



Quest for the Origin of Life – Experiments towards the Formation of Sugar through Small Molecules

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DIP – Haifa – Technion

The sweet world - sugars

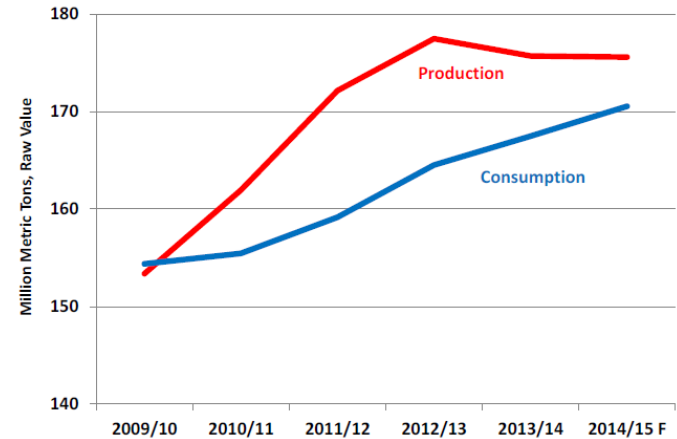


enjoyment

food }
fuel } energy

~ 33.1 kg/a consumption of adults

disacchriade: glucose + fructose $\equiv$ saccharose



175.7 million tons/a



36.7 million tons/a



27.0 million tons/a

1801: the Chemist Franz Carl Achard

1850: industrial revolution; the „white gold“ became common

Carbohydrates



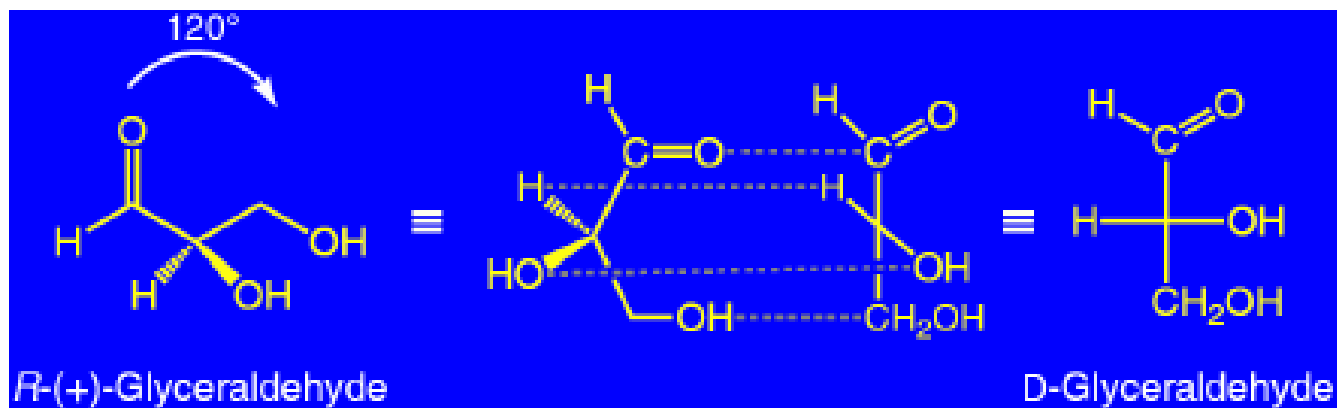
Sugars: „A loose term applied to monosaccharides and lower oligosaccharides.

(IUPAC, Gold Book)

Aldoses and ketoses $\equiv$ „hydrates of carbon“

Monosaccharides $C_n(H_2O)_n$

Oligosaccharides $C_n(H_2O)_m$



(IUPAC, Gold Book)

Oligosaccharides $C_n(H_2O)_m$

(+)- α -D-Glucopyranose
 Schmp. 146 °C
 $[\alpha]_D = +112$
 36%

D-Glucose
 0,02%

(+)- β -D-Glucopyranose
 Schmp. 150 °C
 $[\alpha]_D = +18,7$
 64%



Sugars: „A loose term applied to monosaccharides and lower oligosaccharides.

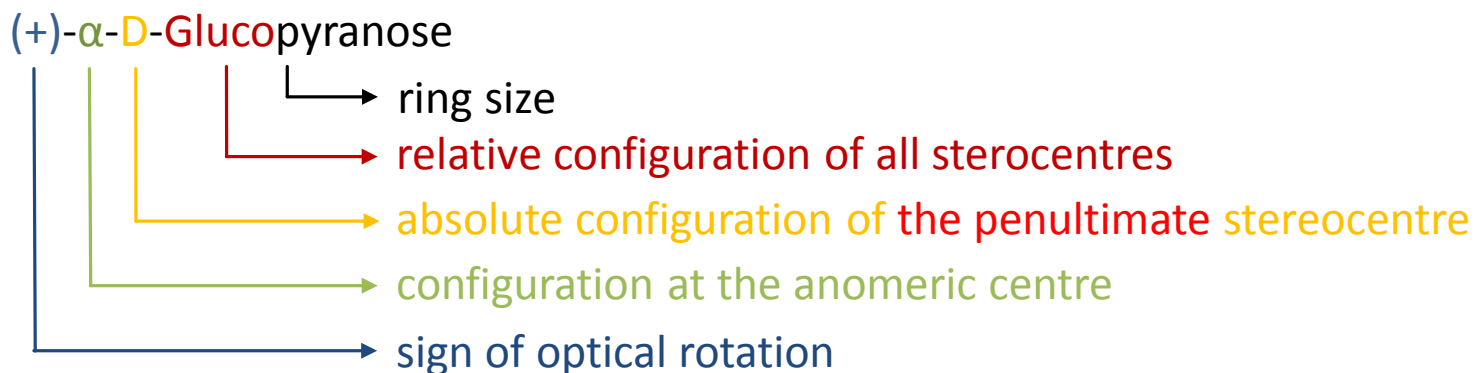
(IUPAC, Gold Book)

Aldoses and ketoses $\equiv$ „hydrates of carbon“

Monosaccharides $C_n(H_2O)_n$

Oligosaccharides $C_n(H_2O)_m$

nomenclature for sugars:

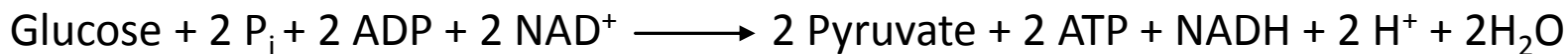


High density of functional groups – polyhydroxyalkanes $\longrightarrow$ great variety of isomers

Carbohydrates

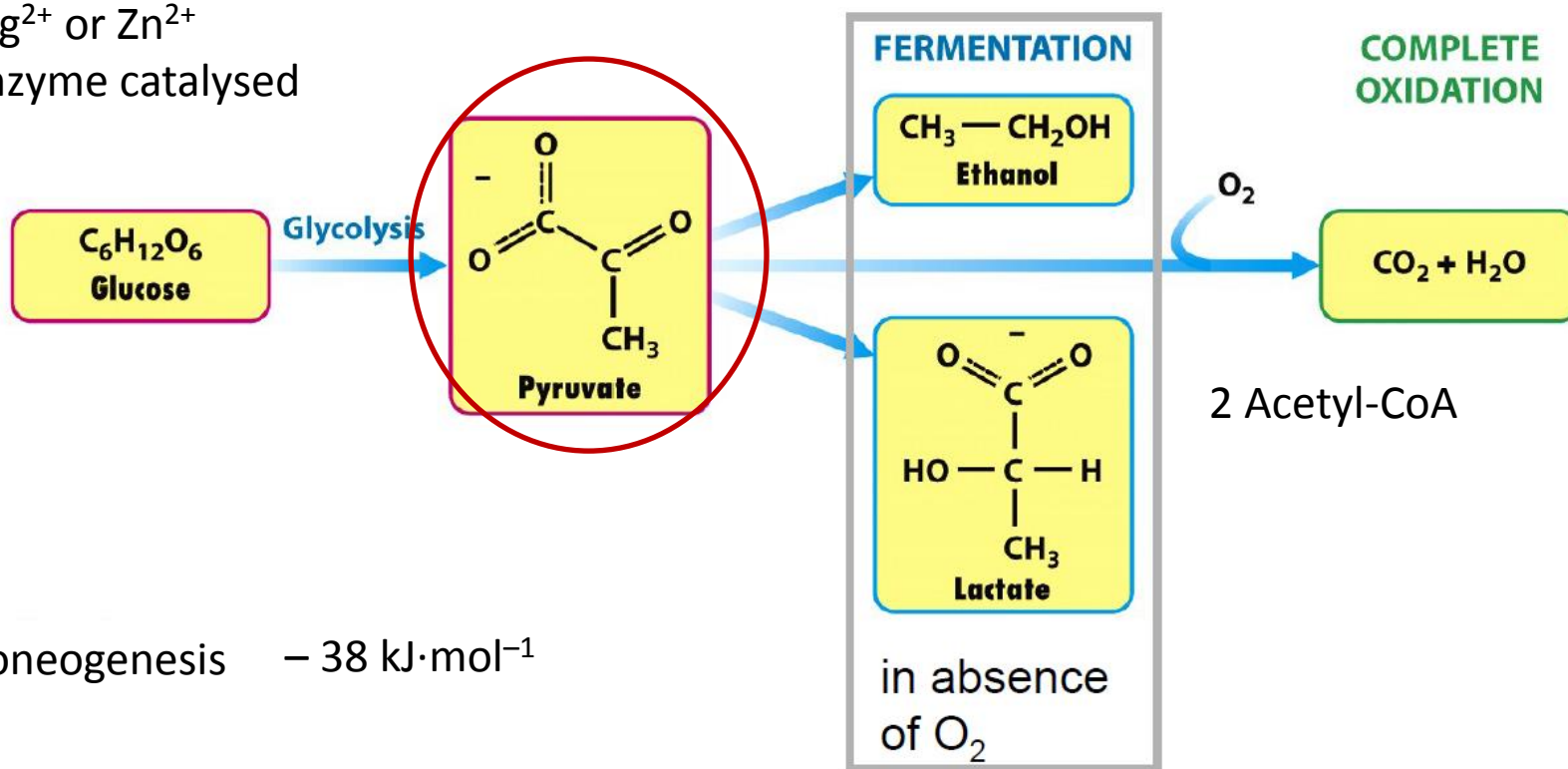


Glycolysis:



- 10 steps
- 3 irreversible
- 3 different stages
- Mg^{2+} or Zn^{2+}
- enzyme catalysed

– 84 kJ·mol⁻¹



Glyconeogenesis – 38 kJ·mol⁻¹

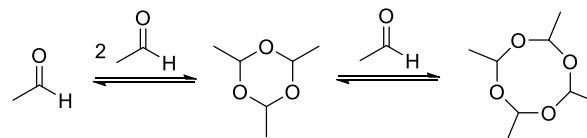
The Origin? Small Molecules in the Interstellar Medium



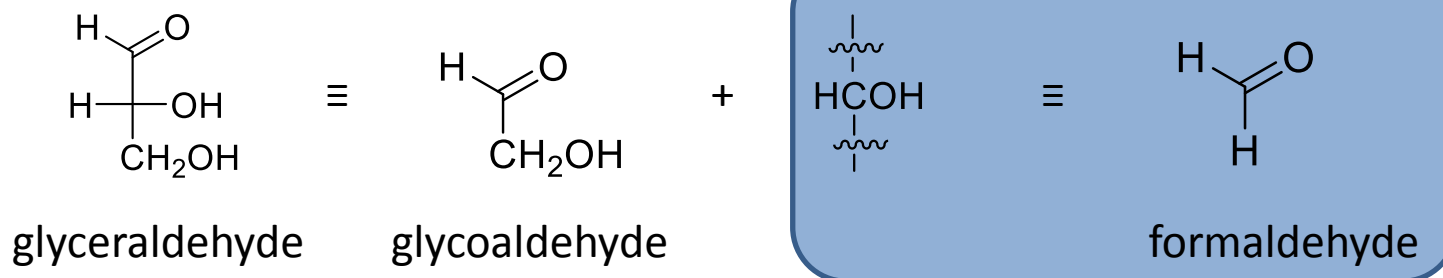
Where do sugars come from?

sugars on earth: autotrophic organisms via photosynthesis

oligo- or polymeres of acetaldehyde



What are the necessary building blocks?



glycolaldehyde was found in interstellar clouds through GHz-spectroscopy

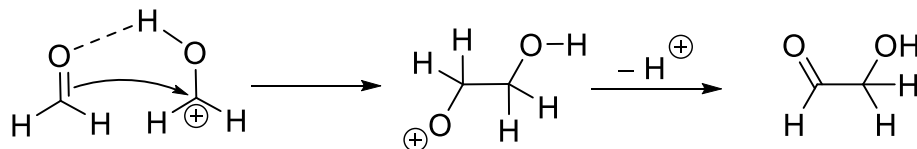
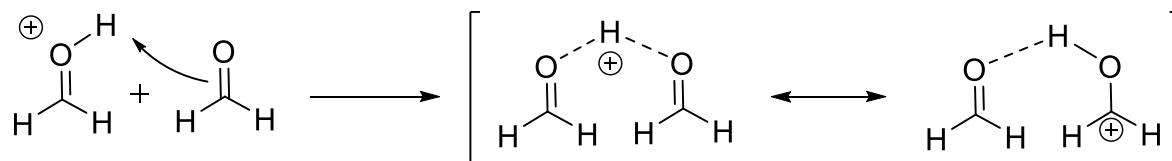
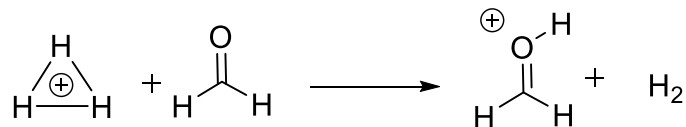
→ next to formaldehyde

high dilution; particle densities $10^{-4} - 10^5 \text{ cm}^{-3}$; $T[\text{K}] = 10 - 150$

The Origin? Small Molecules in the Interstellar Medium



de Groot et al.: emission spectrum of H_3^+



→ mechanism Halfen et al.
supported by theoretical investigations of Schaefer et. al and Munoz-Caro et al.

