Reactivity of atmospheric radicals with functionalised surfaces

RADICAL
A Fundamental Breakthrough in Detecting Atmospheric Radicals.

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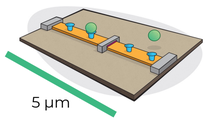
Introduction

NOW
- Currently, detecting radicals is complex, cumbersome and expensive.
- Only a few labs worldwide can detect radicals.

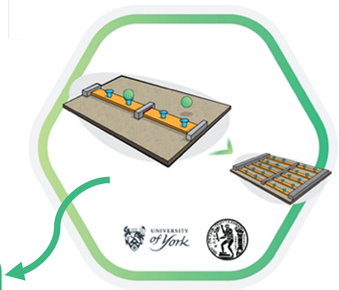
FUTURE
- RADICAL is developing a break-through way of detecting radicals with a small, low-cost electronic sensor that can be deployed globally.
- Self-assembled monolayers (SAMs) are going to be used to functionalise the sensor surface for enabling the detection of specific gas phase molecules.

Silicon semiconductor sensor



OUR AIM

FUNCTIONALISING



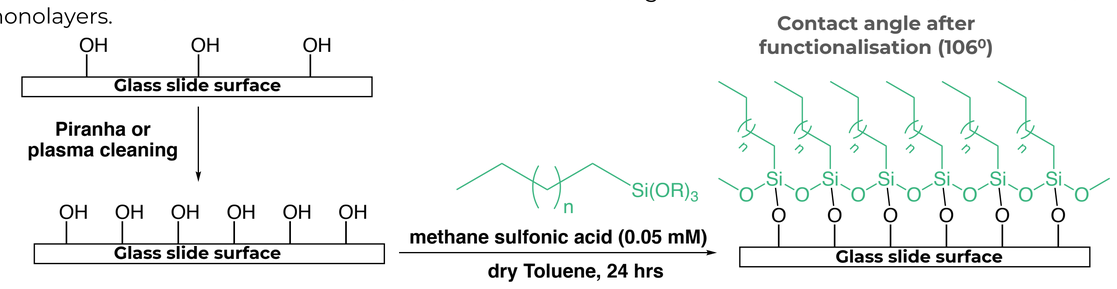
Organic layer to trap atmospheric radicals
- Simulating
- Testing

Monitoring reaction of radicals with SAMs

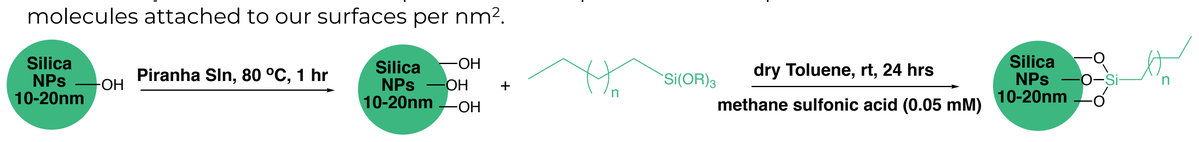
Methodology

Functionalisation of silica surfaces

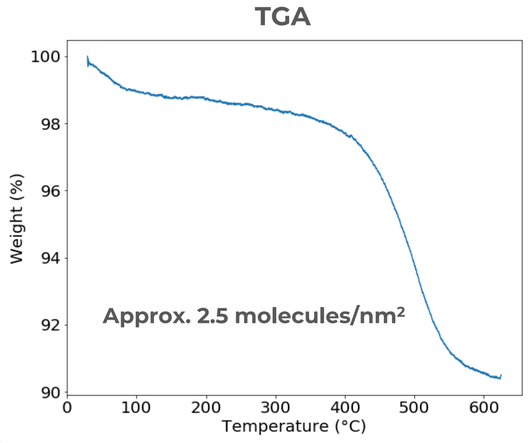
Glass slides were used as a model substrates to attach the organic molecules and form self-assembled monolayers.



