On the determination of the activation energies for the thermal relaxation of photoisomers by state-of-the-art mass spectrometry methods

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Context

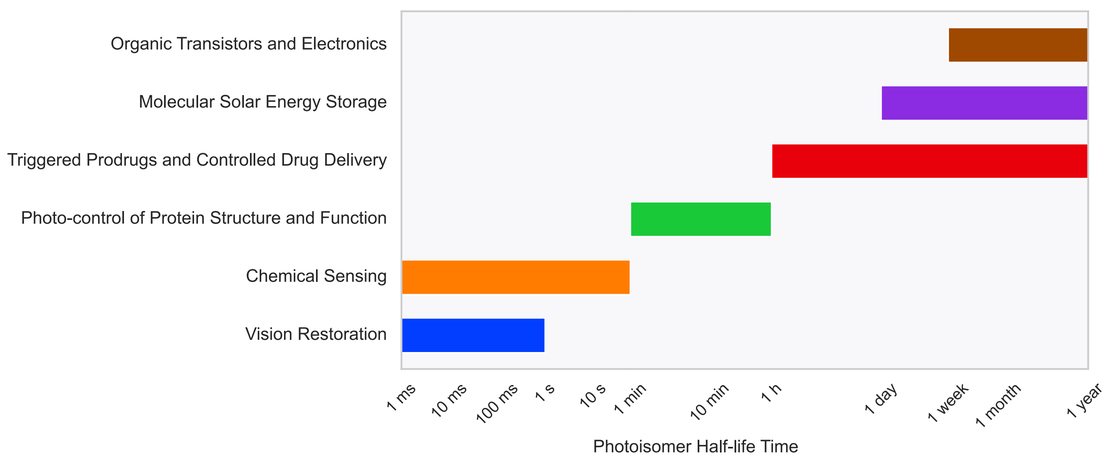


Figure 1. Ideal half-life times of different applications of azobenzene-based photoswitches.[1-4]

Photoswitching molecules allow reversible control of their structure and properties using light. Their effective design, however, requires precise tuning of key parameters, particularly the half-life time of the metastable photoisomer.[4] Conventional solution-based methods to measure back-isomerization kinetics are limited by time and temperature constraints. To address this, we explore gas-phase strategies using tandem ion mobility spectrometry and collisional activation, offering a faster and more efficient way to study thermal back-isomerization kinetics of photoswitching systems.

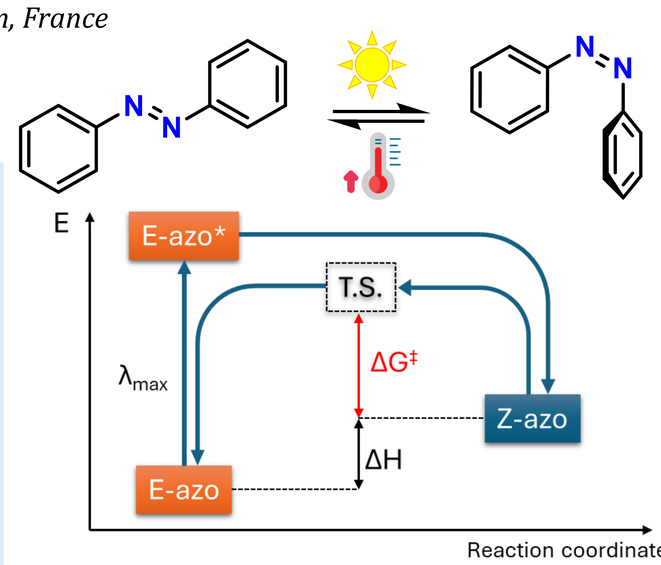


Figure 2. Schematic representation of azobenzene photoswitching and thermal back-isomerization processes.[5]

