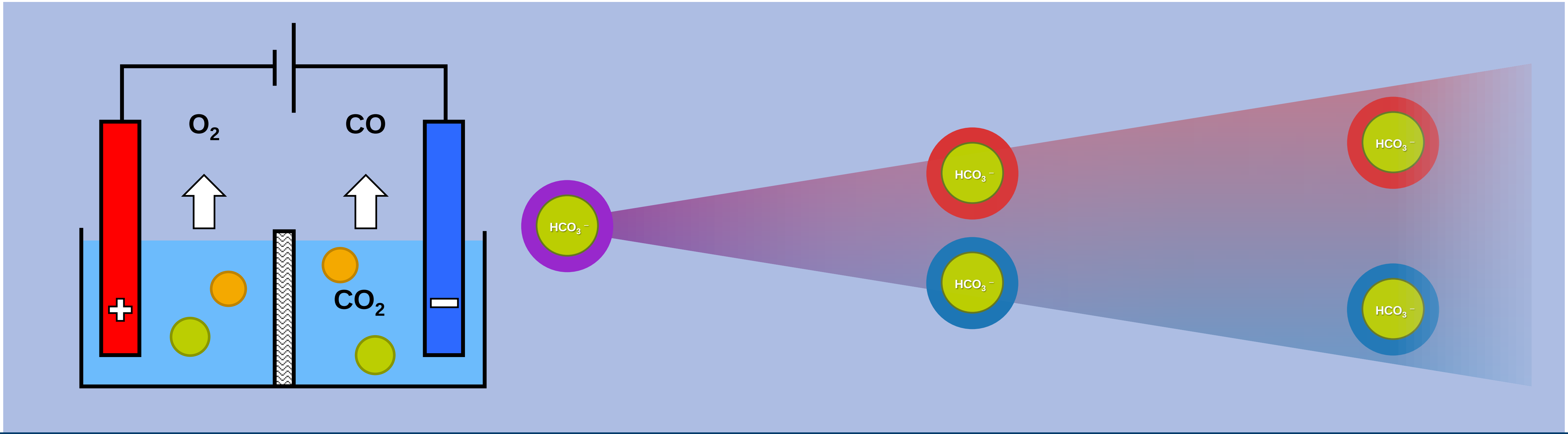
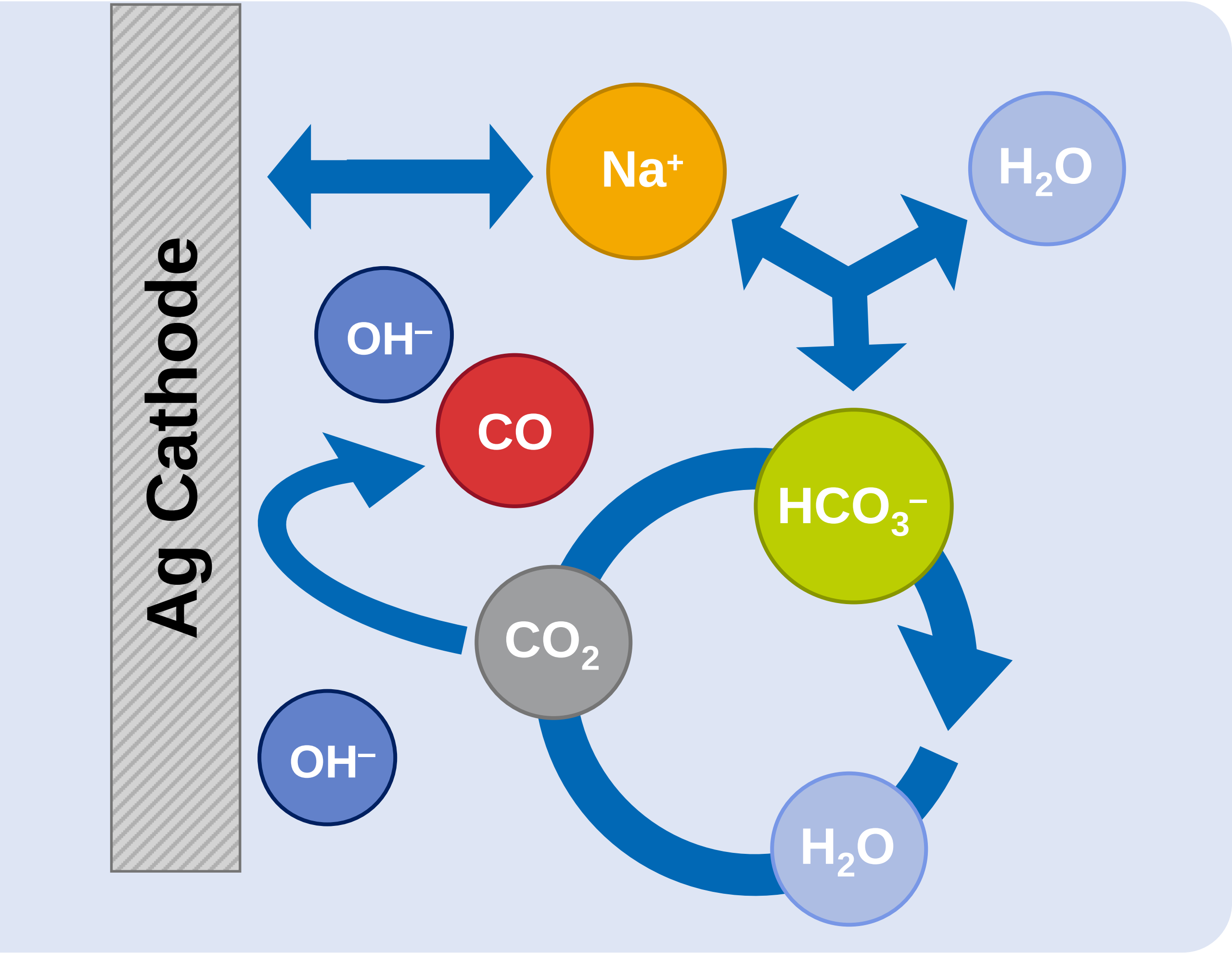


In operando NMR investigations of electrolyte chemistry during CO_2 electrolysis

ICCDU | 26th June 2023 I S. Jovanovic, P. Jakes, S. Merz, R.-A. Eichel, J. Granwehr

JÜLICH Forschungszentrum

Motivation

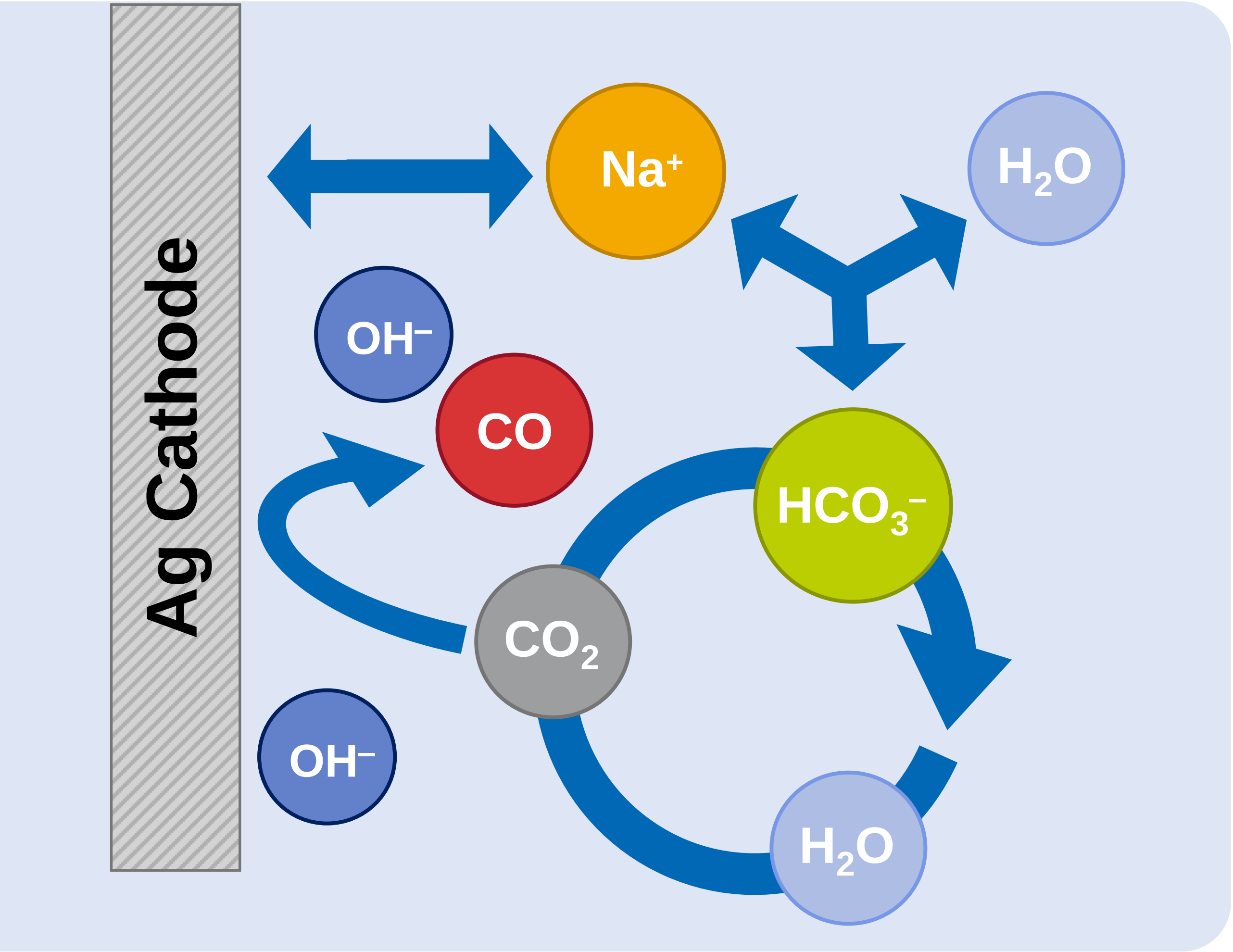


Local pH and **electrolyte chemistry** play a critical role for CO_2 electrolysis!

- **Local pH**
  affects catalytic pathways
- **CO_2/HCO_3^- equilibrium**
  affects CO_2 resupply
- **Cation chemistry**
  affects product selectivity

JÜLICH Forschungszentrum

Motivation



Local pH and **electrolyte chemistry** play a critical role for CO_2 electrolysis!

