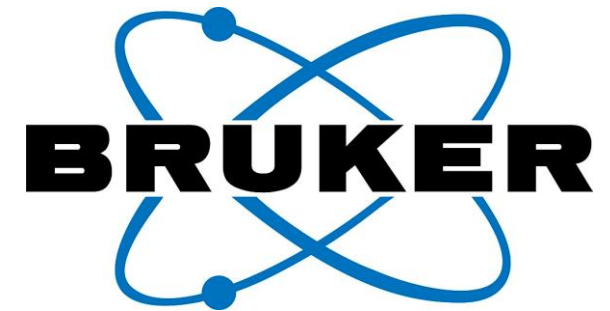
School Education

- Primary school No. 1655 / No. 15 (Khersonskaya, Moscow)
- School No. 562 / No. 15 (Perekopskaya, Moscow)
- School No. 1073 (Varshavskoe, Moscow) with its program authored by **Vladimir Myskin**
- Information Technology Lyceum No. 1533 “LIT” (Lomonosovsky, Moscow) from 2000 to 2002 – **UNESCO** Associated Schools Project Network (ASPnet)
 - Mathematics, computer science and IT
 - Diploma thesis @ **Aleksandr Giglavyj**: “Information and communication technology (ICT) market of the Baltic states” (2002)



University Years: 2002–2008

- Uni: **Gubkin Russian State University** of Oil and Gas (Moscow)
 - Faculty of Chemical Engineering and Ecology
 - Department of Organic Chemistry and Petrochemistry
 - Major / specialty: chemistry and technology of **natural gas**
- Scientific collaborations:
 - **Bruker Optics** (Bremen, Germany)
 - ITERA / ARETI Group (Geneva, Switzerland)
 - Department of Physics, **Umea University** (Sweden)
 - Institute of Problems of Chemical Physics (Chernogolovka)
 - Nesmeyanov Institute of Organoelement Compounds



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- Uni: **Gubkin Russian State University** of Oil and Gas (Moscow)
 - Faculty of Chemical Engineering and Ecology
 - Department of Organic Chemistry and Petrochemistry
 - Major / specialty: **natural gas** chemistry and technology
- Industrial partners:
 - **Lumex** Instruments (St. Petersburg)
 - Orsknefteorgsintez / RussNeft (Orenburg Oblast)
 - Kirishinefteorgsintez / Kinef (Leningrad Oblast)
 - Astrakhan Gas Processing Plant / Gazprom
 - Kuibyshevsky Refinery (Samara Oblast)



Pre-doc Studies: 2007–2008

- Georg August University of **Göttingen** (Germany)
 - Institute of Physical Chemistry
 - Graduate school: Spectroscopy of molecular aggregates (GRK 782 PCGG, GEPRIS 273443)
 - Group of Prof. Dr. **Martin Suhm** / Philipp Zielke
 - Topic: Raman spectroscopy of normal alkanes

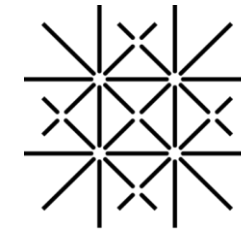
- Ruprecht Karl University of **Heidelberg** (Germany)
 - Institute of Applied Physical Chemistry
 - Group of Prof. Dr. **Michael Grunze** / Patrick Koelsch
 - Topic: sum-frequency-generation spectroscopy (SFGS) of biofilms



Pre-doc Studies: 2007–2008

- University of **Basel** (Switzerland)
 - Department of Chemistry
 - Group of Prof. Dr. **John Paul Maier** / Egor Chasovskikh
 - Topic: electronic spectroscopy of carbon radicals and ions (SNSF 115864)
 - Theoretical calculations: Université Paris-Est, Laboratoire de Chimie Théorique (France)

- Max Planck Institute for Polymer Research in **Mainz**
 - Experimental Physics of Interfaces @ MPI-P
 - Group of Prof. Dr. **Hans-Jurgen Butt** / Gunter Auernhammer
 - Invited talk on dielectric spectroscopy of macromolecular petroleum systems



Universität
Basel

Max-Planck-Institut
für Polymerforschung

Max Planck Institute
for Polymer Research



PhD Studies: 2008–2012

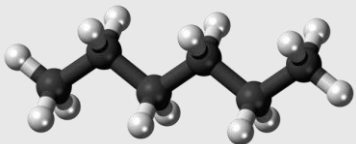
- Uni: **ETH Zurich** (Switzerland)
 - Department of Chemistry and Applied Biosciences (CHAB)
 - Group of Prof. Dr. **Renato Zenobi**
 - Vibrational spectroscopy and mass-spectrometry
 - PhD thesis: “Development of express methods for analysis of petroleum refining products and petrochemicals based on vibrational spectroscopy” (Gubkin University, 2013)
- Industrial partners:
 - **Danone** Research Centre Daniel Carasso (Paris)
 - Unimilk (Moscow Oblast)
 - NT-MDT (Zelenograd, Moscow)





