European Network on New Sensing Technologies for Air Pollution Control and Environmental Sustainability - *EuNetAir*

COST Action TD1105

4th International Workshop *EuNetAir* on

Innovations and Challenges for Air Quality Control Sensors

FFG - Austrian Research Promotion Agency - Austrian COST Association

Vienna, Austria, 25 - 26 February

MSDI HETEROJUNCTIONS, HOW CONDUCTIVITY AND IMPEDANCE ALLOW FOR DISCRIMINATION BETWEEN AMMONIA AND HUMIDITY

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Scientific context and objectives in the Action

- **Background / Problem statement:** Guidelines for Best Coupling Air-Pollutant and Transducer (SIG 3)

- **Objective:** To operate a same conductometric device in different ways to achieve a better selectivity ?

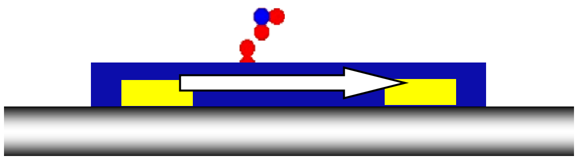
- **Outline:** - Presentation of the device

  - Current = f(time): Sensitivity to NH_3 and relative humidity

  - Impedance = f(frequency): Discrimination between NH_3 and relative humidity

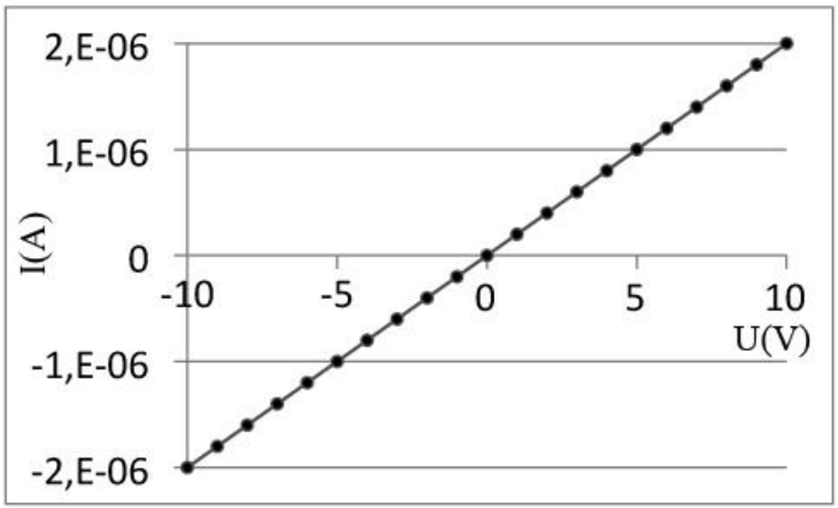
This is following my talk in Sofia, in Dec. 2015

Conductometric Gas Sensors



Conductivity: σ = n e μ

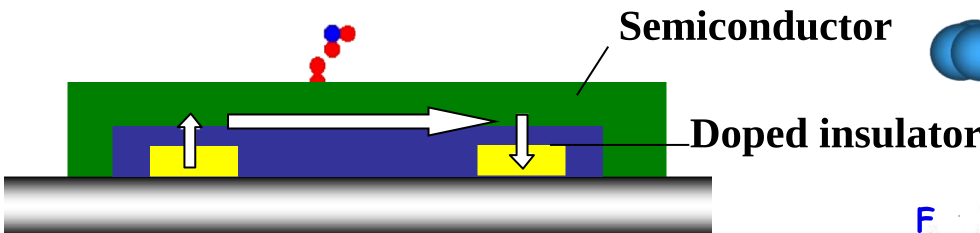
For redox active species, variation of n by doping or neutralization of charge carriers: $\Delta[Gas] \Rightarrow \Delta n \Rightarrow \Delta\sigma$

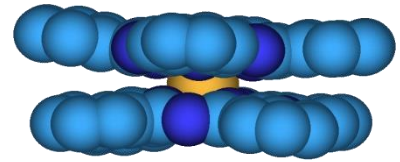


Thus, in a p-type material, a donating species like NH_3 can give 1 electron to the material, neutralizing the positive charge carriers, leading to a decrease of σ.

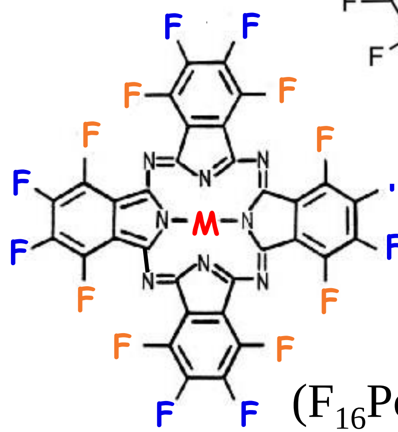
M. Bouvet, A. Pauly, "Molecular Semiconductor - Based Gas Sensors" in The Encyclopedia of Sensors, ed. by C.A. Grimes, E.C. Dickey, M. V. Pishko, American Scientific Publishers, vol 6, 2006, pp 227-270.