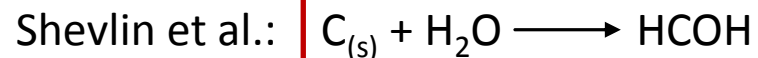
De Groot, M. J. H.; Lamers, H. J. G. L. M. *Nature*, **1992**, 355, 420-422. Halfen, D. T.; Apponi, A. J.; Woolf, N.; Polt, R.; Ziurys, L. M. *Astrophys. J.* 2006, 639, 237-245. Hoffmann, M. R.; Schaefer, H. F. *Astrophys. J.* **1981**, 249, 563-565. Castro, M. E.; Nino, A.; Munoz-Caro *Theor. Chem. Account* **2008**, 119, 343-354.

The Origin? Small Molecules in the Interstellar Medium

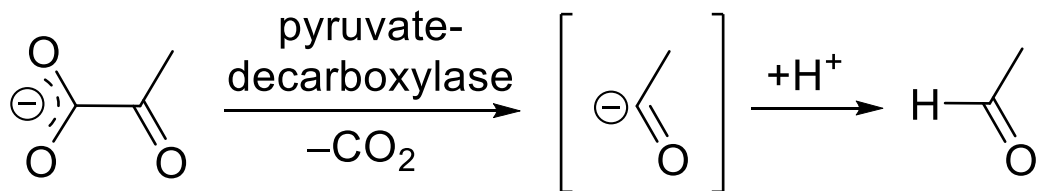


To perform a condensation of sugarlike compounds, an activation of one aldehyde is needed

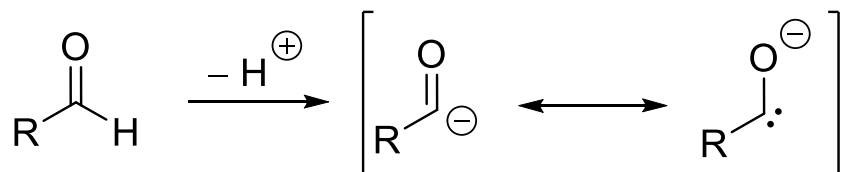
→ Umpolung, acidic, cationic or NHC



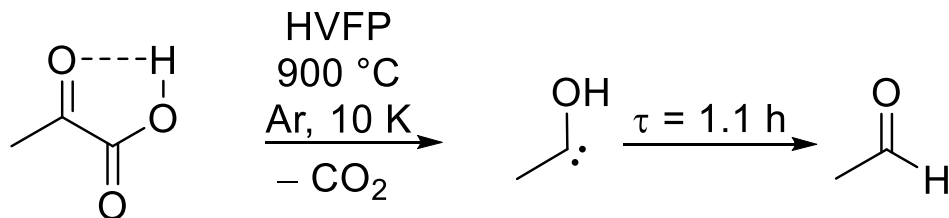
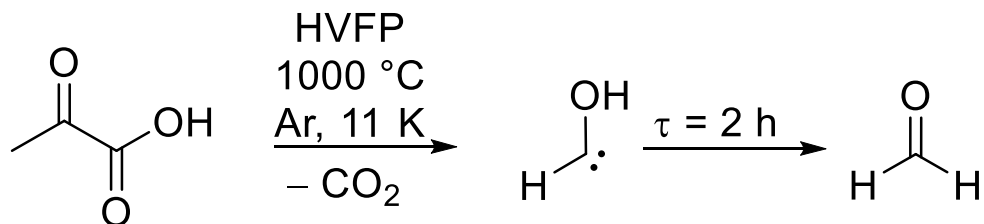
Schreiner et al.: only $\text{C}(^1\text{D}) + \text{H}_2\text{O}$; $\text{C}(^3\text{P}) + \text{H}_2\text{O} \longrightarrow \text{Clusters}$



The Origin? Small Molecules in the Interstellar Medium



Schreiner et al.:



Enders aminoacid reaction

Wanzlick, H.-W. *Angew. Chem. Int. Ed.*, **1962**, 74, 129. Schreiner, P. R.; Reisenauer, H. P.; Pickard, F. C.; Simonett, A. C.; Allen, W. D.; Mátyus, E.; Czásár, A. G. *Nature*, **2008**, 453, 906-909. Ley, D.; Gerbig, D.; Schreiner, P. R. *Org. Biomol. Chem.*, **2012**, 10, 3781-3790. Thaddeus, P.; Gottlieb, C. A.; Mollaaghababa, R.; Vrtilek, J. M. *J. Chem. Soc., Faraday Trans.* **1993**, 89, 2125-2129. Schreiner, P. R.; Reisenauer, H. P.; Ley, D.; Gerbig, D.; Wu, C.-H.; Allen, W. D. *Science* **2011**, 332, 1300-1303. Carpenter, B. K. *Science* **2011**, 332, 1269-1270.

State of the Art - Formose Reaction

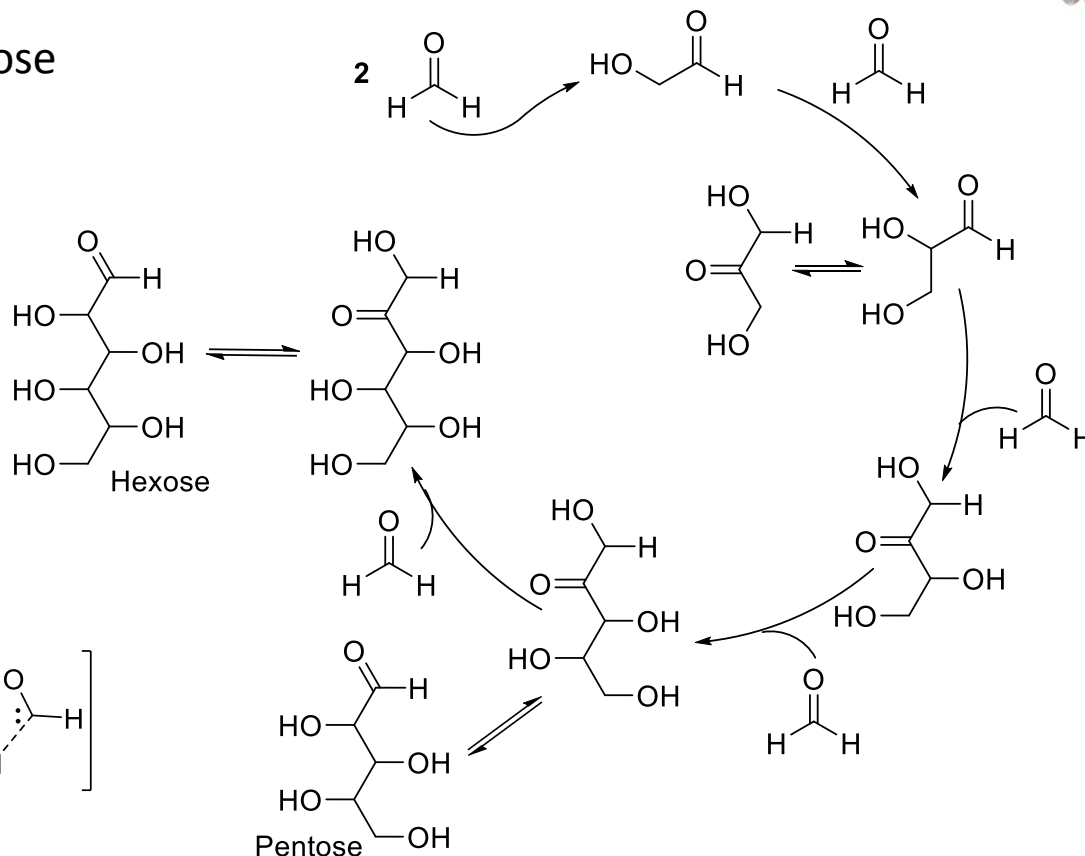
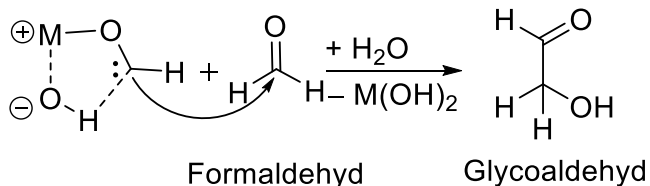
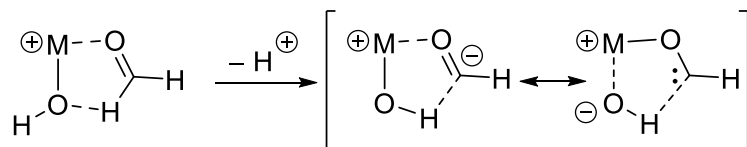