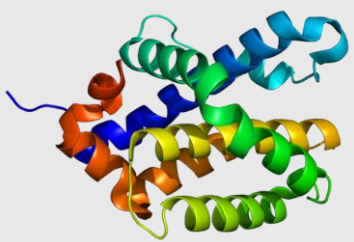
Scientific and industrial results

- Machine learning for **vibrational spectroscopy** data:
 - A series of papers on near-infrared spectroscopy of petrochemicals, products of petroleum refining and biofuels:
 - [Fuel \(2007\) 323](#), [Energy Fuels \(2007\) 2460](#), [Chemom Intell Lab Syst \(2007\) 183](#), [Fuel \(2008\) 1096](#), [Chemom Intell Lab Syst \(2008\) 58](#), [Fuel \(2008\) 2745](#), [Neural Comput Appl \(2009\) 557](#), [ACA \(2010\) 27](#), [Analyst \(2011\) 1703](#), [ACA \(2011\) 190](#), [ACA \(2011\) 63](#), [Fuel \(2011\) 2007](#), [Microchem J \(2011\) 121](#), [Energy Fuels \(2011\) 2373](#), [Analyst \(2012\) 1604](#).
 - Practical implementation for laboratory analysis at Kinef (Kirishi), Samara, **Gazprom** (Astrakhan) and Mozyr Refinery (Belarus)
- **Petroleum macromolecules** and surface science:
 - A series of papers on asphaltenes, petroleum resins and other colloid systems:
 - [JDST \(2007\) 419](#), [JNIRS \(2007\) 343](#), [JDST \(2008\) 457](#), [JCIS \(2008\) 167](#), [JDST \(2008\) 1505](#), [Energy Fuels \(2009\) 1230](#), [Energy Fuels \(2011\) 189](#), [JDST \(2011\) 1502](#), [Phys Wave Phen \(2015\) 143](#).
 - Colloid state control of **Kumkol oil** (Kazakhstan)



Scientific and industrial results

- Physical chemistry of **normal alkanes**:
 - A series of papers on quantum chemistry and Raman spectroscopy of alkanes:
 - [Chem Phys \(2008\) 267](#), [JCP \(2008\) 164101](#), [JPCA \(2009\) 1012](#), [JPCA \(2010\) 6729](#), [Mol Phys \(2011\) 943](#).
 - The **benchmark** experimental value for the enthalpy difference between *trans* and *gauche* conformations of normal butane: $\Delta H = 660 \pm 22 \text{ cal mol}^{-1}$
 - Used by Bachrach in [Computational Organic Chemistry](#) (2014), Vogel & Houk in *Organic Chemistry* (2019), AMBER FF for biomolecules, etc.
- **Machine learning** for quantum chemistry:
 - One of the **earliest** attempts to combine ML and QC:
 - [JCP \(2009\) 074104](#), [PCCP \(2011\) 11710](#).
 - Almost zero interest after publication, but became a large separate field of studies in 2020s: ML-DFT, ML-FF, Δ -learning, etc.
 - Review by Dral in [Quantum Chemistry in the Age of Machine Learning](#) (2022) 698 pp.



Scientific and industrial results

- Physical chemistry of **biomolecules**:
 - A series of papers on QC and Raman spectroscopy of gas-phase **amino acids**:
 - [Chem Phys Lett \(2009\) 195](#), [PCCP \(2010\) 5980](#), [JPCL \(2010\) 20](#), [JCP \(2010\) 231101](#), [JPCB \(2010\) 15075](#), [Comput Theor Chem \(2011\) 15](#), [PCCP \(2012\) 99](#).
 - The very first measurement of **conformation equilibrium in free glycine**
 - QC of other biomolecules – triazoles, tetrazole, formic acid, aldehydes, etc.:
 - [JCP \(2009\) 154307](#), [JPCA \(2009\) 4910](#), [JPCA \(2010\) 3698](#), [JCP \(2010\) 211103](#), [JASMS \(2011\) 1167](#), [Struct Chem \(2011\) 1047](#), [Mol Phys \(2011\) 2341](#), [PCCP \(2023\) 22089](#).
- **Mass-spectrometry** and electronic spectroscopy:
 - Food samples, dyes, peptides, biocomplexes, etc.:
 - [Analyst \(2010\) 773](#), [PCCP \(2010\) 11710](#), [PCCP \(2010\) 14121](#), [JASMS \(2010\) 172](#), [Angewandte \(2010\) 2358](#), [Anal Chem \(2010\) 7394](#), [ABC \(2010\) 405](#), [IJMS \(2011\) 241](#), [RSCA \(2011\) 1962](#).
 - Proof that electrospray ionization (ESI) generates **gaseous analytes at ambient conditions**

Journalist

- **Business-Swiss**, Zurich
 - Edited by Marad Widmer, LL.M.
 - Shveytsariya Delovaya / Widmer Strategy GmbH
- **Nasha Gazeta**, Geneva
 - Edited by Dr. Nadia Sikorsky (Nadezhda Sikorskaya)
- **Wikinews**, Miami, FL
 - Interviews with Profs. Jonathan Gruber (MIT), Clive Spash (CSIRO), Stephen Ward (UBC), Robert Costanza (UCL), Dimie Ogoina (WHO)
- **Eyewitness News (EWN)**, Johannesburg, SA

Швейцария Деловая



Part II. Brainware Analytics

Brainware Analytics: formal

- Formal: **Brainware Analytics GmbH** (Switzerland)
 - BWAN = BrainWare Analytics LLC
 - Commercial register CH-170.4.011.342-9
 - EU VAT: CHE-202.748.777
 - Statutory date: 10 Jul 2012
 - Daily register No. 9743 / Publication number: 6791860
 - Official address: Rathausstrasse 14, 6340 Baar, Zug
 - Industry: computer hardware, provision of IT services
 - Share capital: 20'000 CHF
 - Registered persons: “Balabin, Roman, Russian citizen, in Schlieren, managing director, with sole signature and shareholder” (SHAB)