Molecular Semiconductor - Doped Insulator heterojunctions (MSDI)

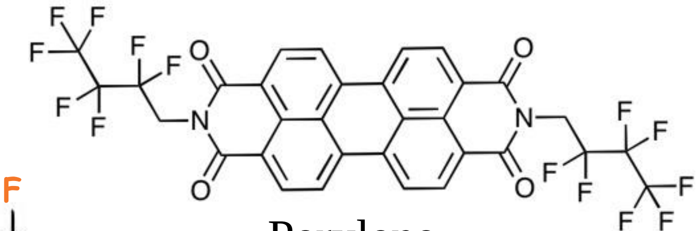




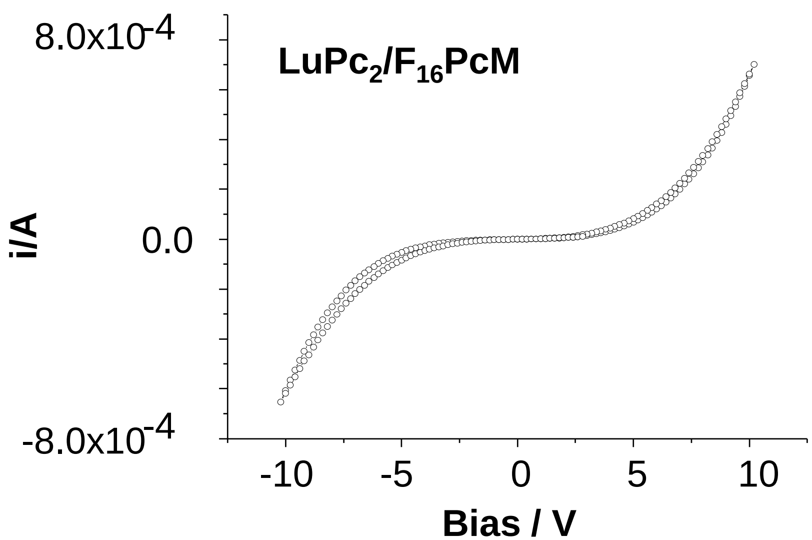
$LuPc_2$
$E_{gap} = 0.5$ eV



$(F_{16}Pc)M$



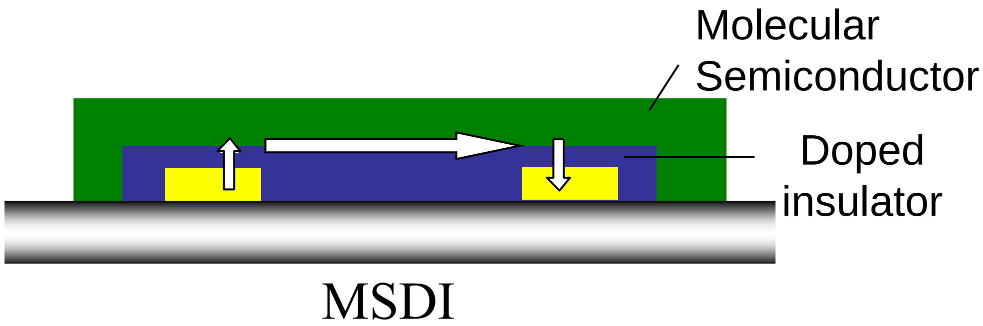
Perylene



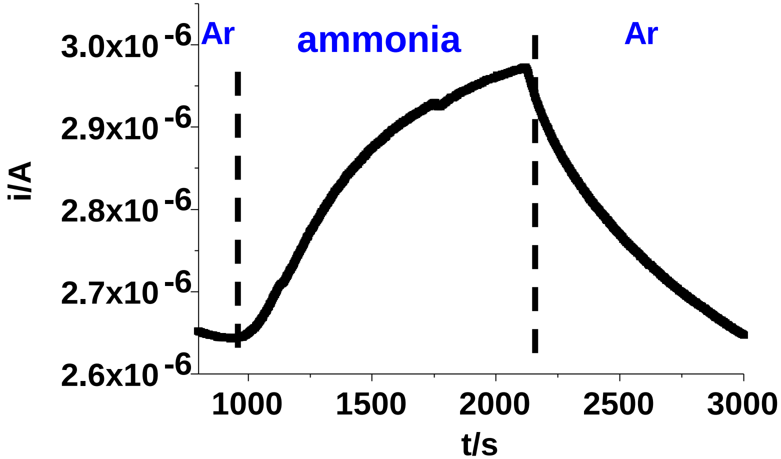
⇒ Device sensitive to redox active gases with a response inverted compared to that of a $LuPc_2$ resistor

V. Parra et al., “Molecular semiconductor - doped insulator (MSDI) heterojunctions: An alternative transducer for gas chemosensing", *Analyst*, 134, 1776-1778, 2009.