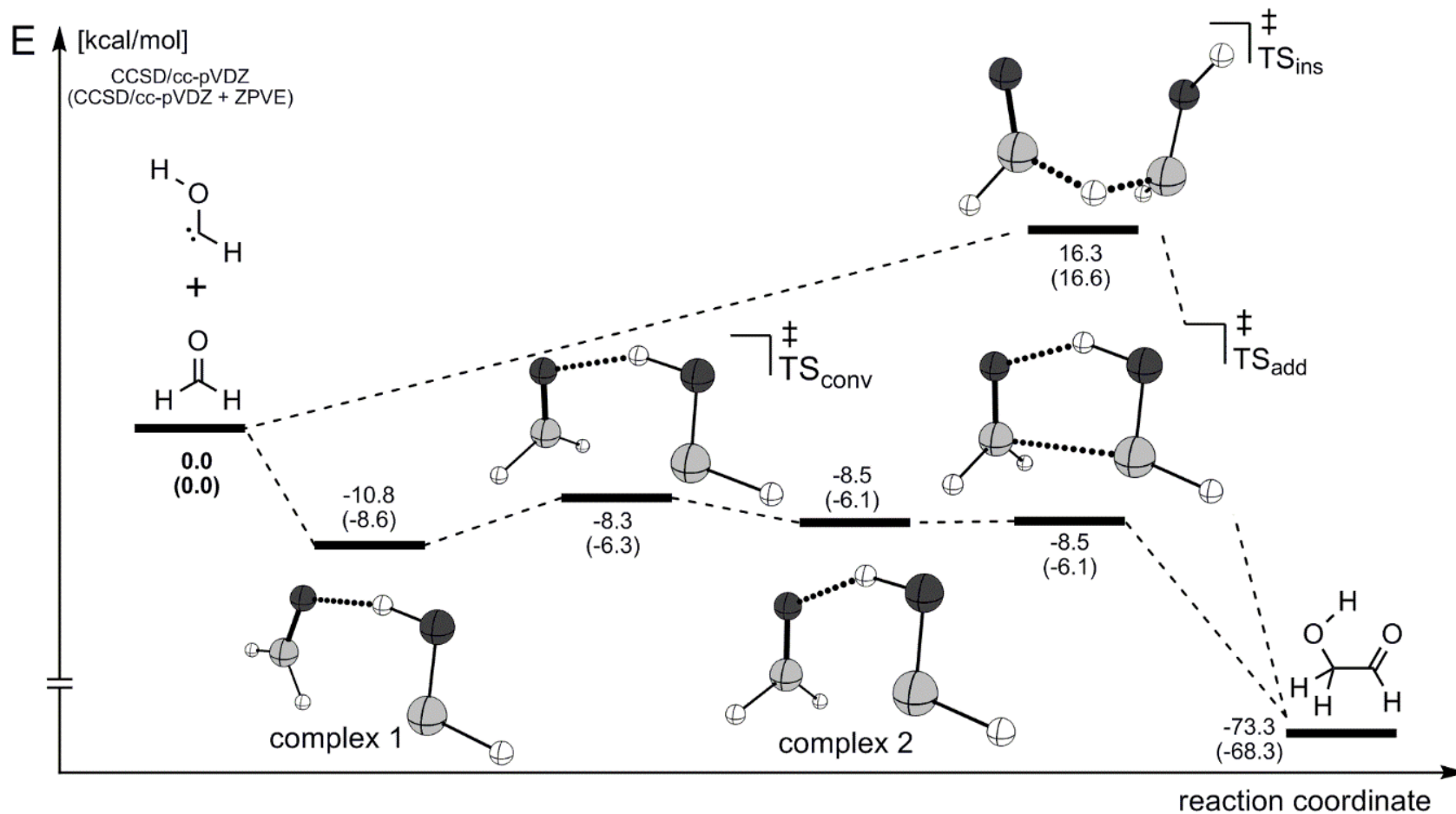
Formose = Formaldehyd und Aldose

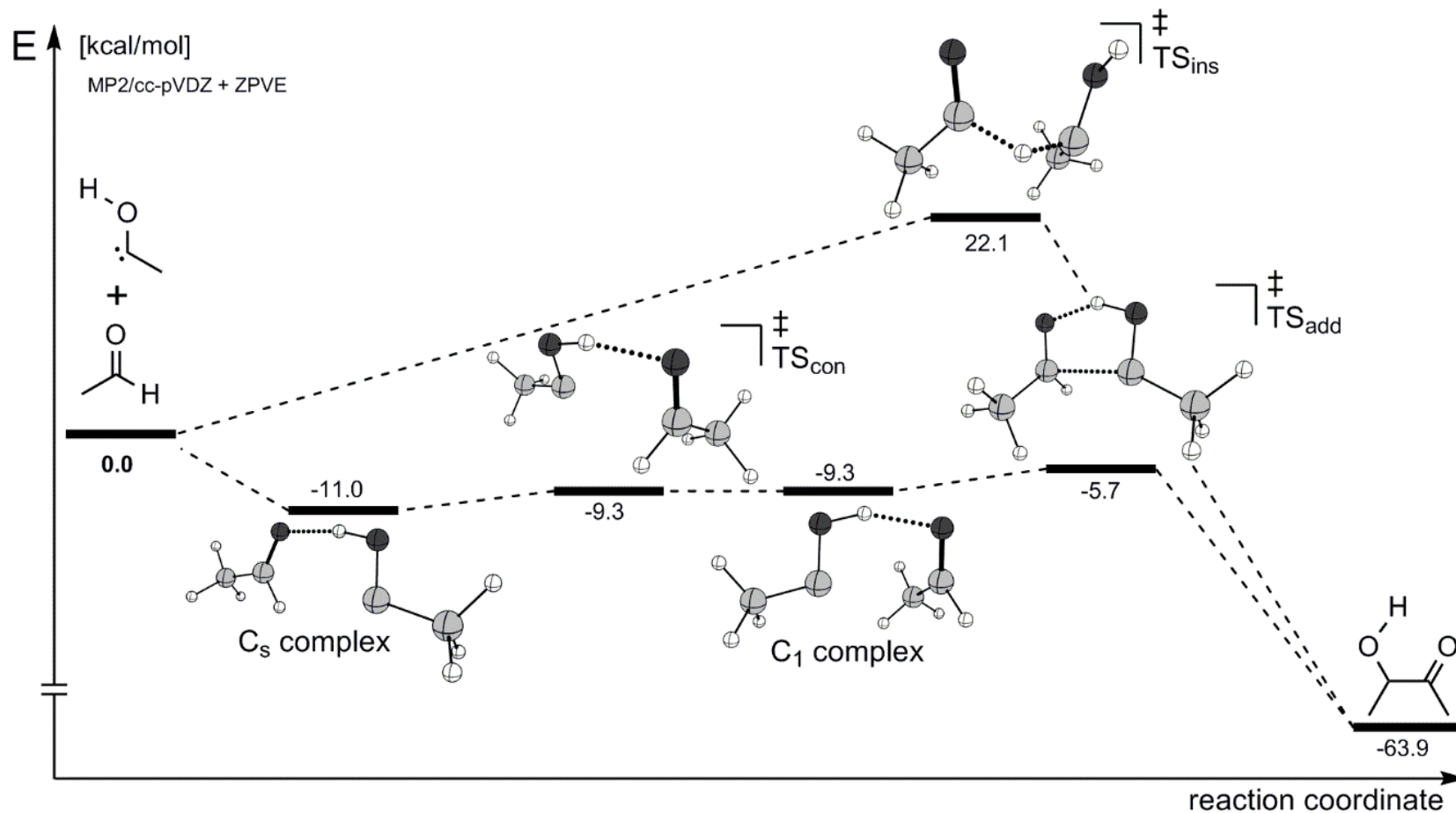
Butlerov reaction –

mixture of different monosaccharides

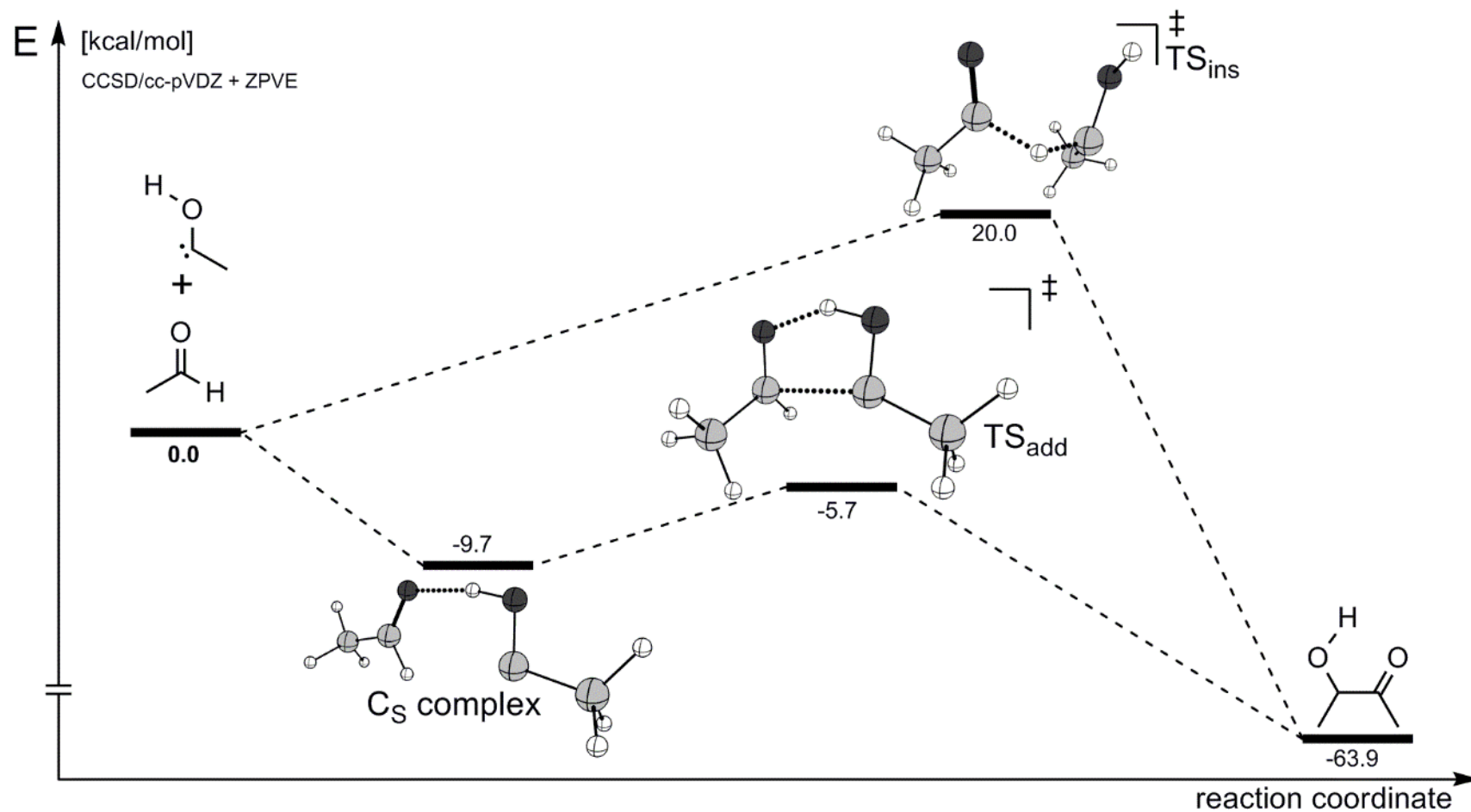
Initial step:



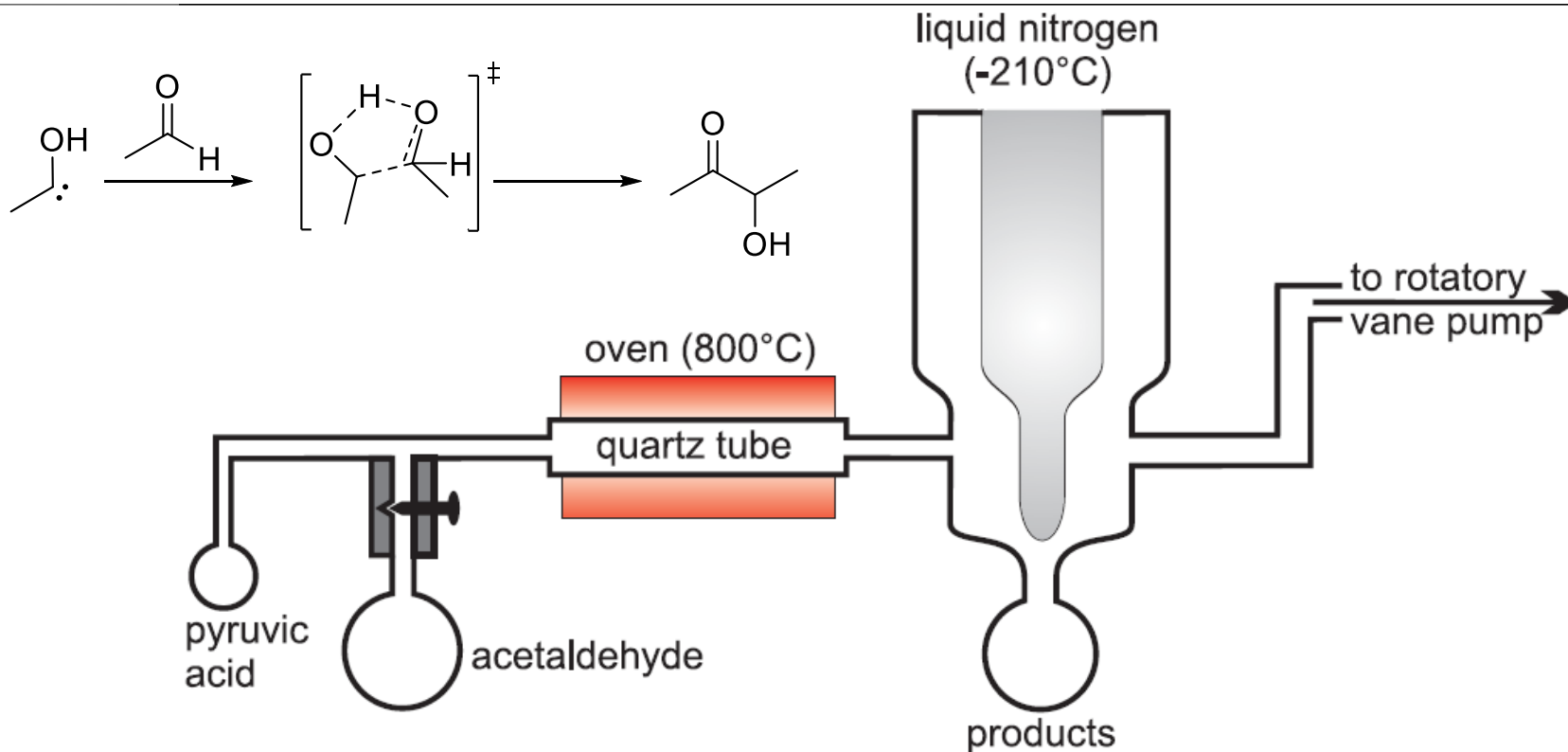




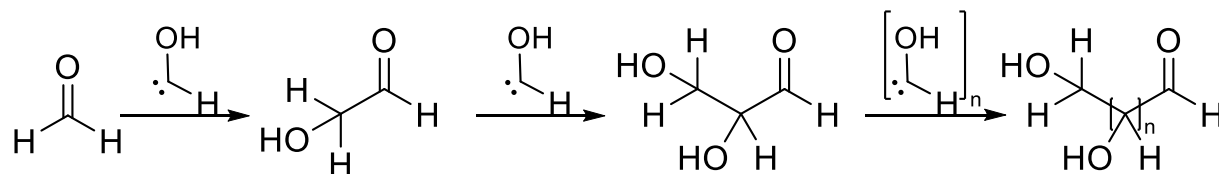
Early Theoretical Consideration



Experimental Approach



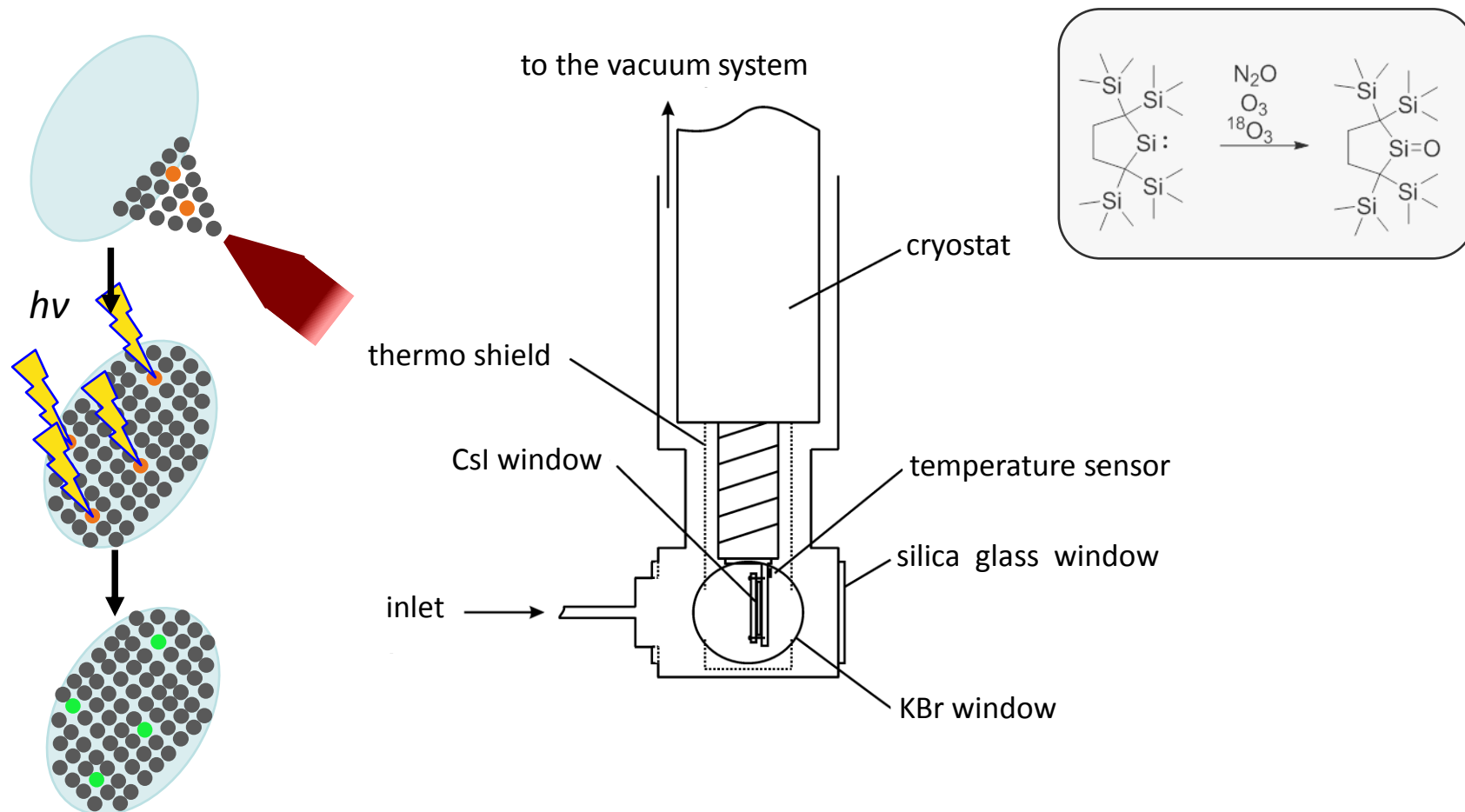
Quest:



Matrix-Isolation Technique

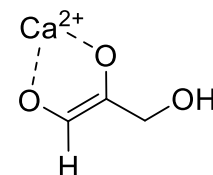
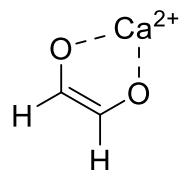
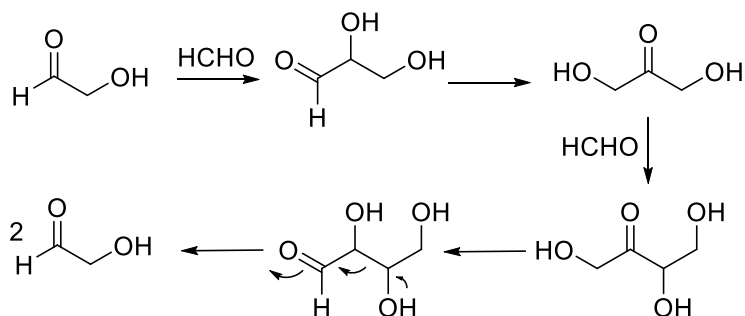


typical matrix materials : Ar, Ne, Kr, Xe, N₂, 3-methylpentane...



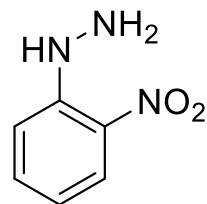
methods : photolysis, pyrolysis, laser flash photolysis...

Experimental Approach



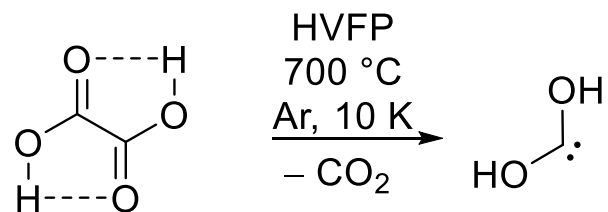
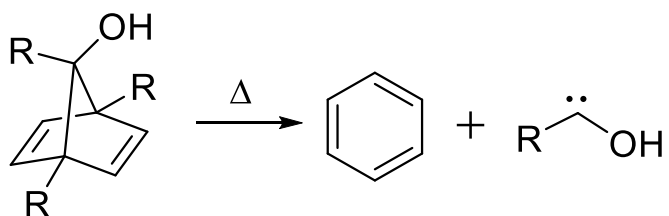
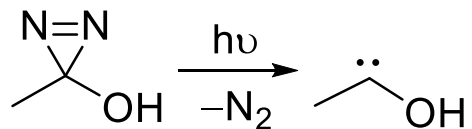
Analysis of reaction mixtures:

- derivatisation and GC
- HPLC
- MS
- etc



Matrix experiments with pyrolysis of pyruvate in an Ar (Kr) : acetaldehyde

hydroxymethylene in He nanodroplets



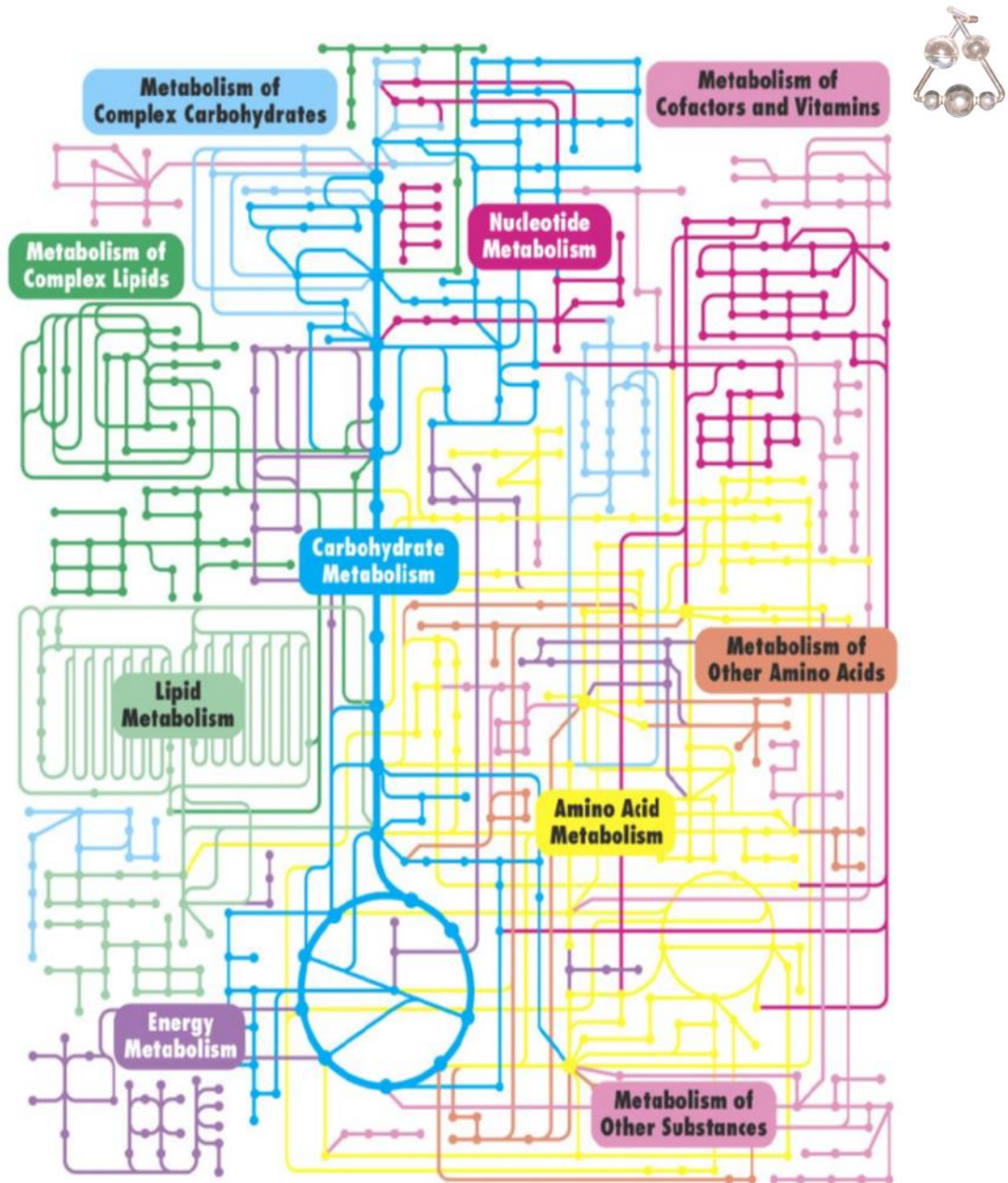
Acknowledgement:

Thanks,...

- Professor Schreiner
- Dr. Reisenauer
- Dennis, David, Philipp
- PRS Group...



Vielen Dank



Referenzen:



Zuckerwürfel --

<http://www0.f1online.de/premid/004672000/4672781.jpg>

http://www.google.de/url?sa=t&rct=j&q=&esrc=s&source=web&cd=3&ved=0CEoQFjAC&url=http%3A%2F%2Fapps.fas.usda.gov%2Fpsdonline%2Fcirculars%2Fsugar.pdf&ei=fdu7U9yRC4T27AaOw4GICg&usg=AFQjCNGBkxILEl8eSsG8N_CieJT9zaGDZA&bvm=bv.70138588,d.ZGU&cad=rja



http://www.ipicture.de/4images/data/media/426/flagge_indien.gif



<http://ecx.images-amazon.com/images/I/41CRz-1OezL.jpg>



<http://wichtelexpress.files.wordpress.com/2013/03/planet-erde.jpg>

Referenzen:

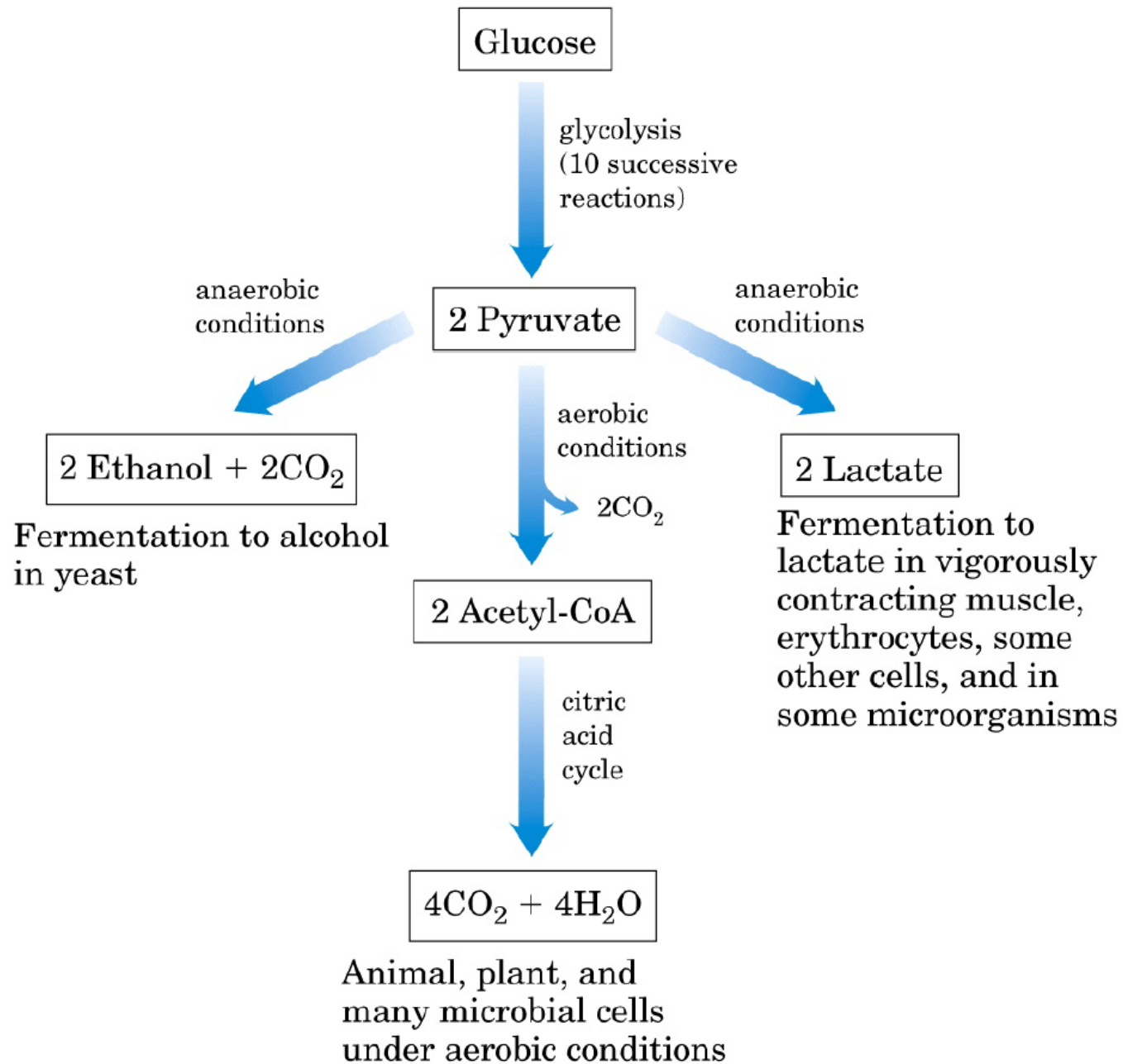


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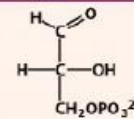
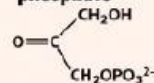
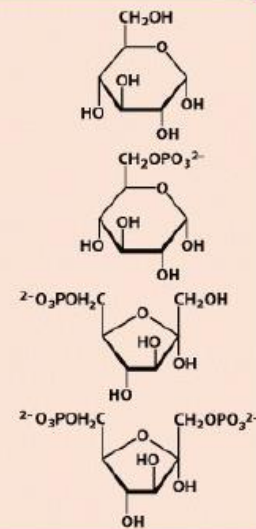
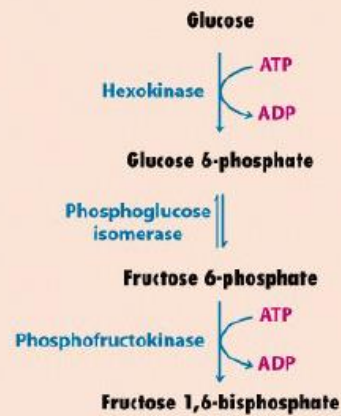