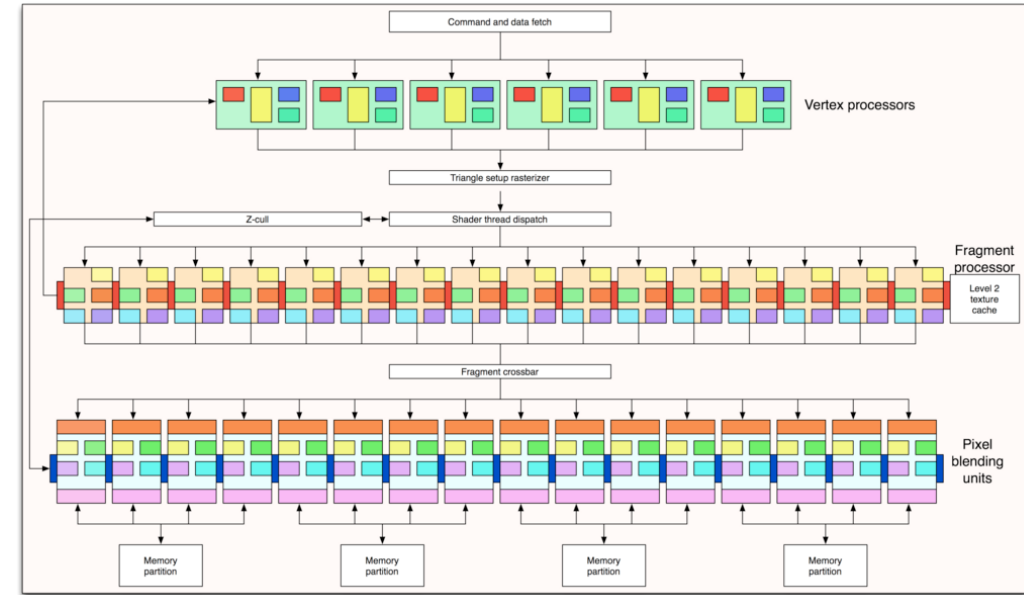
Brainware Analytics: locations

- Office in **Schlieren**, 2013–2014:
 - Address: Grabenstrasse 11a, 8952 Schlieren, Zurich
 - Partner: Dualsystems Biotech AG
 - proteomics for industry and academia
- Office at **Technopark Zurich**, 2014–2017:
 - Address: Newton 1.OG, Technopark Zurich, Technoparkstrasse 1, 8005 Industriequartier, Zurich
 - Five people in Jul 2014:
 - two scientists with PhDs, two computer engineers and an expert in GPU-based computer simulations
 - “Balabin, Roman, Russian citizen, in Schlieren, managing director, with sole signature and shareholder... Kornilov, Pavel, Russian citizen, in Zurich, shareholder, without signatory power” (SHAB)



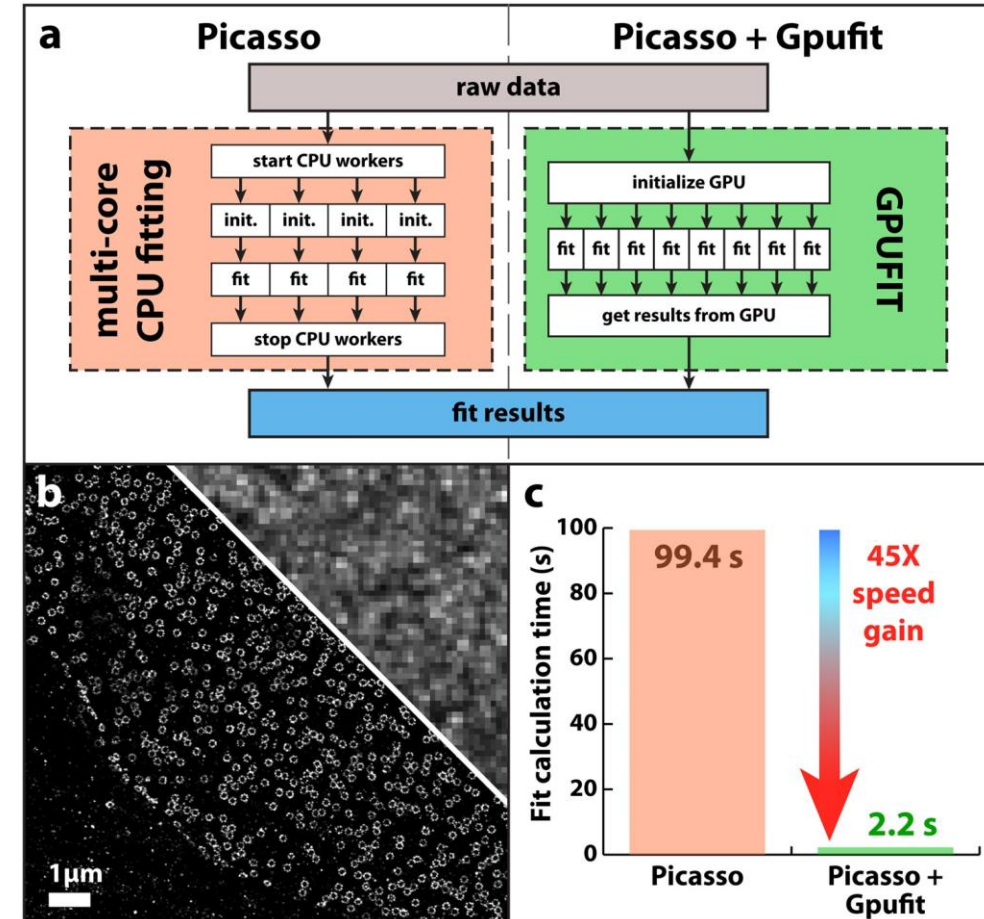
General-purpose computing on GPUs

- **GPGPU** = the use of a graphics processing units (GPUs) beyond computation of computer graphics only
- GPUs could perform computation in applications traditionally handled by the central processing unit (CPU)
- Fits **scientific computing**
- The use of multiple video cards in one computer further parallelizes the processing



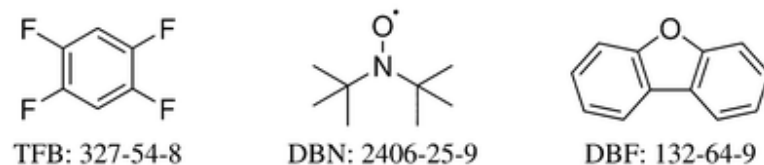
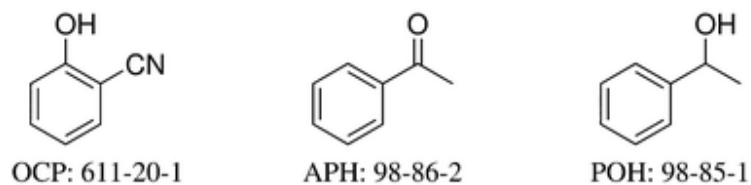
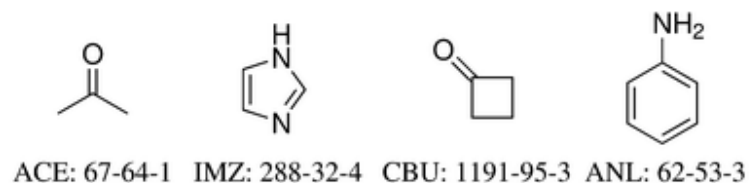
General-purpose computing on GPUs

