

# *Outlook for Potential Third Generation Immersion Fluids*

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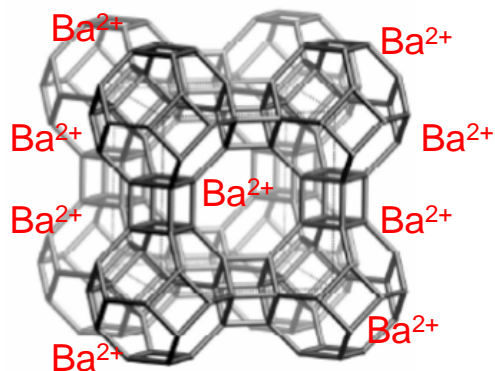


## Gen 3 Goals

	<u>Goal 3rd Gen</u>
Refractive Index	~1.8-2.0
Abs/cm (base 10)	<0.15
dn/dt (ppm/K)	<250
Viscosity (cP)	<3
Scatter @ 193 nm	<0.2%mm
ESH Issues	none
Contact Angle on Bare Si	equal to water
Absorption Stability (cm-min) <sup>-1</sup>	0.01
Cost per Layer	<\$1
Organic/Aqueous	Either
Imaging Demo (IL)	

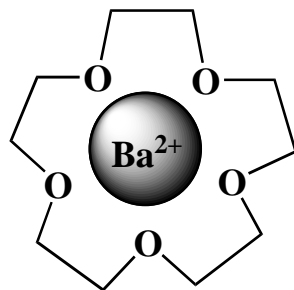


# Possible candidates



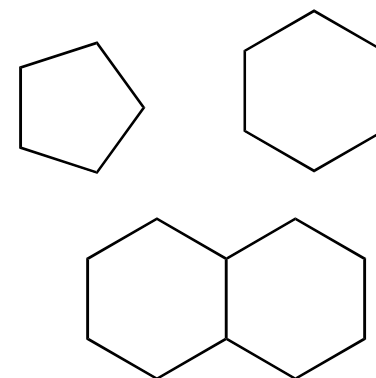
## Nanoparticles

- Flexibility to include any cation
- Large scattering
- Instability of nanoparticles dispersions



## Crown-Ethers

- Low scattering
- High refractive index
- Flexible structure
- Low transparency



## Cyclic alkanes

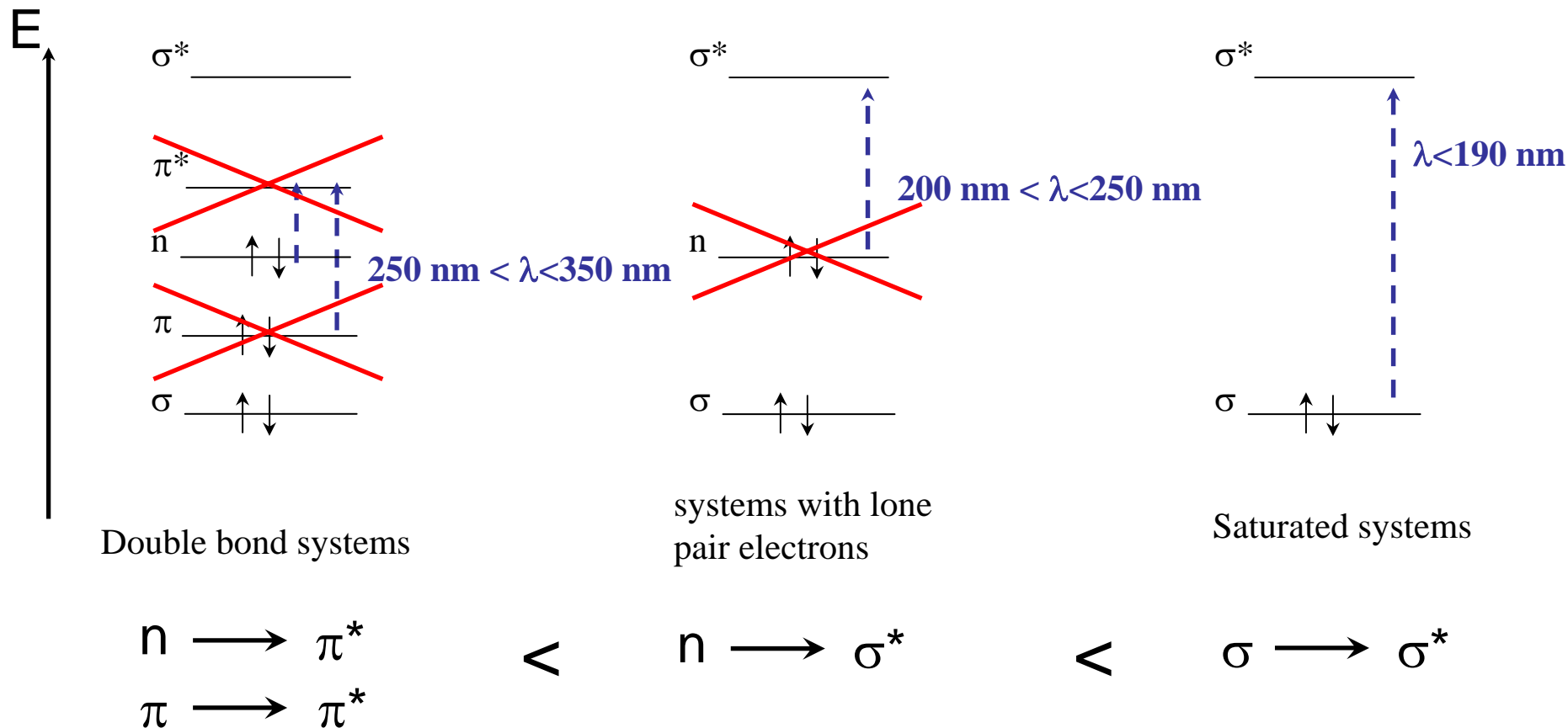
- ?
- ?

In general the main problem is the low transparency of most of the candidates because of the scattering or absorption.



