Transient Spectroscopy and Kinetics

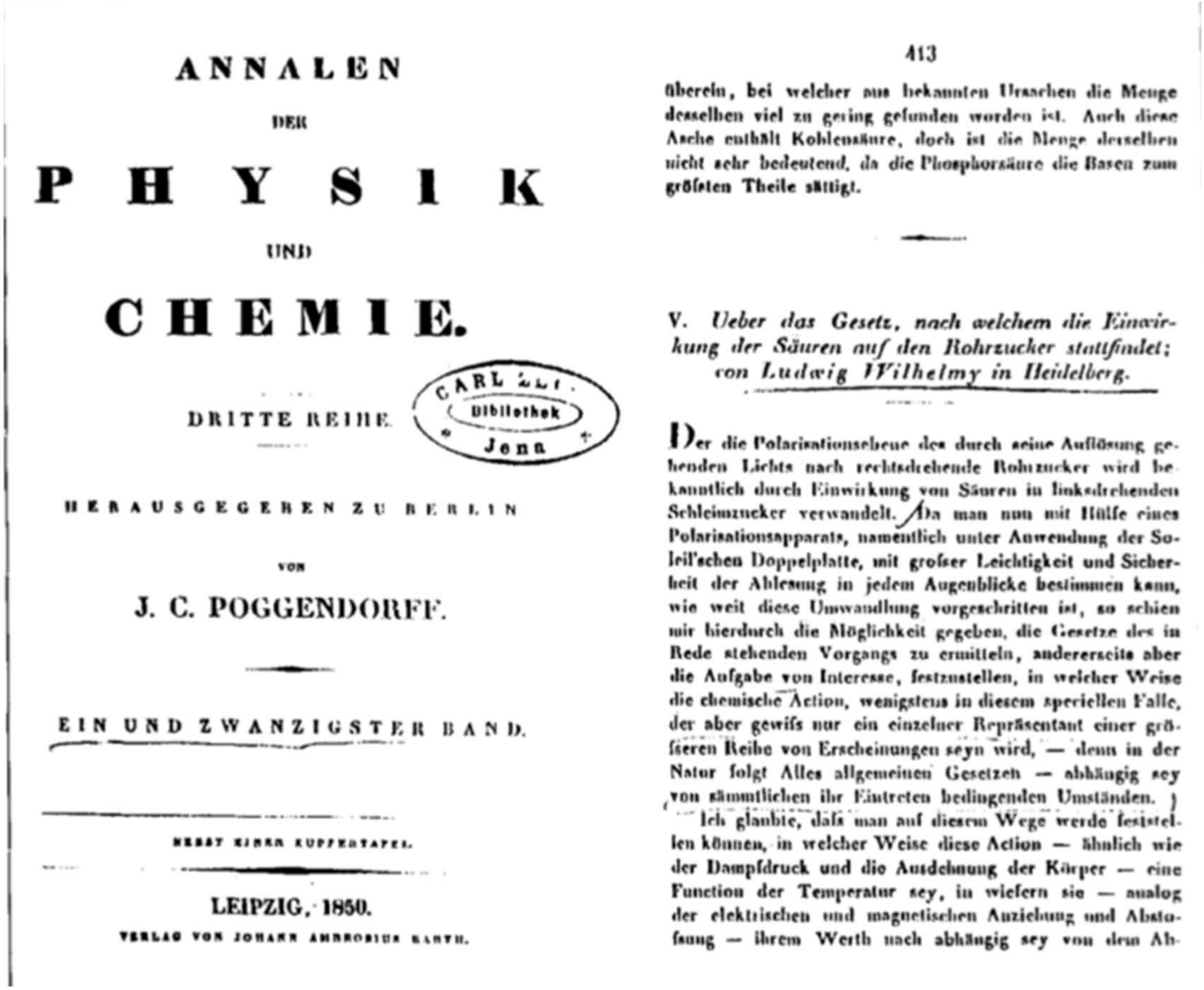
Aim:

- Techniques
- Determination of reaction mechanisms; WHAT FOR?
  - Understanding, chemical systematics.
  - How to interfere with (photo)reactions (e.g., by trapping, quenching) and improve the desired yield or suppress an unwanted reaction.
- Basic knowledge of kinetic laws and fitting procedures
- Practical applications, pH–rate profiles

Historical Notes

First consideration of reaction kinetics:

Ludwig Ferdinand Wilhelmy, *1812 – †1864:



ANNALEN
DER
PHYSIK
UND
CHEMIE.

DRITTE REIHE.

HERAUSGEGEBEN ZU BERLIN
VON
J. C. POGGENDORFF.

EIN UND ZWANZIGSTER BAND.

NEBST EINER KUPFERTAFEL.

LEIPZIG, 1850.
VERLAG VON JOHANN AMBROSIUS BARTH.

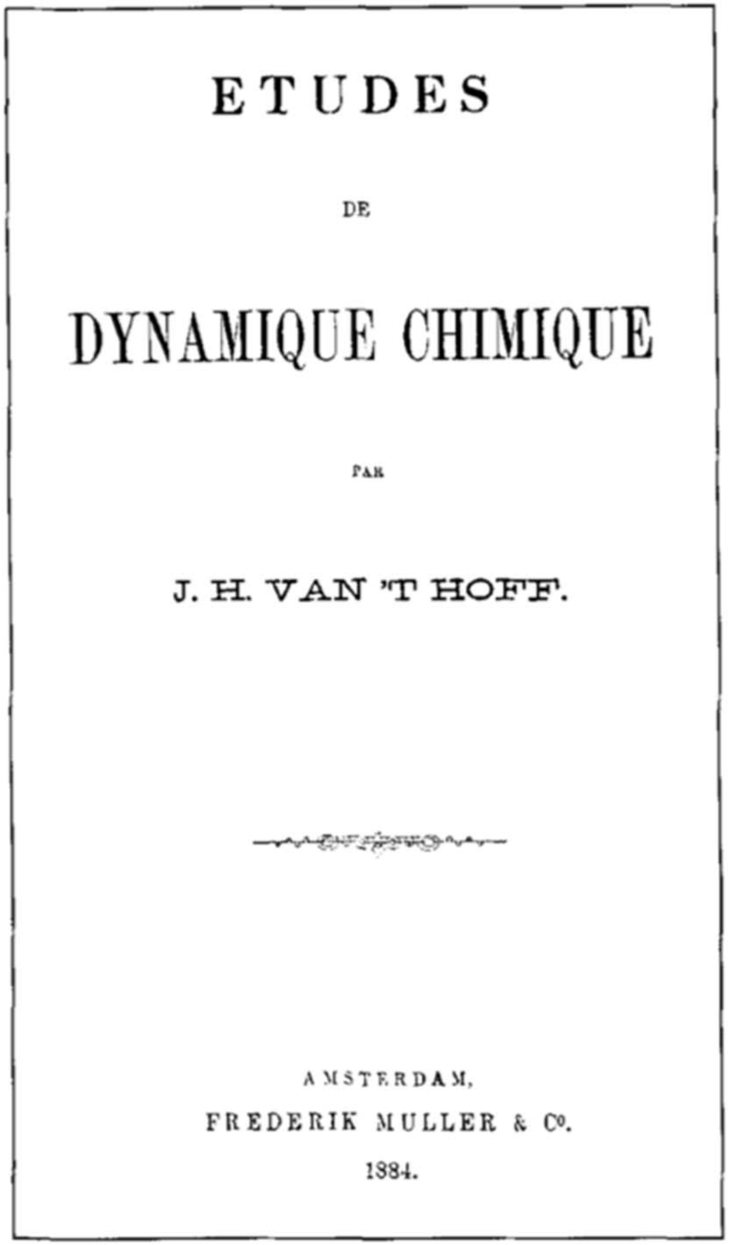
überein, bei welcher aus bekannten Ursachen die Menge desselben viel zu gering gefunden worden ist. Auch diese Asche enthält Kohlensäure, doch ist die Menge desselben nicht sehr bedeutend, da die Phosphorsäure die Basen zum gröſsten Theile sättigt.