Investigation of local electrolysis phenomena requires ***in operando* methods!**

Overview *In Operando* NMR spectroscopy

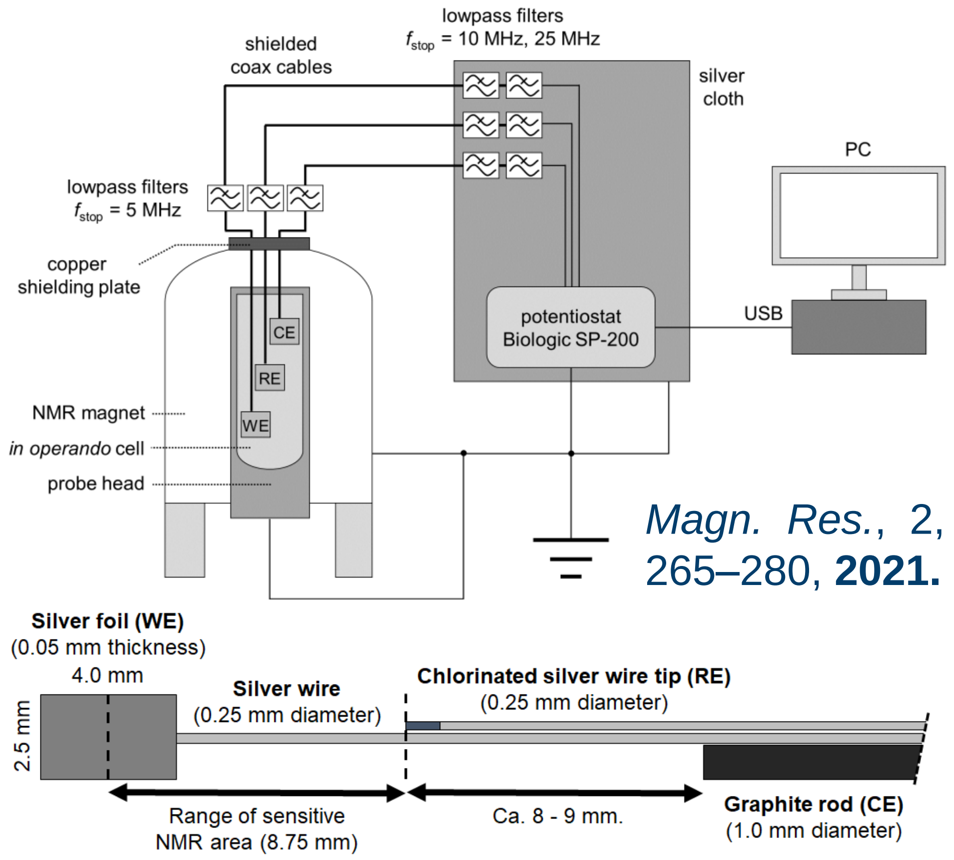
Benefits

1. **Wide toolset of experiments**
   to investigate system interactions
2. **Straightforward assessment**
   of chemical species
3. **Selective studies**
   of molecular properties

Challenges

1. **Magnetic field distoration**
   by conductive cell components
2. **Amplification of external RF noise**
   by cables & wires
3. **Compatibility**
   between equipment

In operando Electrolysis Setup



Magn. Res., 2, 265–280, **2021.**

JÜLICH Forschungszentrum

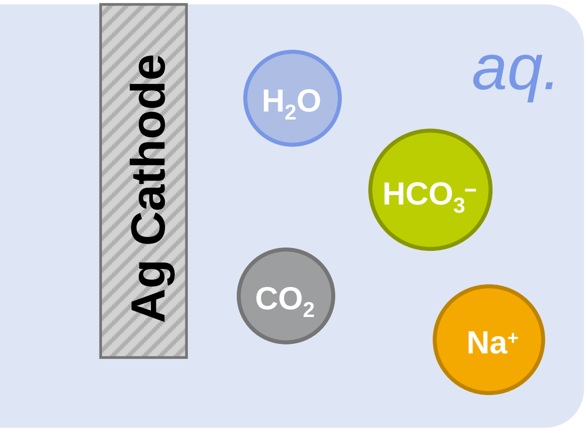
In operando Experimental Procedure

Increasingly negative potential   Increasing reaction rate

Open Circuit Voltage
$U \approx -0.04$ V

Under-potential
$U = -1.10$ V

Electrolysis Conditions
$U \approx -1.4$ V



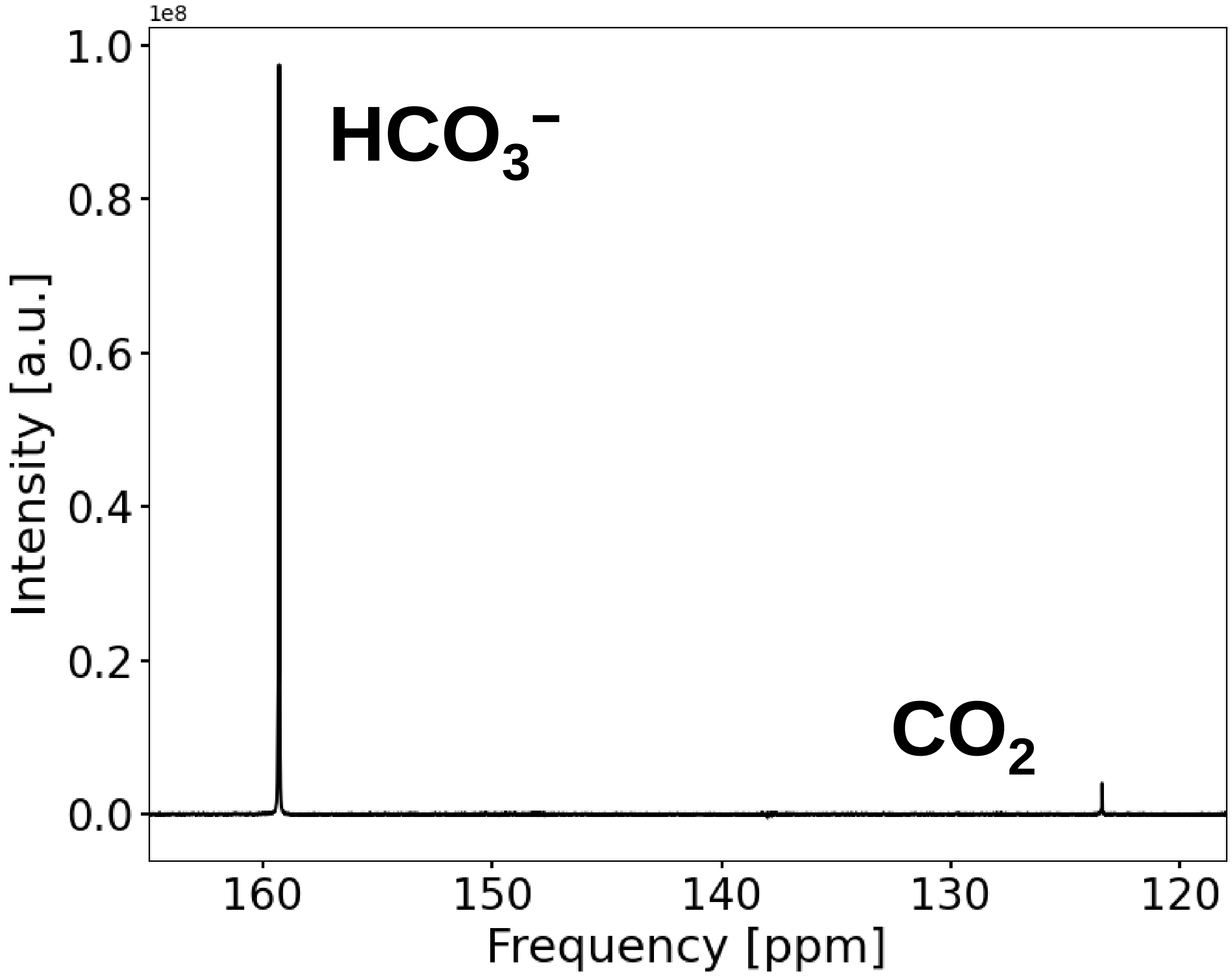
Ag Working Electrode

1M K/NaH^{13}CO$_3$(aq) Electrolyte

Saturated with **$^{13}CO_2$**

1. **^{13}C/^{23}Na Spectra recording** for 12 hours (10 min resolution)
2. ***T_1* & *T_2*** Relaxation Experiments
3. **Exchange Experiment** (CO_2/HCO_3^-)