# Electronic transitions

## Molecular orbital theory

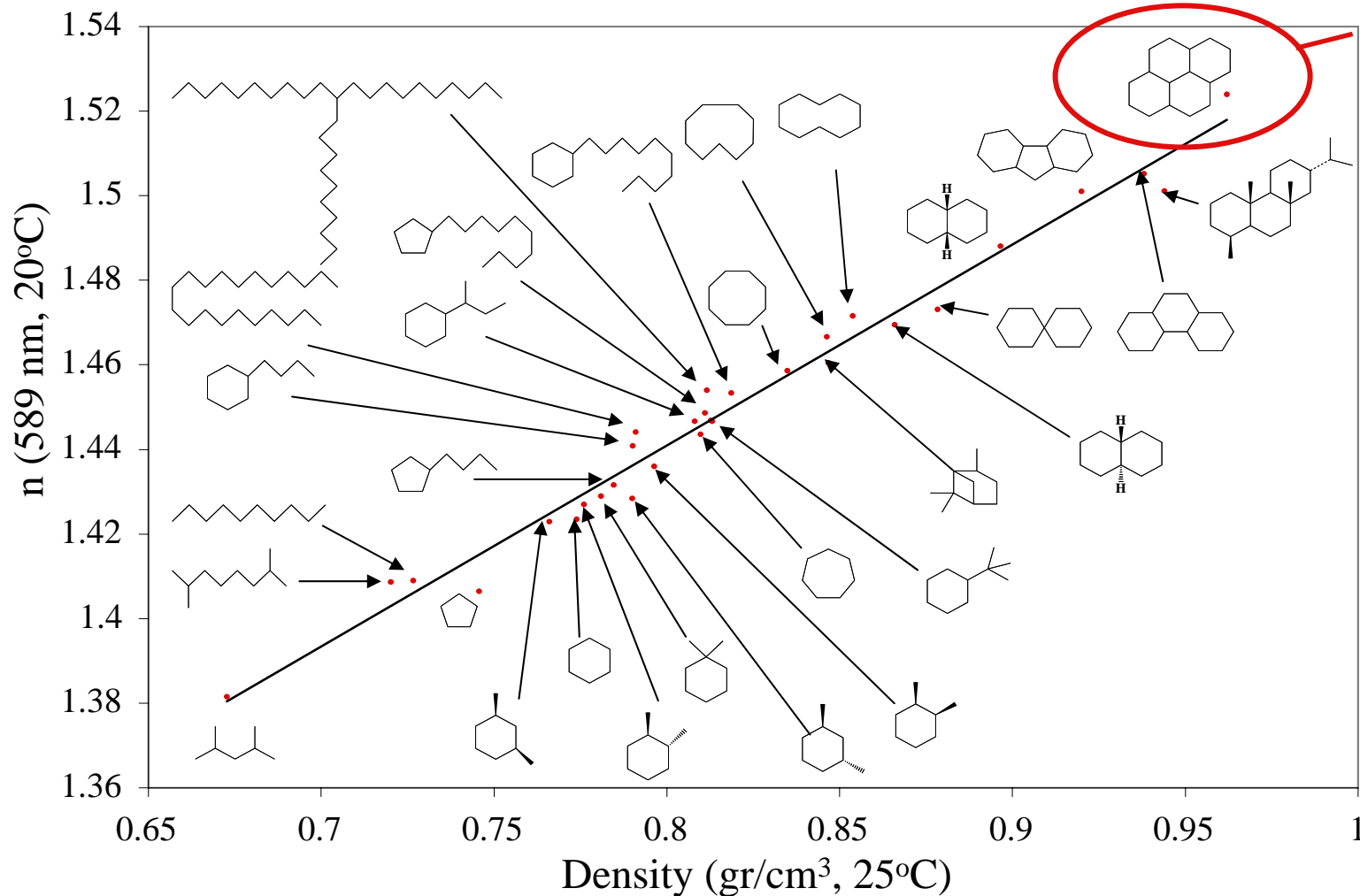


Double bond and lone pair systems should be excluded to avoid absorption. **Alkanes** and **cycloalkanes**.



# Alkanes: Density vs Refractive index

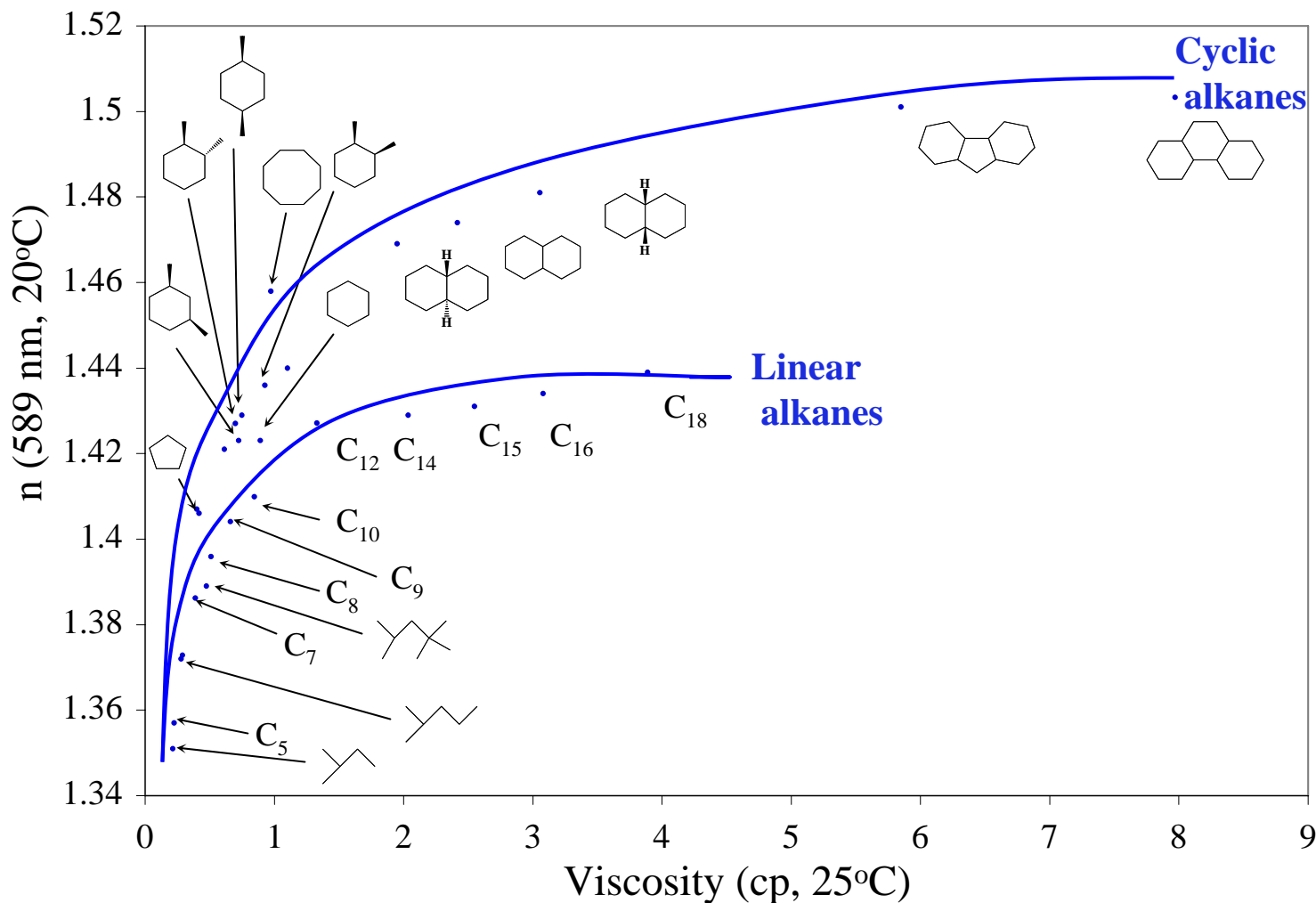
Promising candidate



- Linear relation between density and refractive index of alkanes
- Cyclic and polycyclic alkanes have a higher RI than linear alkanes.



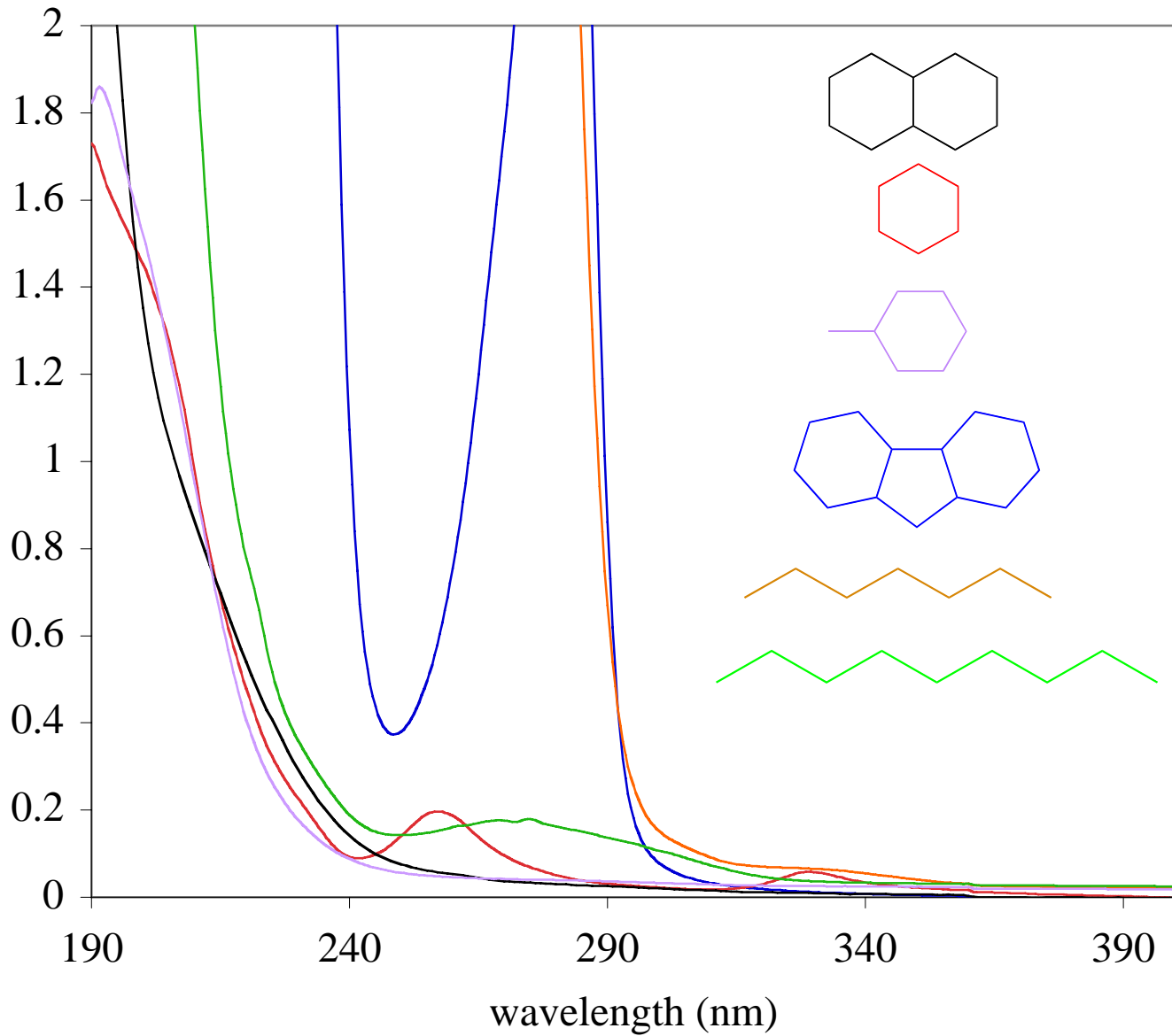
# Alkanes: Viscosity vs Refractive index



