Chemical storage of solar energy: measurement of activation energies by ion mobility and mass spectrometry

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MOST design

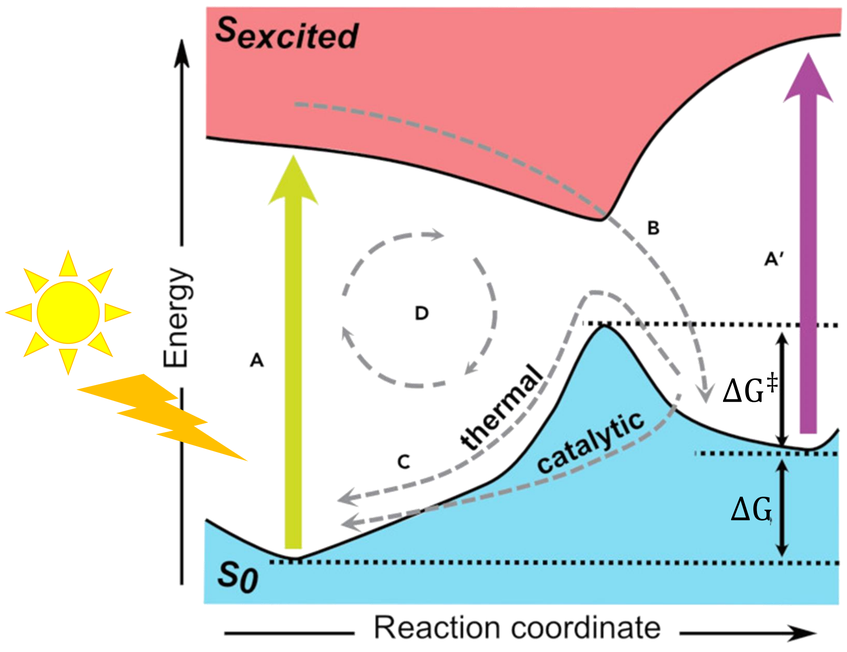


Figure 1. Principle of a MOST system consisting of two photoisomers [1].

Features of an ideal MOST system:

A. Absorption
The system's main absorption band must close to the maximum of the solar irradiation wavelength (~ 500 nm)

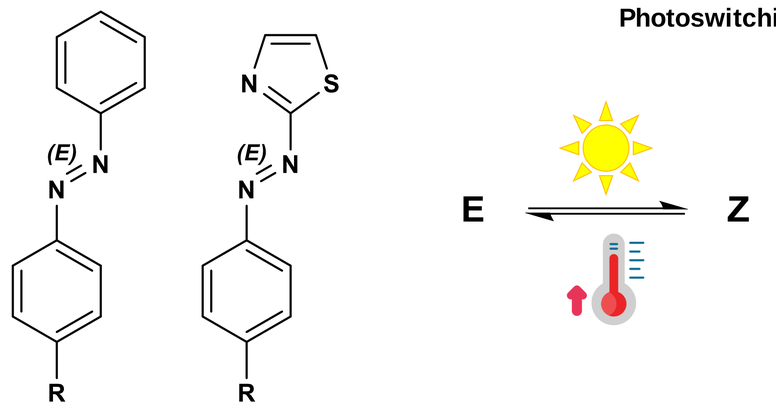
A'. Absorption bands overlap
Absorption bands must not overlap to avoid the photochemical back-isomerization

B. Photoconversion efficiency
The quantum yield of the photoconversion process must be as close as possible to 1

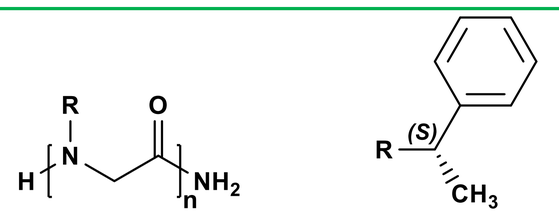
C. Thermal back-conversion
The metastable isomer must be thermally stable at ambient temperature for storage purpose

D. Cyclability
The system must withstand numerous charge/discharge cycles

Photoswitching unit



Peptoid backbone



How to measure thermal back-isomerization rates quickly and efficiently?