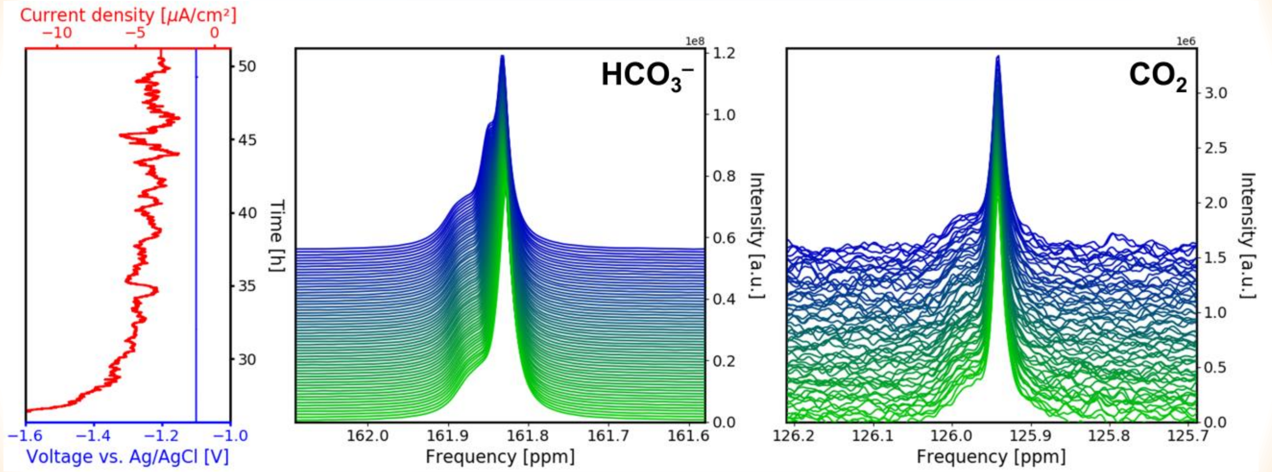
Observation #1 ^{13}C Signal Evolution

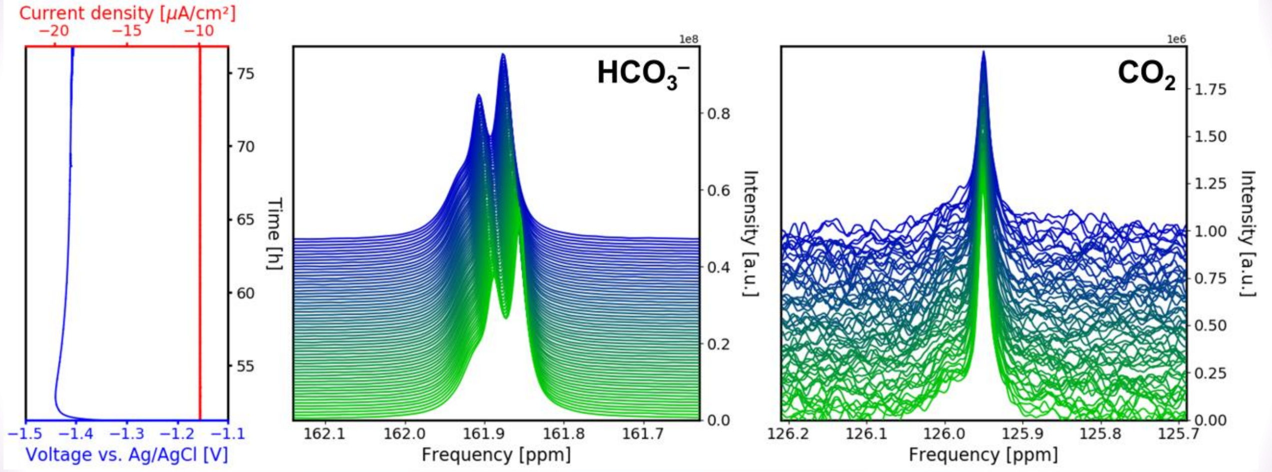


^{13}C spectrum of CO_2 saturated electrolyte

Observation #1 ^{13}C Signal Evolution

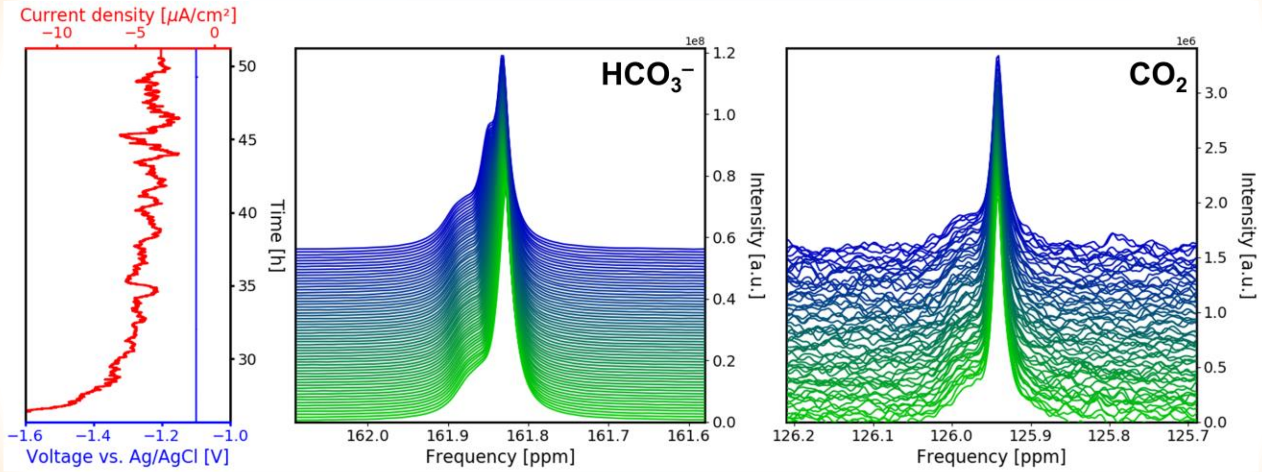
OCV | Under-potential | Electrolysis

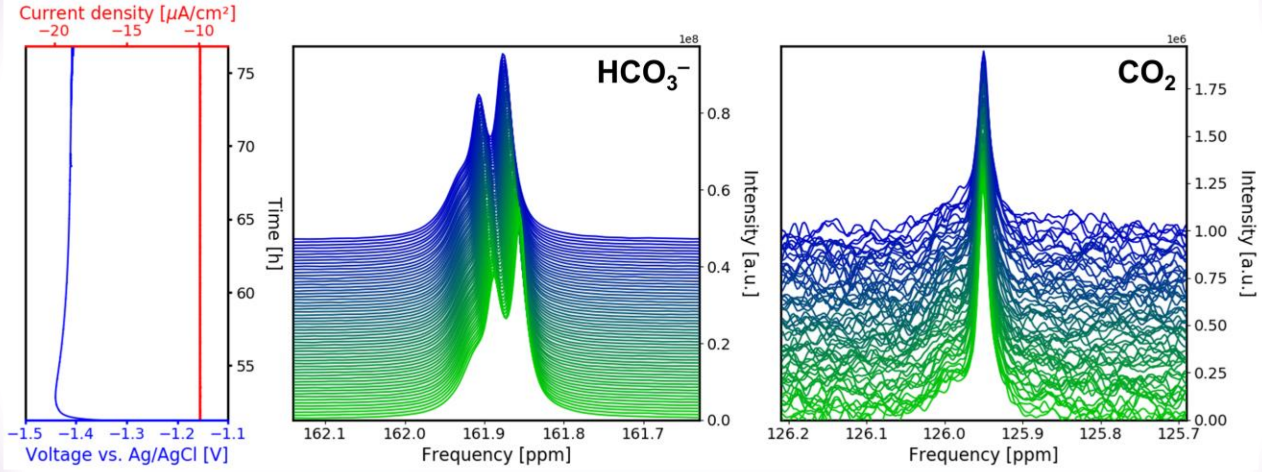




Observation #1 ^{13}C Signal Evolution

OCV → Under-potential → Electrolysis



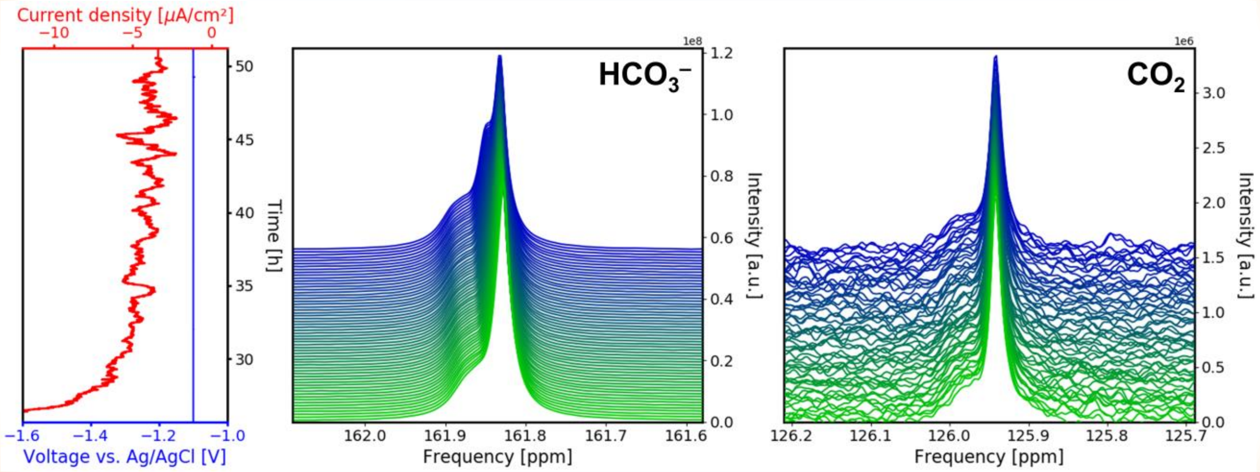


CO_2 signal only decreases in intensity, shape stays constant

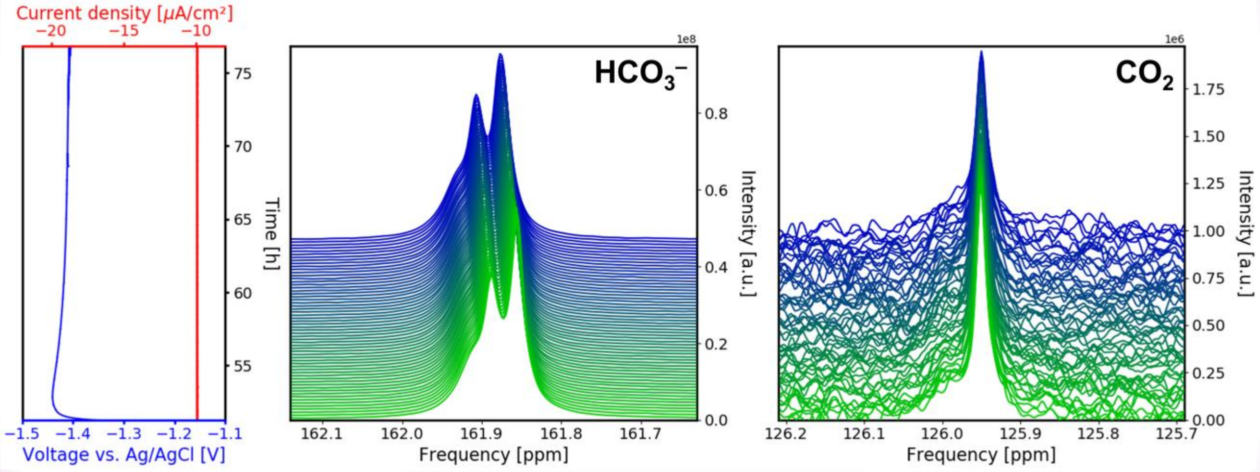
JÜLICH Forschungszentrum

Observation #1 ^{13}C Signal Evolution

OCV → Under-potential → Electrolysis



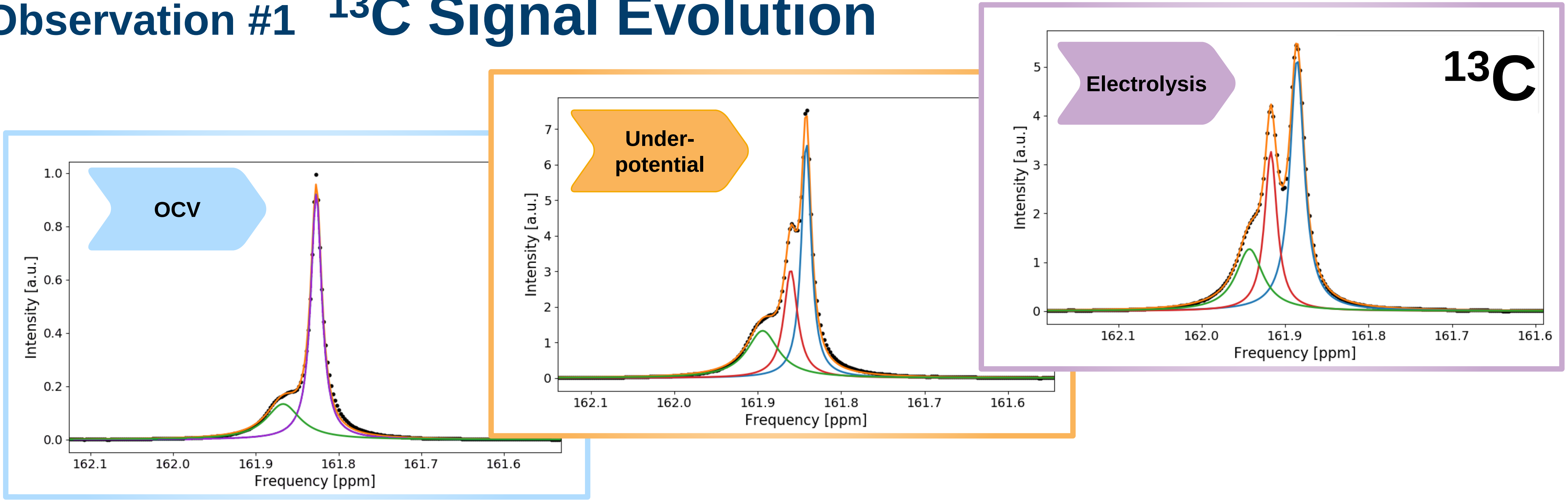
CO_2 signal only decreases in intensity, shape stays constant