• No linear relation between viscosity and refractive index of alkanes

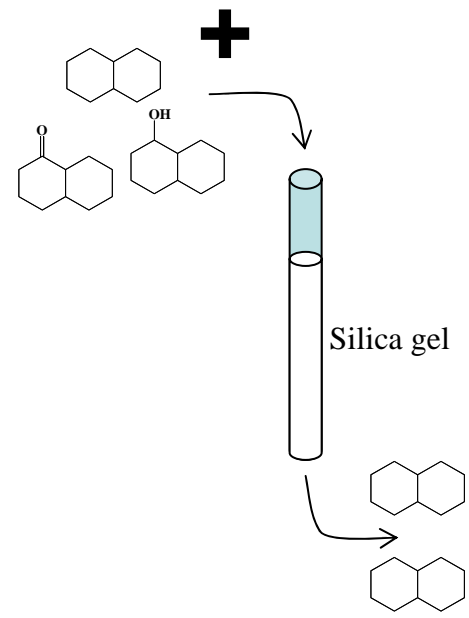
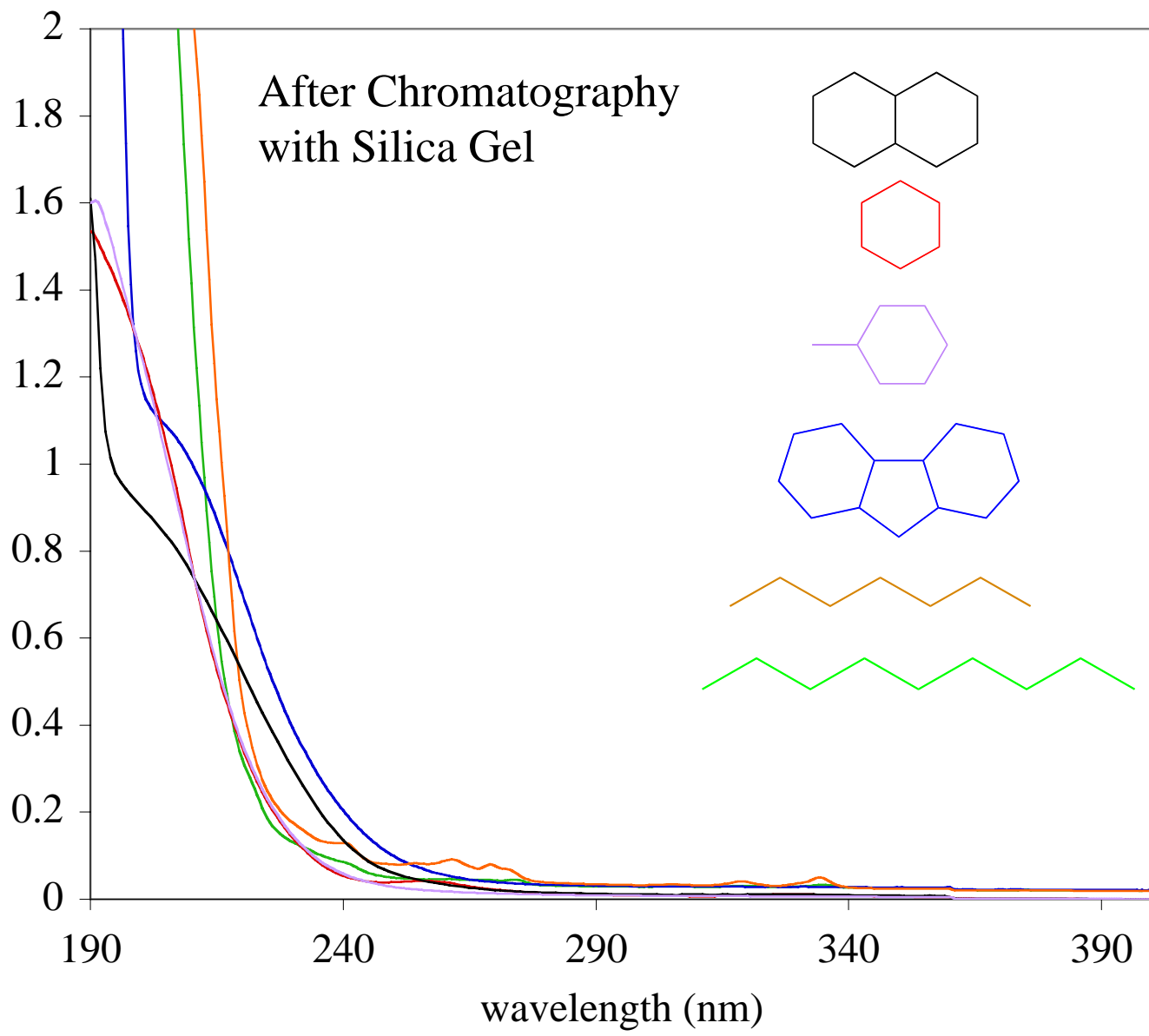