http://commons.wikimedia.org/wiki/File:Sugar_Beet.jpg

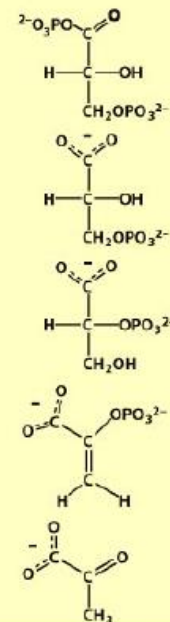
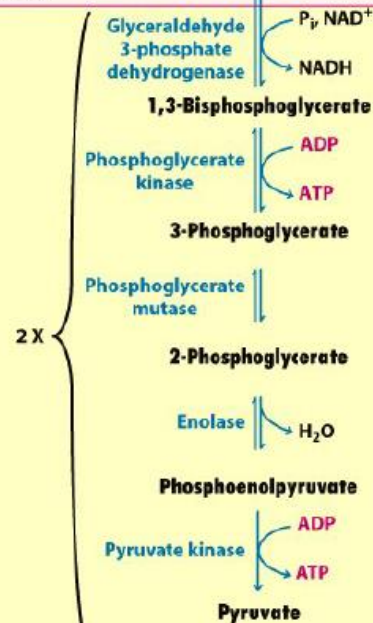


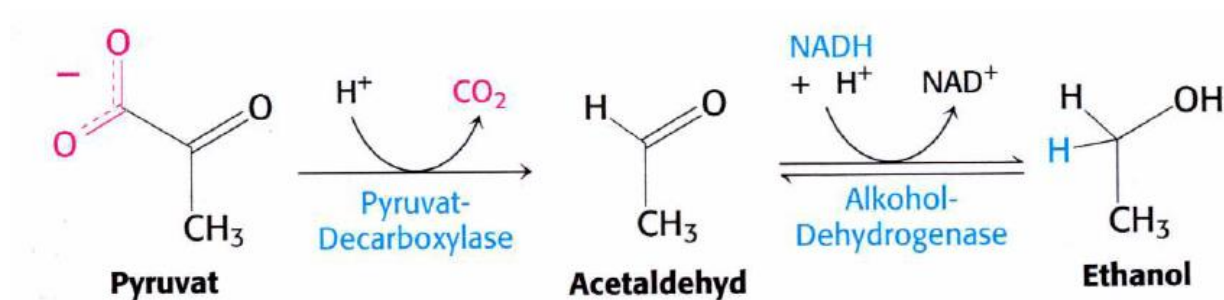


Stage 1



Stage 3





Please note the special nomenclature for sugars: (+)- α -D-Glucopyranose

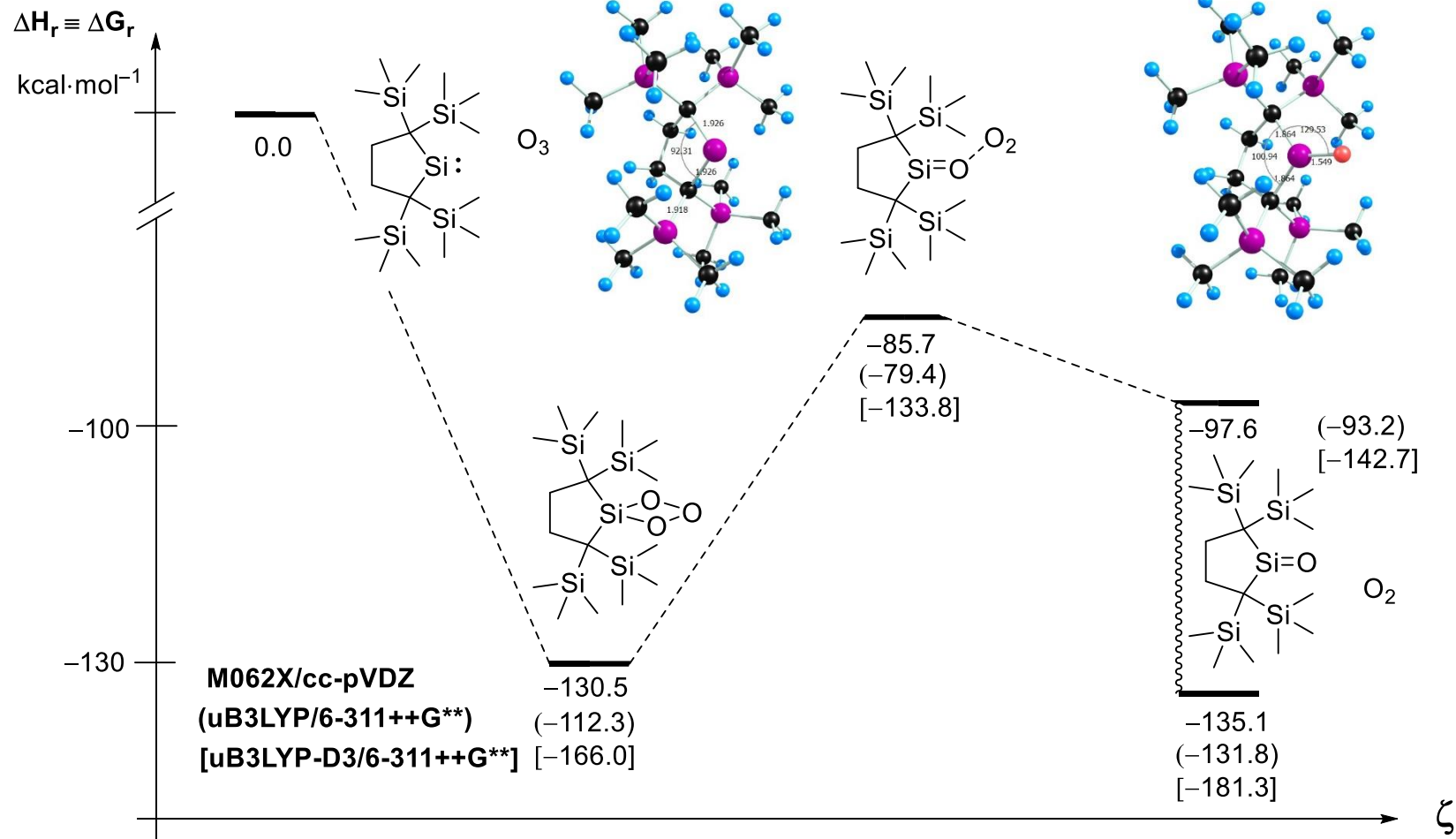
(+) $\rightarrow$ sign of optical rotation

α $\rightarrow$ configuration at the anomeric centre

D $\rightarrow$ absolute configuration of the penultimate stereocentre of the carbon chain

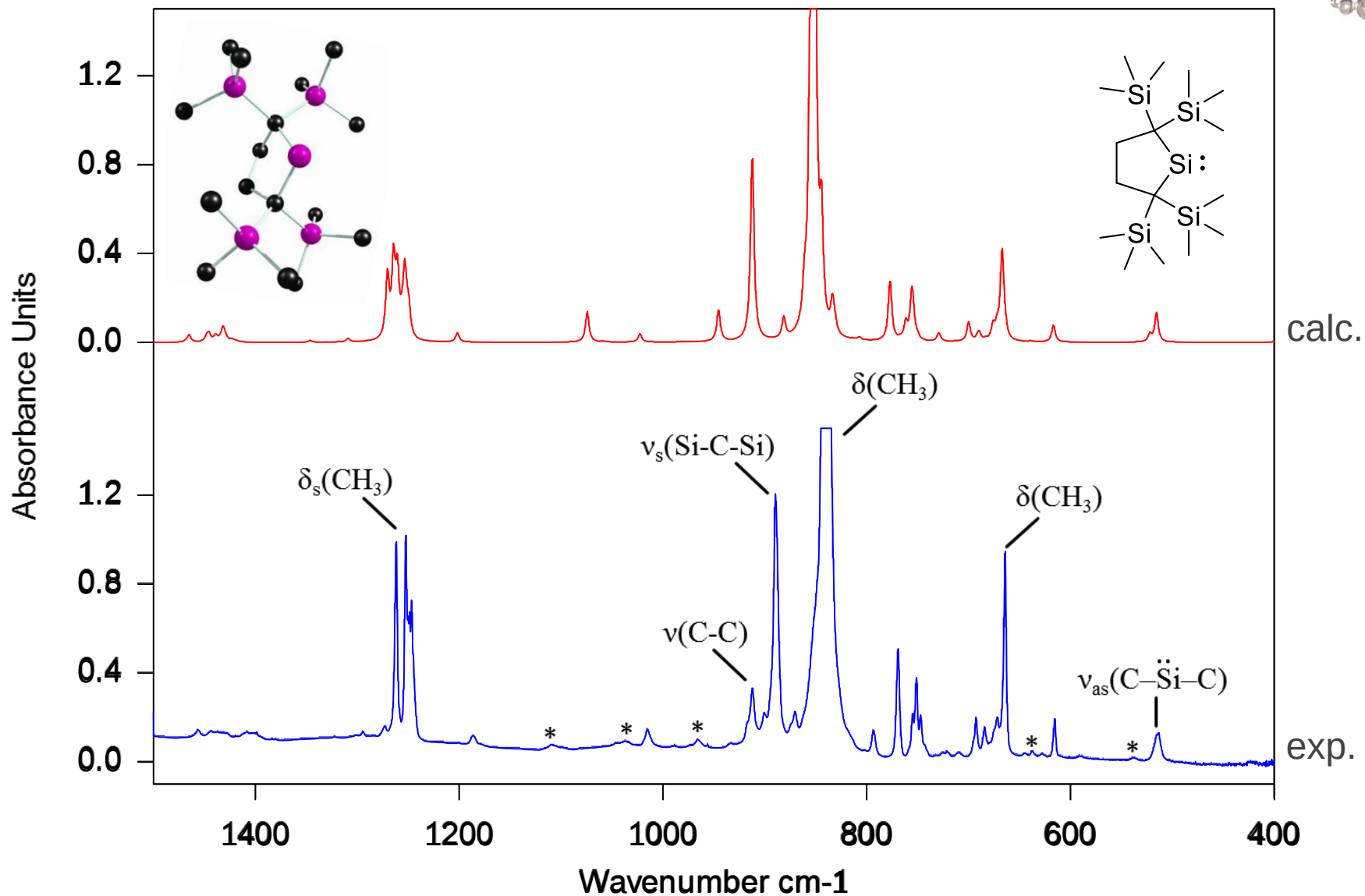
Glucose $\rightarrow$ relative configuration of all stereocentres bearing a secondary alcohol