Half-life time of the metastable isomers

$$t_{1/2} = \frac{\ln 2}{k}$$

$$k = \frac{k_B\,T}{h}\,e^{\frac{-\Delta G^{\ddagger}}{RT}}$$

Activation barrier

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

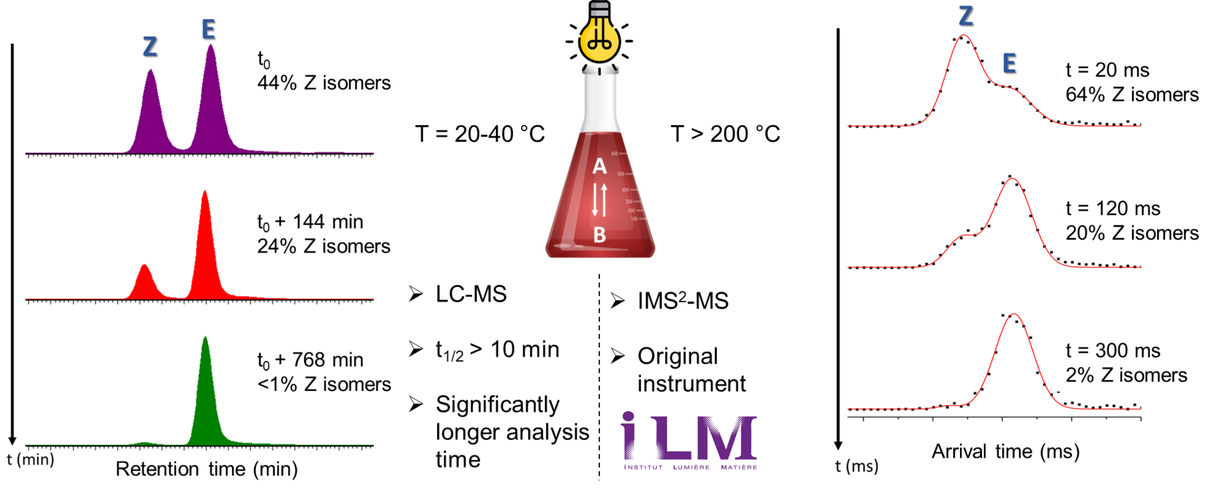
Eyring plot

$$\ln\left(\frac{k}{T}\right) = \frac{-\Delta H^{\ddagger}}{R}\frac{1}{T} + \frac{\Delta S^{\ddagger}}{R} + \ln\frac{k_B}{h}$$

Photoisomer separation

Back-isomerization in solution
Liquid Chromatography LC

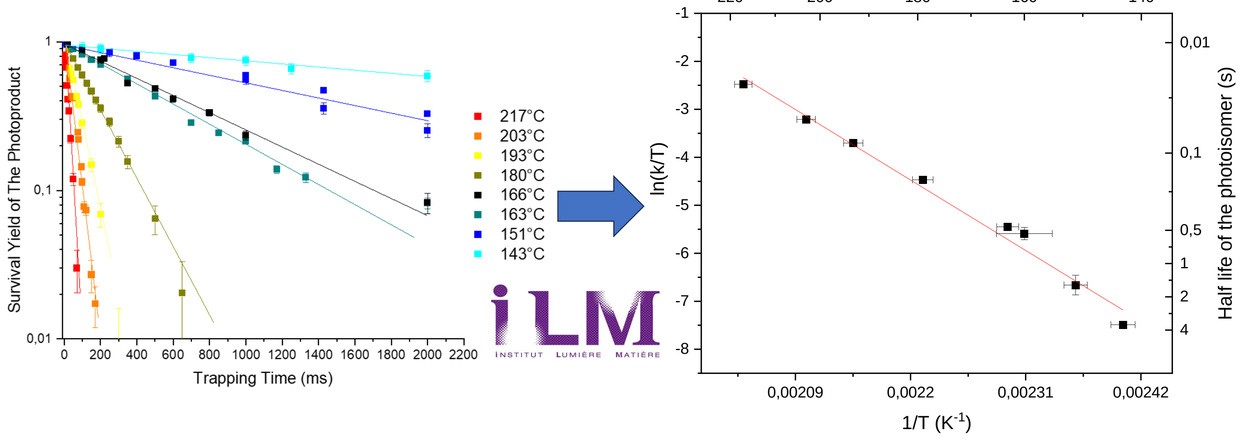
Back-isomerization in the gas phase
Ion mobility spectrometry IMS