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- GPUs could perform computation in applications traditionally handled by the central processing unit (CPU)
- Fits **scientific computing**
- Example: estimation of non-linear parameters by the **Levenberg-Marquardt algorithm**



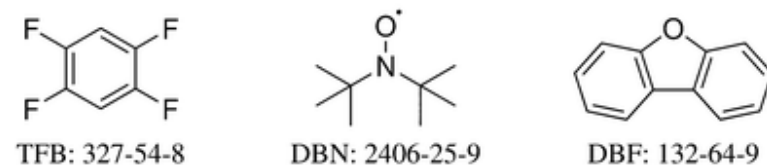
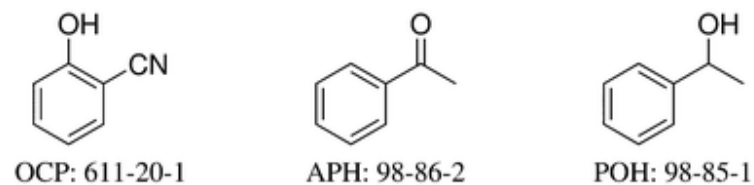
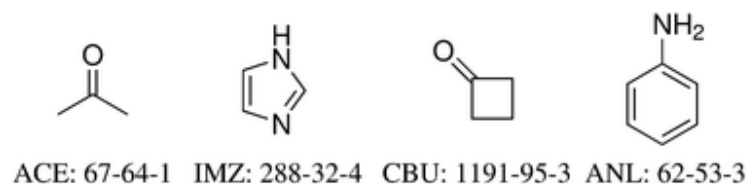
Part III. The HyDRA Challenge

The HyDRA Challenge: 2021



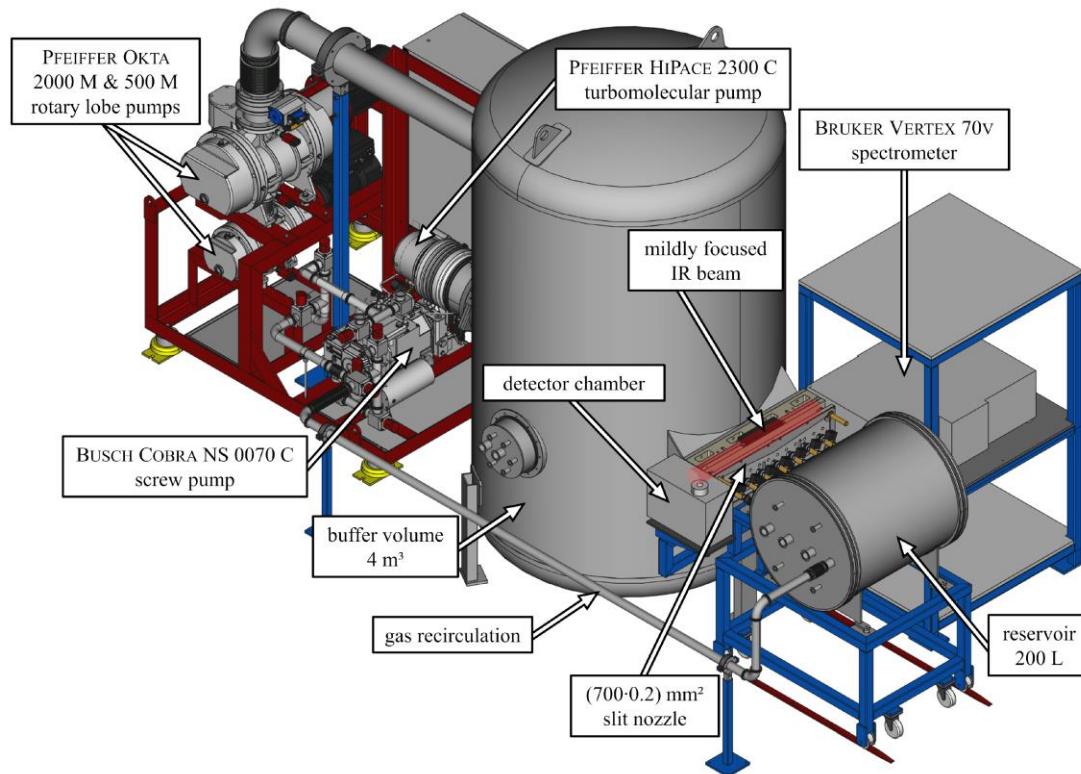
- **Hydrate Donor Redshift Anticipation (HyDRA)** blind challenge for the microhydration
- Organizers:
 - University of Göttingen / Paris-Saclay University
 - Prof. Dr. **Ricardo Mata** (theor) / Prof. Dr. **Anne Zehnacker-Rentien** (exp)
- Ten complexes of organic molecules with water
- No experimental information prior to predictions' submission (before Mar 2022)