# Absorption spectra of alkanes



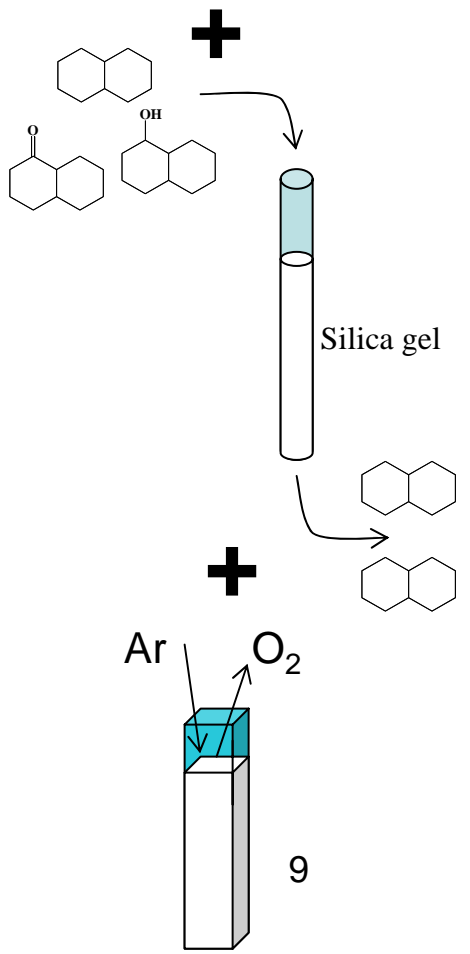
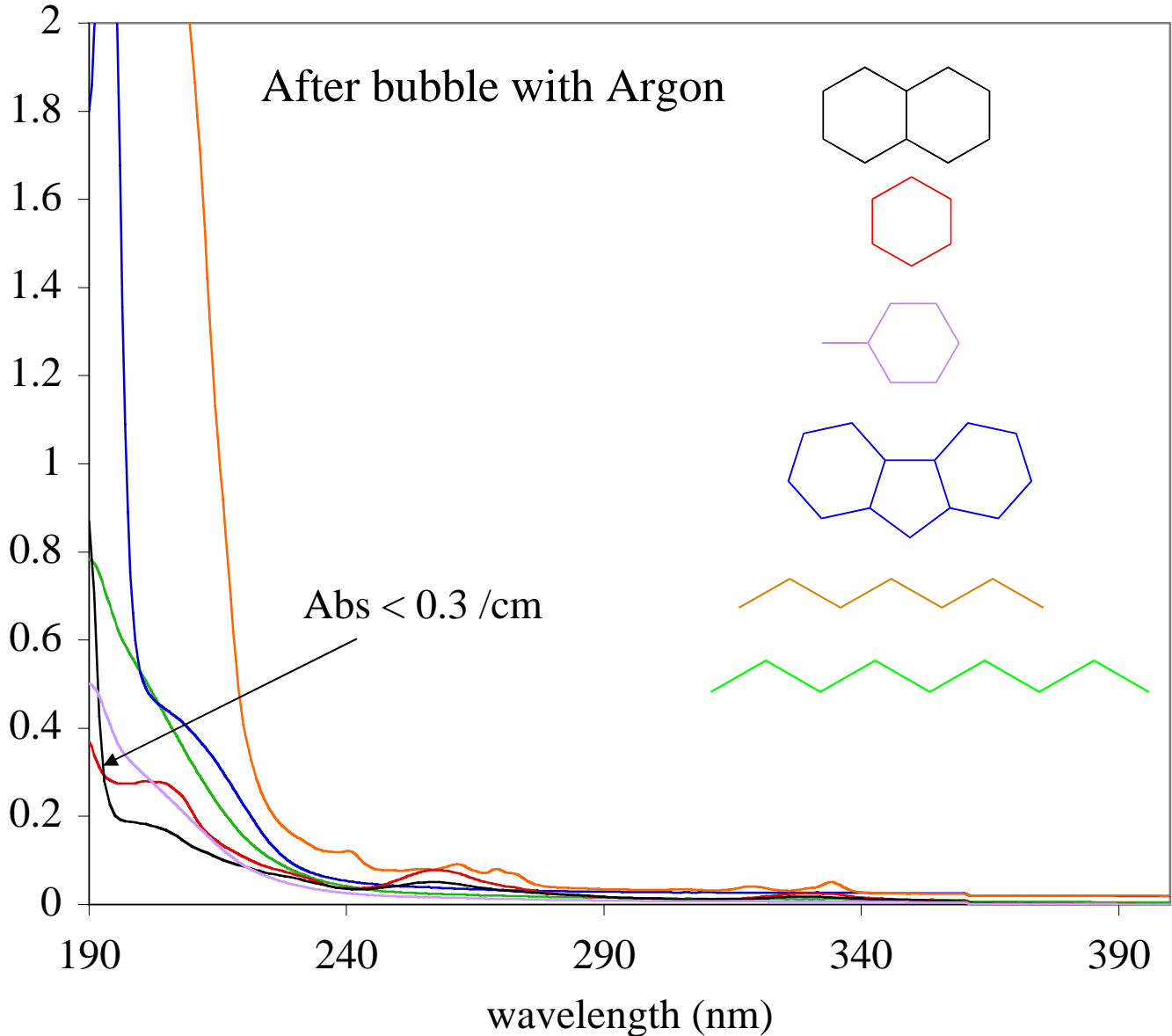