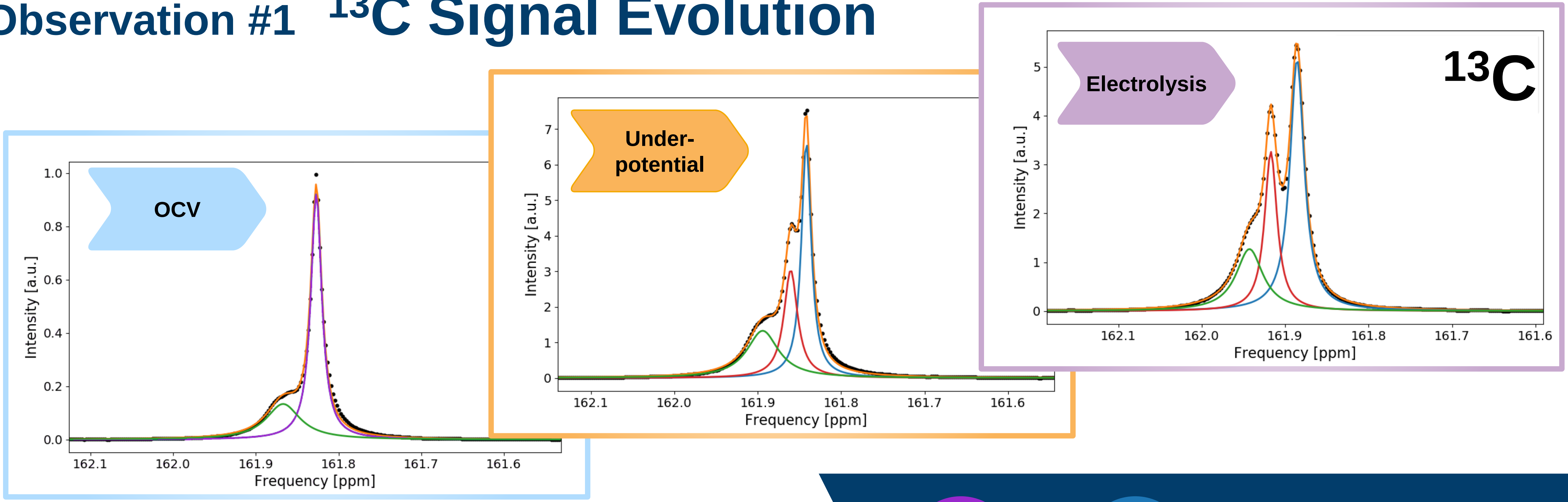
HCO_3^- signal splits during underpotential and electrolysis stage

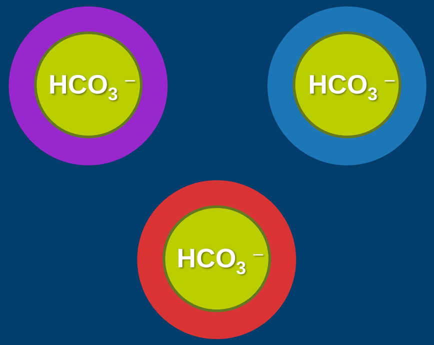
JÜLICH Forschungszentrum

Observation #1 ^{13}C Signal Evolution



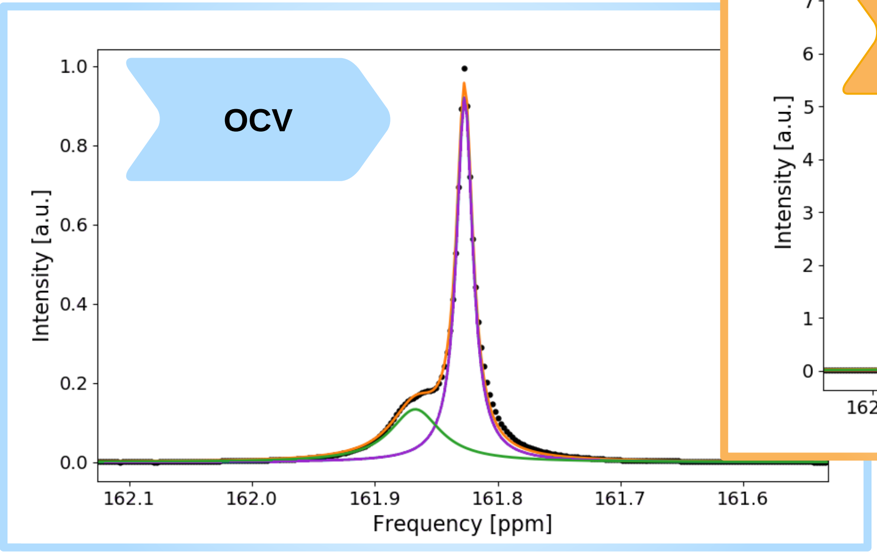
Observation #1 ^{13}C Signal Evolution

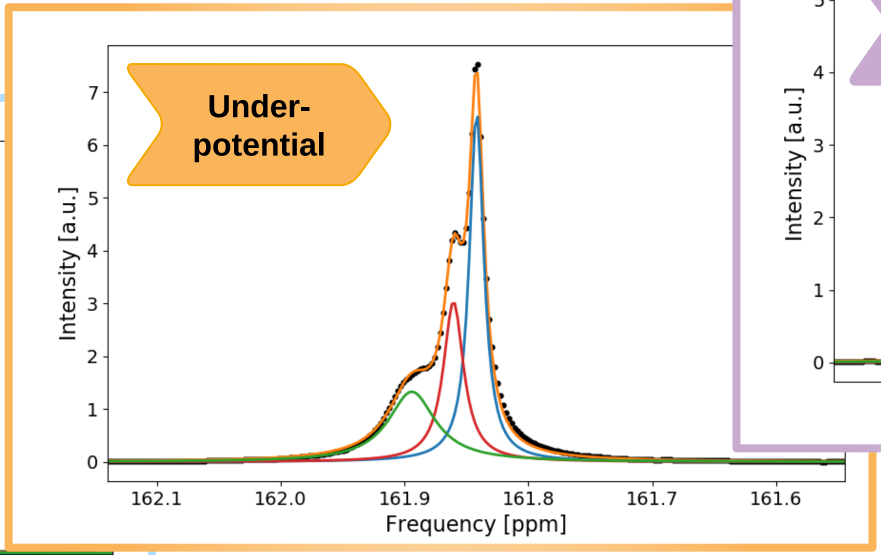


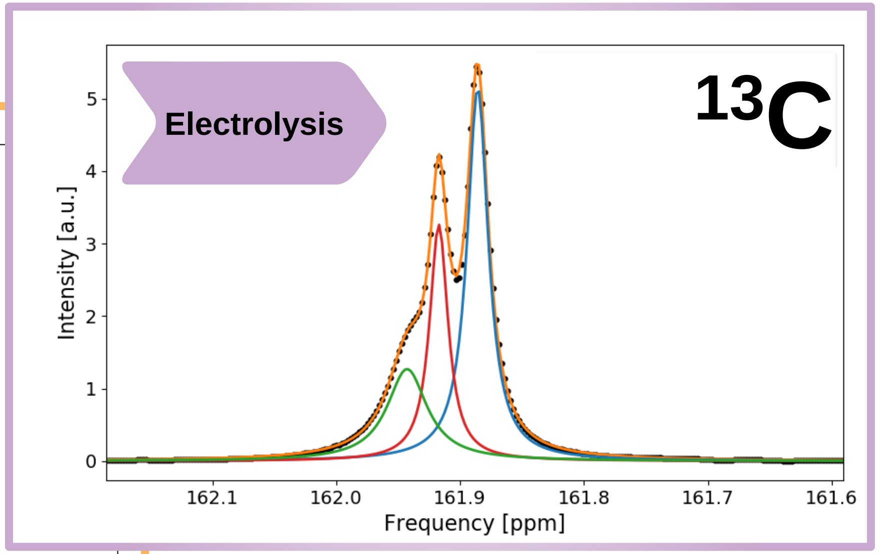


Different HCO_3^- environments

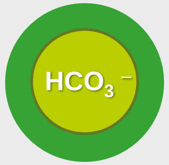
Observation #1 ^{13}C Signal Evolution

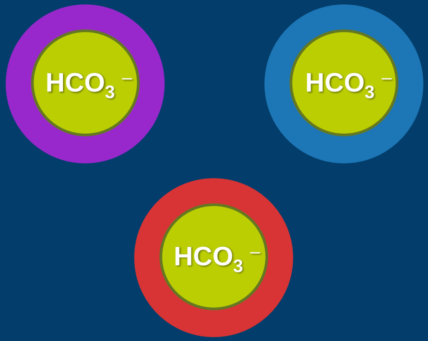






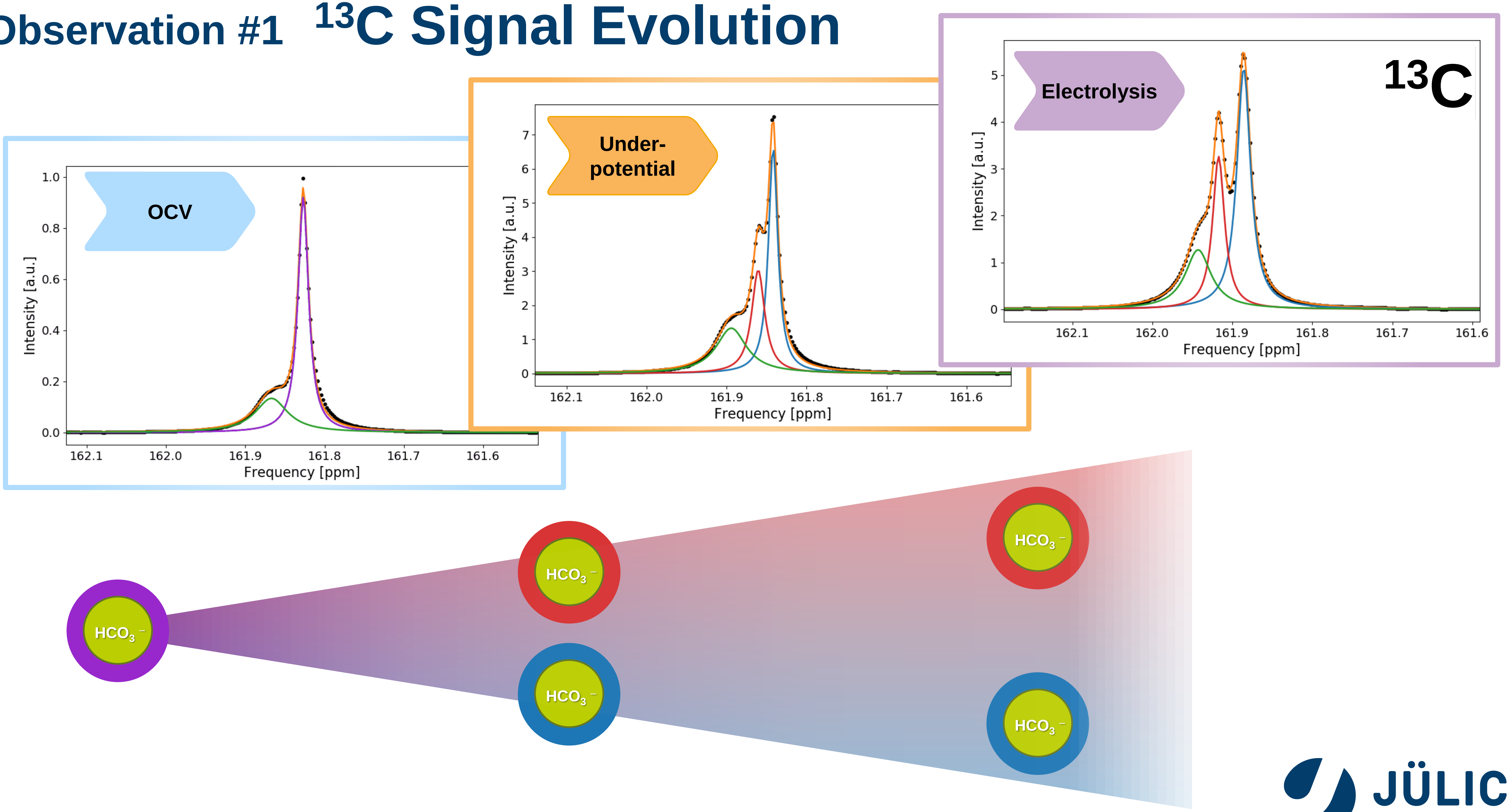
Artifact
distortion of main magnetic field B_0