The HyDRA Challenge: 2021



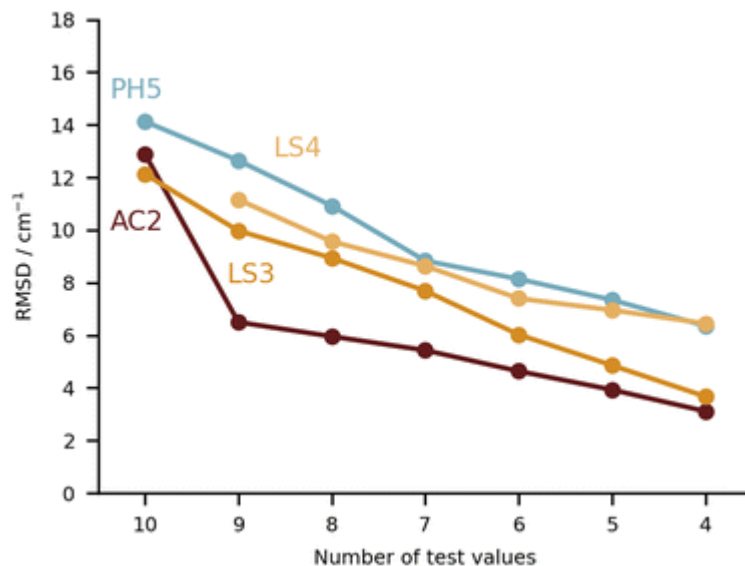
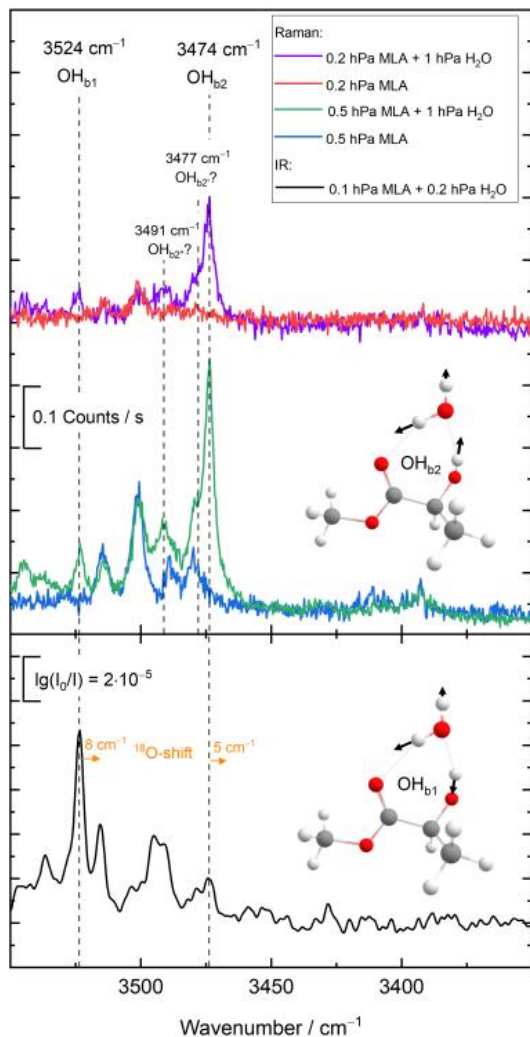
- The role of theory in understanding hydration is multifaceted:
 - Helps to **assign** the experimental spectral data
 - Could even replace experiment (to some extent)
- A need for **unbiased** tests of different predictive theoretical approaches by experiment

The HyDRA Challenge: 2023



- Submitted:
 - 18 models from 12 groups
 - mostly DFT
- Three (3) best models were selected
- Model **LS4** based on a novel DFT learning strategy that included water geometrical parameters is among **top-3**
- My idea: PBE0-D3BJ/aVT(Q)Z adjusted with a five-parameter regression function
 - Good for GPU-based calculations

The HyDRA Challenge: 2023



- Submitted:
 - 18 models from 12 groups
 - Mostly DFT
- Three (3) best models were selected by the jury
- Model **LS4** based on a novel DFT learning strategy that included water geometrical parameters is among **top-3**
- My idea: PBE0-D3BJ/aVT(Q)Z adjusted with a five-parameter regression function

Part IV. Nitrogen Fixation by Ambient Plasma

The Project

- **Experimental part:**

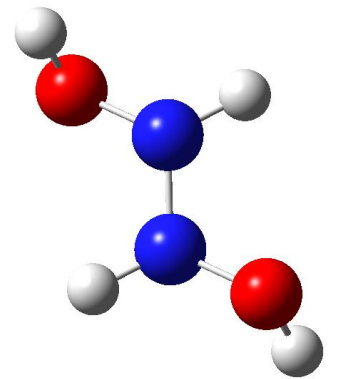
- Spectroscopic analysis of the long-lived intermediates in the process of ambient catalyst-free nitrogen fixation with water dimer
- Investigation of formic acid synthesis in CO/water plasma
- Investigation of CO₂/water & N₂O/water plasma configurations

- **Theoretical part:**

- Calculation of N₂ fixation by water radical-cations at CCSD(T) level
- Plasma parameters estimation by numerical methods

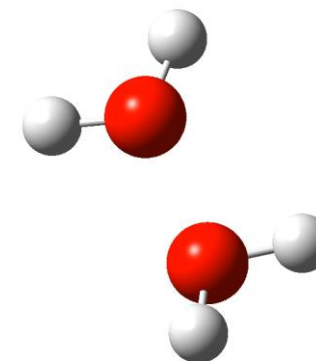
- **Industrial part:**

- Contact with hydroxylamine/nitroxyl producers
- Obtaining the grant of a patent
- Industrial project detailing