Photoswitches studied

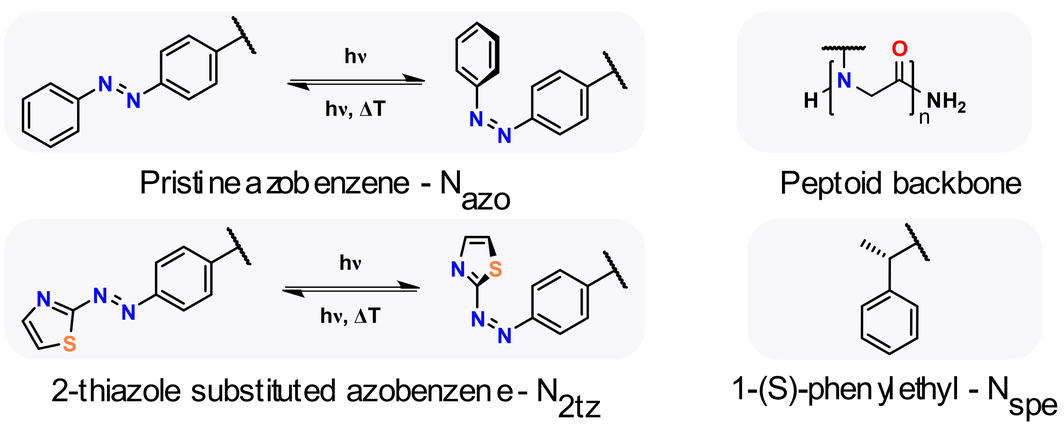
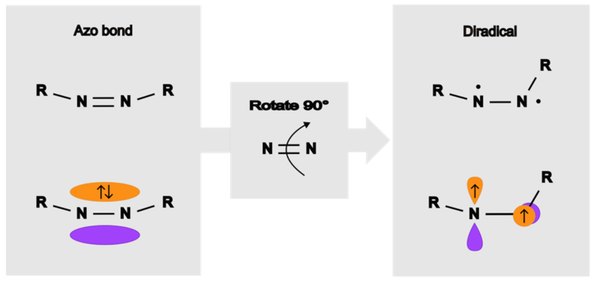


Figure 3. General structure of the systems studied, which consist of selected side chains grafted onto a backbone (top right) in a sequence-defined peptoid. Sequences are given from the N- to C-terminus.[6]

The entropy puzzle

What does happen when the N=N bond rotates?



$$k = \gamma \frac{k_B T}{h} e^{-\left(\frac{\Delta H^{\ddagger} - T\Delta S^{\ddagger}}{RT}\right)}$$

Transmission coefficient, traditionally ≃ 1 but...

$$\Delta H^{\ddagger}_{measured} = \Delta H^{\ddagger}_{Eyring}$$

$$\Delta S^{\ddagger}_{measured} = \Delta S^{\ddagger}_{Eyring} + R\ln(\gamma)$$

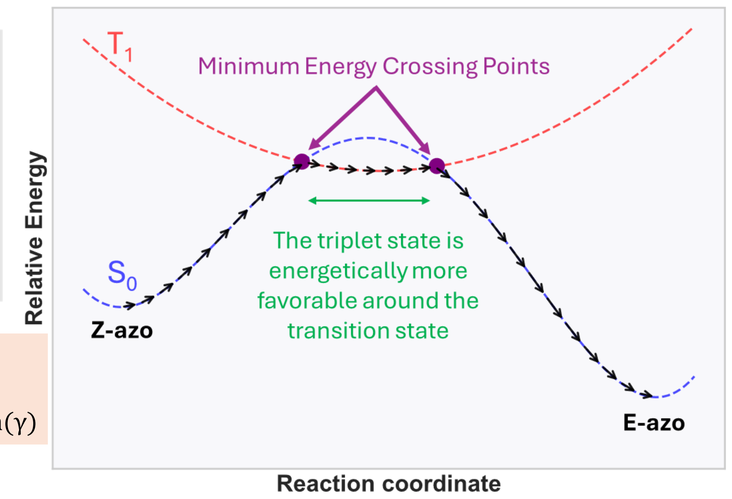


Figure 4. Schematic representation of the intersystem crossing process involved in the AZO bond rotation.[7]

Kinetics in the gas phase – thermal activation

1) Z-photoisomers selection in **IMS1**
2) Trapped ions relaxation at a controlled temperature for a variable time = **kinetic monitoring** (different **T**)
3) Photoisomers population sampling by **IMS2**