V. *Ueber das Gesetz, nach welchem die Einwirkung der Säuren auf den Rohrzucker stattfindet;* *von Ludwig Wilhelmy in Heidelberg.*

Der die Polarisationsebene des durch seine Auflösung gehenden Lichts nach rechtsdrehende Rohrzucker wird bekanntlich durch Einwirkung von Säuren in linksdrehenden Schleimzucker verwandelt. Da man nun mit Hülfe eines Polarisationsapparats, namentlich unter Anwendung der Soleil'schen Doppelplatte, mit groſser Leichtigkeit und Sicherheit der Ablesung in jedem Augenblicke bestimmen kann, wie weit diese Umwandlung vorgeschritten ist, so schien mir hierdurch die Möglichkeit gegeben, die Gesetze des in Rede stehenden Vorgangs zu ermitteln, andererseits aber die Aufgabe von Interesse, festzustellen, in welcher Weise die chemische Action, wenigstens in diesem speciellen Falle, der aber gewiſs nur ein einzelner Repräsentant einer gröſseren Reihe von Erscheinungen seyn wird, — denn in der Natur folgt Alles allgemeinen Gesetzen — abhängig sey von sämmtlichen ihr Eintreten bedingenden Umständen.

Ich glaubte, daſs man auf diesem Wege werde feststellen können, in welcher Weise diese Action — ähnlich wie der Dampfdruck und die Ausdehnung der Körper — eine Function der Temperatur sey, in wiefern sie — analog der elektrischen und magnetischen Anziehung und Abstoſsung — ihrem Werth nach abhängig sey von dem Ab-

Van’t Hoff (Nobel prize 1901)
$v = kAB / \mathrm{V}$ (i.e., rate is prop. to species conc’s c_{A} and c_{B})



ETUDES

DE

DYNAMIQUE CHIMIQUE

PAR

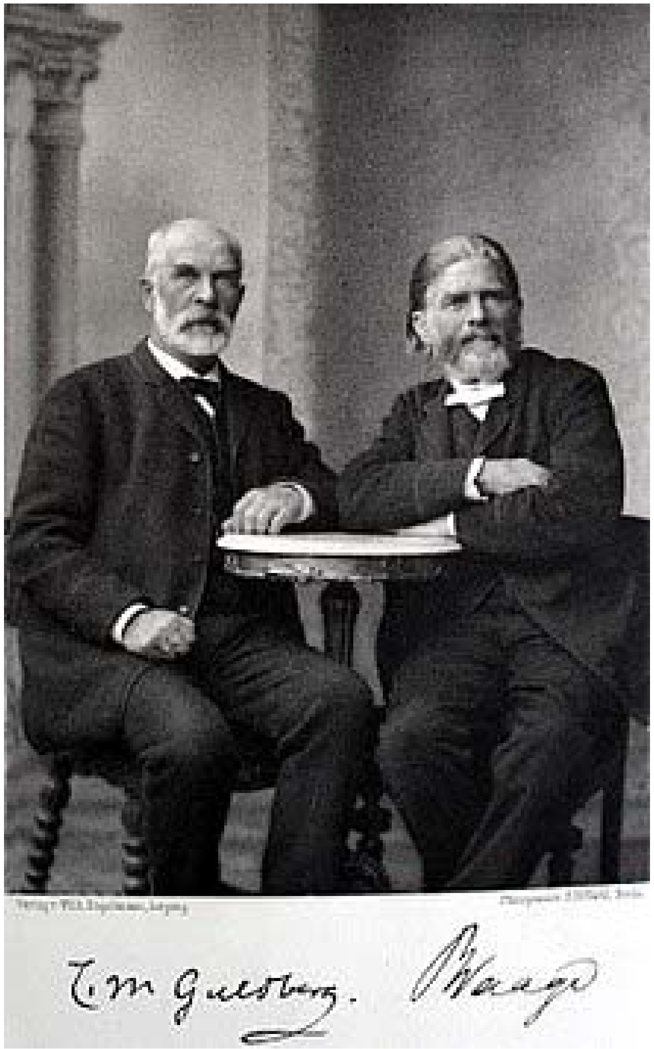
J. H. VAN 'T HOFF.

AMSTERDAM,
FREDERIK MULLER & C°.
1884.

Jacobus Henricus van’t Hoff (1852–1911).

Relationship between *k* and *K*

Guldberg and Waage (1863): Ester hydrolysis (reversible)



Mathematician Chemist

$$\text{E(ster)} + \text{W(ater)} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \text{A(cid)} + \text{Al(cohol)}$$

At equilibrium: $v = 0 = k_f[E][W] - k_b[A][Al]$

Hence: $k_f/k_b = ([A][Al])/([E][W]) = K$

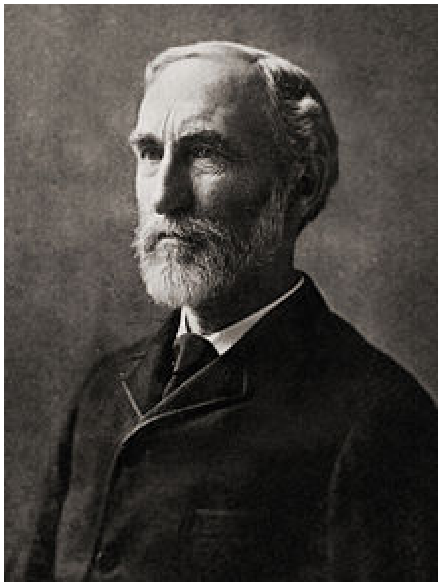
"Law of mass action"

Note: This "derivation" is not general and not quite correct (why?)