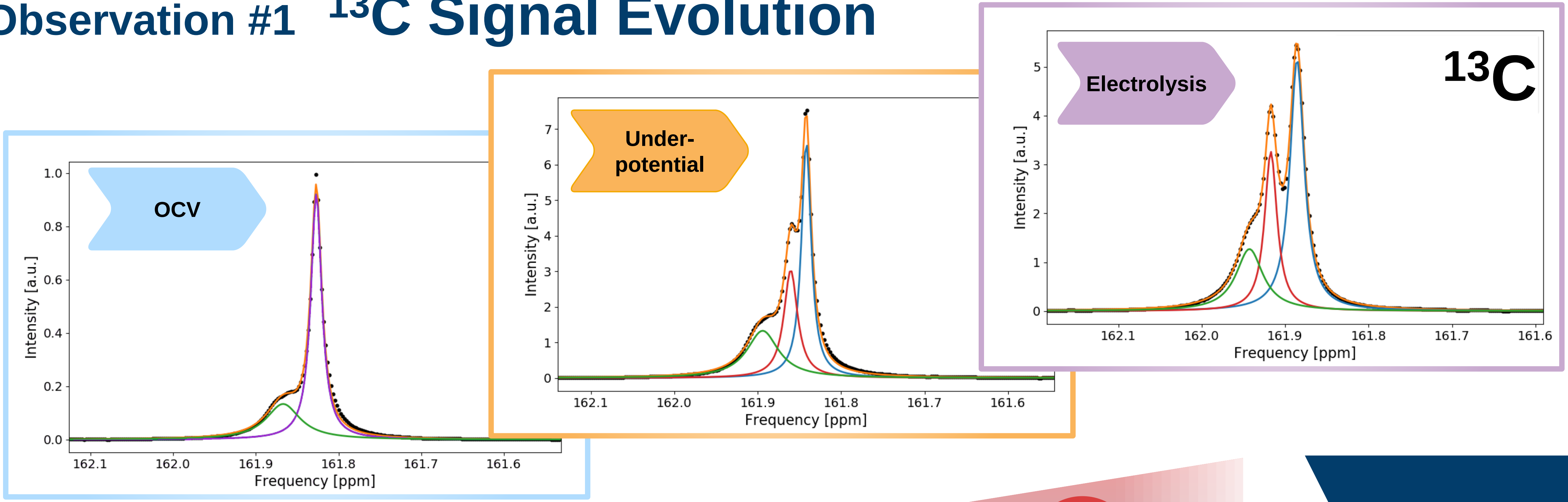
Different HCO_3^- environments

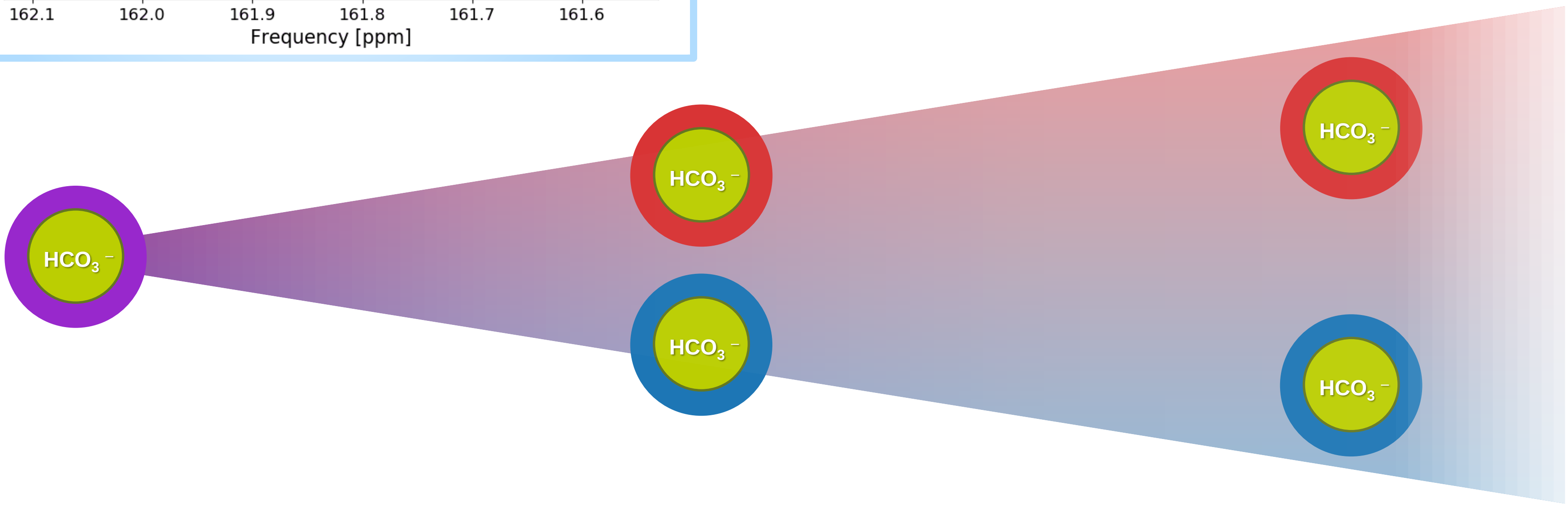
Observation #1 ^{13}C Signal Evolution



JÜLICH
Forschungszentrum

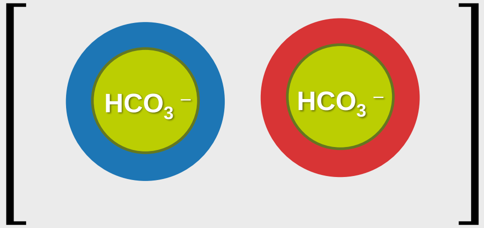
Observation #1 ^{13}C Signal Evolution

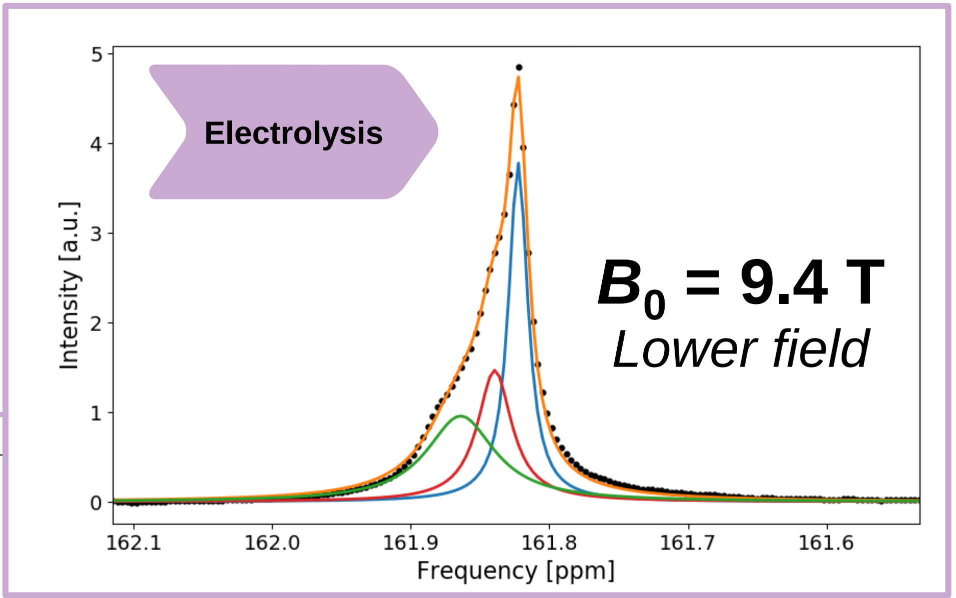


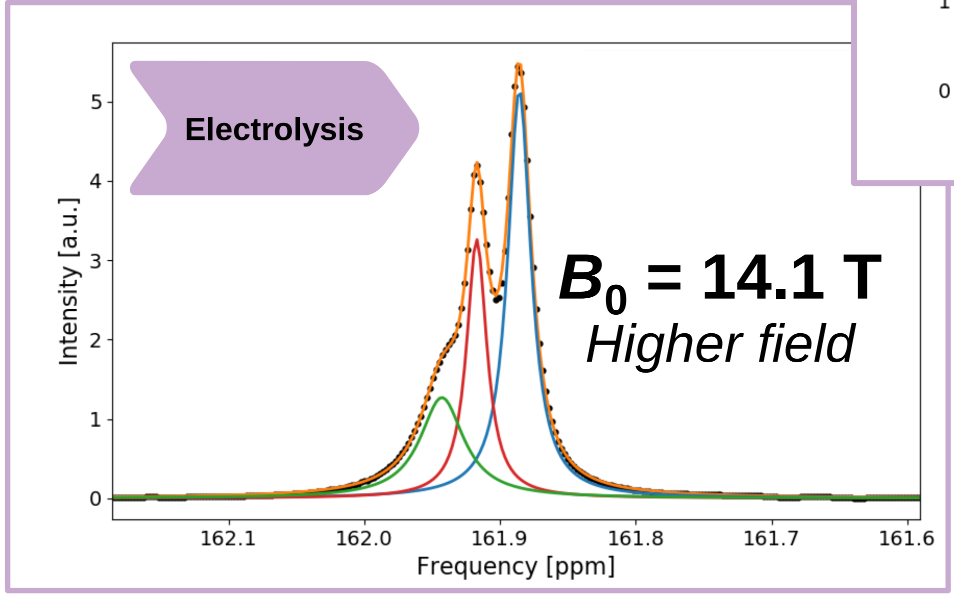


Changes in local HCO_3^- environment!