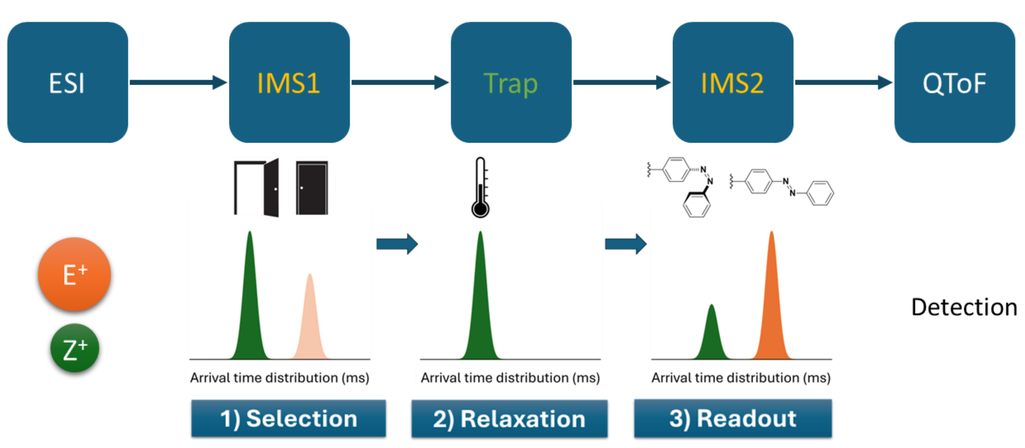


Figure 5. Principle of the tandem-IMS experiments.[8]

Peptoid sequence	Ion	ΔH‡ Gas phase kJ mol⁻¹	ΔS‡ Gas phase J mol⁻¹ K⁻¹	ΔG‡ (293K) Gas phase kJ mol⁻¹	Mechanism pathway identified
$N_{spe}N_{spe}N_{azo}$	$[M+H]^+$	101.6 ± 1.8	-25.4 ± 0.5	109.0 ± 1.9	Rotation
	$[M+Na]^+$	98.1 ± 0.9	-32.9 ± 0.3	107.9 ± 1.0	Rotation
$N_{spe}N_{spe}N_{2tz}$	$[M+H]^+$	93.1 ± 0.5	9.85 ± 0.05	90.2 ± 0.5	Inversion
$N_{spe}N_{2tz}N_{spe}N_{spe}$	$[M+H]^+$	91.7 ± 2.2	-41.6 ± 1.1	103.8 ± 2.5	Rotation

Table 1. Activation parameters for thermal gas-phase back-isomerization measured by tandem IMS experiments and the corresponding relaxation mechanism.[8]

Kinetics in the gas phase – collisional activation

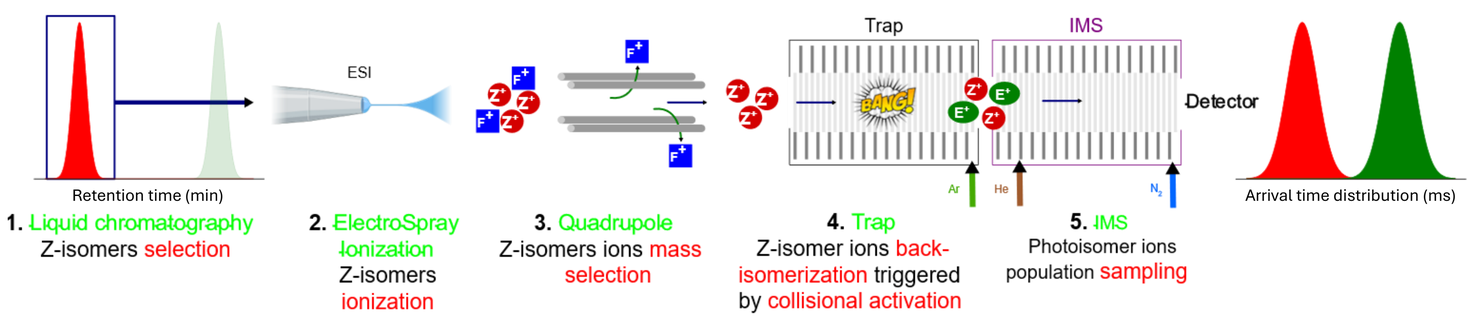


Figure 6. Principle of the collision-induced back-isomerization experiments.