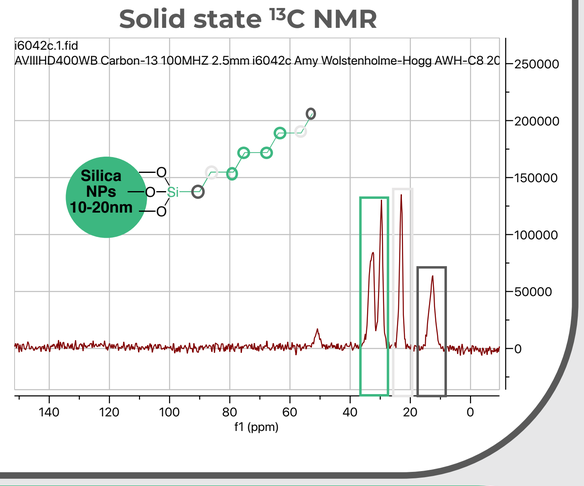
Silica Nanoparticles were used to provide further quantitative and qualitative information about the molecules attached to our surfaces per nm².



TGA



Solid state ^{13}C NMR



•OH generation via plasma

- **Atmospheric pressure plasma jet** (APPJ) has been used to generate reactive species.
- The generation of ·OH occurs through several processes including:

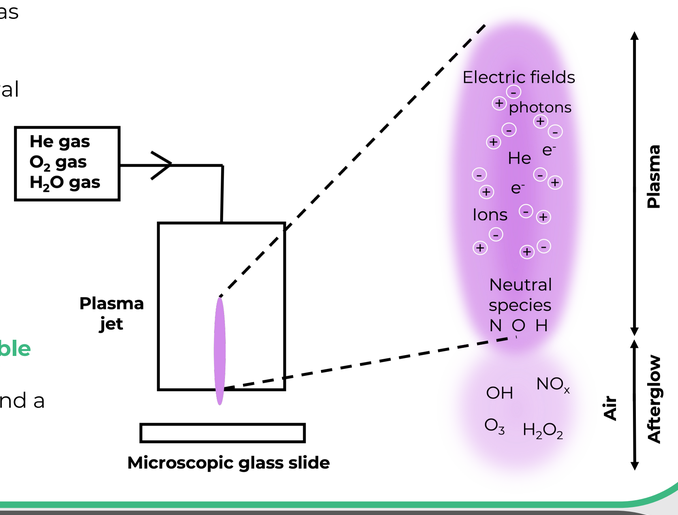
$H_2O + e^- \rightarrow OH + H + e^-$

$H_2O + O^* \rightarrow 2OH$

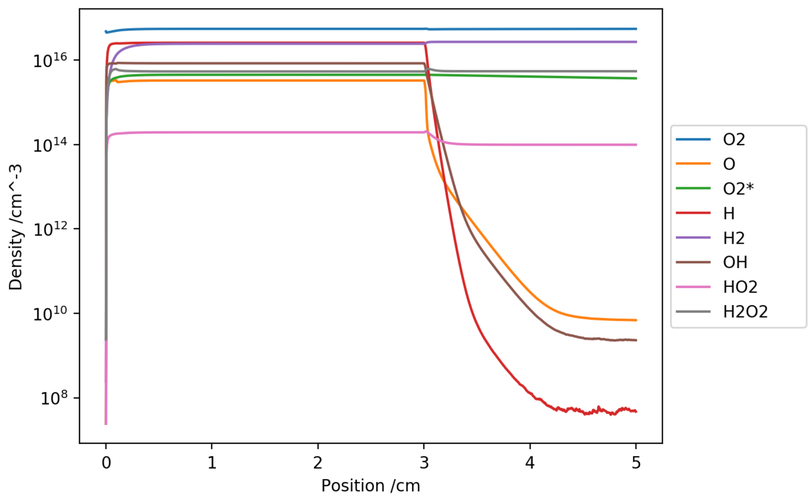
$H + H_2O_2 \rightarrow OH + H_2O$

$H + HO_2 \rightarrow 2OH$

- The **benefit** of using plasma is that **reasonable estimations** can be made for the **density** of atomic O and OH radicals being produced and a relatively **high OH concentration can be achieved** in the gas phase.