pyranose $\rightarrow$ ring size of the cyclic acetal



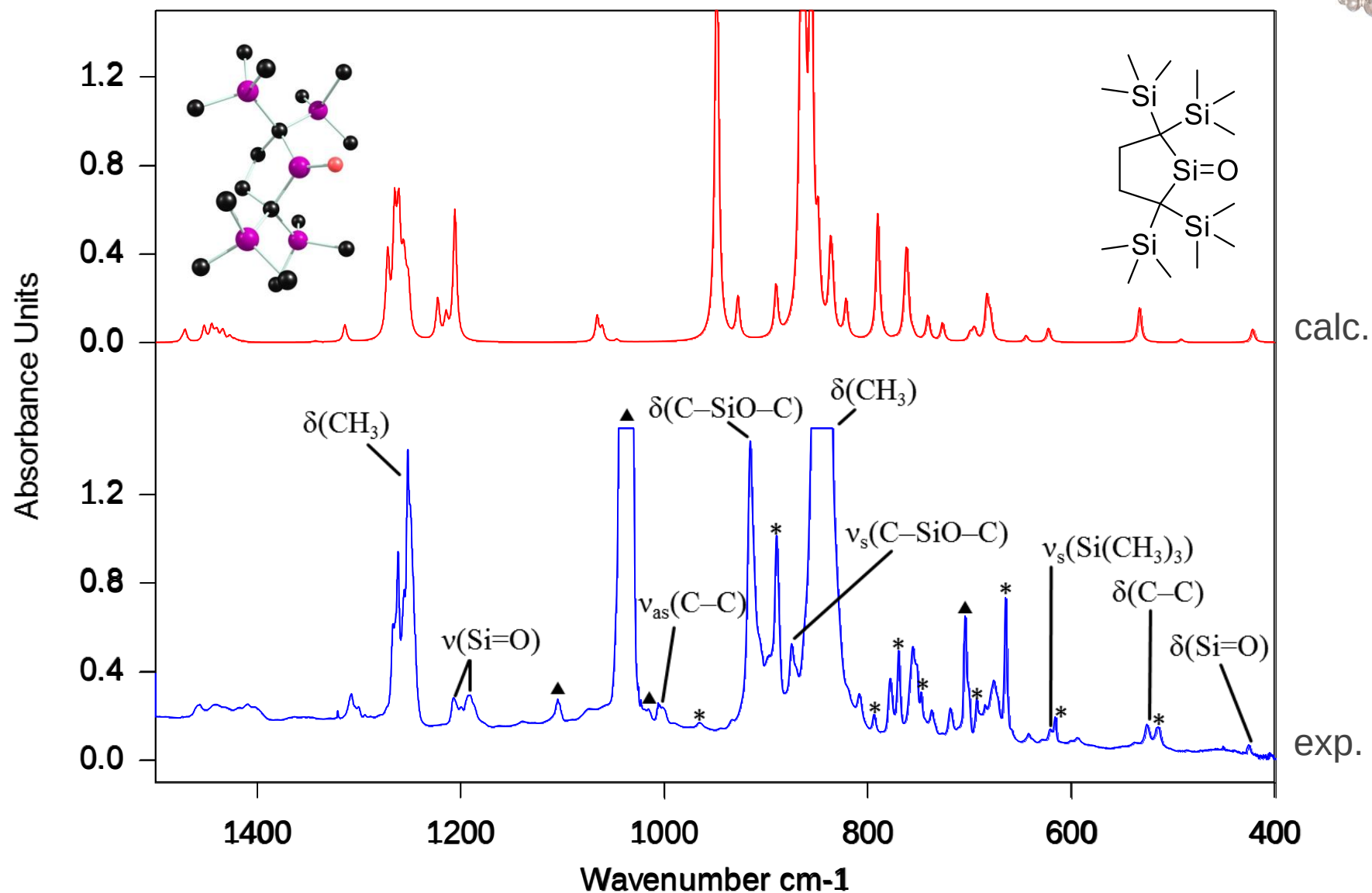
Problem : high polarity $\longrightarrow$ tendency to oligomerize with „no activation barrier“

Experimentals



* referring to silaethene

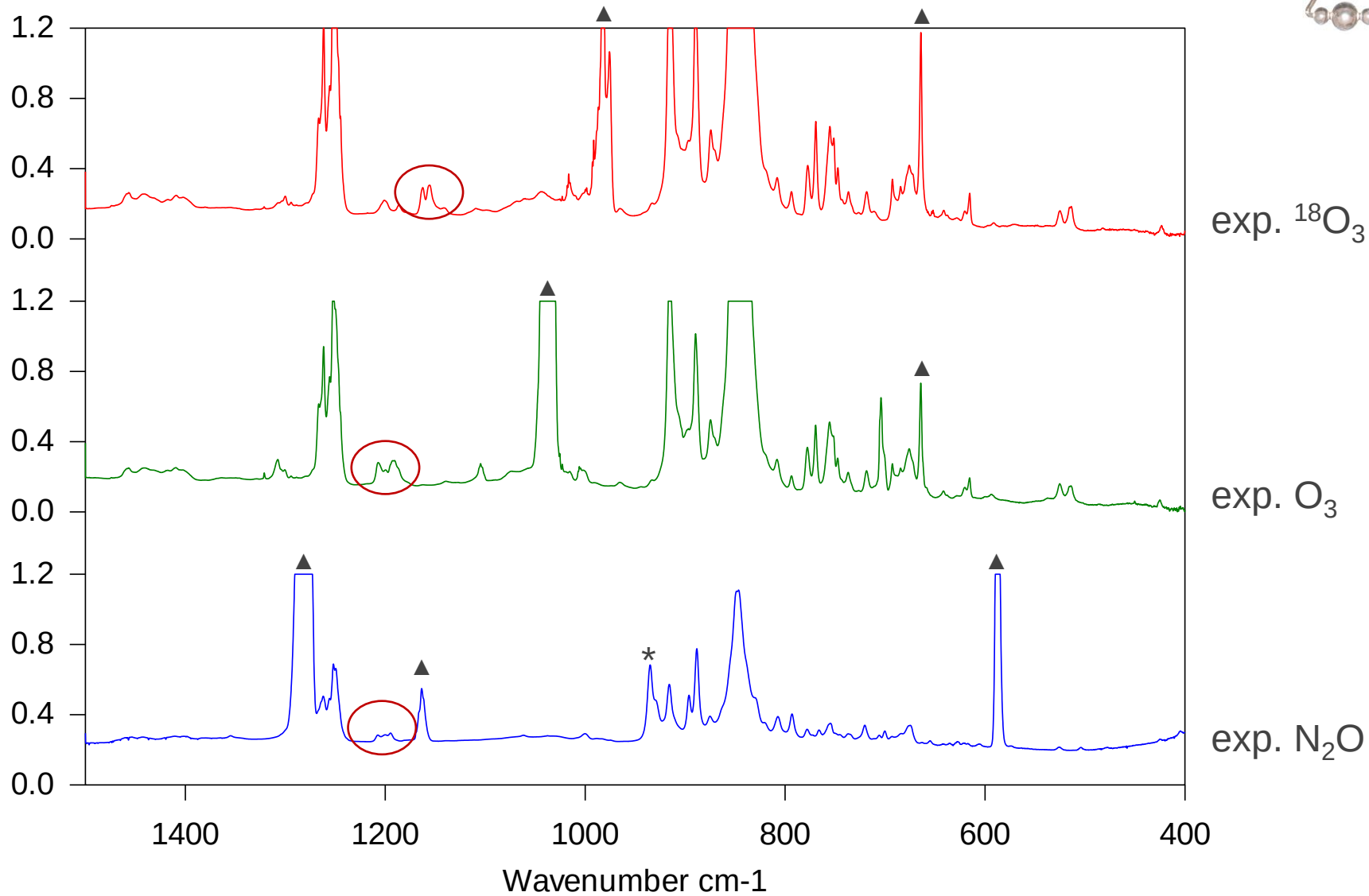
Experimentals

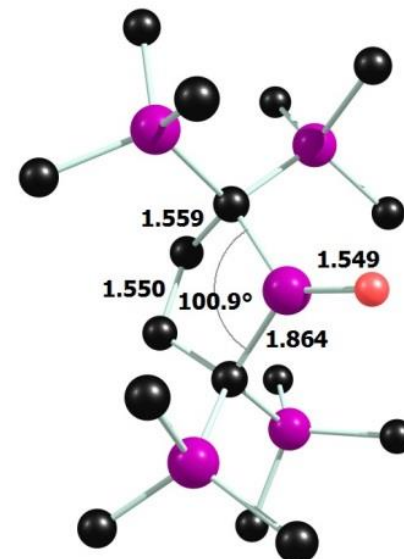
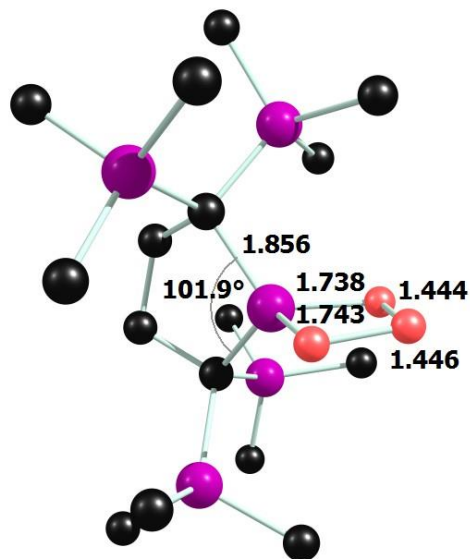
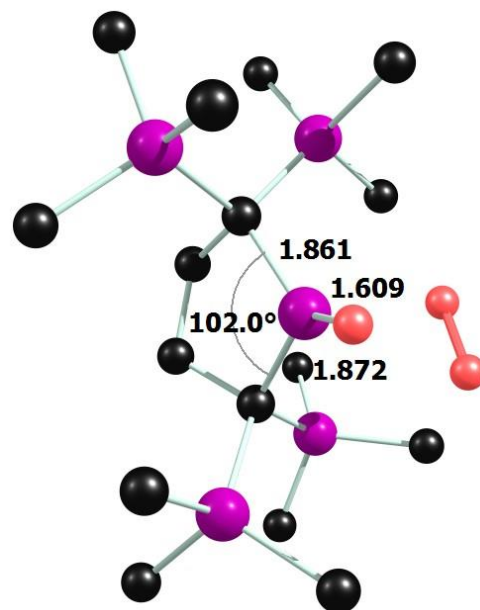
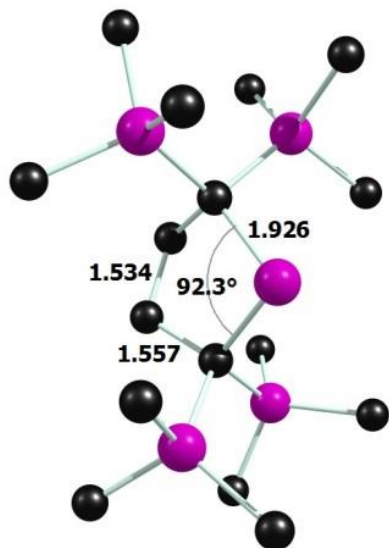