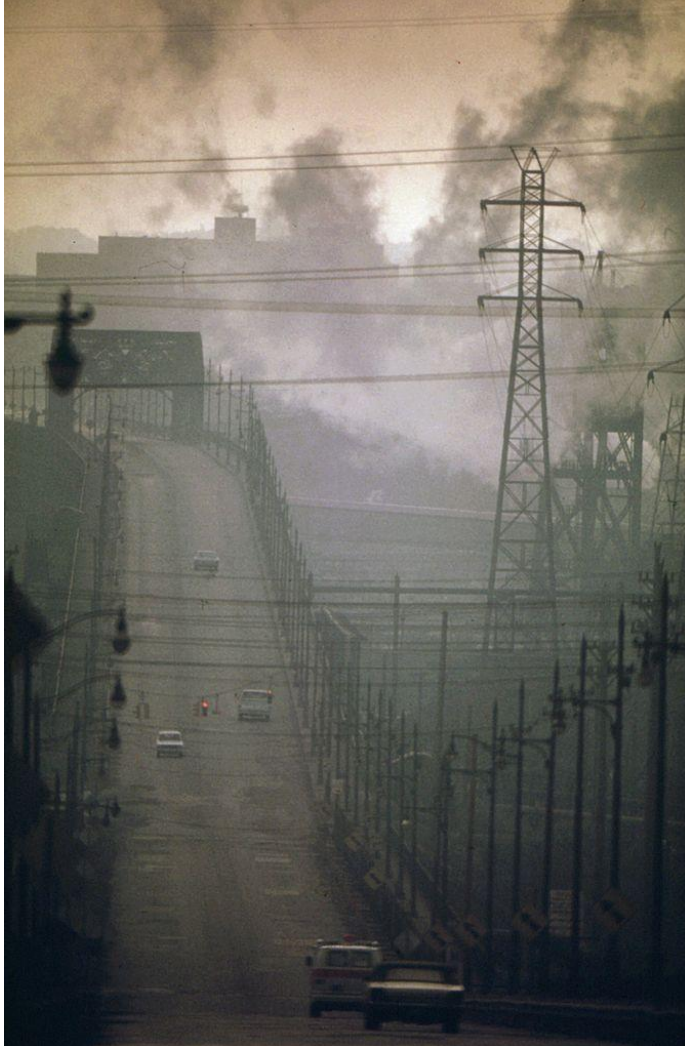


WDRAC: Water dimer radical-cation

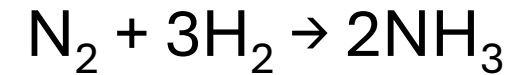
- The WDRACs, $(\text{H}_2\text{O})_2^{+\bullet}$, react with organic substances in three rather different ways:
 - as electron acceptors
 - as **proton donors**
 - as reagents for the OH^\bullet moiety exchange
- WDRACs could co-exist in two different conformations:
 - ion-radical structure, $\text{H}_3\text{O}^+\cdots\text{OH}^\bullet$, with standard hydrogen bond
 - two-center-three-electron non-classical **hemibonded** configuration, $(\text{H}_2\text{O}\cdots\text{OH}_2)^{+\bullet}$.



“Modern” nitrogen fixation: Haber-Bosch process

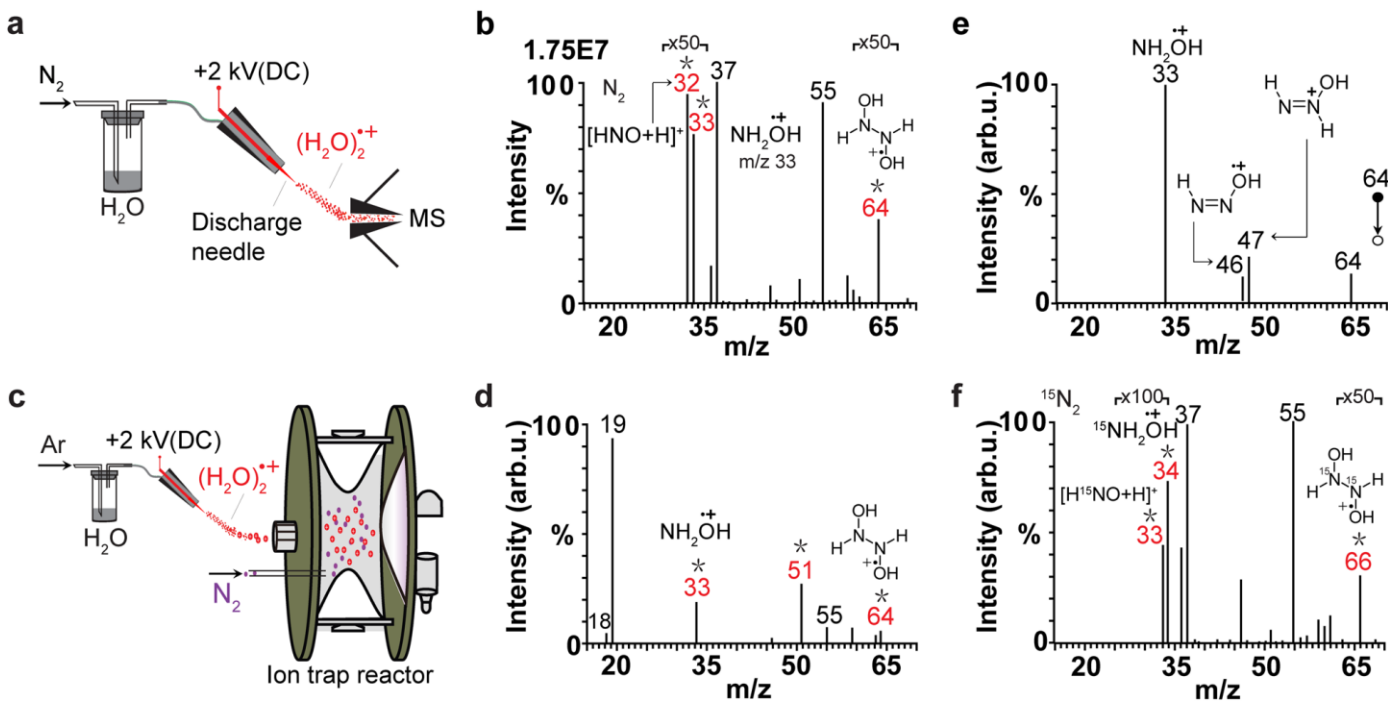


- **Haber-Bosch process** (1909) is the main industrial procedure for nitrogen fixation:



- Parameters:
 - Catalyst: Fe/FeO
 - Pressure: ~200 bar
 - Temperature: ~**500** °C