Observation #2 Magnetic field dependent effects

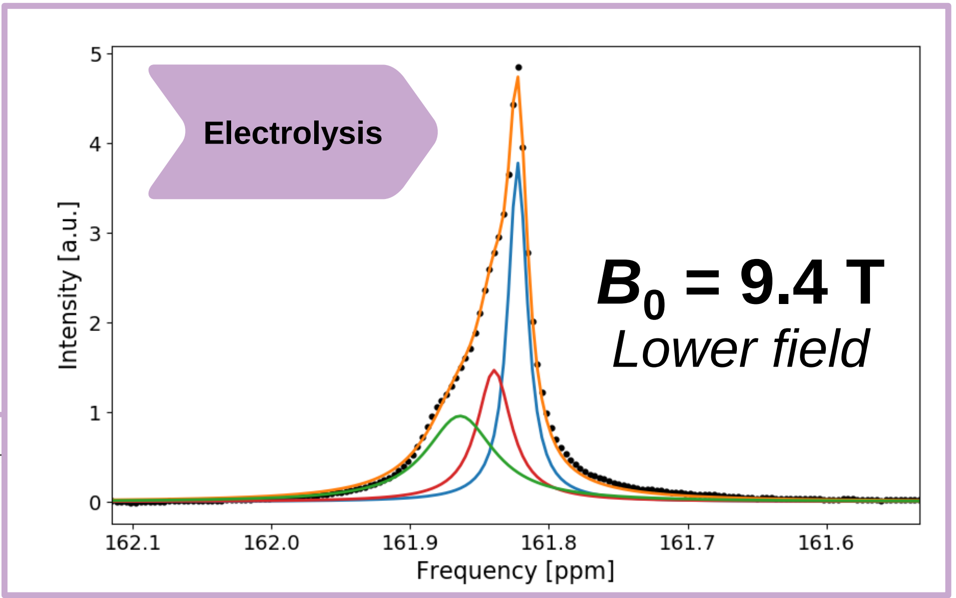
$\Delta\delta$  $= f(B_0)$

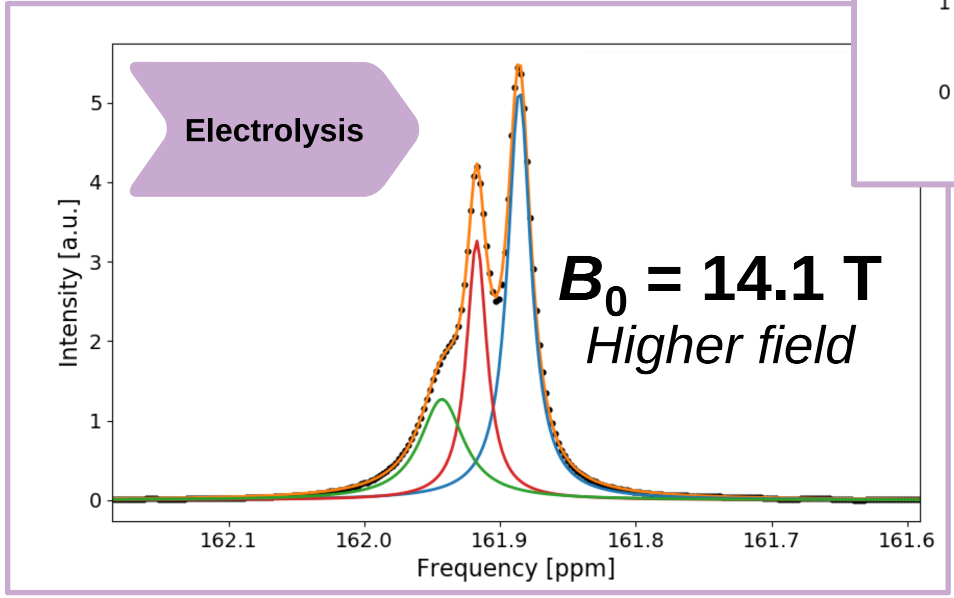




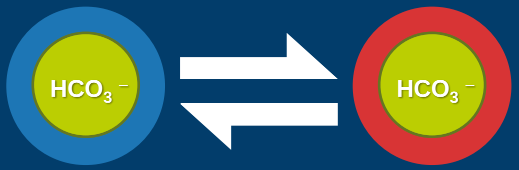
JÜLICH Forschungszentrum

Observation #2 Magnetic field dependent effects



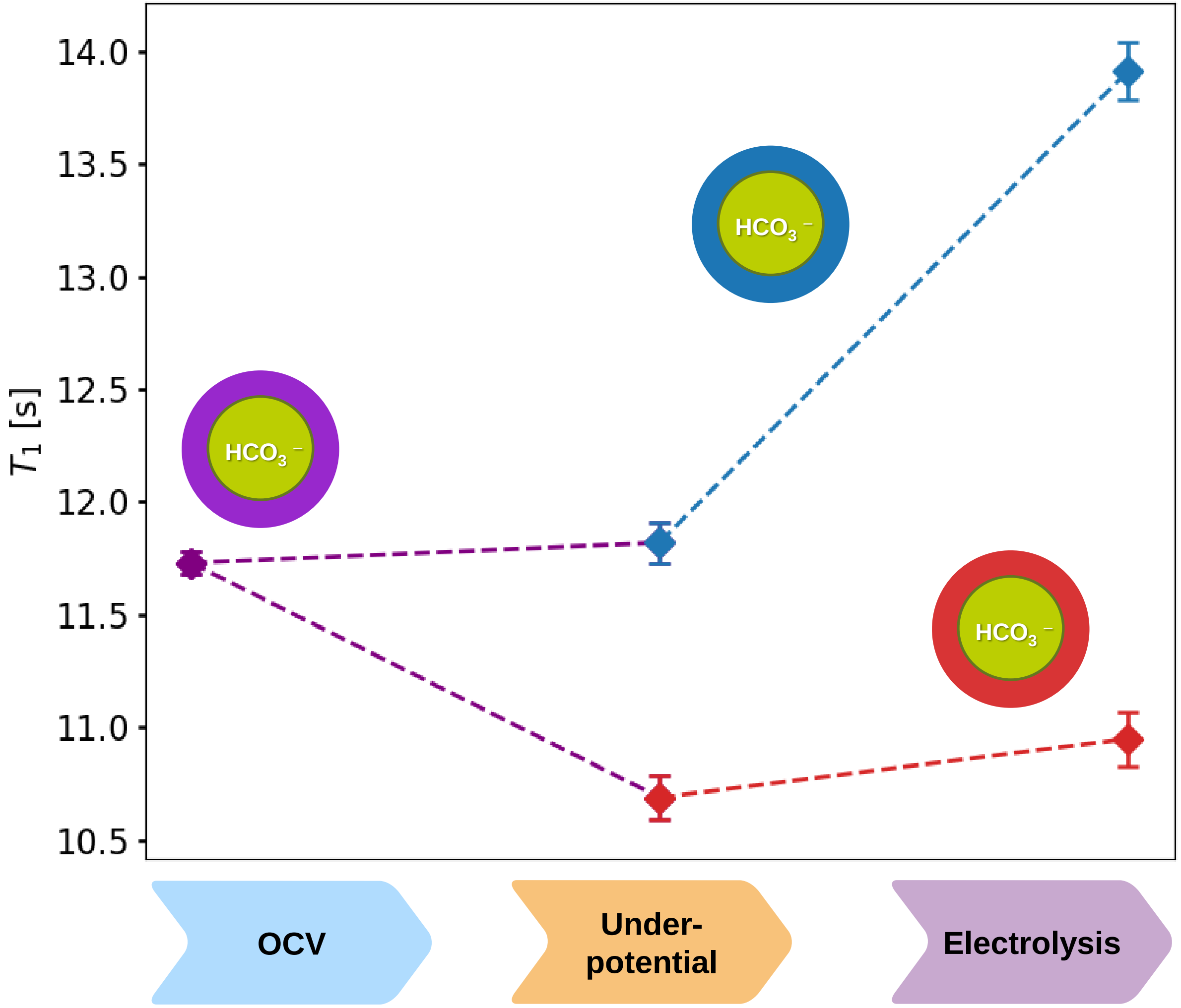


Field dependent peak separation
→**Exchange!**



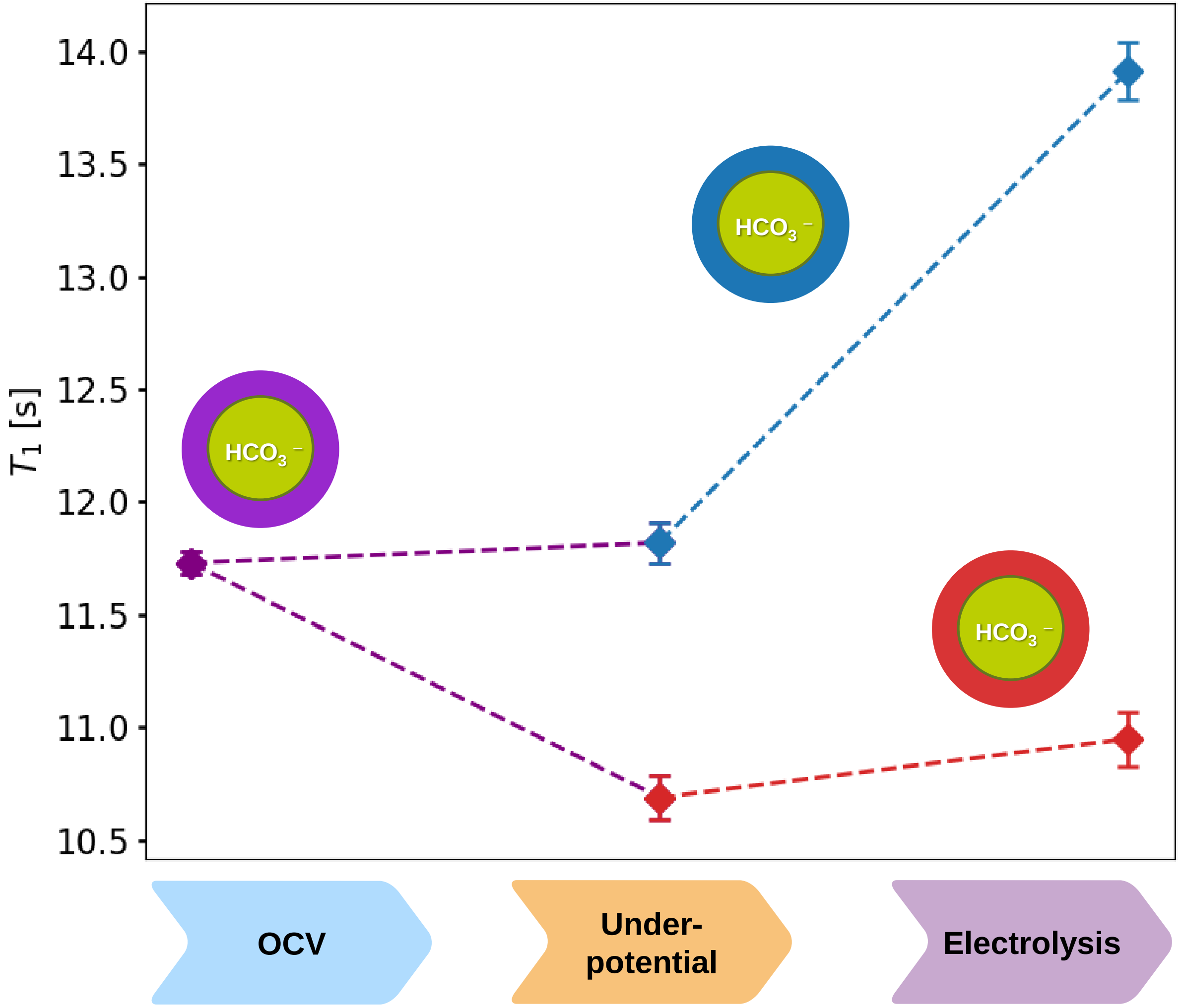
JÜLICH Forschungszentrum

Observation #3 T_1 relaxation constants