J. W. Gibbs, 1876

$$K^{\circ} \equiv \prod_{i=1}^{n} (a_i)^{\nu_i}$$

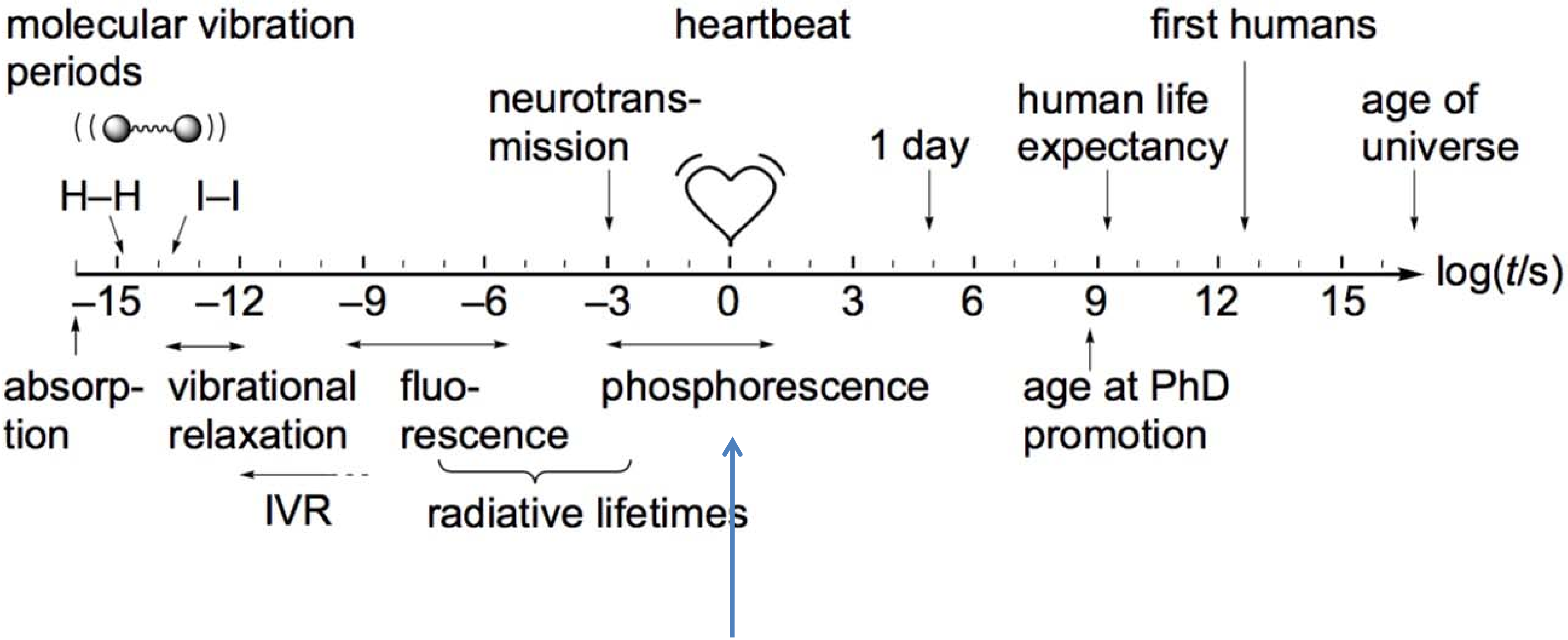
$$\Delta_r G^{\circ} = -RT \ln K^{\circ}$$



Determination of reaction mechanisms

1. Define the stoichiometry (reactants, products, equilibrium constant)
2. Measure the observed (integrated) rate laws: $c_i = c_i(t)$.
    - Dependence on T, p, solvent, catalysts, …
3. Propose a hypothesis for the reaction mechanism
    - State the differential rate law for that mechanism: $dc_i/dt = \ldots$
    - Respect thermodynamic restriction: $k_f/k_b = K$
4. Verification (or falsification: then back to 3.)
    - Compare model and experimental data (curve fitting, determine parameters)
    - Observe postulated reaction intermediates
    - Vary reaction conditions (trap intermediates or independent generation of intermediates)
    - Kinetic isotope effects and isotopic labeling
5. Theoretical calculation (QM)
6. Structure–reactivity relationships

Time scales



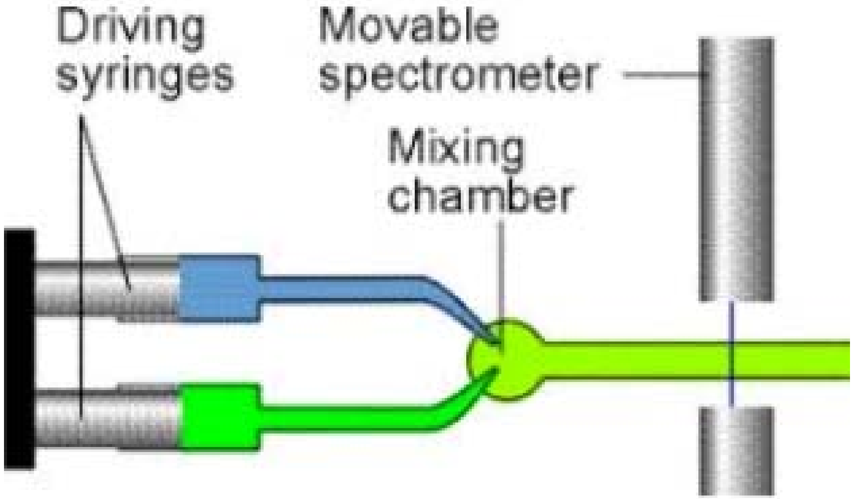
Prior to ~1950, reactions with a lifetime ≤ 1 s were considered to be “fast”

Methods to observe "fast" reactions

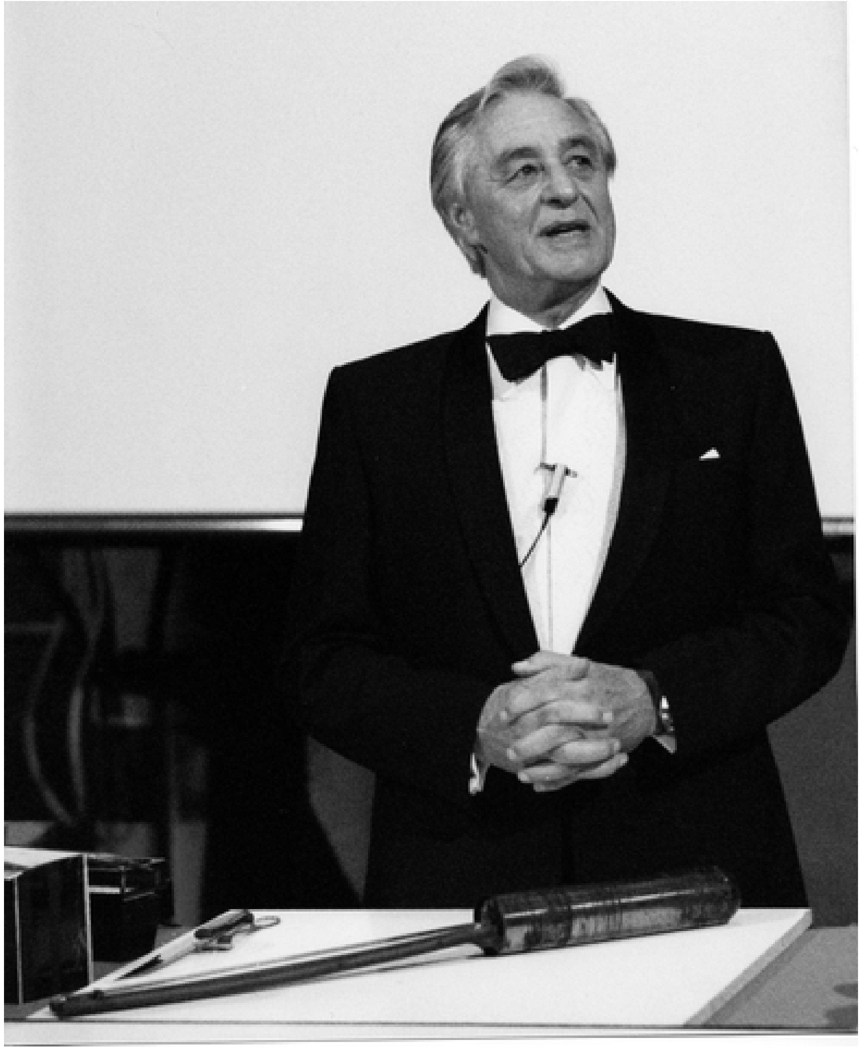
Requires generation of non-equilibrated samples within <<1s

Essential for the time resolution is not the time required for the measurement, but how accurately the signal generation is defined.