Sensitivity of n-MSDIs to Ammonia

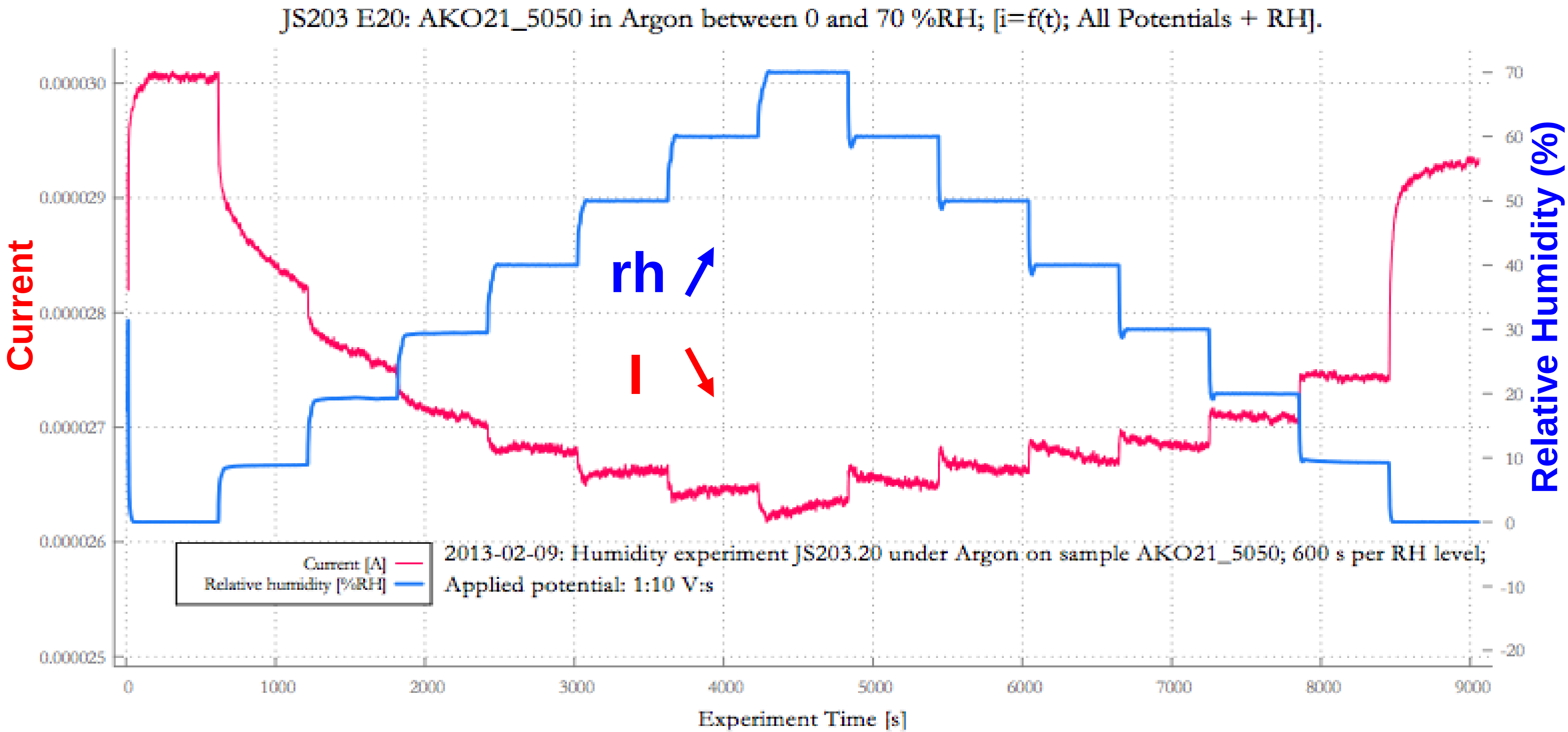


An energy barrier $E_{p\text{-}n}$ exists at the interface between the two layers



n-MSDI, $E_{p\text{-}n}$ ↘ and I ↗

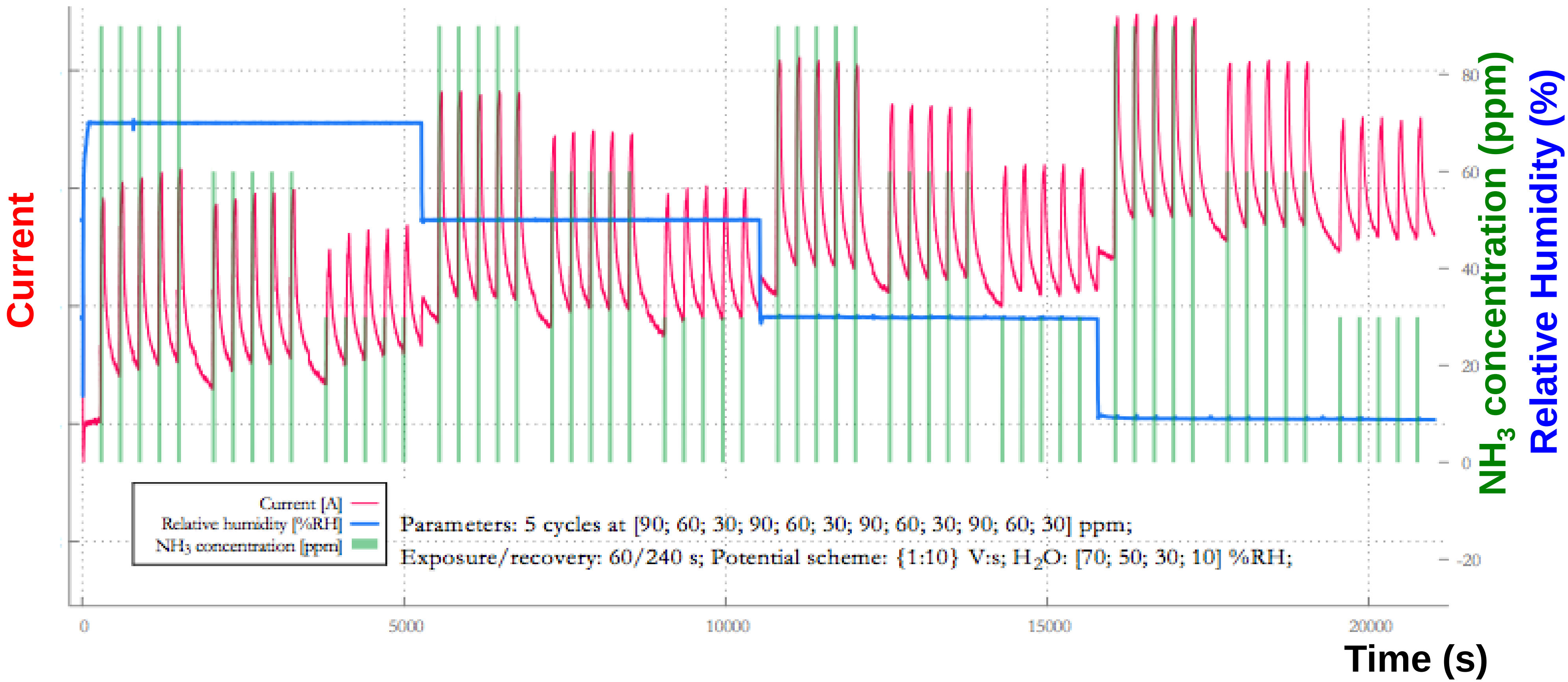
Sensitivity of n-MSDIs to Humidity



H_2O is a donating species like NH_3 , but I ↘

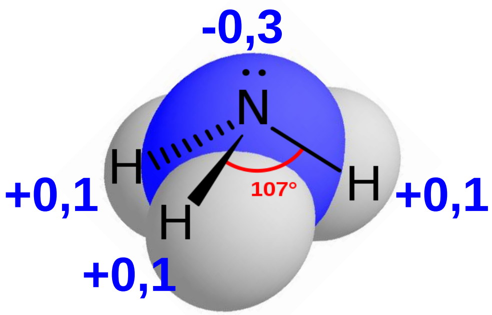
but the effect is very weak between 10 and 70 % rh