* referring to silylene; ▲ referring to O_3

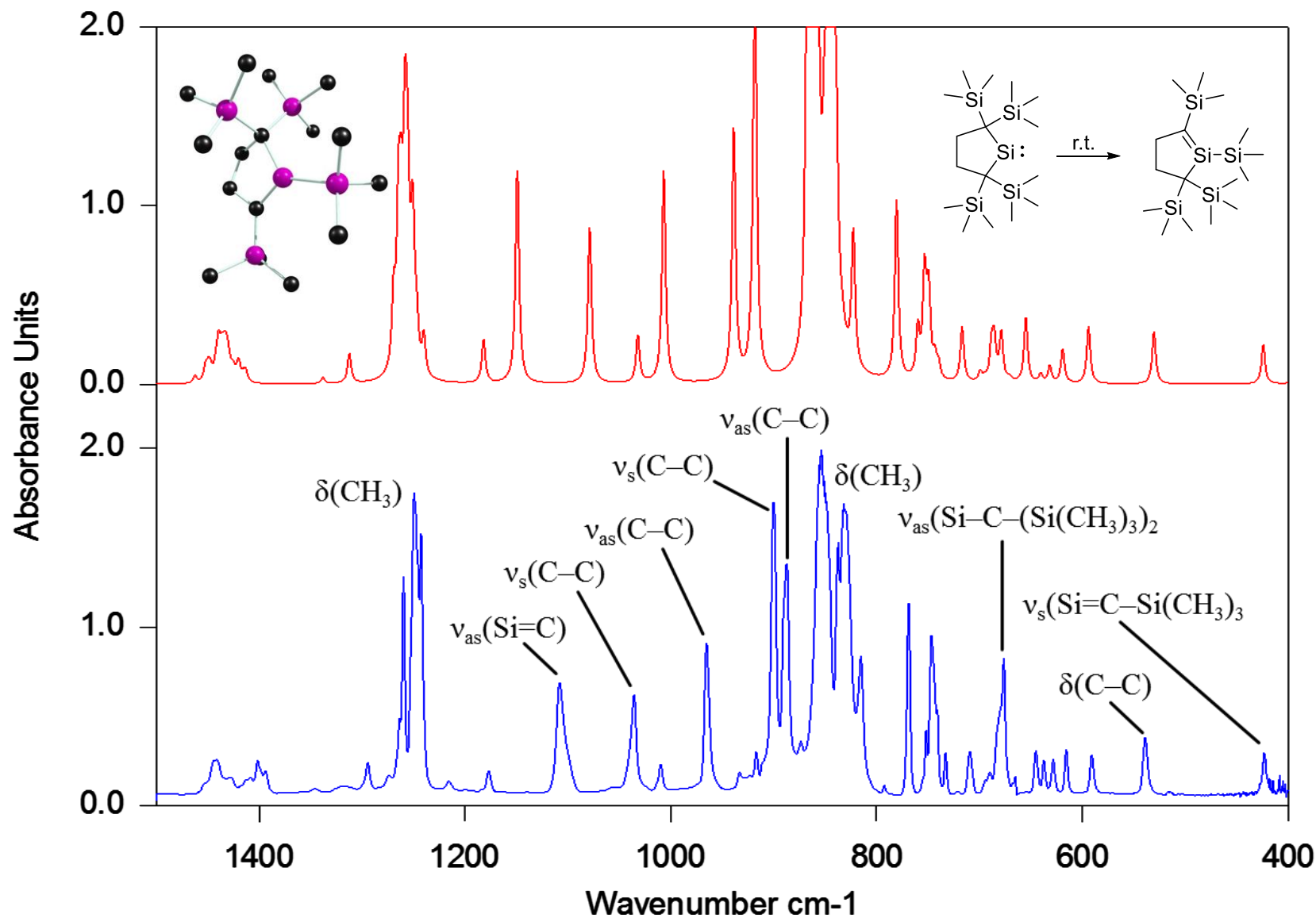


Experimentals

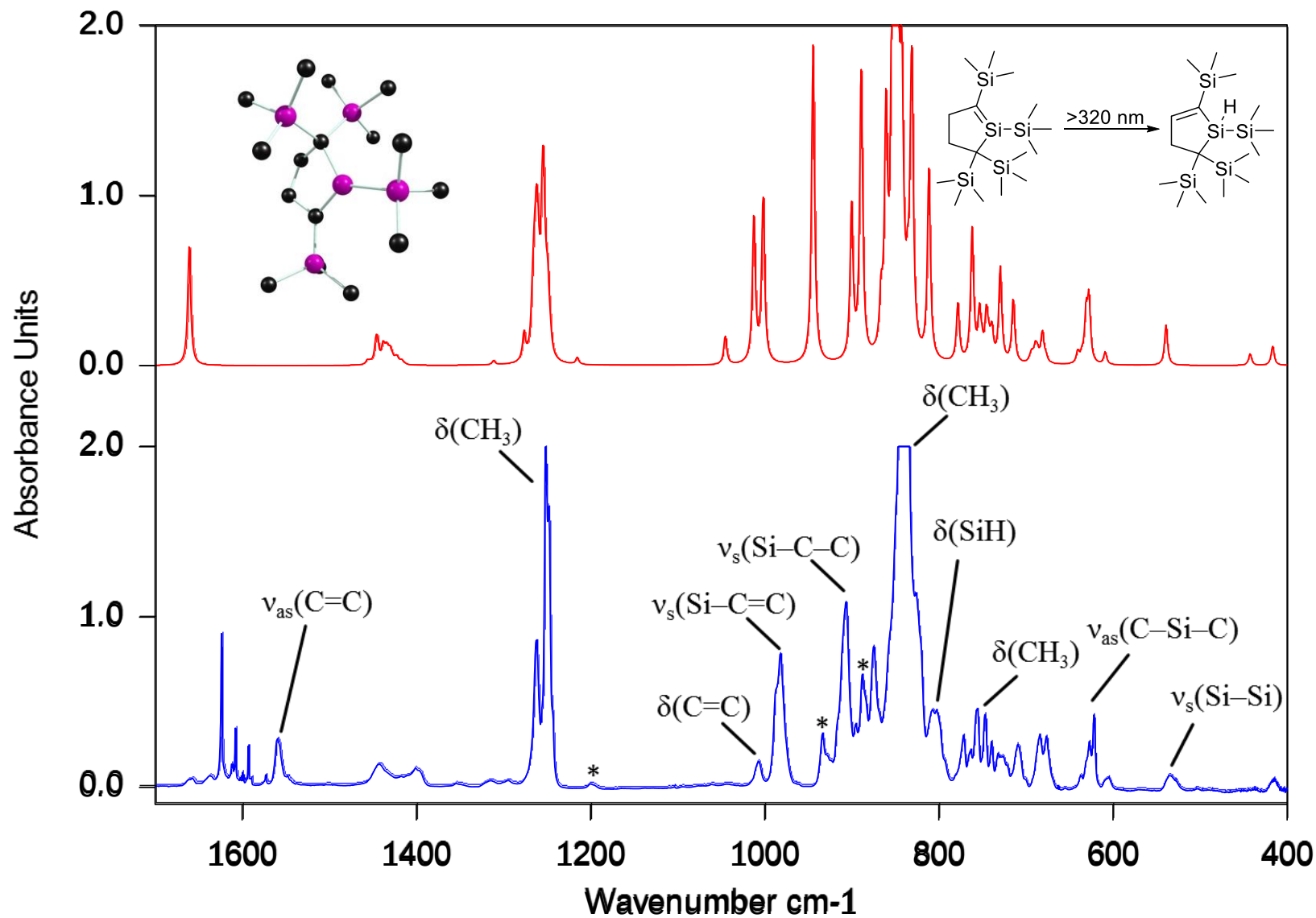




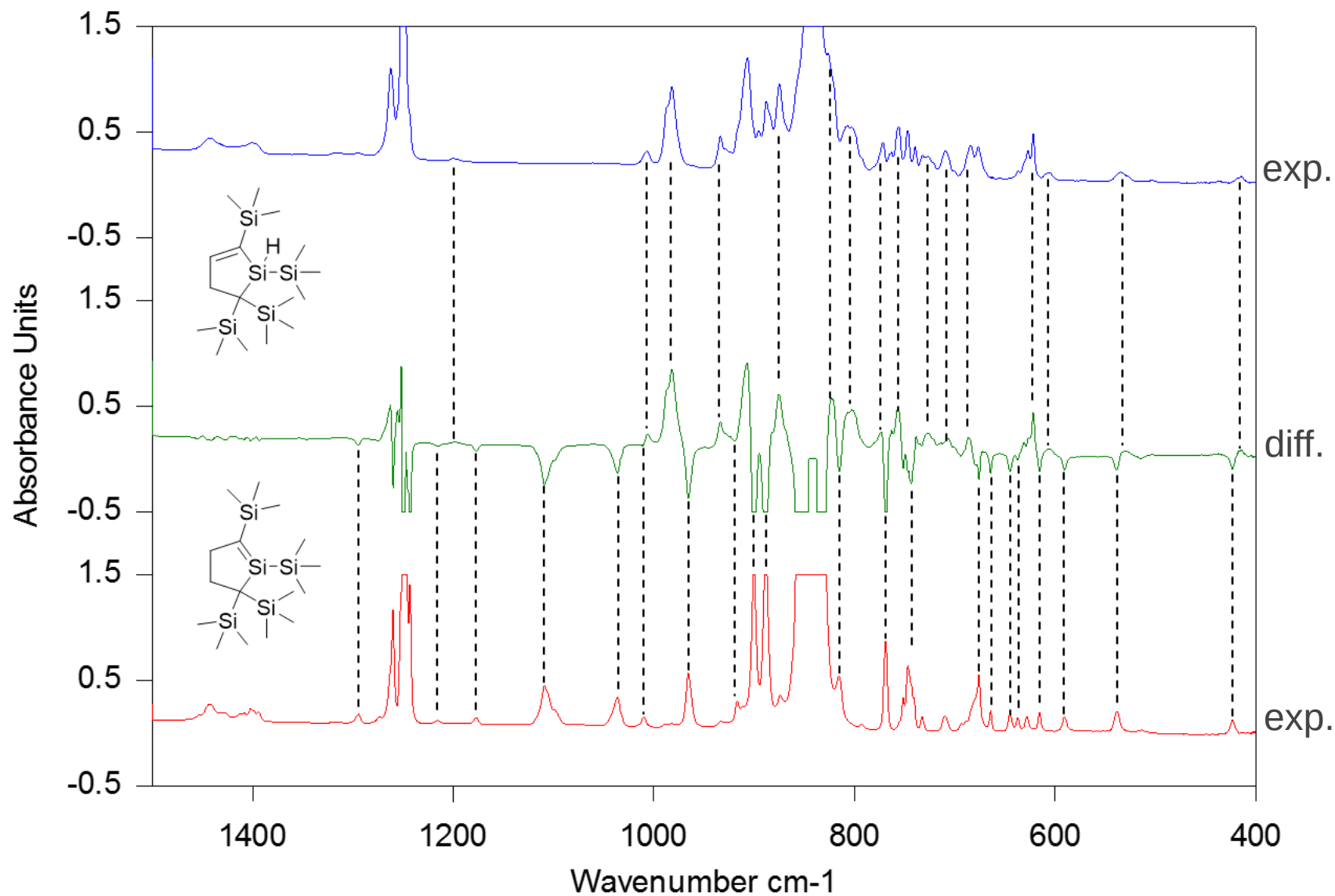
Experimentals



Experimentals

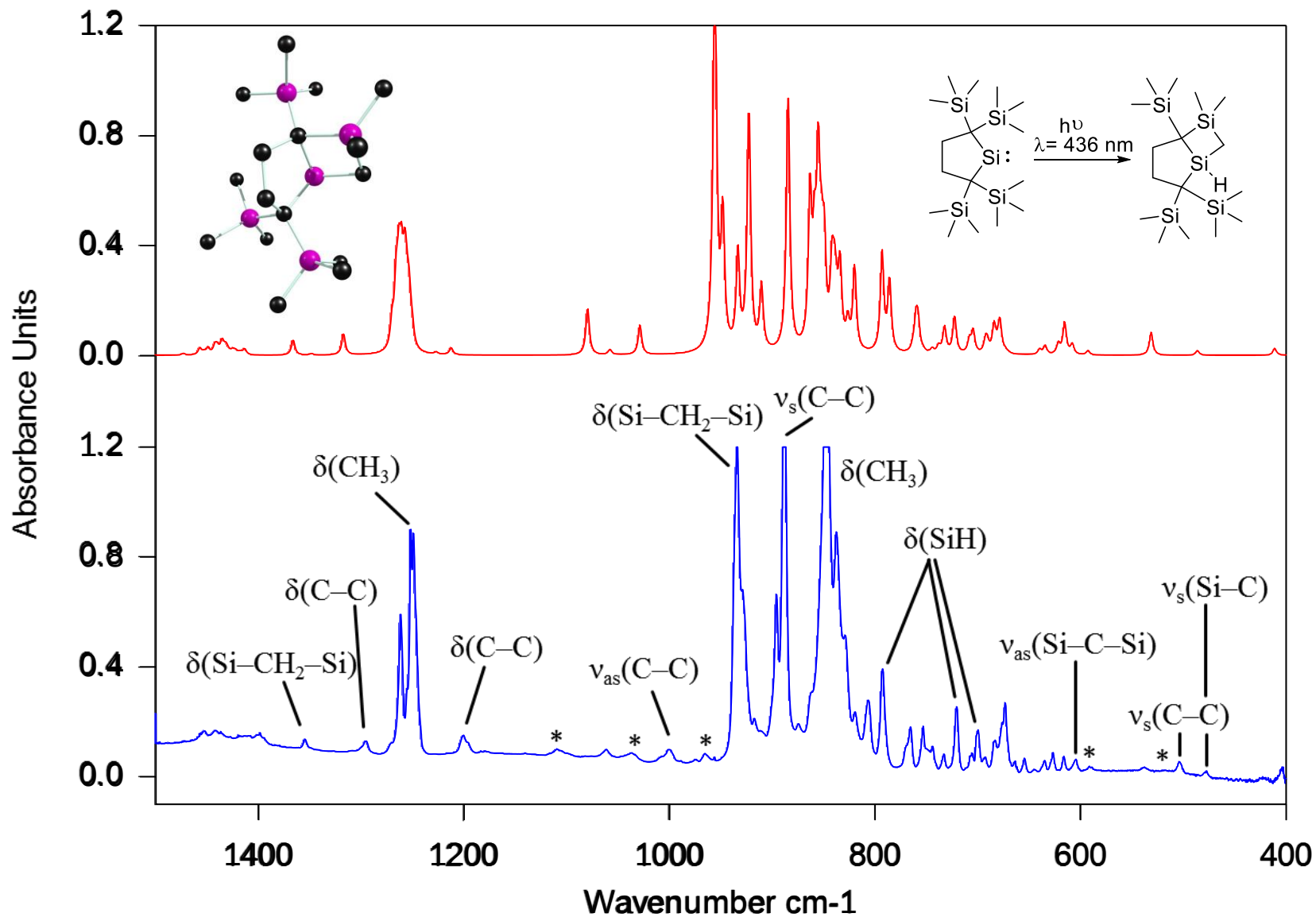


Experimentals

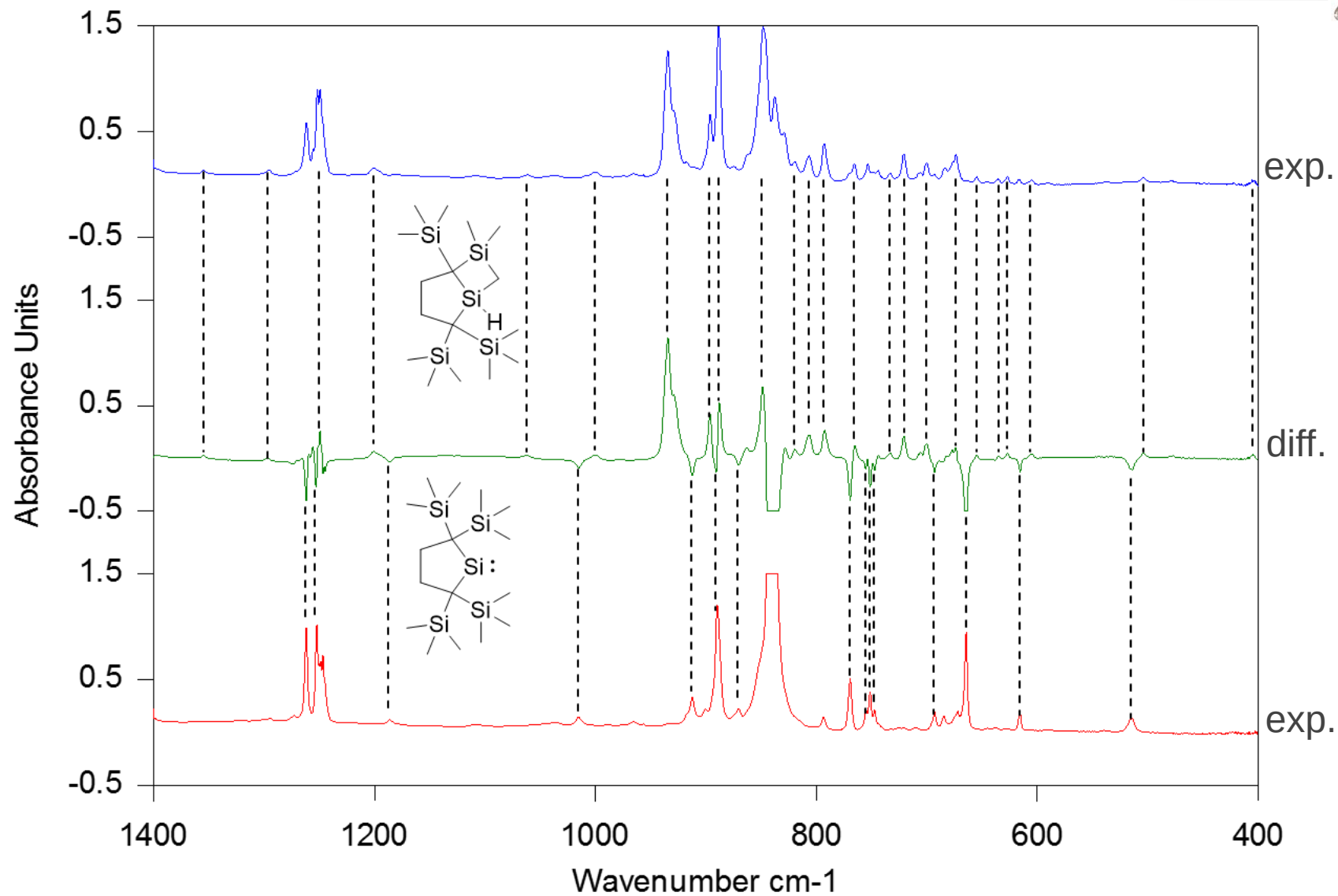


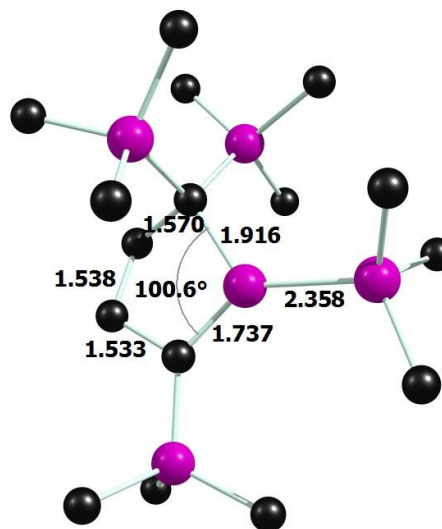
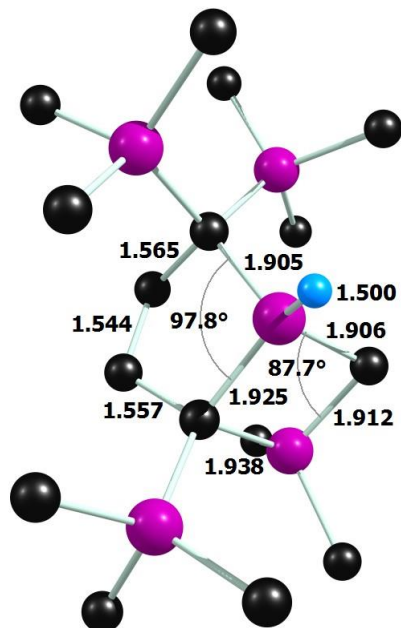
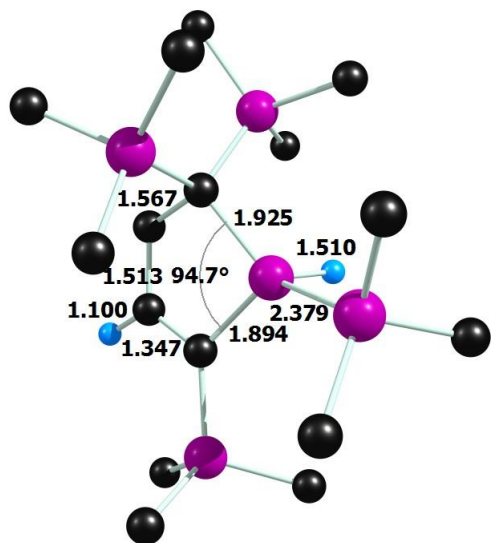
$\nu(\text{Si-H}) = 2030\text{--}2080 \text{ cm}^{-1}$

Experimentals

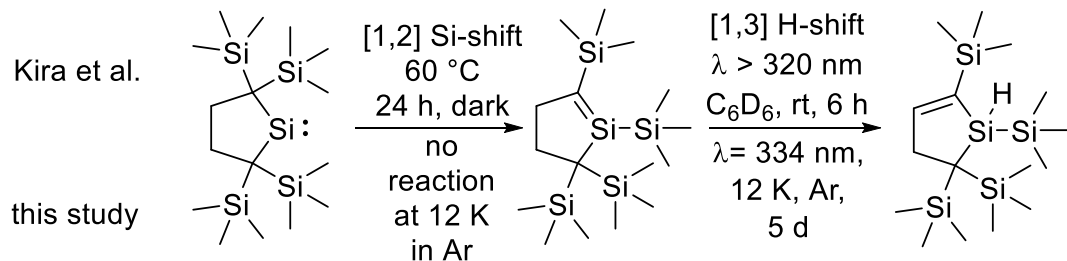


Experimentals