- Fast mixing ("flow") ~ms
- Pressure drop (membrane) ~ms
- *T*-Jump (e^- or *hv*) ~ms
- Pulse radiolysis (fast e^-,) αıs
- Modulated perturbation ~ps (*hv*, *p* {sound waves}, lock-in amplifiers)
- Flash photolysis: ms, ns, ps, fs
- MS, X-ray, IR, el. diffraction, ….



George Porter $^*1920 – ^\dagger2002$



Nobel prize in chemistry: 1967

The Royal Institution

Kinetic Flash Photolysis

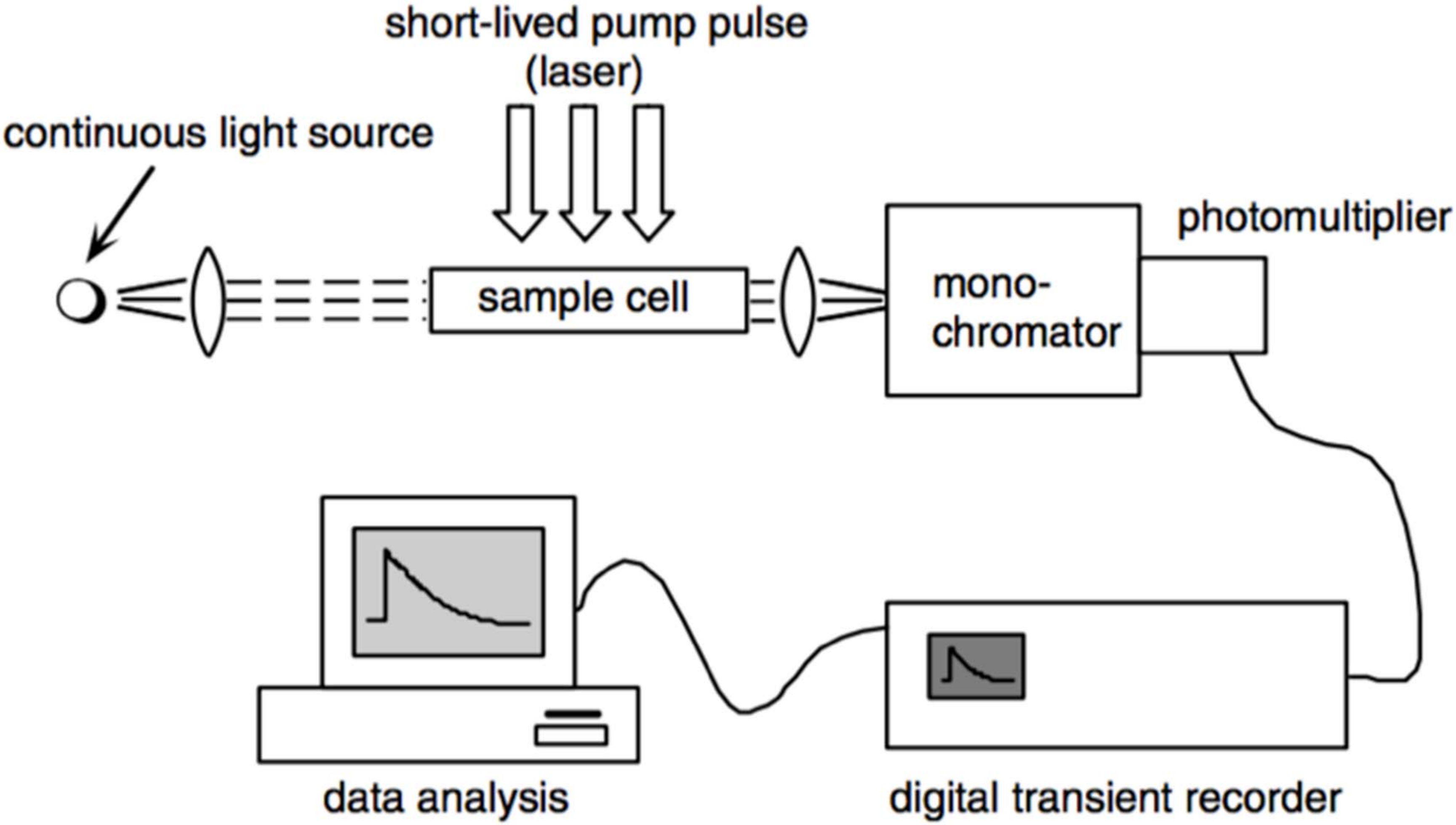


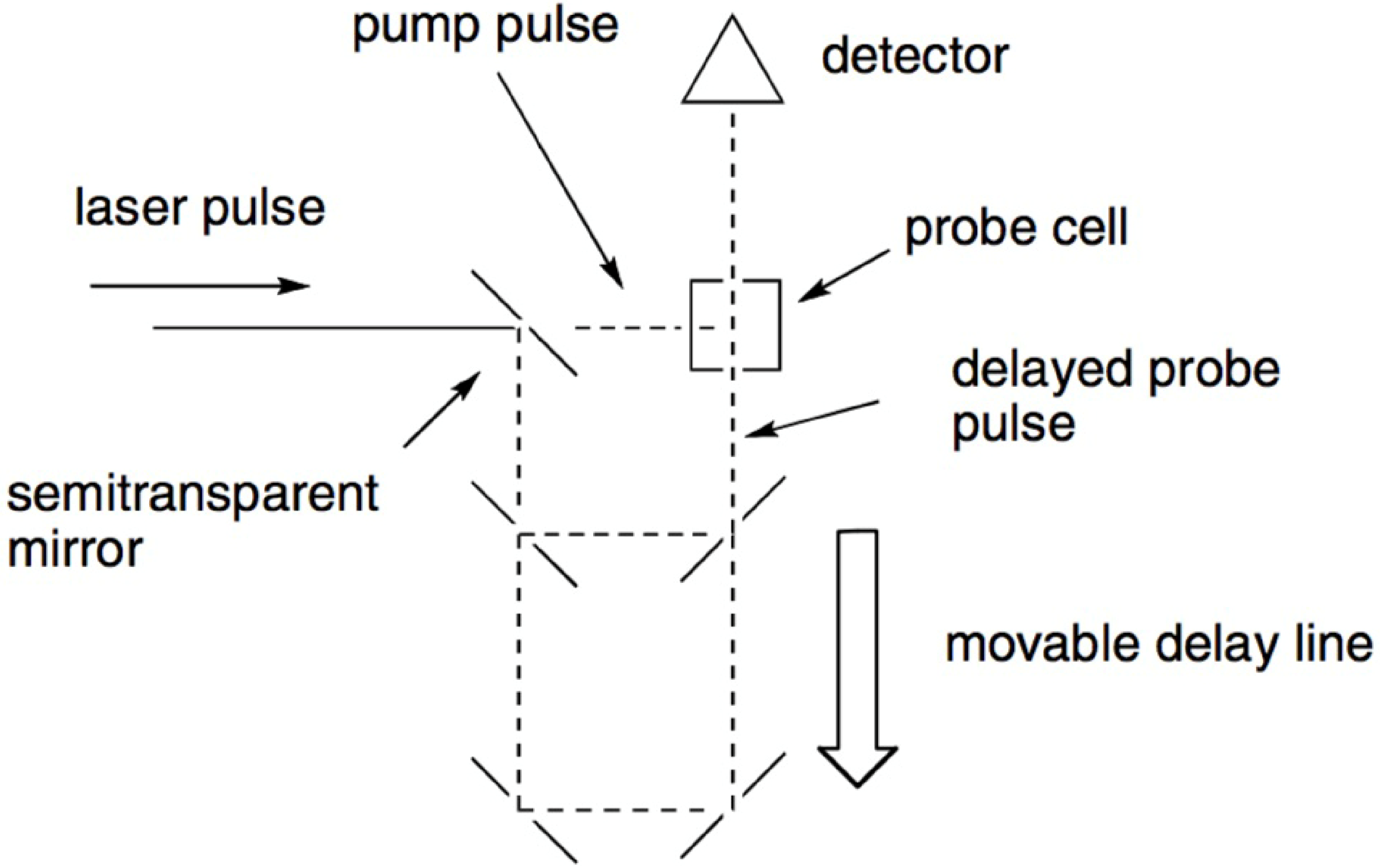
Figure 3.14 Kinetic setup for flash photolysis

Spectrographic flash photolysis

Originally (Porter): monitoring light provided by a second delayed flash passing the sample and a spectrograph, photographic plates; ~0.1 ms.