# Absorption spectra of alkanes



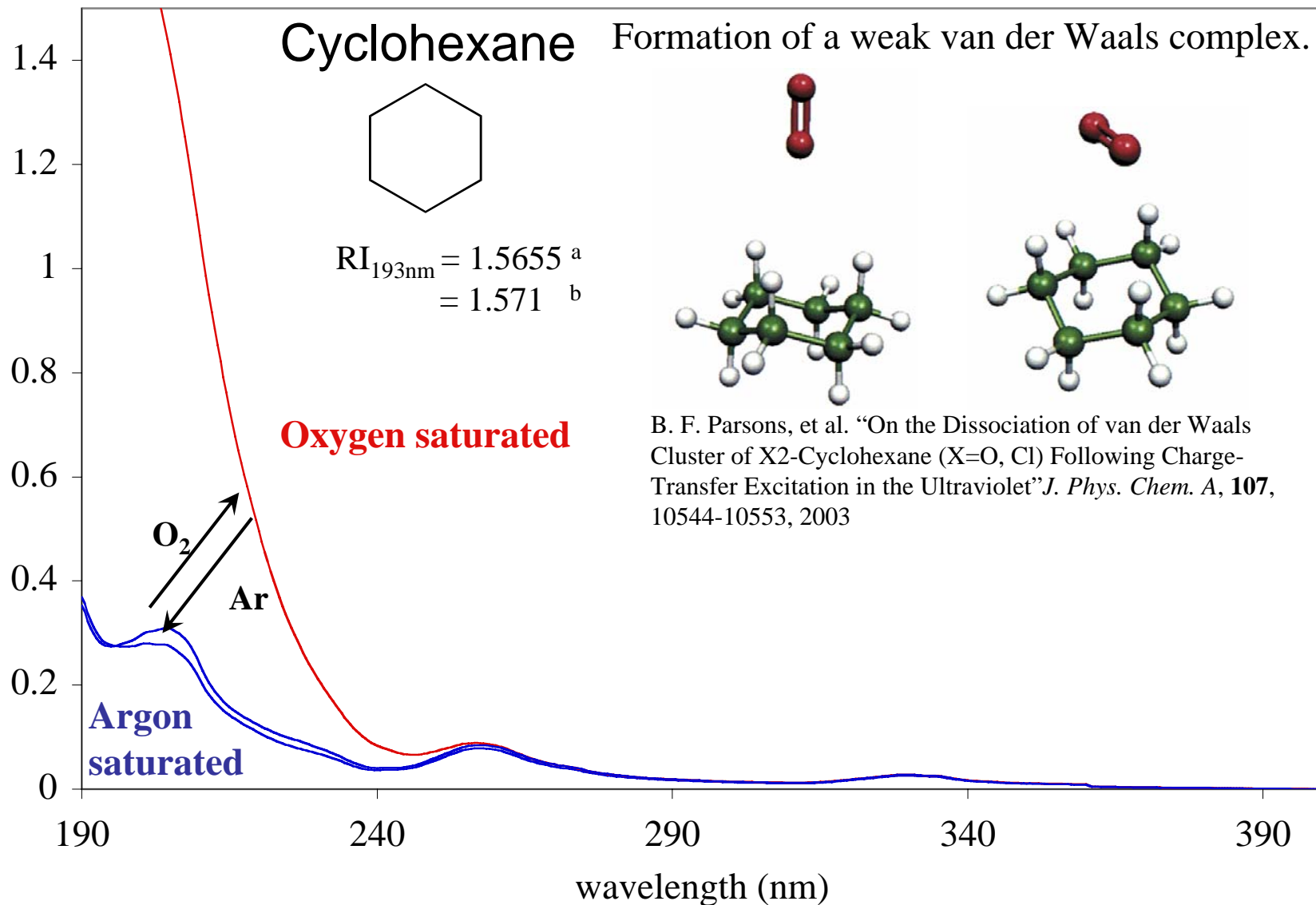


# Absorption spectra of alkanes





# Formation of a Oxygen-complex

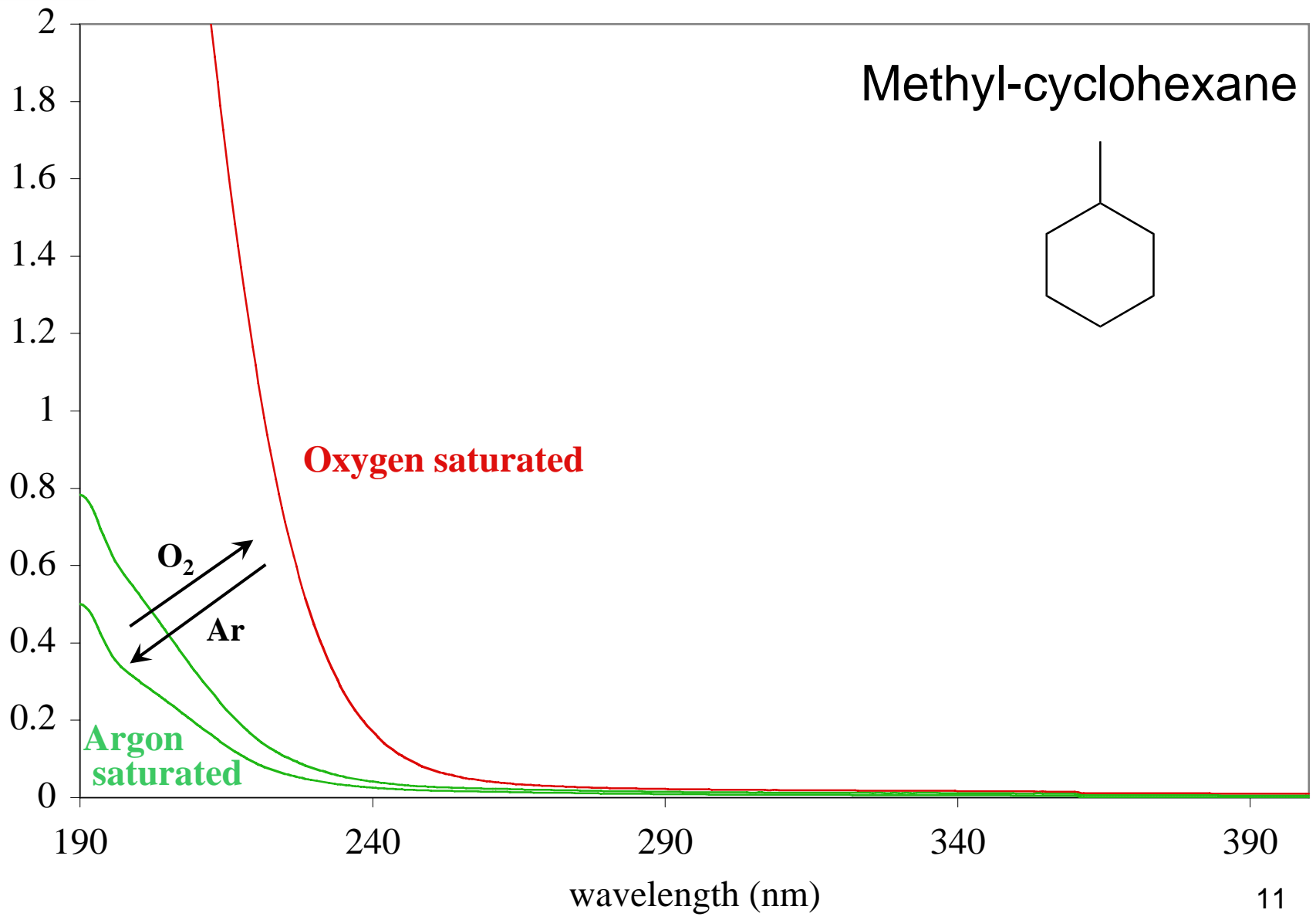


<sup>a</sup> Zhang et al. "Immersion Lithography Fluids", Patent Appl. US2005/0173682 A1

<sup>b</sup> R. French et al. "Ultraviolet Transparent alkanes and Processes using same in vacuum and deep ultraviolet applications", WO 2005/119371 A1



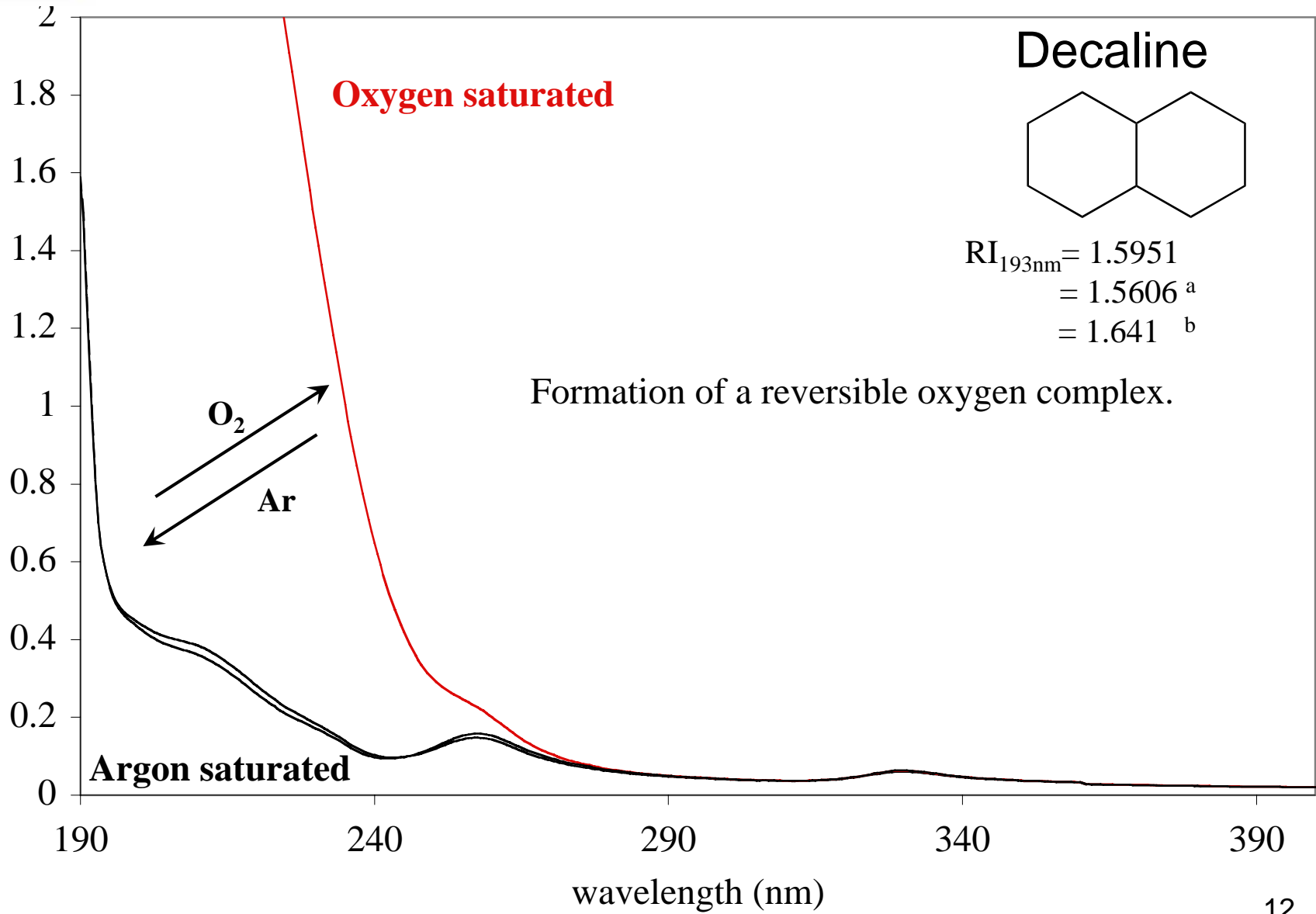
# Formation of a Oxygen-complex



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# Formation of a Oxygen-complex



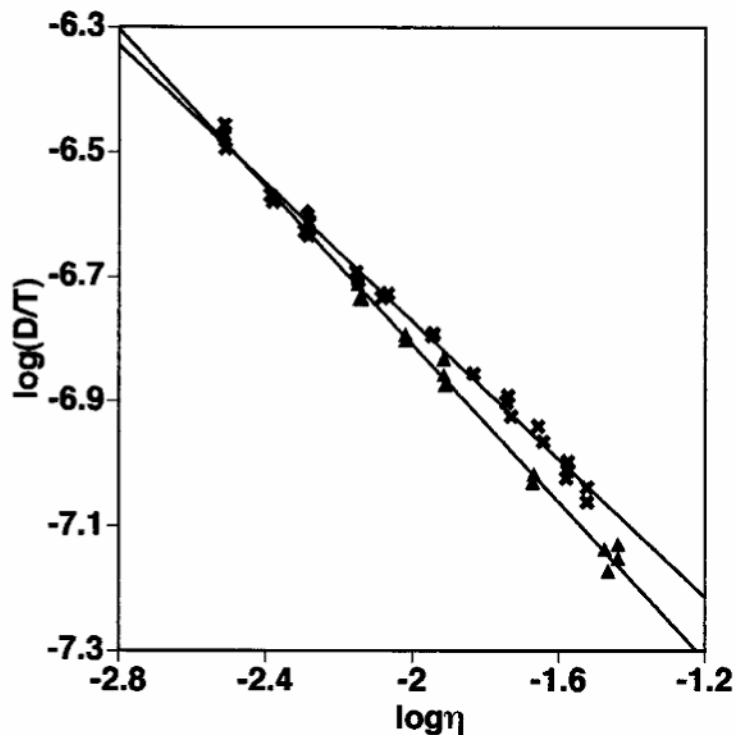
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# Oxygen diffusion and solubility