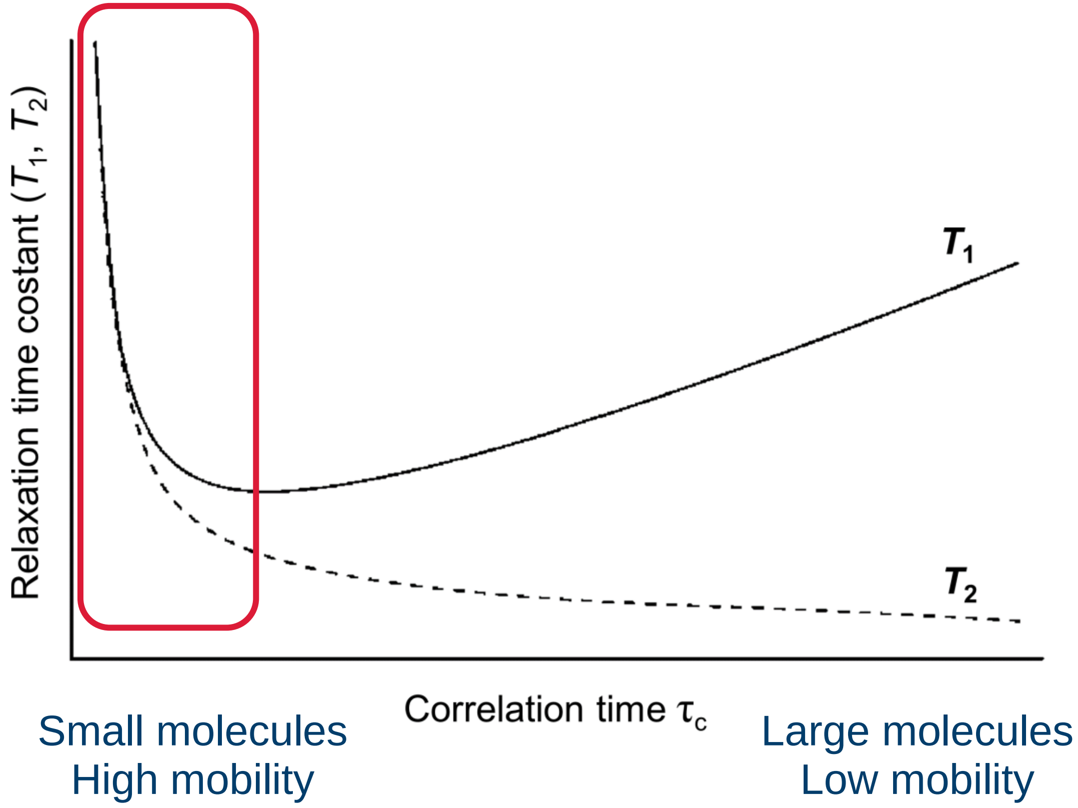


JÜLICH Forschungszentrum

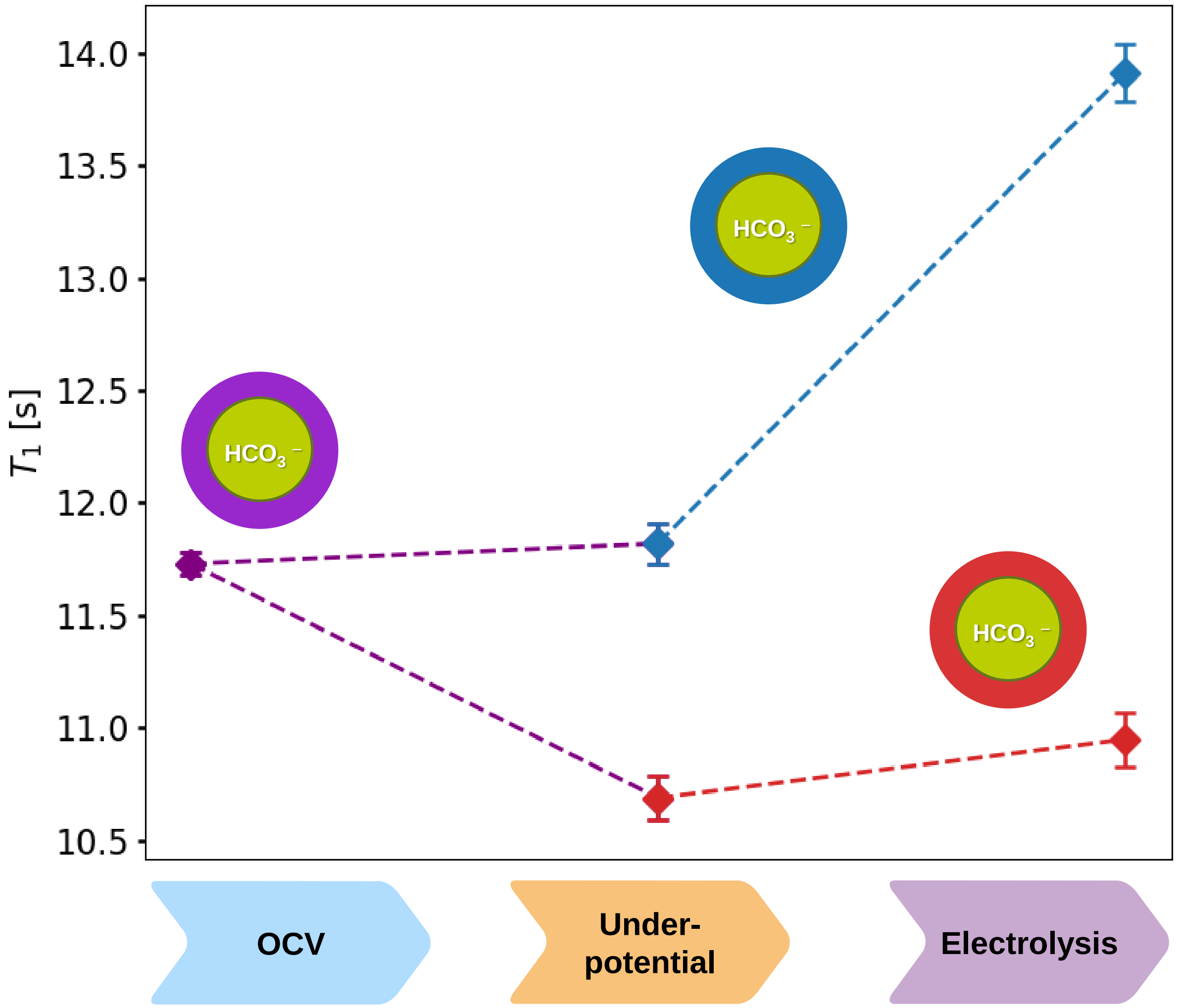
Observation #3 T_1 relaxation constants

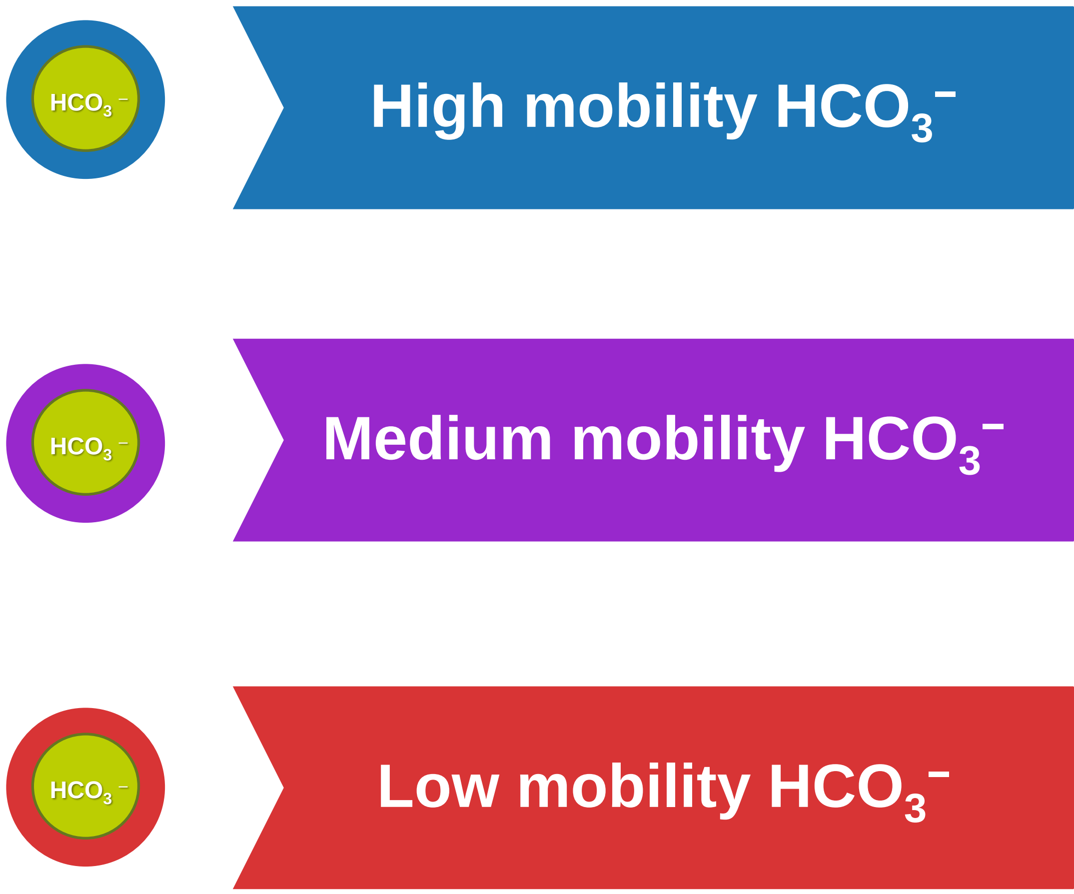


BPP theory



Observation #3 T_1 relaxation constants





Discussion HCO_3^- Environments

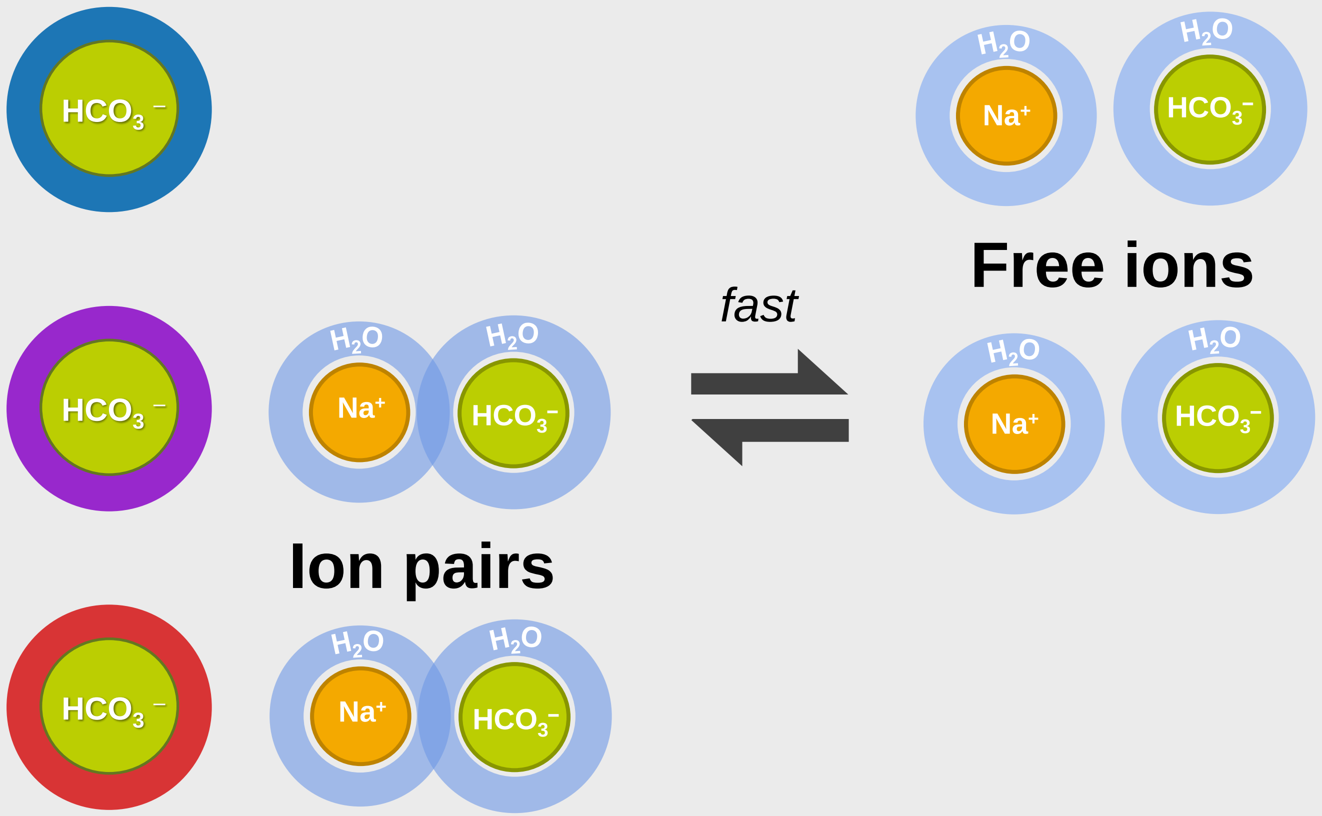
Na^+/HCO_3^- must be…

1. in two chemical environments
2. that are exchanging in solution
3. and exhibit different mobilites