- LC-MS
- $t_{1/2}$ > 10 min
- Significantly longer analysis time

- IMS²-MS
- Original instrument

Kinetics in the gas phase using thermal activation



Temperature calibration as proposed by Donor *et al.* [2]

$$T_{eff} = T_0 + \frac{\alpha\, q\, Trap\, CV}{3\, N_{at}\, k_B}$$

	Back-isomerization	Fast	Commercially available
LC-MS	In solution	✗	✓
Tandem IMS	In gas phase	✓	✗
Collisional activation	In gas phase	✓	✓

Kinetics parameters measured by collisional activation

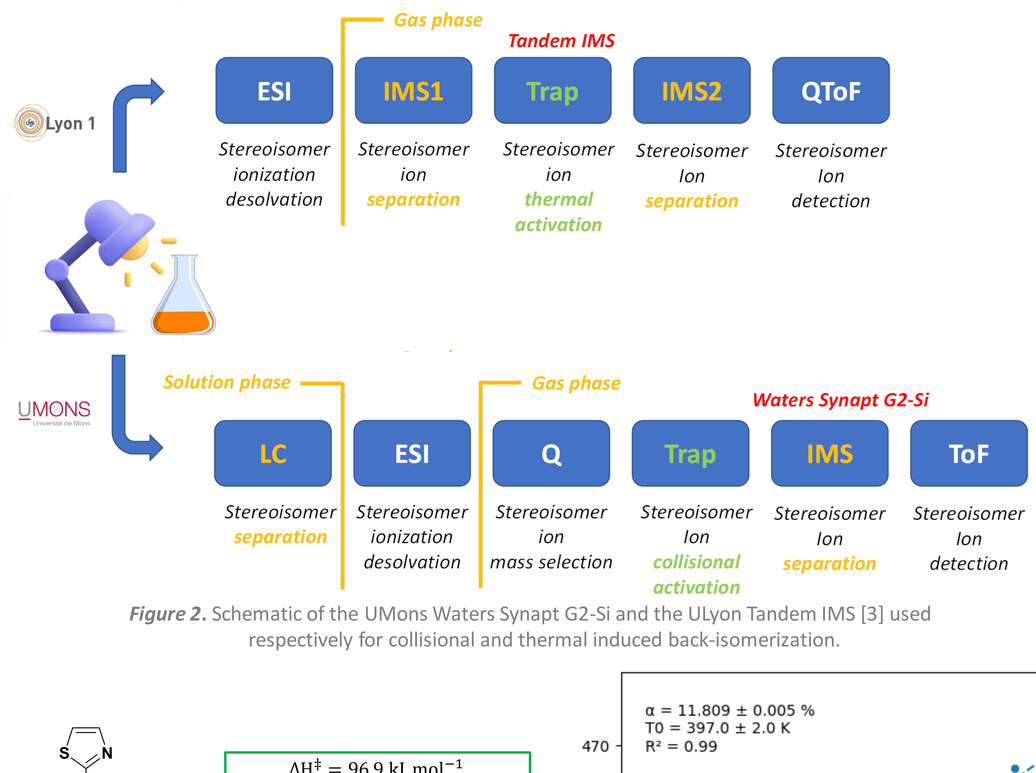
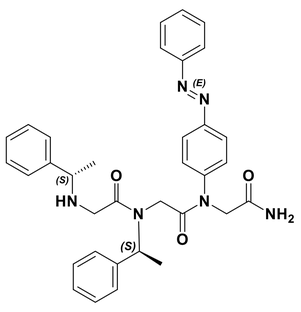


Figure 2. Schematic of the UMons Waters Synapt G2-Si and the ULyon Tandem IMS [3] used respectively for collisional and thermal induced back-isomerization.