Sensitivity to Ammonia of n-MSDIs



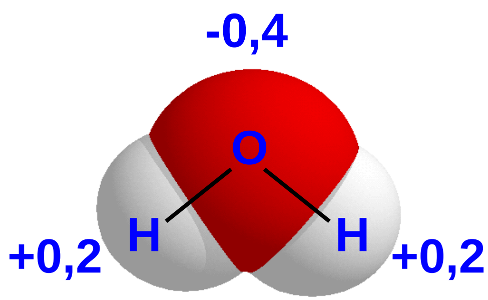
NH_3: I ↗   **H_2O : I ↘**

Discrimination between NH_3 and H_2O



μ = 1,49 D

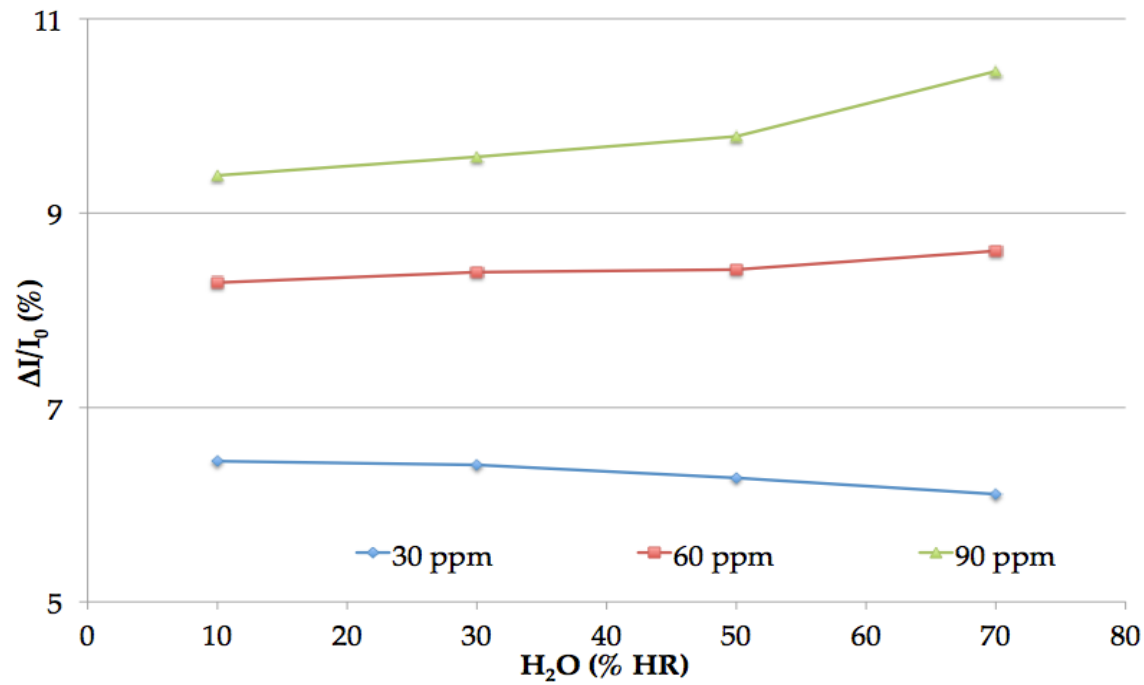
ε = 22



μ = 1,85 D

ε = 80

Relative response: $\Delta I/I_0 = (I - I_0)/I_0$ =f(Relative Humidity)

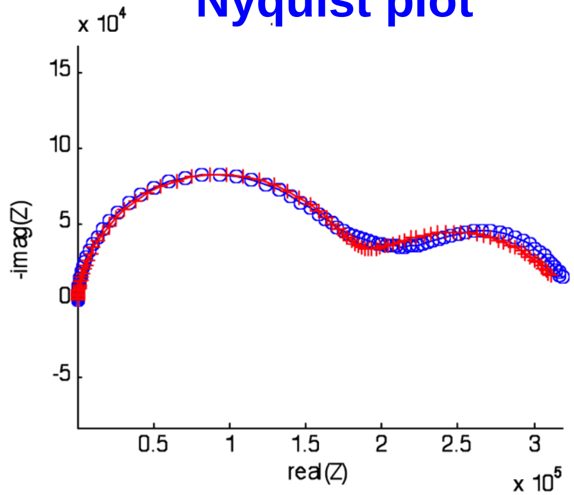


⇒ Good discrimination of NH_3 concentrations whatever the rh in the 10-70 % range