Later: ns-laser with a gated image intensifier, ~10 ns.

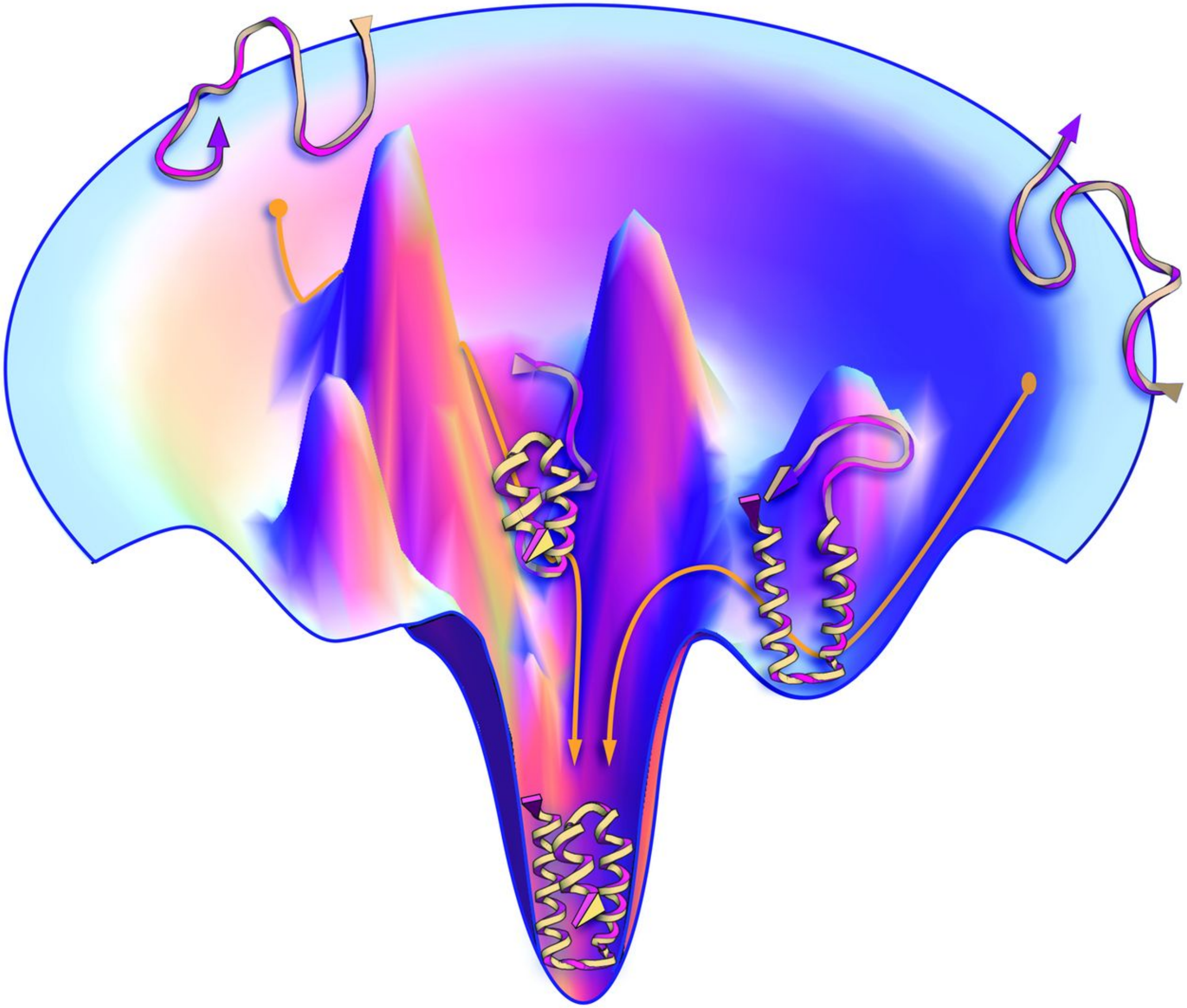
Pump–probe: ~ps, ~fs



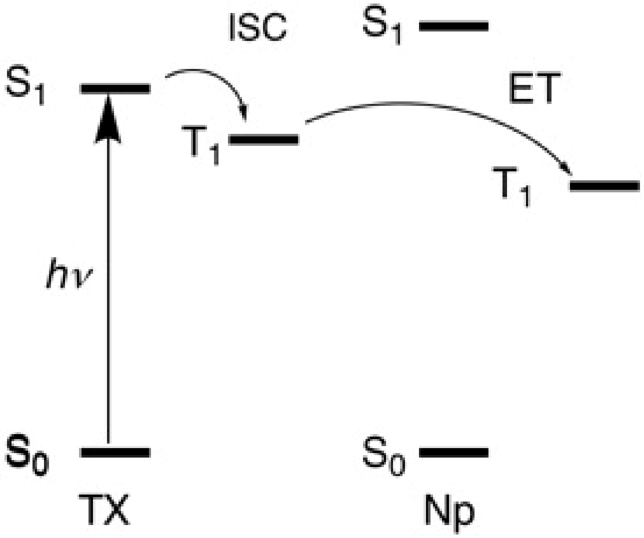
Beware of Artefacts!