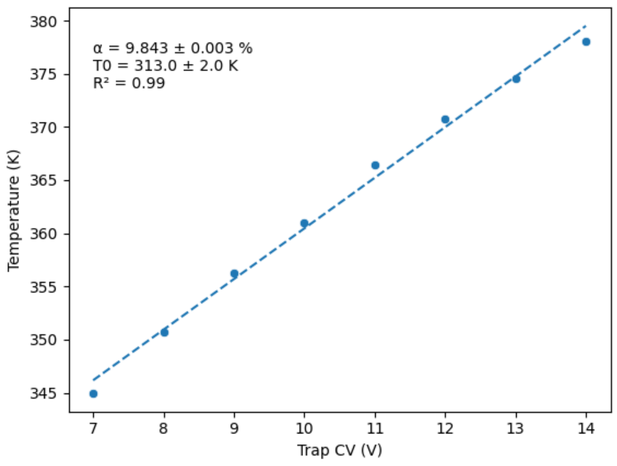


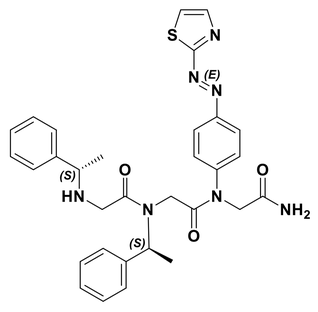
$$\Delta H^{\ddagger} = 96{,}8\ \text{kJ.mol}^{-1}$$
$$\Delta S^{\ddagger} = -34\ \text{J.mol}^{-1}.\text{K}^{-1}$$

In solution (MeOH)

$$\Delta H^{\ddagger} = 101{,}6 \pm 1{,}8\ \text{kJ.mol}^{-1}$$
$$\Delta S^{\ddagger} = -25{,}4 \pm 0{,}5\ \text{J.mol}^{-1}.\text{K}^{-1}$$

In gas phase (protonated)



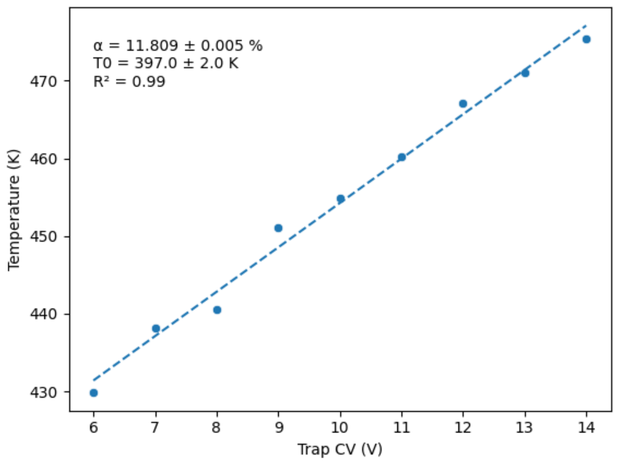


$$\Delta H^{\ddagger} = 96{,}9\ \text{kJ.mol}^{-1}$$
$$\Delta S^{\ddagger} = 3{,}9\ \text{J.mol}^{-1}.\text{K}^{-1}$$

In solution (MeOH)

$$\Delta H^{\ddagger} = 93{,}1 \pm 0{,}5\ \text{kJ.mol}^{-1}$$
$$\Delta S^{\ddagger} = 9{,}85 \pm 0{,}05\ \text{J.mol}^{-1}.\text{K}^{-1}$$

In gas phase (protonated)



Conclusions

Mass spectrometry represents a powerful tool to measure the activation energies of MOST systems in solution thanks to the coupling with liquid chromatography. But this technique has some limitations, especially due to its time scale. We therefore turned to another tool offered by mass spectrometry with the use of ion mobility devices. First, we induce the back-isomerization of the studied systems by direct heating or "thermal activation" within an original tandem IMS instrument at Ulyon [3]. Collisional activation is then investigated using a method recently proposed by Donor *et al.* to calibrate the Synapt G2-Si in temperature [2] using reference values measured in the gas phase by thermal activation.

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References

[1] Wang, Z. et al. Storing energy with molecular photoisomers. Joule 5, 3116–3136 (**2021**).
[2] Donor, M. T., Mroz, A. M. & Prell, J. S. Experimental and theoretical investigation of overall energy deposition in surface-induced unfolding of protein ions. Chem. Sci. 10, 4097–4106 (**2019**).
[3] Simon, A.-L. et al. Tandem ion mobility spectrometry coupled to laser excitation. Rev. Sci. Instrum. 86, 094101 (**2015**).

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