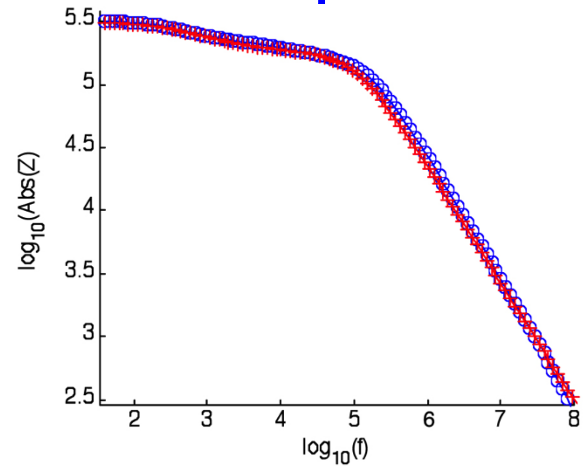
Impedance = f(frequency)

n-MSDI

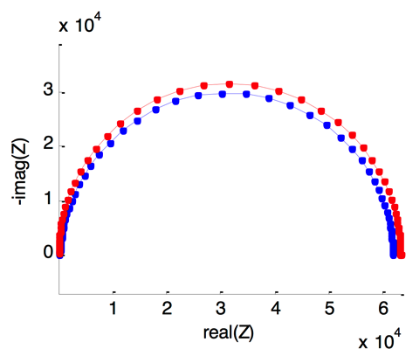
Nyquist plot

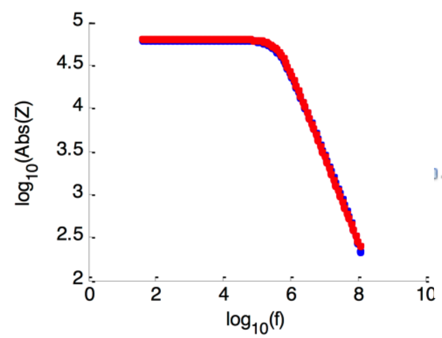


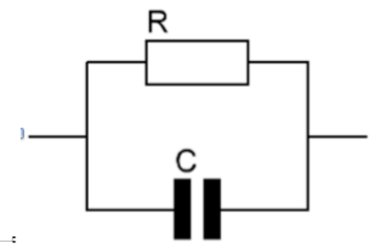
Bode plot



$LuPc_2$ resistor

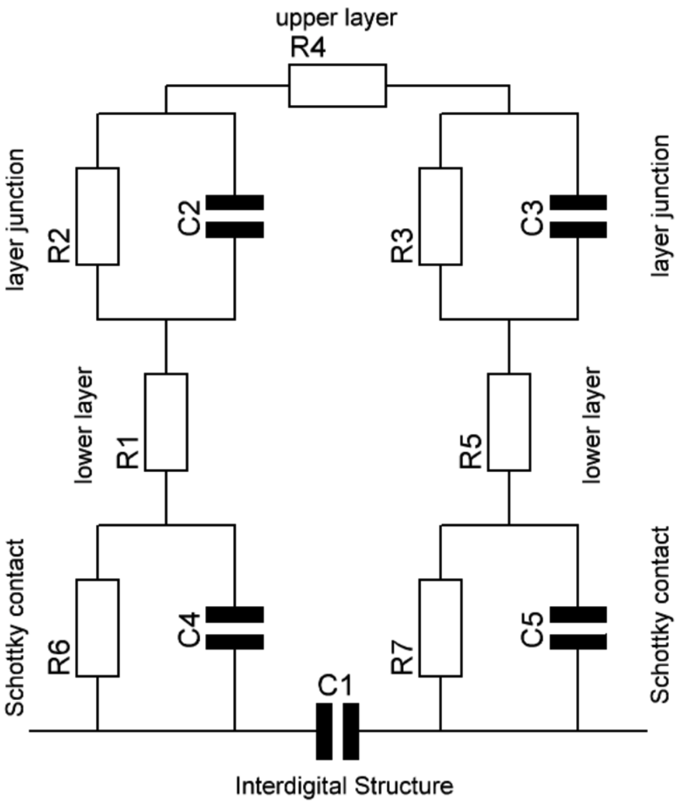




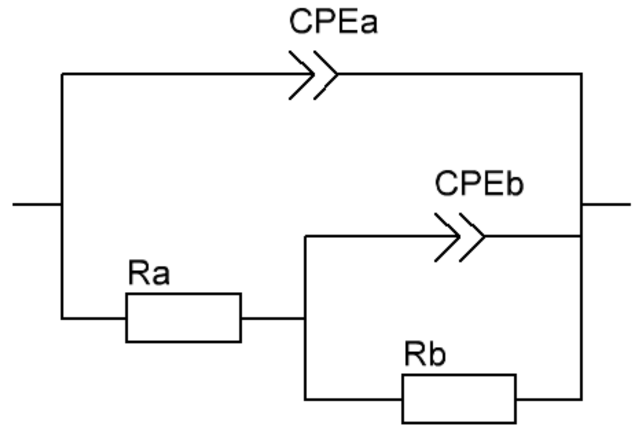


M. Bouvet*, P. Gaudillat, A. Kumar, T. Sauerwald, M. Schüler, A. Schütze*, J.-M. Suisse, "Revisiting the electronic properties of Molecular Semiconductor – Doped Insulator (MSDI) heterojunctions through impedance and chemosensing studies", Org. Electron., 26 (2015), 345-354.