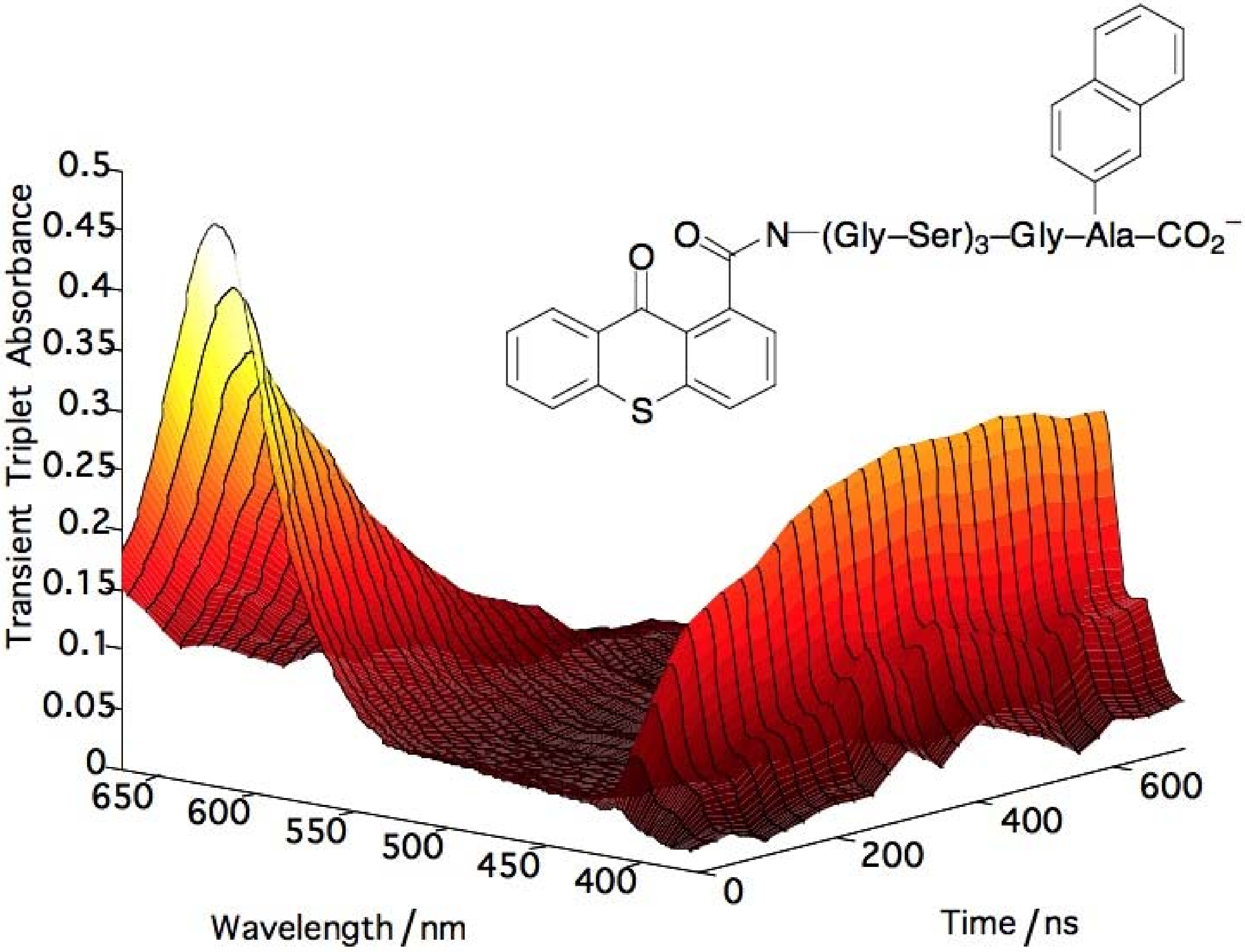
- Stray light (use filters)
- Fluorescence of the sample (false “bleaching”)
- Acoustic shock waves (microseconds)
- Inhomogeneous sample distribution (laser pulses), distort mainly strong signals
- Electronic pulses from flash lamp or Q-switches (Faraday cage)
- Electronic signal echoes

The speed limit of protein folding



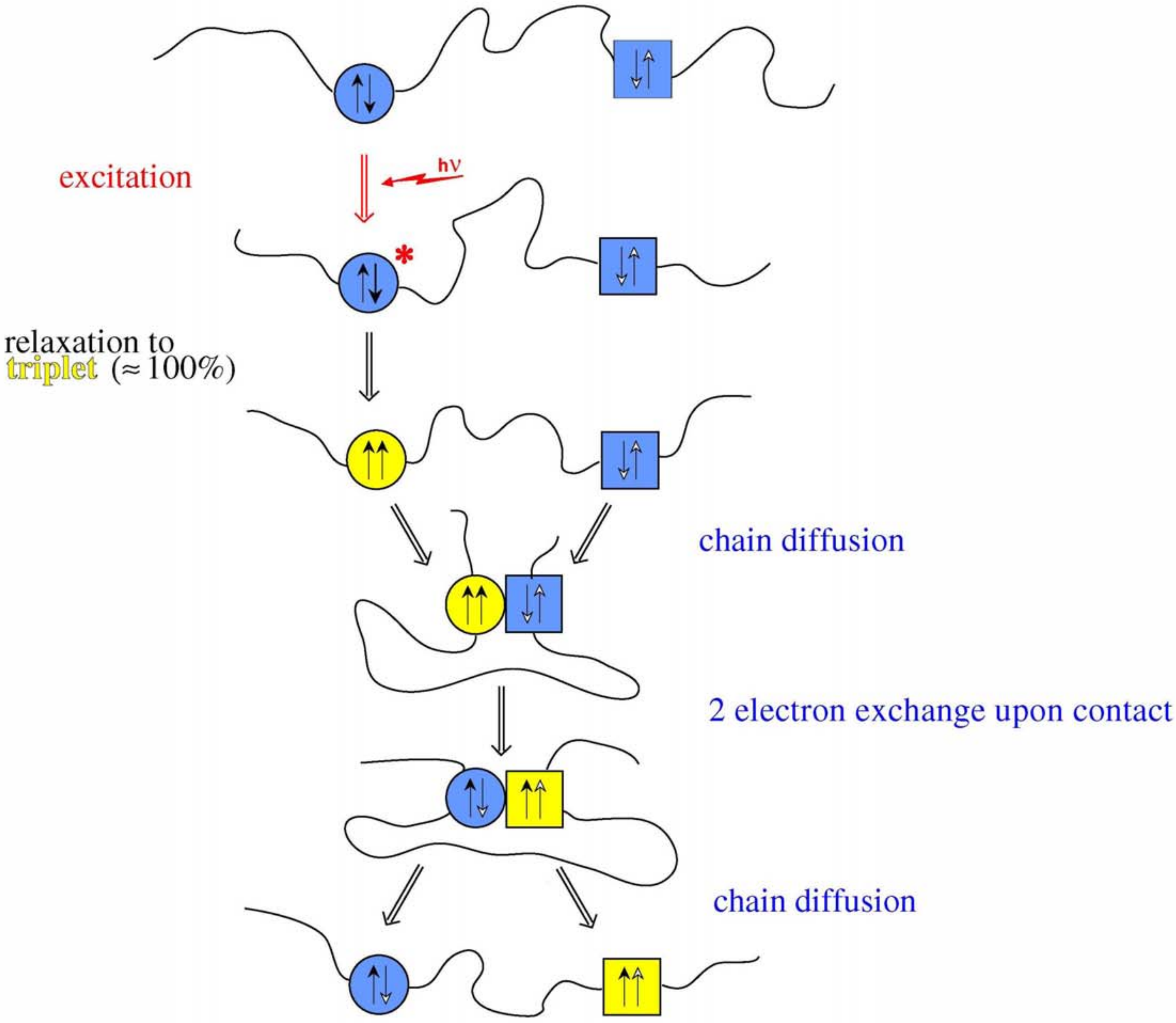
Spectrographic monitoring of triplet energy transfer from xanthone to naphthalene