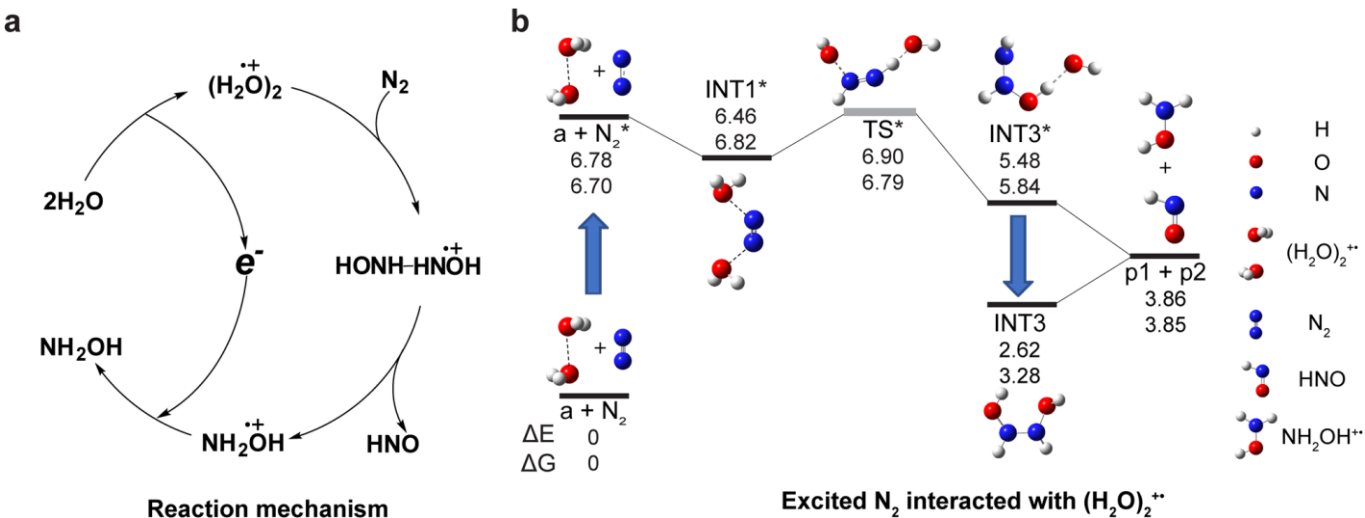
Ambient catalyst-free nitrogen fixation



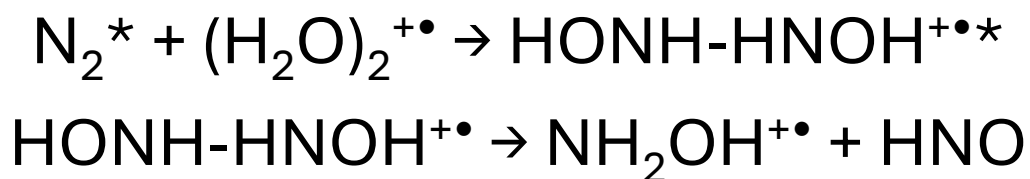
- **Ambient** disproportionation reaction of N_2 with water dimer radical-cation:



Ambient catalyst-free nitrogen fixation

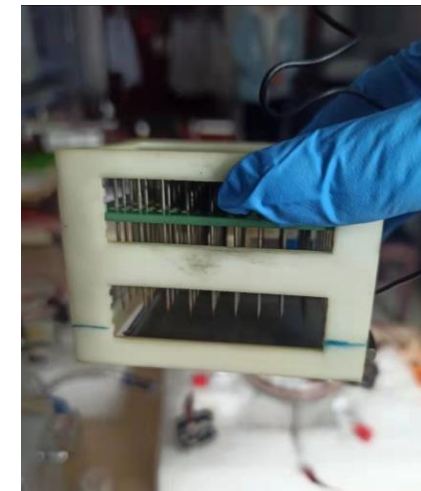
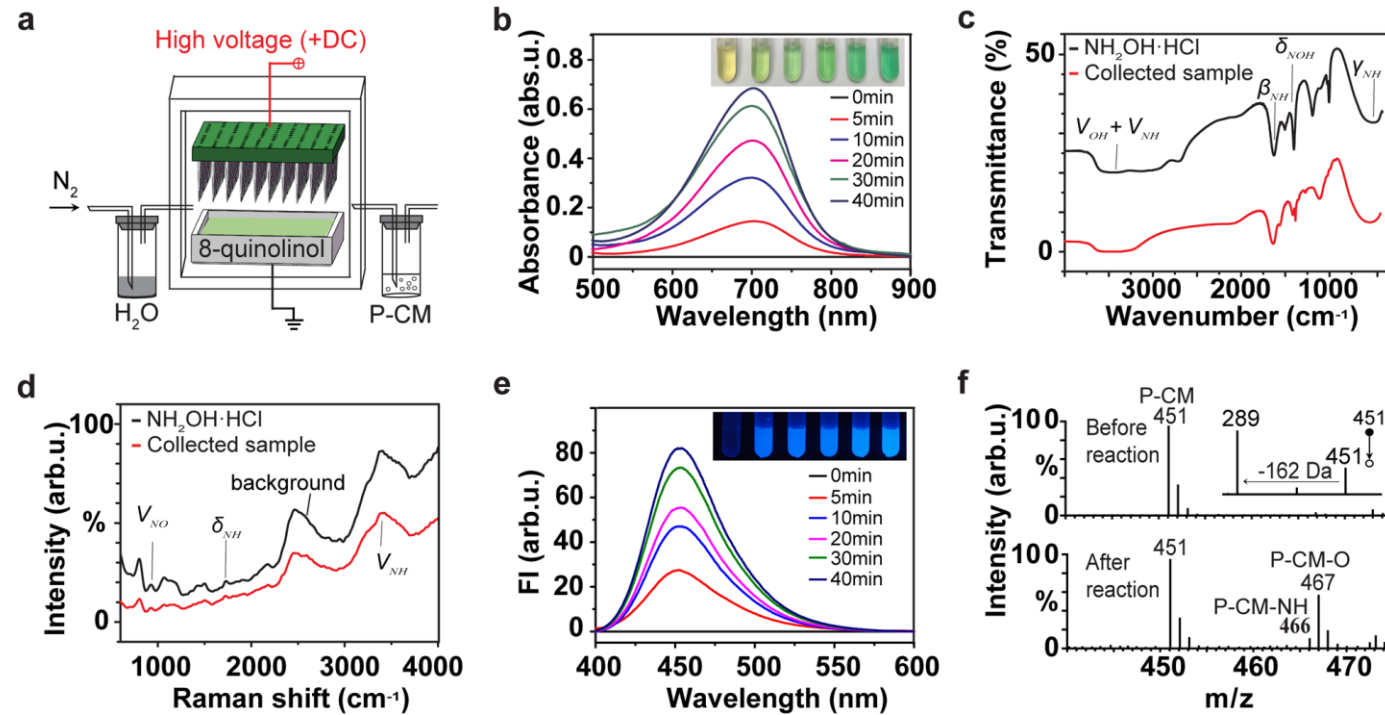
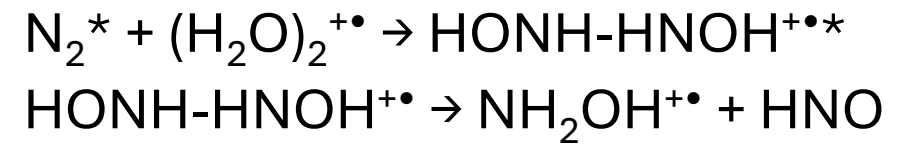