Equivalent circuit



Simplified equivalent circuit,
including Component Principal Element



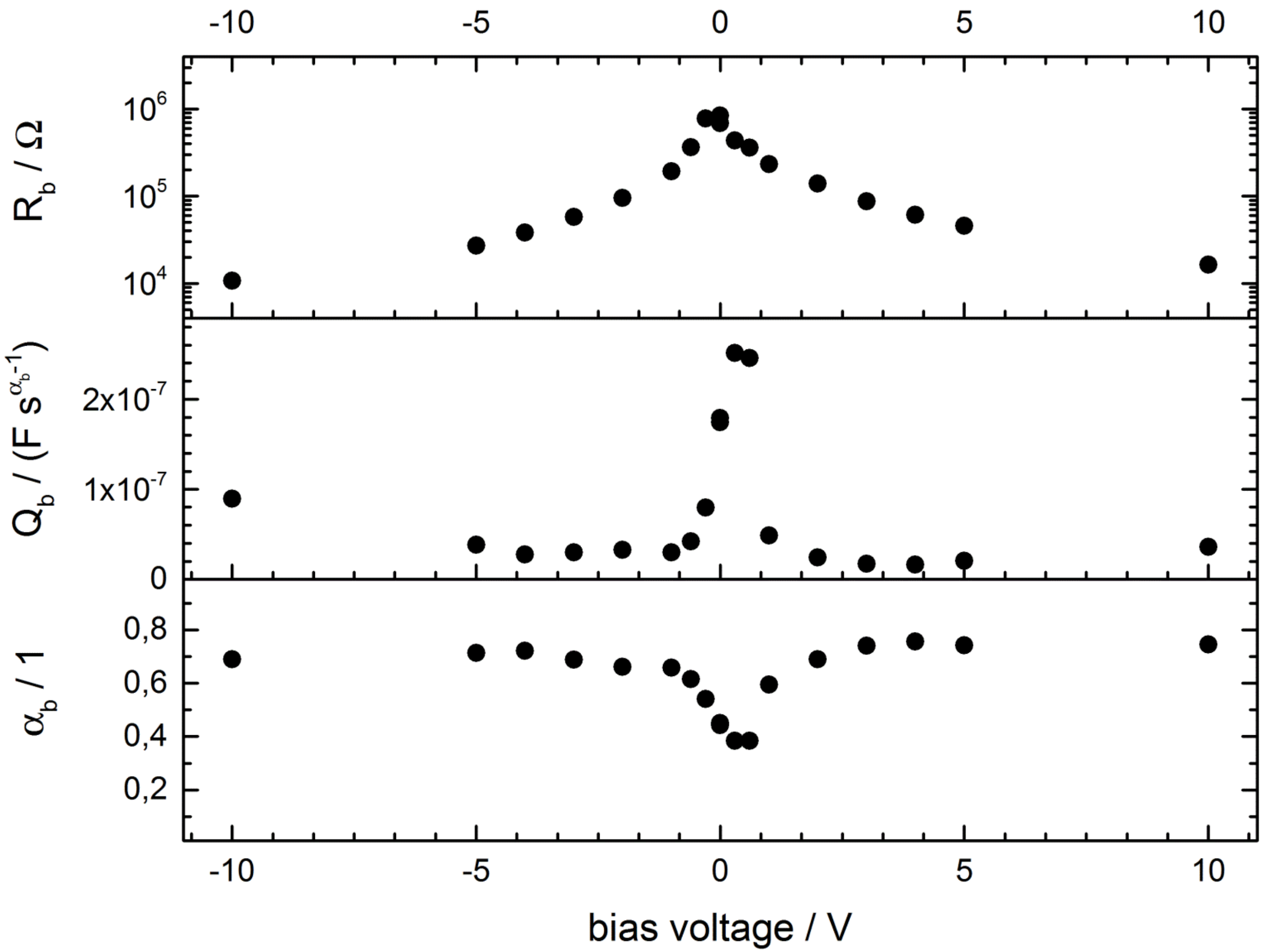
Impedance: $Z_{CPE} = 1/(Q \cdot (j\omega)^{\alpha})$

with $\omega = 2\pi f$, where Q is the capacity, f the frequency and α a coefficient.

For the special case of $\alpha = 1$, a CPE equals an ideal capacitor with Q = C.
It can also represent a normal resistor ($\alpha = 0$),
or a so-called Warburg element ($\alpha = 0.5$).

M. Bouvet*, P. Gaudillat, A. Kumar, T. Sauerwald, M. Schüler, A. Schütze*, J.-M. Suisse, "Revisiting the electronic properties of Molecular Semiconductor – Doped Insulator (MSDI) heterojunctions through impedance and chemosensing studies", Org. Electron., 26 (2015), 345-354.