HCO_3^- Environments

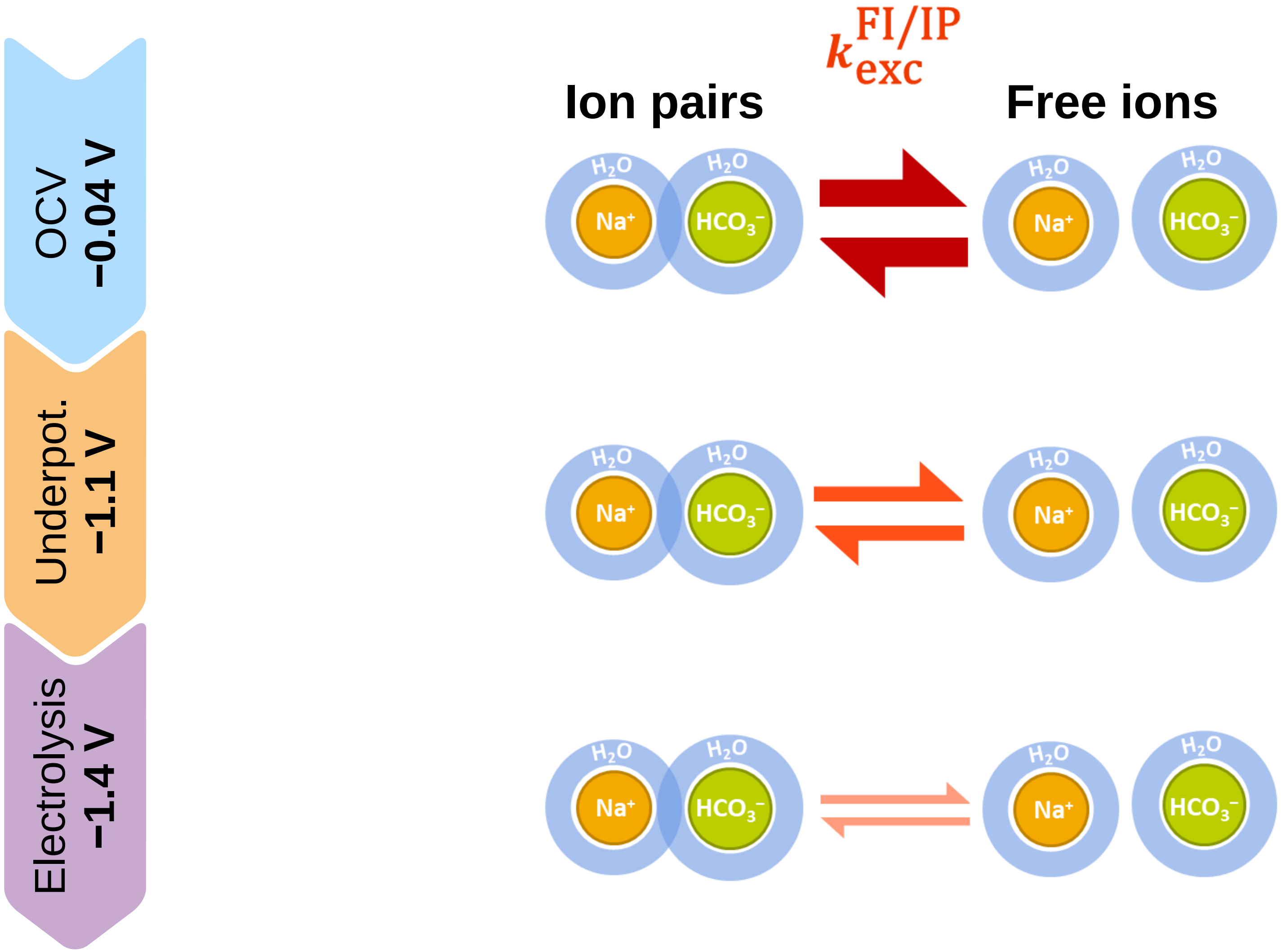
Na^+/HCO_3^- must be…

1. in two chemical environments
2. that are exchanging in solution
3. and exhibit different mobilites



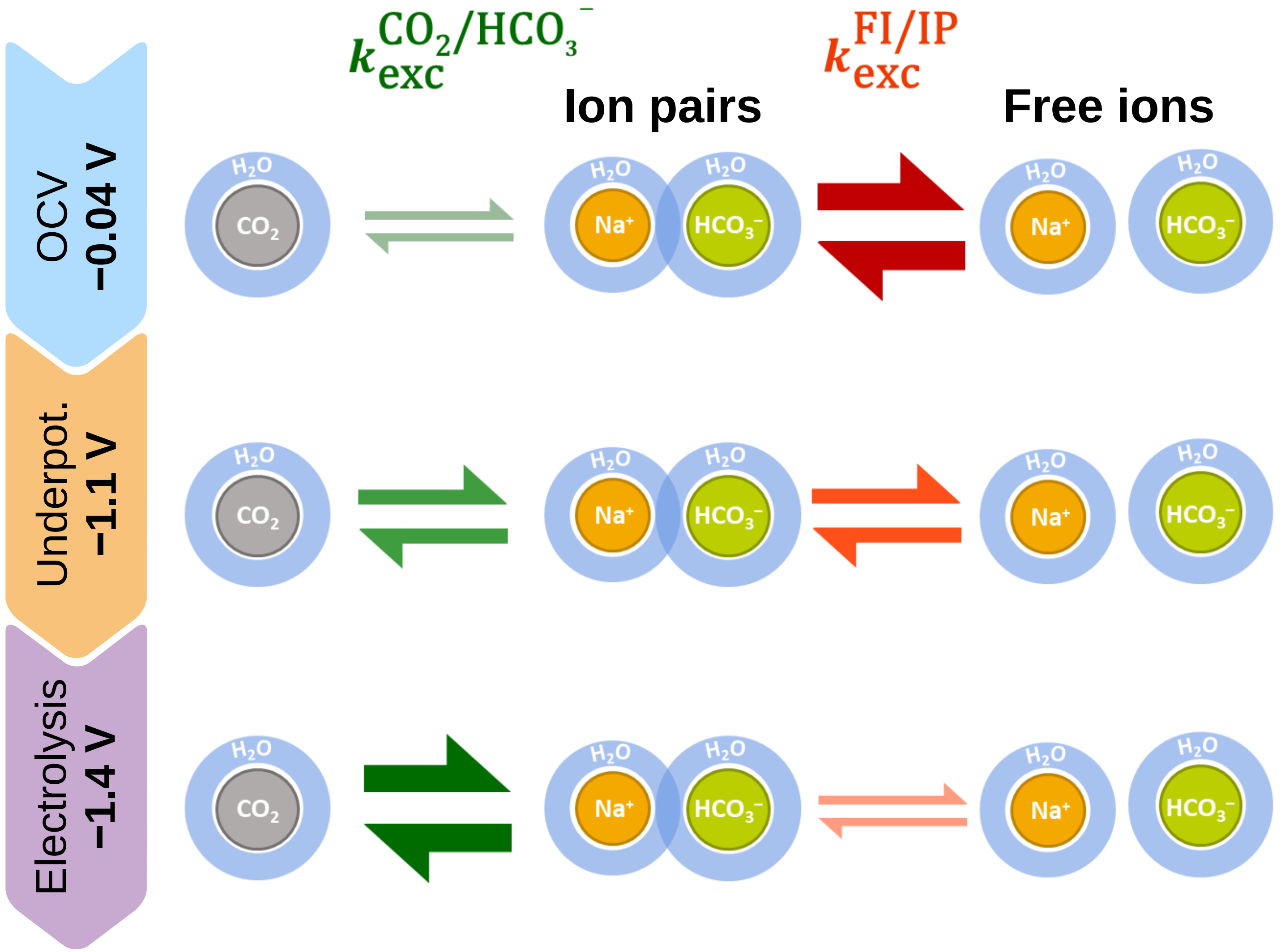
JÜLICH Forschungszentrum

Conclusion Potential Dependent Electrolyte Chemistry



Exchange rate between IP and FI decreases with increasingly negative potential

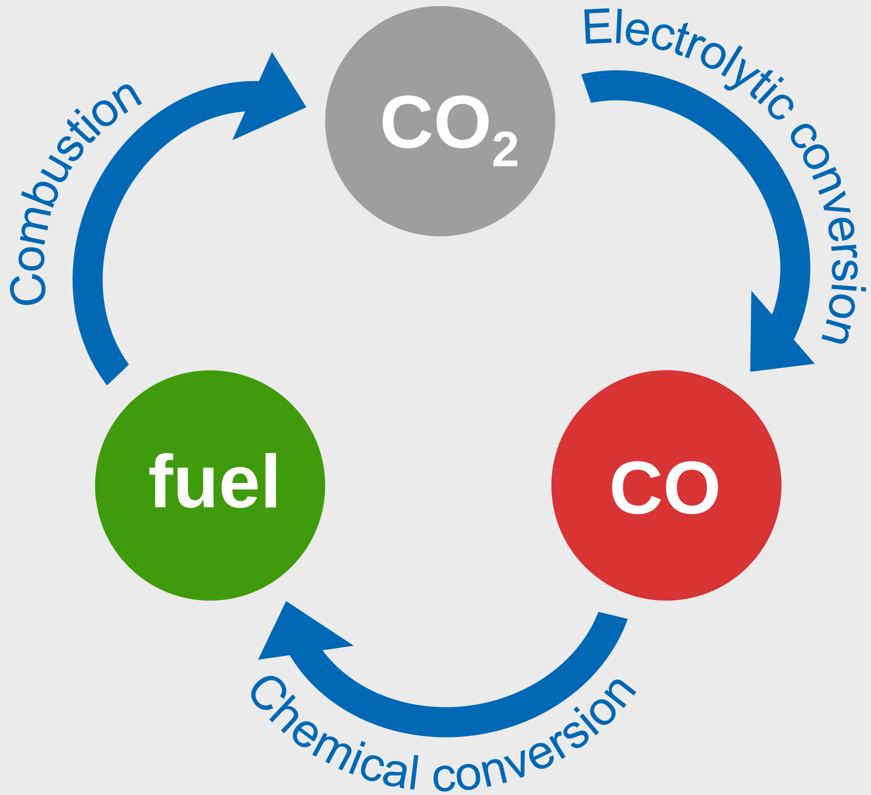
Conclusion Potential Dependent Electrolyte Chemistry



Exchange rate between IP and FI decreases with increasingly negative potential

Life time of IPs affects CO_2 resupply by catalyzing the HCO_3^- dehydration

IEK-9: Fundamental Electrochemistry



Prof. Rüdiger-A. Eichel
Head of Institute

Prof. Josef Granwehr
Head of Department

Michael Schatz
PhD Candidate

FSC

DFG Deutsche Forschungsgemeinschaft

Ionic On-and-Off Relationships in CO_2 Electrolysis