1-D kinetics modelling of plasma afterglow

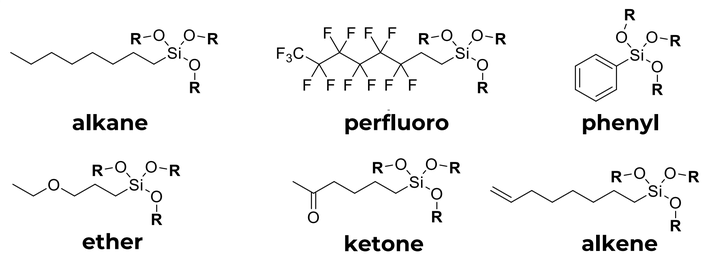


- Used a **1-D GlobalKin model** to simulate the formation of reactive species in the **afterglow** of the plasma jet (position **3-5 cm**).
- Shows the **density of •OH and atomic O** reaching our glass slides is approximately **10^{10} molecules/cm³.**

Reactivity of plasma-generated species

•OH exposure to a library of surface-bound organic molecules

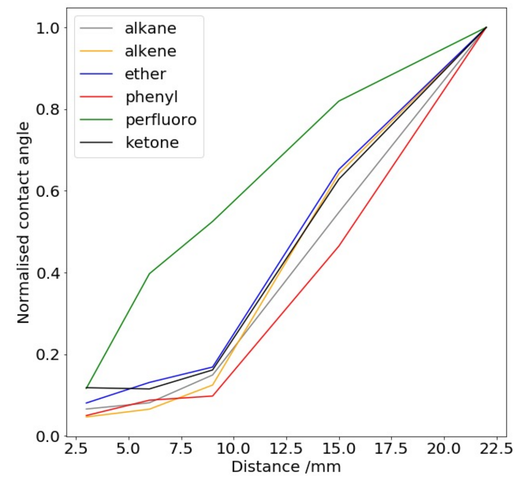
Glass slides were functionalised with a library of organic molecules.



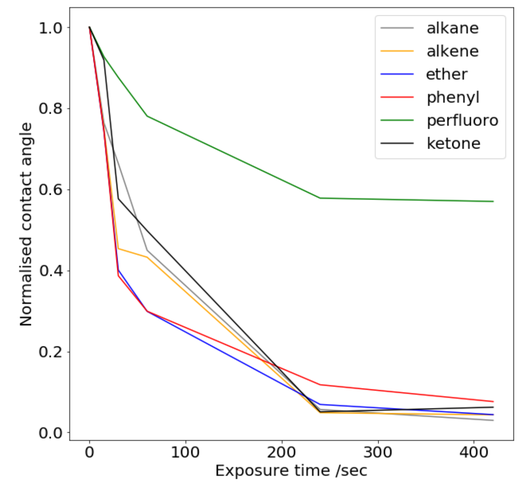
Molecule	Contact angle /degrees
alkane	100 ±2
perfluoro	117 ±3
ketone	65 ±2
ether	70 ±2
alkene	85 ±2
phenyl	75 ±2

Their **rates of decay upon plasma exposure** were analysed using **contact angle analysis**.

Distance from plasma jet



Exposure time



Most molecules gave a **similar rate of decay** upon exposure to ·OH radicals. Only the **perfluoro alkane** chains gave a **slower rate** of decay. C-F bonds are unreactive towards ·OH radicals, so the decay of the perfluorinated derivative is likely due to the reaction with the underlying C-H bonds.

Ether reacts slightly faster than the other compounds. This could be due to H-abstraction from the adjacent chains by the ROO· which forms following hydroxyl radical attack (**autoxidation**).

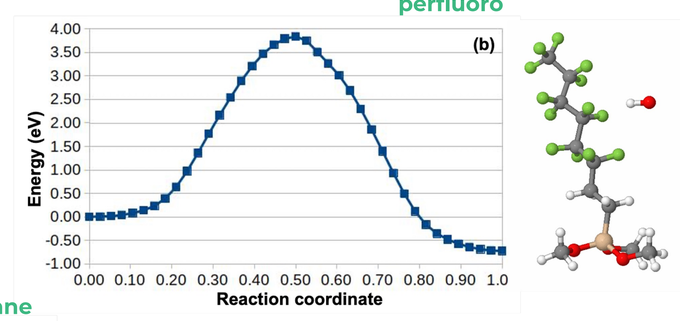
The reasons for the high reactivity of the phenyl derivative is not clear.