Effect of the bias voltage on electrical parameters

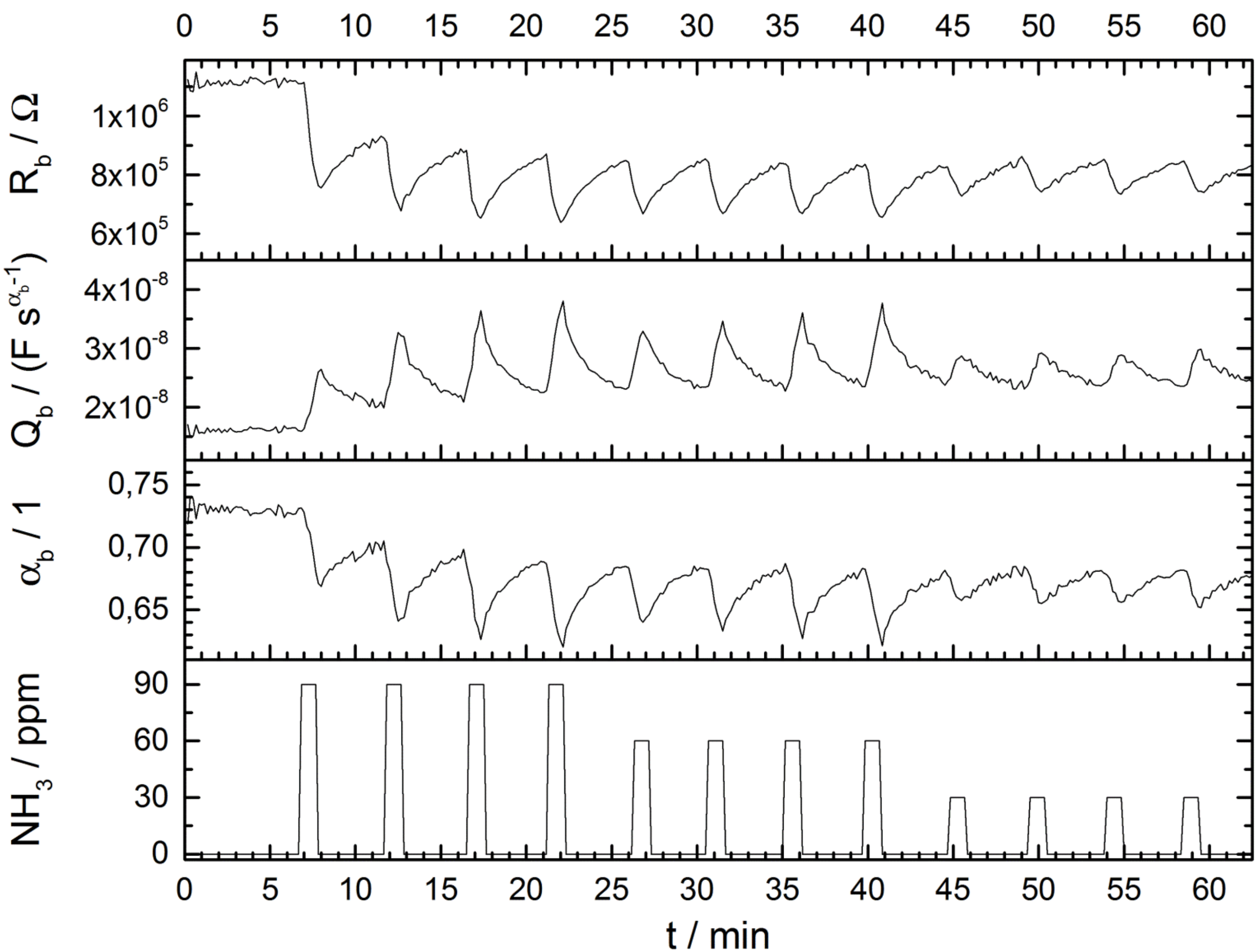


Strong effect of the bias potential

Due to the existence of an energy barrier at the interface

M. Bouvet*, P. Gaudillat, A. Kumar, T. Sauerwald, M. Schüler, A. Schütze*, J.-M. Suisse,
"Revisiting the electronic properties of Molecular Semiconductor – Doped Insulator (MSDI) heterojunctions through impedance and chemosensing studies", Org. Electron., 26 (2015), 345-354.

Effect of NH_3 on the different electrical parameters



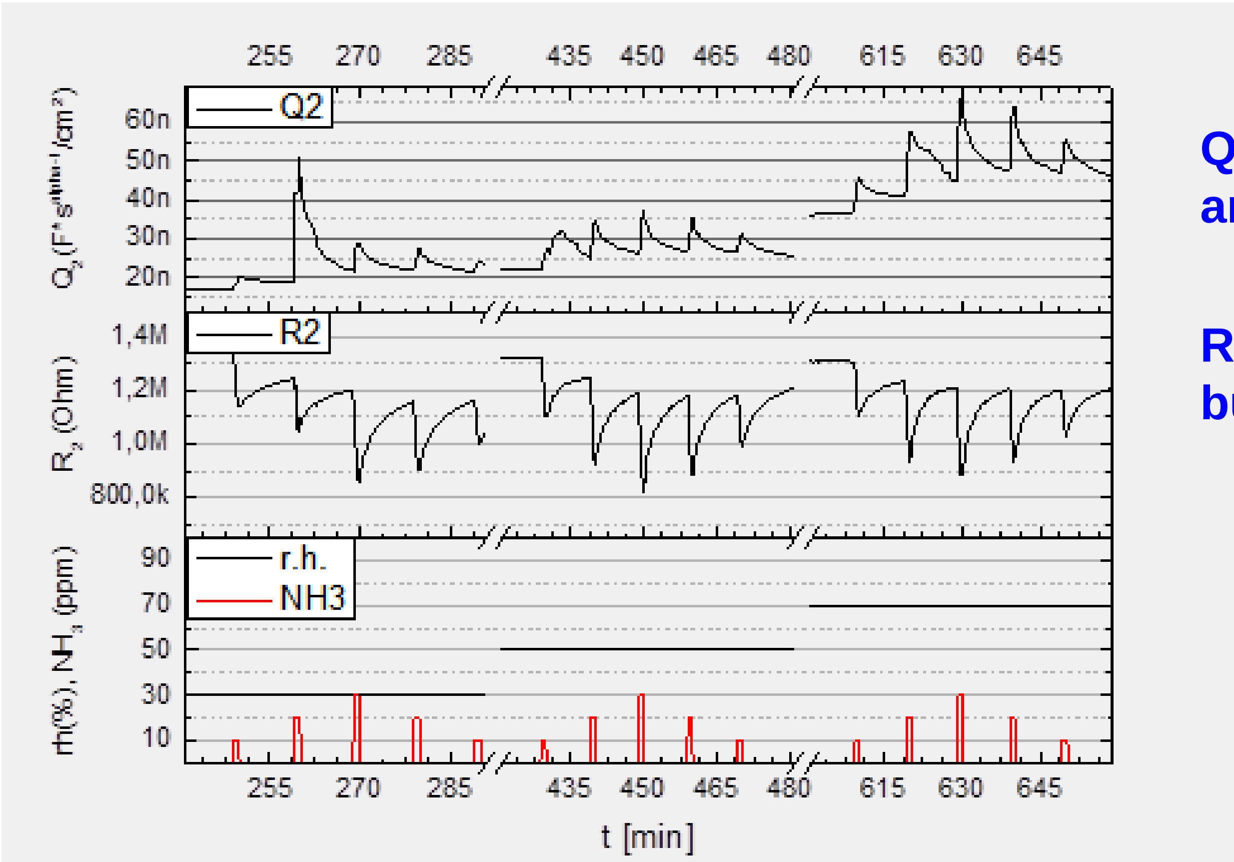
R decreases under NH_3,

Q increases under NH_3,

α decreases under NH_3,

M. Bouvet*, P. Gaudillat, A. Kumar, T. Sauerwald, M. Schüler, A. Schütze*, J.-M. Suisse, "Revisiting the electronic properties of Molecular Semiconductor – Doped Insulator (MSDI) heterojunctions through impedance and chemosensing studies", Org. Electron., 26 (2015), 345-354.