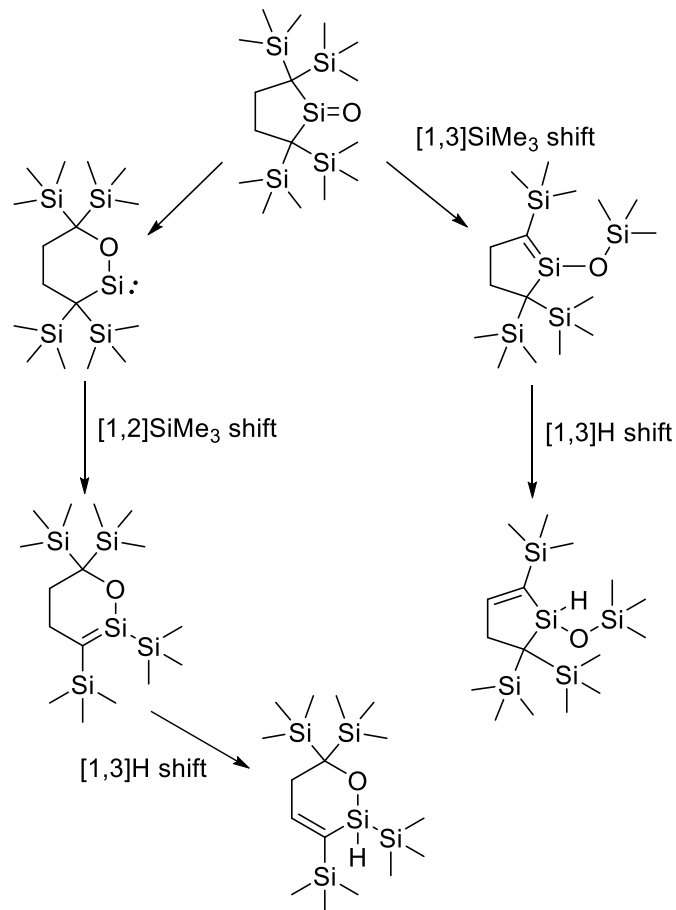
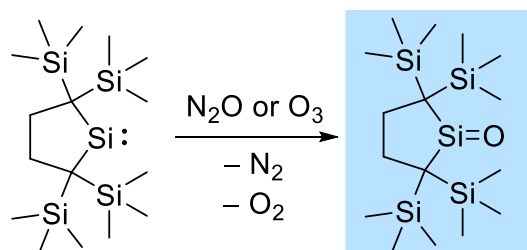
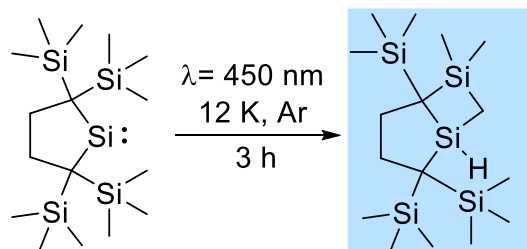




Summery

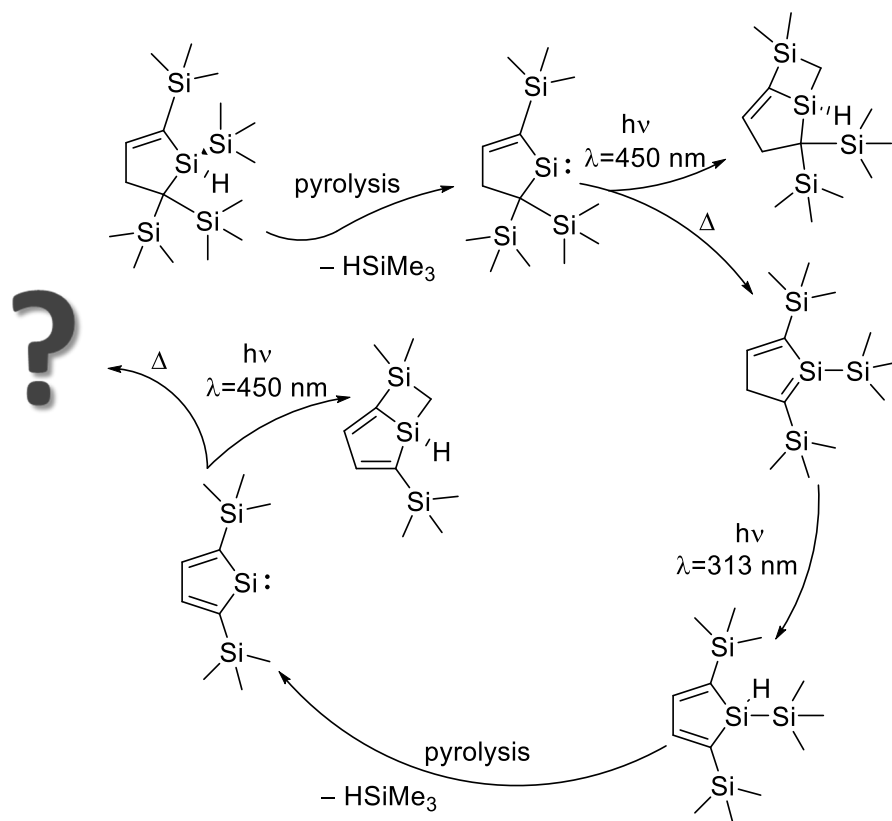
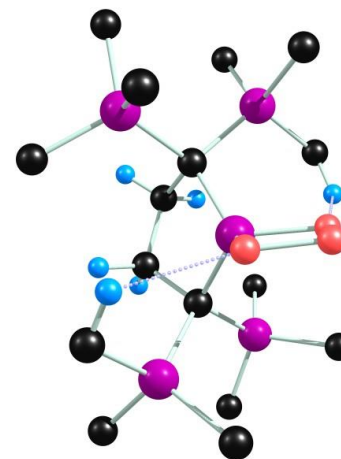


* 14 d at r.t., dark / $T_{\text{evap}} = 60^\circ\text{C}$



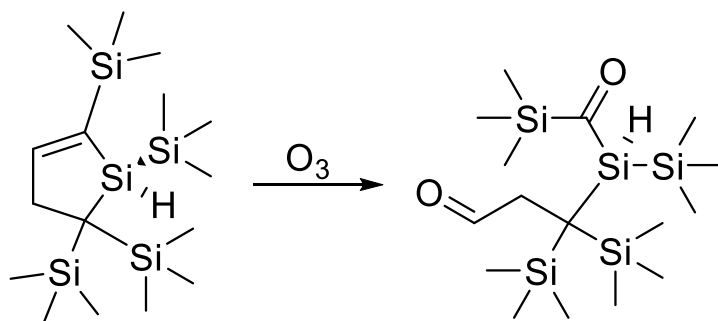
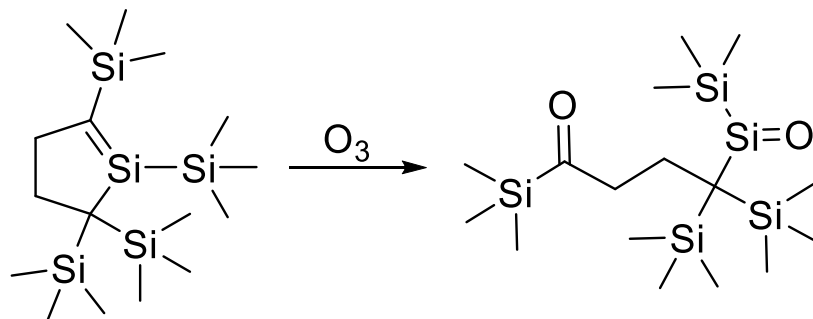


- photochemical fate of the silanone
- crystal structure of silanone
- role of dispersion interactions





What happen to the side products during the treatment with ozone



?

Impression



Todá