- **Ambient** disproportionation reaction of N_2 with water dimer radical cation:

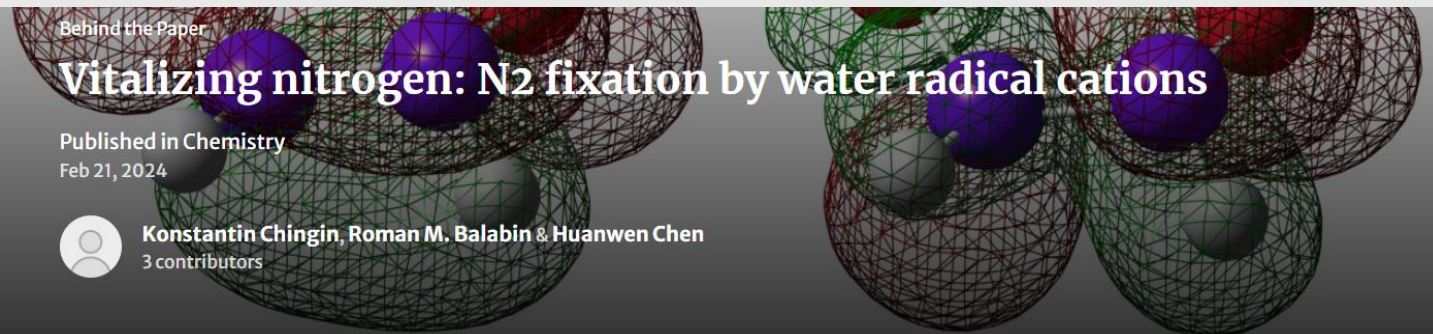


Ambient catalyst-free nitrogen fixation

- Scaled-up setup and vibrational spectroscopy:



Reaction: Press



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Жигулёвец стал соавтором нового метода связывания азота

22 февраля 2024 09:40 328

Открыт новый плазменный метод связывания атмосферного азота водой. Среди авторов – два россиянина, один из которых родился в Жигулёвске.

ПРОБЛЕМЫ И МЕТОДЫ НАУКИ

Как вода связала азот



НОВОСТИ НАУКИ

Биодоступный азот можно получить связыванием в водной плазме

18.03.2024 • РОМАН БАЛАБИН • ХИМИЯ • 68 КОММЕНТАРИЕВ



N+1

| 15:42 | 27.02.24 | * 51

| Химия

[Ссылка](#)

Молекулярный азот прореагировал с водяной плазмой
При этом образовались гидроксилламин и нитроксил

[Михаил Бойм](#)

Part V. Project Timeline

Project Timeline

Time		Field		
		Experimental	Theoretical	Industrial
2024	Q1	Building of a new plasma setup with optical profiling	Calculation of nitrogen fixation by water dimer radical-cation at CCSD(T) level	General market analysis
	Q2			Gathering of leads and ideas
	Q3	The new setup optimization	Going beyond CC-methods: application of Weizmann-1 scheme, iFCI, and MBE-FCI on (H ₂ O) ₂ ⁺⁺	SWOT matrix analysis
	Q4	Investigation of water-plasma parameters		Contact with hydroxylamine/nitroxyl producers, wholesalers, and consumers in South Central China
2025	Q1	Investigation of methanol-plasma parameters & CH ₃ OH dimer production	Plasma parameters estimation by numerical methods	Contact with hydroxylamine/nitroxyl producers, wholesalers, and consumers in East China
	Q2	Investigation of MTBE-plasma parameters & MTBE dimer production		
	Q3	Investigation of formic acid synthesis in CO/water plasma	Calculation of formic acid synthesis in plasma at CCSD(T) level	Creation of a launch strategy
	Q4	Investigation of CO ₂ /water & N ₂ O/water plasma configurations		Initiating the process of obtaining the grant of a patent
2026	Q1	Building of a new plasma reactor based on the previous findings	Calculation of the long-lived intermediates in CO ₂ /water plasma at CCSD(T) level	Getting declarations of intent (LOIs) from the potential shareholders
	Q2			
	Q3	The reactor test & optimization	Benchmarking of recent DFT methods: SCAN, B05, and B13+ functionals	Acquiring third-party funds
	Q4			Industrial project detailing: Process engineering for nitrogen fixation by water plasma

Thank you for your attention!

感谢您的关注!

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