Fits of diffusion constants for O<sub>2</sub> to  $D/T=A/\eta$ . C<sub>6</sub>-C<sub>16</sub> (x), the cycloalkanes (▲) and isooctane (◆)

Compound	Viscosity (cp, 290 K)	Diff. O <sub>2</sub> (cm <sup>2</sup> s <sup>-1</sup> )	O <sub>2</sub> (Mol Fraction)
Cyclohexane	0.98	4.65 10 <sup>-5</sup> <sup>b</sup>	1.24 10 <sup>-3</sup> <sup>a</sup>
Methyl-CH	0.67	5.74 10 <sup>-5</sup> <sup>b</sup>	1.57 10 <sup>-3</sup> <sup>a</sup>
trans-decalin	2.2720	2.74 10 <sup>-5</sup> <sup>b</sup>	7.978 10 <sup>-3</sup> <sup>c</sup>
cis-decalin	3.657	4.65 10 <sup>-5</sup> <sup>b</sup>	7.978 10 <sup>-3</sup> <sup>c</sup>
nonane		5.98 10 <sup>-5</sup> <sup>b</sup>	2.09 10 <sup>-3</sup> <sup>a</sup>
Perhydropyrene	?	?	?

<sup>b</sup> B. A. Kowert et al. "Diffusion of Dioxygen in Alkanes and Cycloalkanes", *J. Phys. Chem.*, **104**, 8823-8828, 2000.

<sup>a</sup> Solubility Data Series, Oxygen and Ozone, **7**, Ed. R. Battino, Pergamon, 1981.

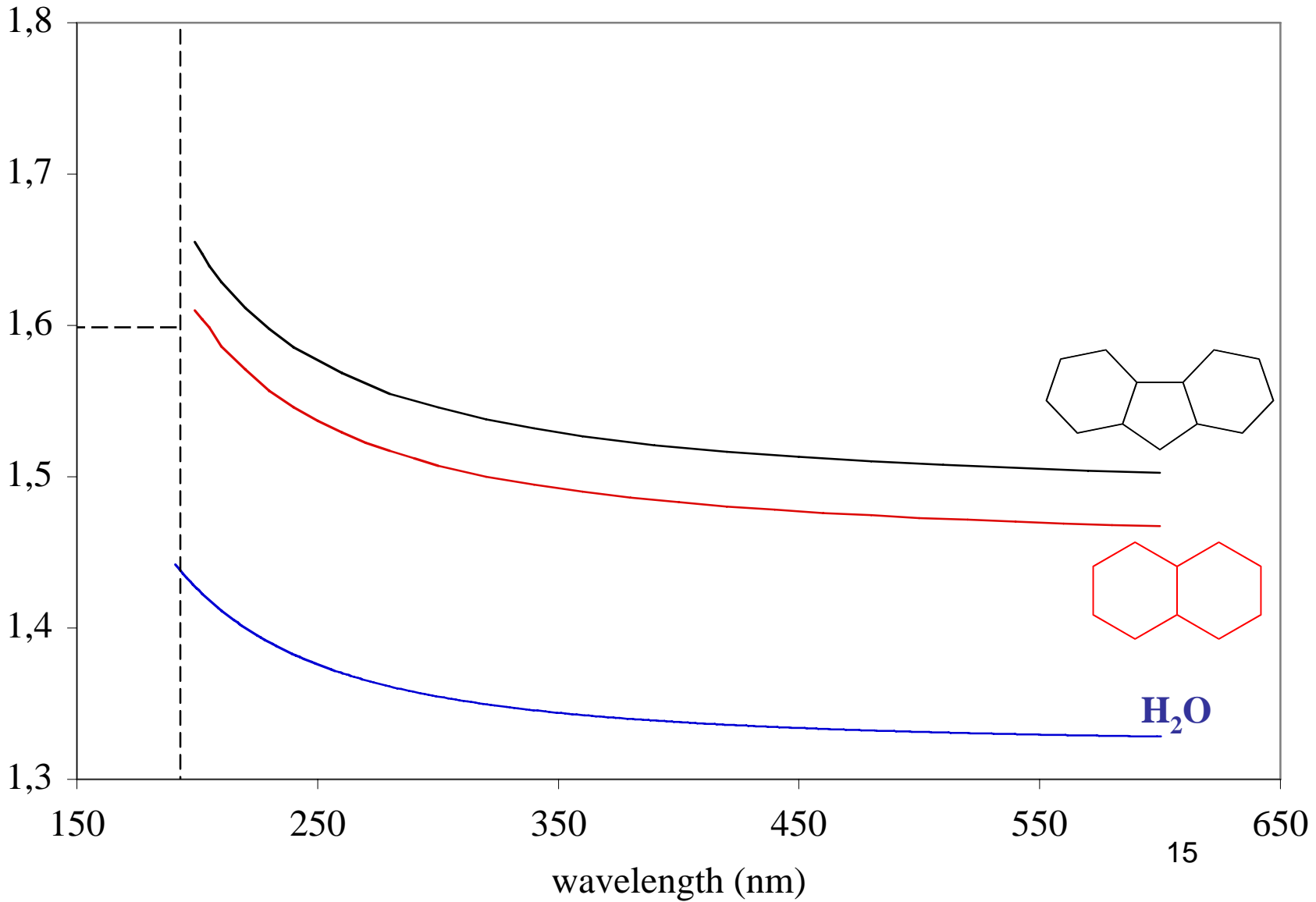
<sup>c</sup> P. Luehring et al. "Gas solubilities (H<sub>2</sub>, He, N<sub>2</sub>, CO, O<sub>2</sub>, Ar, CO<sub>2</sub>) in Organic Liquids at 293.2 K, *J. Chem. Eng. Data*, **34**, 250, 1989.

- Higher is the viscosity lower is the oxygen diffusion.
- Viscosity of perhydropyrene may be higher than the one of decalin. The oxygen diffusion should be lower.



# RI of Cycloalkanes at 193 nm

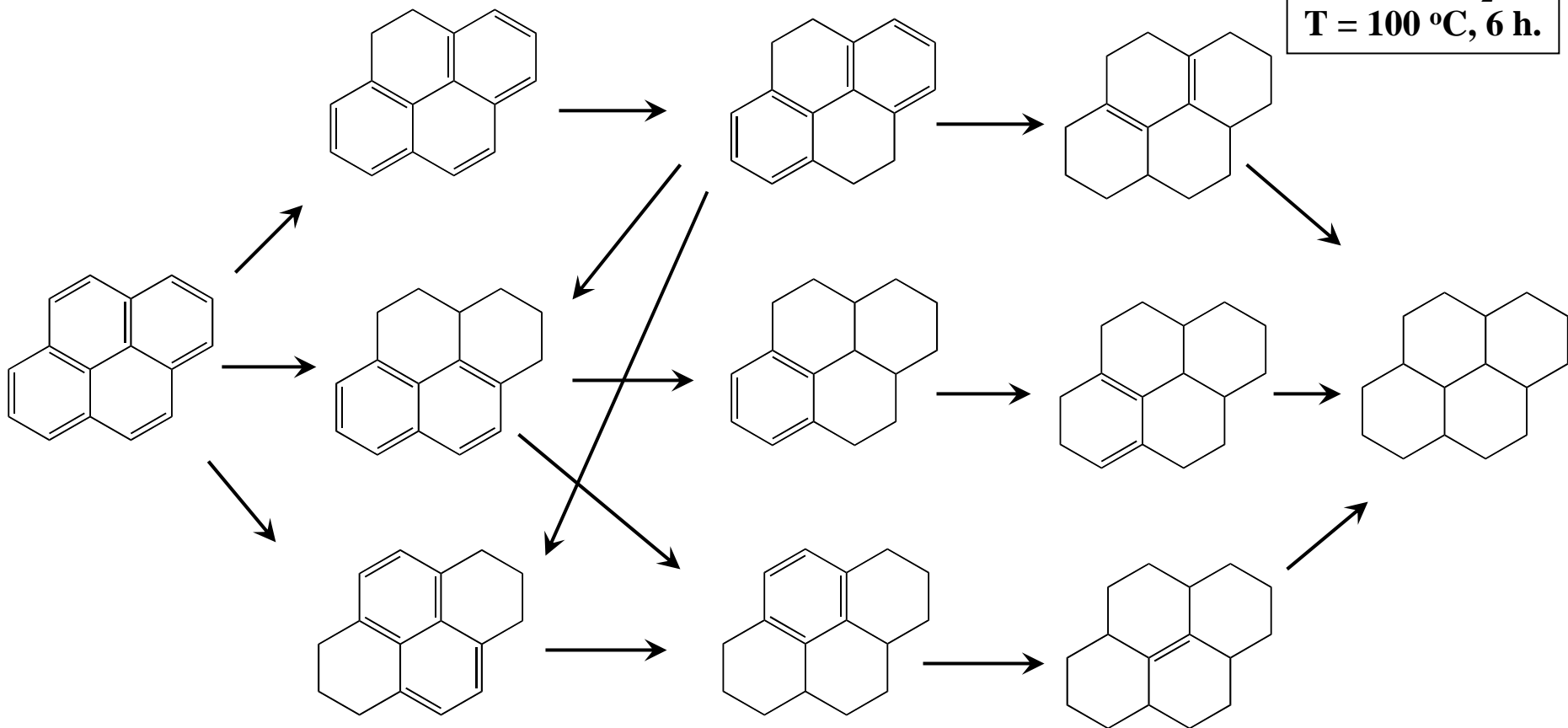
2<sup>nd</sup> Gen.