Discrimination between NH_3 and rh



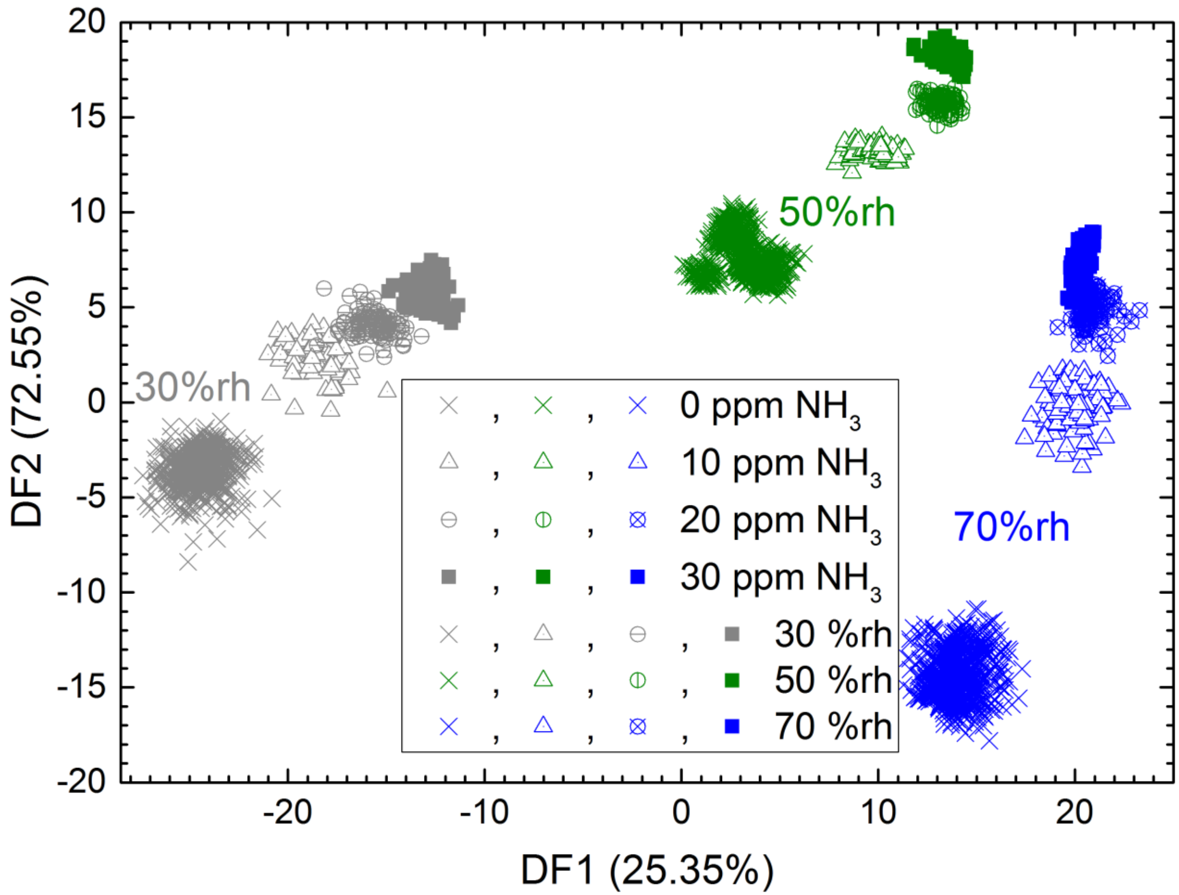
Q increases under NH_3, and depends on rh

R decreases under NH_3, but is not affected by rh

M. Schüler, T. Sauerwald, A. Wannebroucq, J.-M. Suisse, M. Bouvet, A. Schütze, "Selective measurement of ammonia and humidity using a cost-efficient Fourier-Based Impedance Spectroscope and molecular semiconductor – doped insulator sensors", submitted.

Discrimination between NH_3 and rh

Example of linear discriminant analysis



M. Schüler, T. Sauerwald, A. Wannebroucq, J.-M. Suisse, M. Bouvet, A. Schütze, "Selective measurement of ammonia and humidity using a cost-efficient Fourier-Based Impedance Spectroscope and molecular semiconductor – doped insulator sensors", submitted.

Conclusion

MSDIs: New heterojunctions based on molecular materials were demonstrated to be promising transducers for gas chemosensing (For NH_3 in the ppm range, but also for O_3 in the ppb range)

MSDIs: New conductometric transducers that can be operated in different ways :

- **Current = f(time): Simple, but exhibits a good discrimination between NH_3 and rh**
- **Impedance = f(frequency): More powerful because of more data, but requires more data treatment**

$LuPc_2$/Cu(F_{16}Pc) n-type MSDI exhibits a very good stability of the response to NH_3 over a broad range of rh.

MSDIs operate at room temperature with a very good stability over several years.

Research directions: **To tune the electrode-sublayer interface, by chemical or electrochemical modifications, and study it by impedance spectroscopy**

Acknowledgments

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