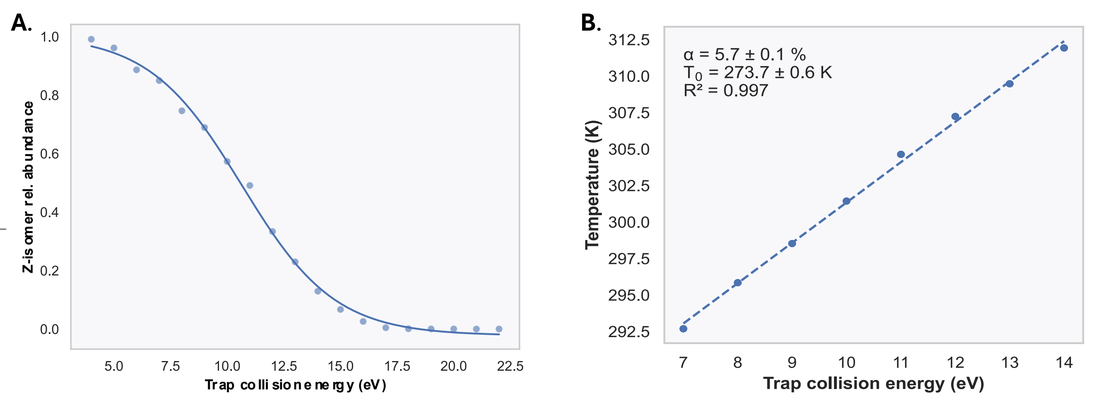
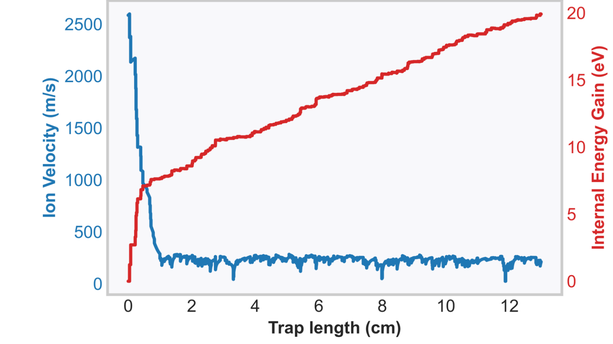


Figure 7. A) Relative abundance of Z photoisomers measured as a function of Trap CE and fitted using a sigmoidal function (solid line). B) Effective temperature calculated from relative abundances for each Trap CE value and fitted using a linear function (dashed line).



Based on dice rolls and models taking into account both heating and cooling by collisions[9]

Monte Carlo (python)

P (Ar) = 2.6 10^{-2} mBar

Trap CV = 20 V

Wave velocity = 200 m/s

Figure 8. Monte Carlo simulations showing the evolution of the velocity and internal energy of an ion within the trap.

Peptoid system	α (%)	T_0 (K)
$[N_{spe}N_{spe}N_{azo} + H]^+$	7.6 ± 0.4	325.8 ± 0.9
$[N_{spe}N_{spe}N_{2tz} + H]^+$	5.7 ± 0.1	273.7 ± 0.6
$[N_{spe}N_{2tz}N_{spe}N_{spe} + H]^+$	8.5 ± 0.3	304.2 ± 1.9
$[N_{spe}N_{spe}N_{azo} + Na]^+$	9.0 ± 0.3	316.8 ± 1.5
$[N_{spe}N_{2tz}N_{spe} + Na]^+$	8.2 ± 0.2	323.1 ± 1.2

Table 2. Temperature calibration parameters measured for reference systems.

$$\ln\frac{-\ln MIA}{T_{eff}} = \frac{-\Delta H^{\ddagger}}{R\,T_{eff}} + \frac{\widetilde{\Delta S^{\ddagger}}}{R} + \ln\frac{k_B}{h} + \ln t$$

with relaxation time window **t = 615 µs**

$$T_{eff} = T_0 + \frac{\alpha\,TrapCV}{3\,N\,k_B} \quad [9]$$

Conclusions and perspectives

- Gas-phase measurements reveal clear structure-dependent differences in activation entropies, reflecting distinct back-isomerization pathways.
- Tandem IMS enables extraction of activation parameters by monitoring gas-phase thermal back-isomerization.
- Collision-induced isomerization provides a fast, calibration-based method to obtain kinetic constants and compare photoswitching systems.
- Expanding the photoswitch library and refining calibration will establish a robust framework for rapid gas-phase kinetic measurements.

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