# Perhydropyrene

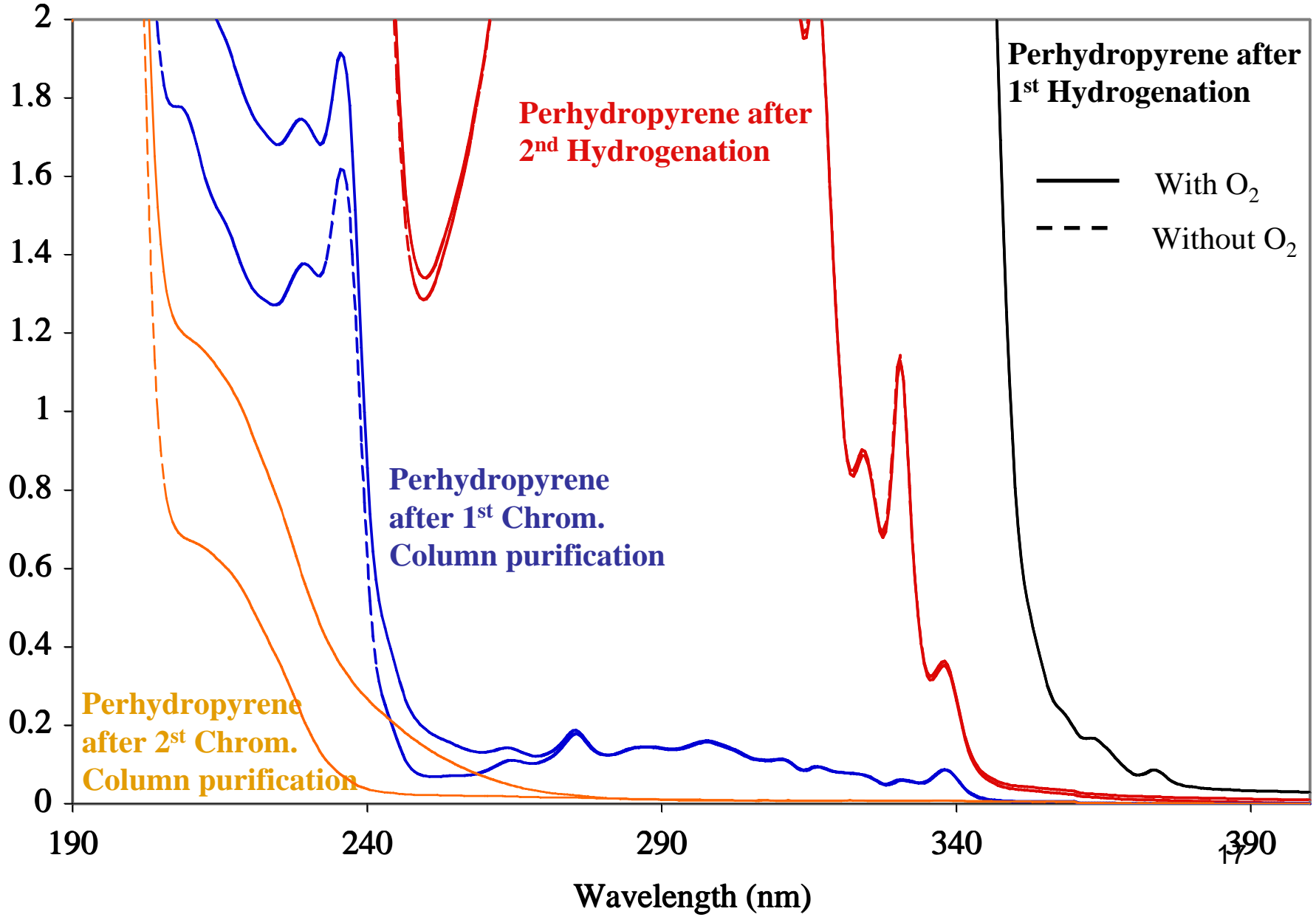
130 Atm. H<sub>2</sub>  
T = 100 °C, 6 h.



- Perhydropyrene is the mayor product of the reaction.
- Small traces of unsaturated perhydropyrenes gives a high absorption on the UV-Vis spectra.
- A complex purification process may be needed.



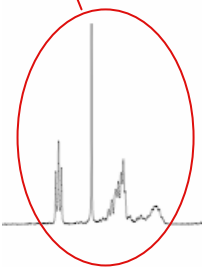
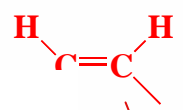
# Absorption spectra of Perhydropyrene



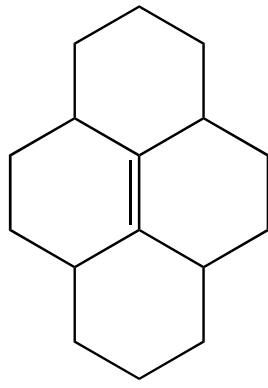


# *H-NMR spectra of Perhydropyrene*

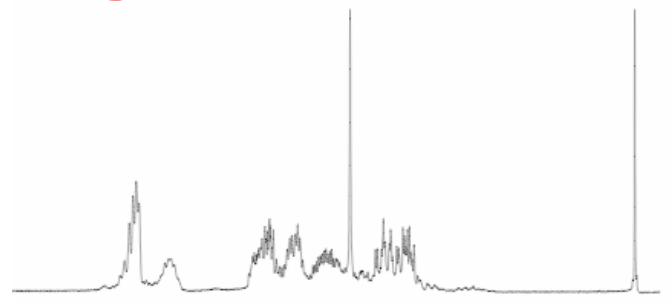
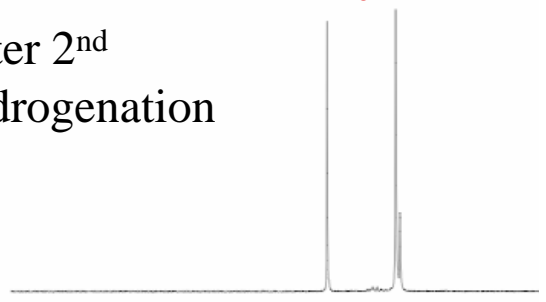
After reaction



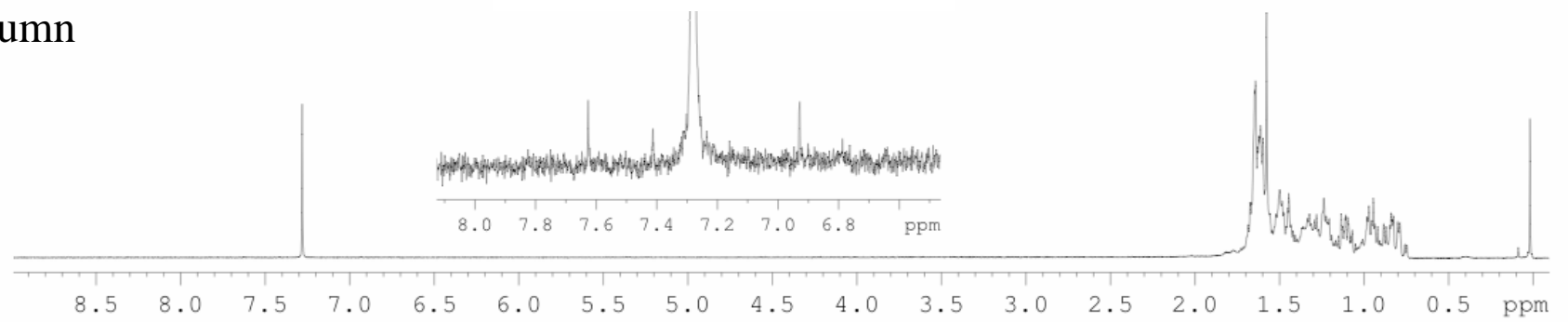
?