DFT calculations for the reaction of •OH with SAMs

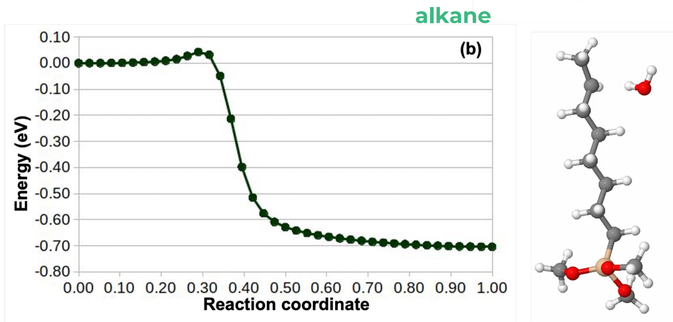
As the ·OH radical approaches a fluorinated alkane, it undergoes **substitution** whereby an O atom replaces a F atom.

The reaction has a **large energy barrier** (>3.5 eV), so it is completely suppressed at normal atmospheric conditions.

perfluoro



alkane

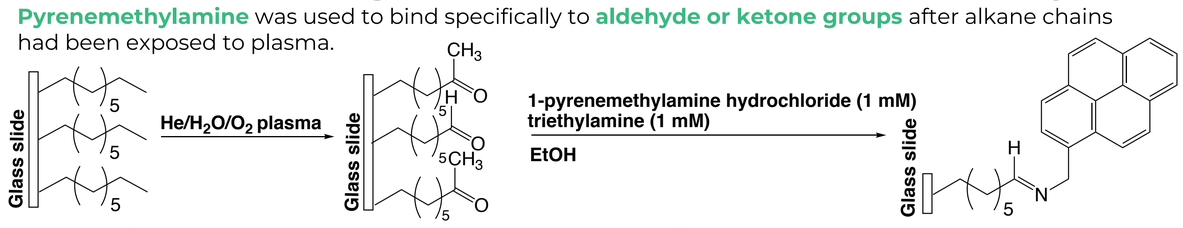


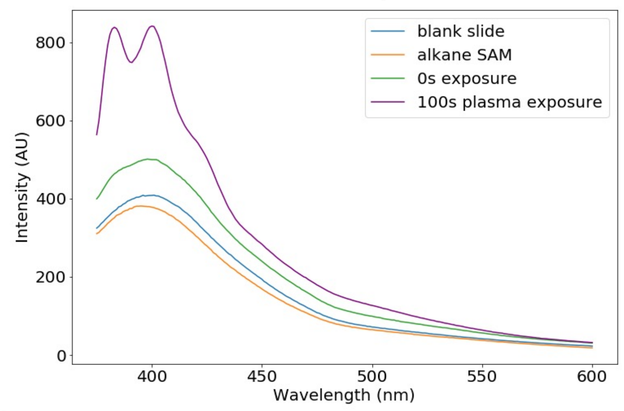
As the ·OH radical approaches an H atom of the alkane, it undergoes **hydrogen abstraction** to form a H_2O molecule.

The DFT results show the reaction is **exothermic** with an energy gain of about **0.70 eV**. Moreover, the **energy barrier** of the reaction is **small** (less than 0.10 eV).

Monitoring the reaction of •OH with alkane SAMs using fluorescence spectroscopy

Pyrenemethylamine was used to bind specifically to **aldehyde or ketone groups** after alkane chains had been exposed to plasma.





Pyrene monomer emission at approx. **390 nm** confirms the presence of **carbonyl groups** after alkane chains have been exposed to plasma.

This technique will be used to **quantify** the **oxygen-containing functional groups** after exposure to plasma and will be used to complement the kinetics study with contact angle analysis. Different linkers will be used to bind fluorophores to other functional groups such as **OH and COOH**.

Conclusions

- Plasma has been used to generate ·OH radicals at a reasonable concentration for reacting with monolayers on glass slides.
- A library of organic molecules have been exposed to ·OH radicals and their rates of decay have been monitored by contact angle analysis.
- Most molecules gave a similar rate of decay upon exposure to ·OH radicals. Only the perfluoro alkane chains gave a slower rate of decay. This result has been supported by the DFT calculations.
- Pyrenemethylamine has been used as a fluorescent probe and has shown the presence of carbonyl groups after alkane chains have been exposed to plasma.
- The fluorescence technique will be used to quantify the oxygen-containing functional groups after exposure to plasma and will be used to complement the kinetics study with contact angle analysis.

References

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