PNAS, **1999**, *89*, 9597

Direct Measurement of Intrachain Diffusion by Triplet-Triplet Energy Transfer



excitation

hν

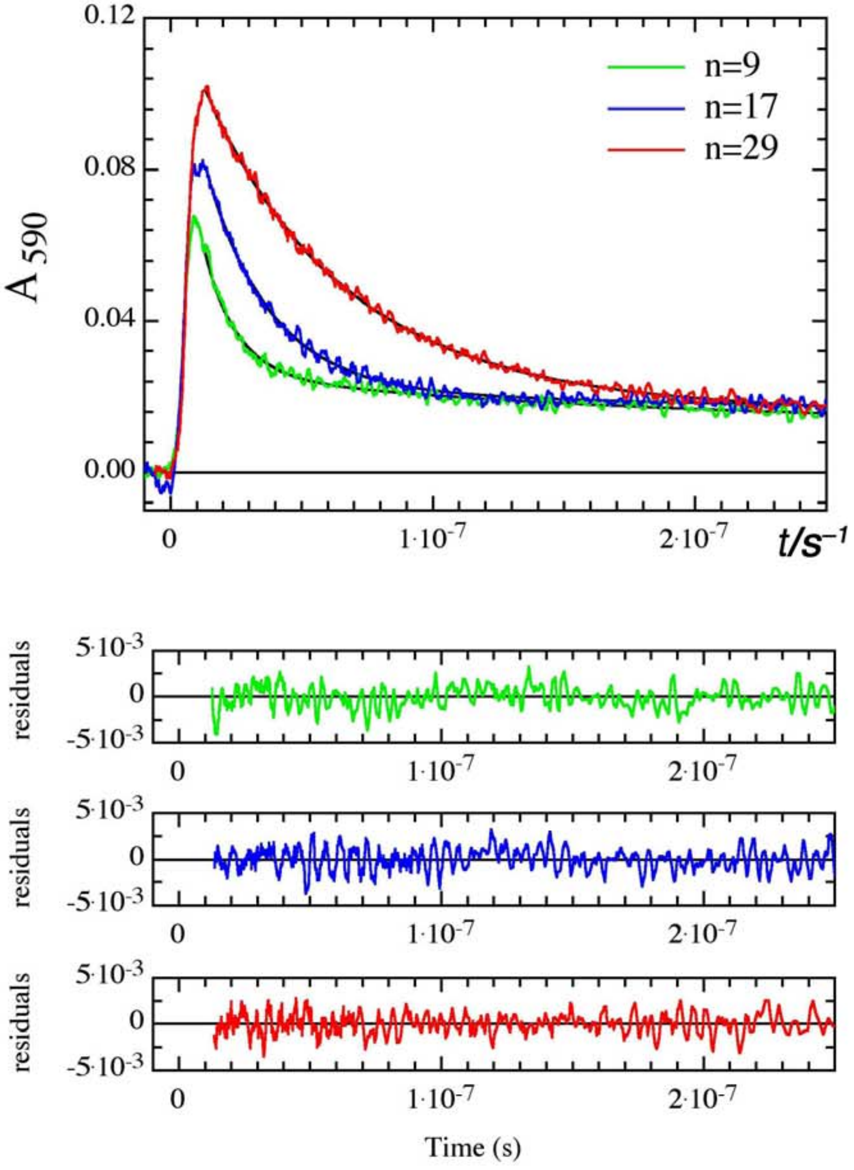
relaxation to triplet (≈ 100%)

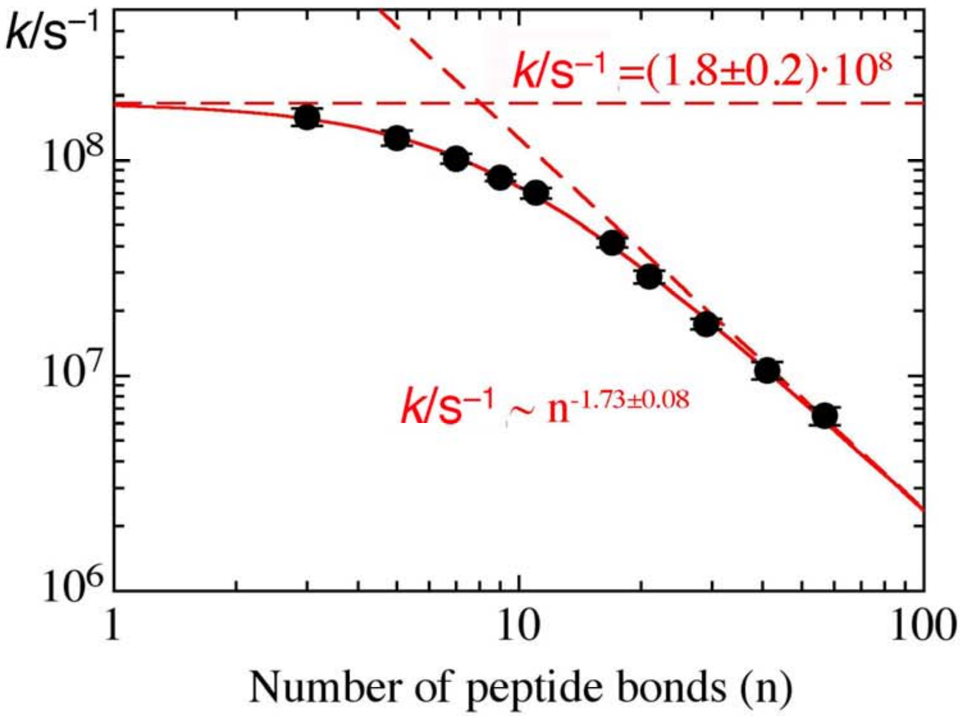
chain diffusion

2 electron exchange upon contact

chain diffusion

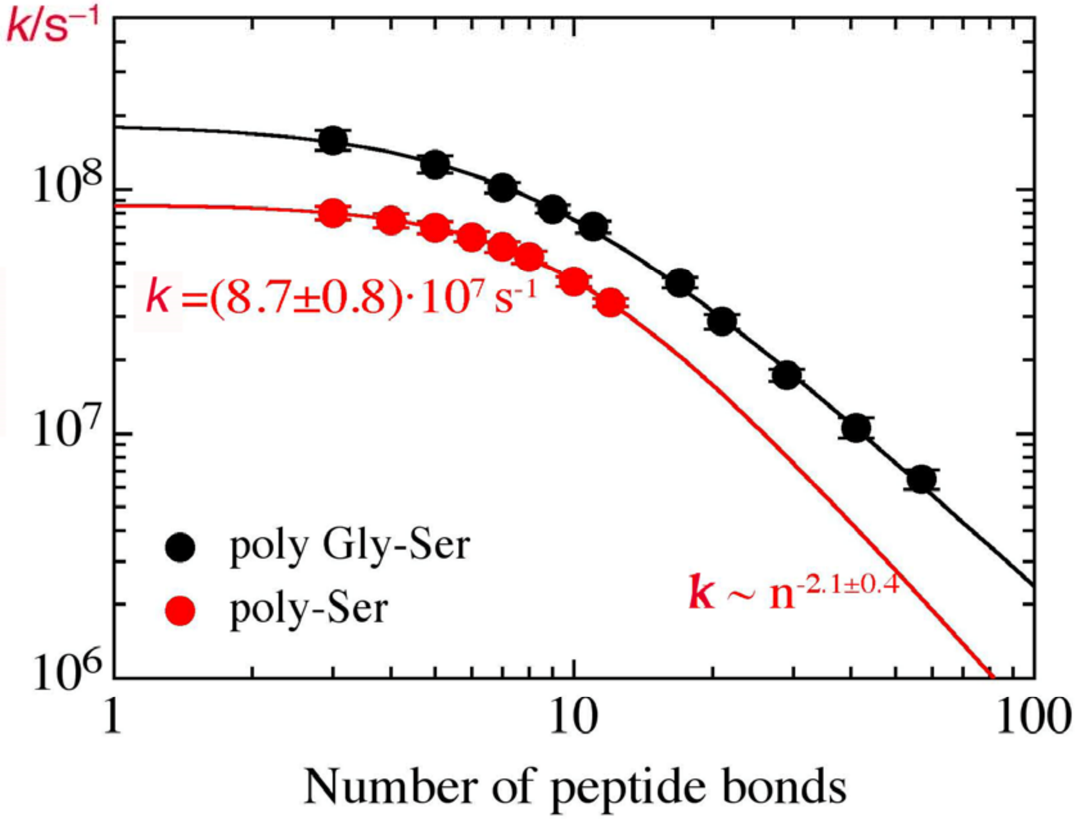
Length-Dependence of the Rate of Contact Formation