After 2<sup>nd</sup> hydrogenation

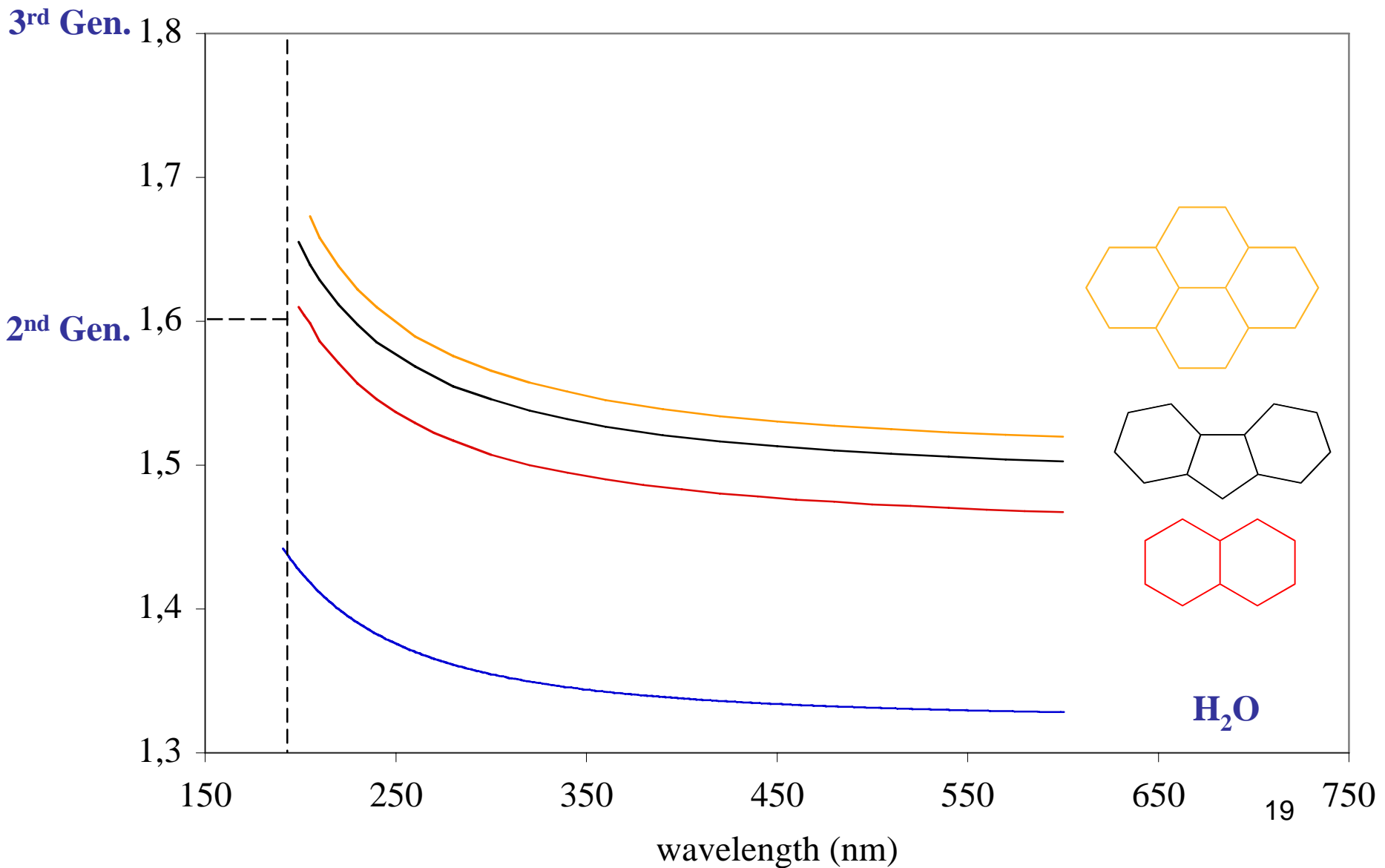


After Chromatography column





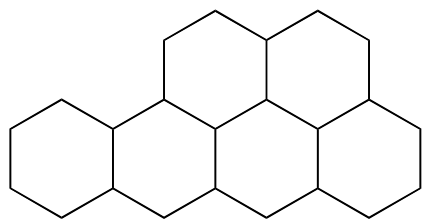
# RI of Cycloalkanes at 193 nm



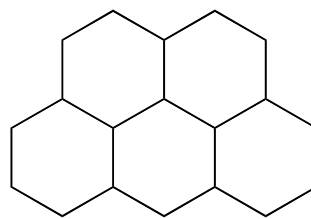


Can be achieve with cycloalkanes  
the desiderate RI of 1.8-1.9?

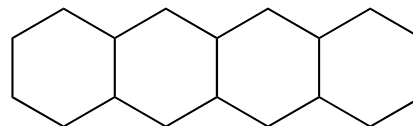
Polycyclo alkanes are **solids** with a higher refractive index....



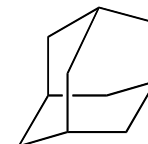
$$\rho = 0.998 \text{ g/cm}^3$$



$$\rho = 0.989 \text{ g/cm}^3$$

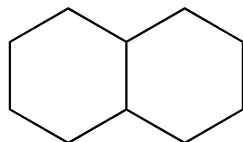
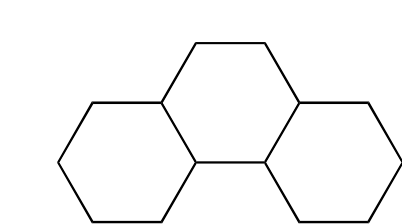


$$\rho = 0.939 \text{ g/cm}^3$$



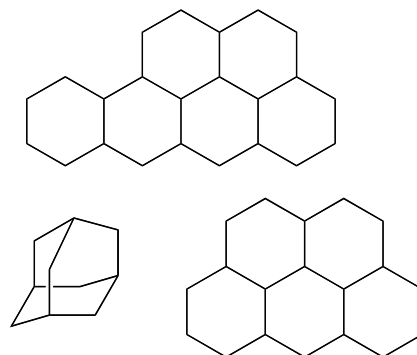
$$\rho = 1.07 \text{ g/cm}^3$$
$$n_{589\text{nm}} = 1.568$$

...but very soluble in liquid cycloalkanes.



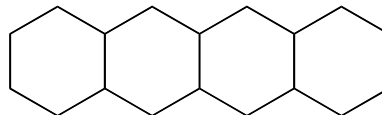
High RI Solvent

+



=

3<sup>rd</sup> generation  
Fluids





## *Conclusion and future work*

- Decalin have been probe as a valid 2<sup>nd</sup> generation immersion fluids with a RI of  $\approx 1.62$  at 193 nm and a absorption of 0.3 /cm.
- Purification of cycloalkanes is a critical issue. Purification method have been develop which provide a high pure-low absorbing fluid.
- Elimination of oxygen should be consider as the critical step. Formation of charge-transfer oxygen-cycloalkane complex with high absorption in the UV-vis have been observed and studied.
- Perhydropyrene can be a potential 3<sup>rd</sup> generation fluid if the absorption can be drop down by further purification, oxygen elimination.
- Addition of solid polycycloalkanes to a high refractive index fluid like decalin should increases the total refractive index of the fluid.
- Photostability of cycloalkanes should be studied. Highly polar oxidation products form during exposure, should be easy to separated by the developed techniques.



# Thank You!!

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