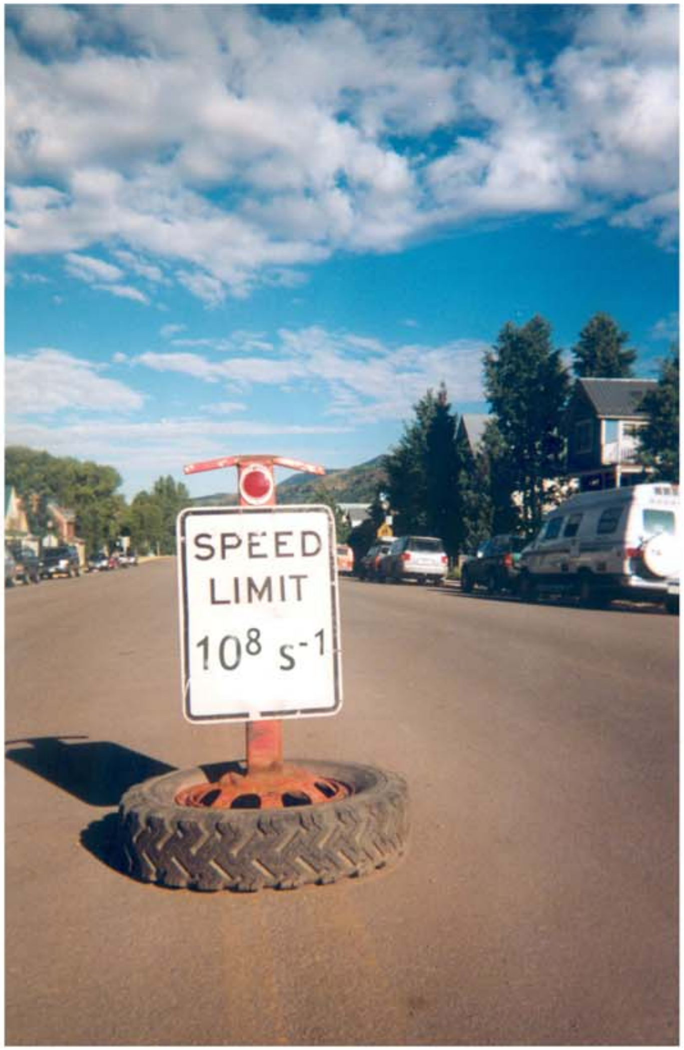
Sequence-dependence of intrachain diffusion

Xan-$(Ser)_n$-NAla-Ser-Gly

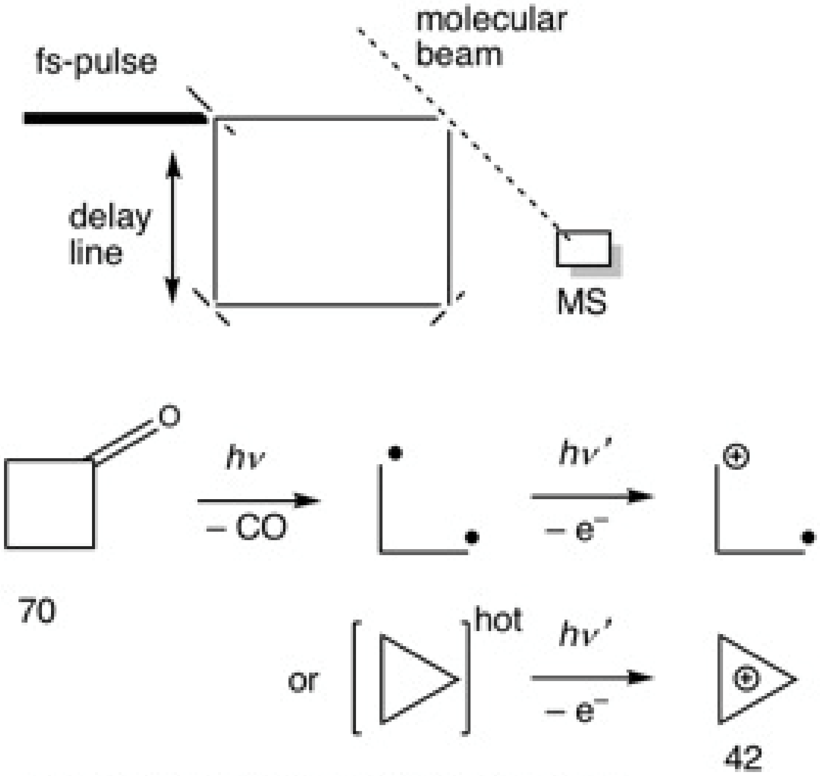


Chain dynamics are only slowed down by a factor of 2 for gycine-free chains, but chain stiffness increases.

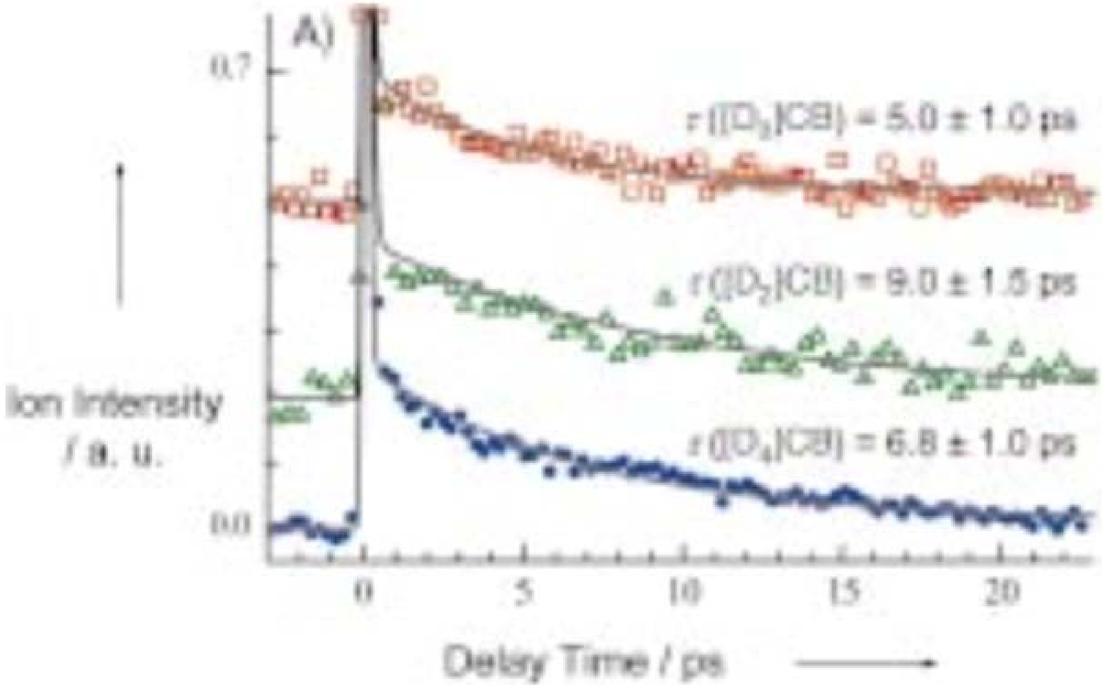
Traveling on the energy landscape



Time-resolved MS



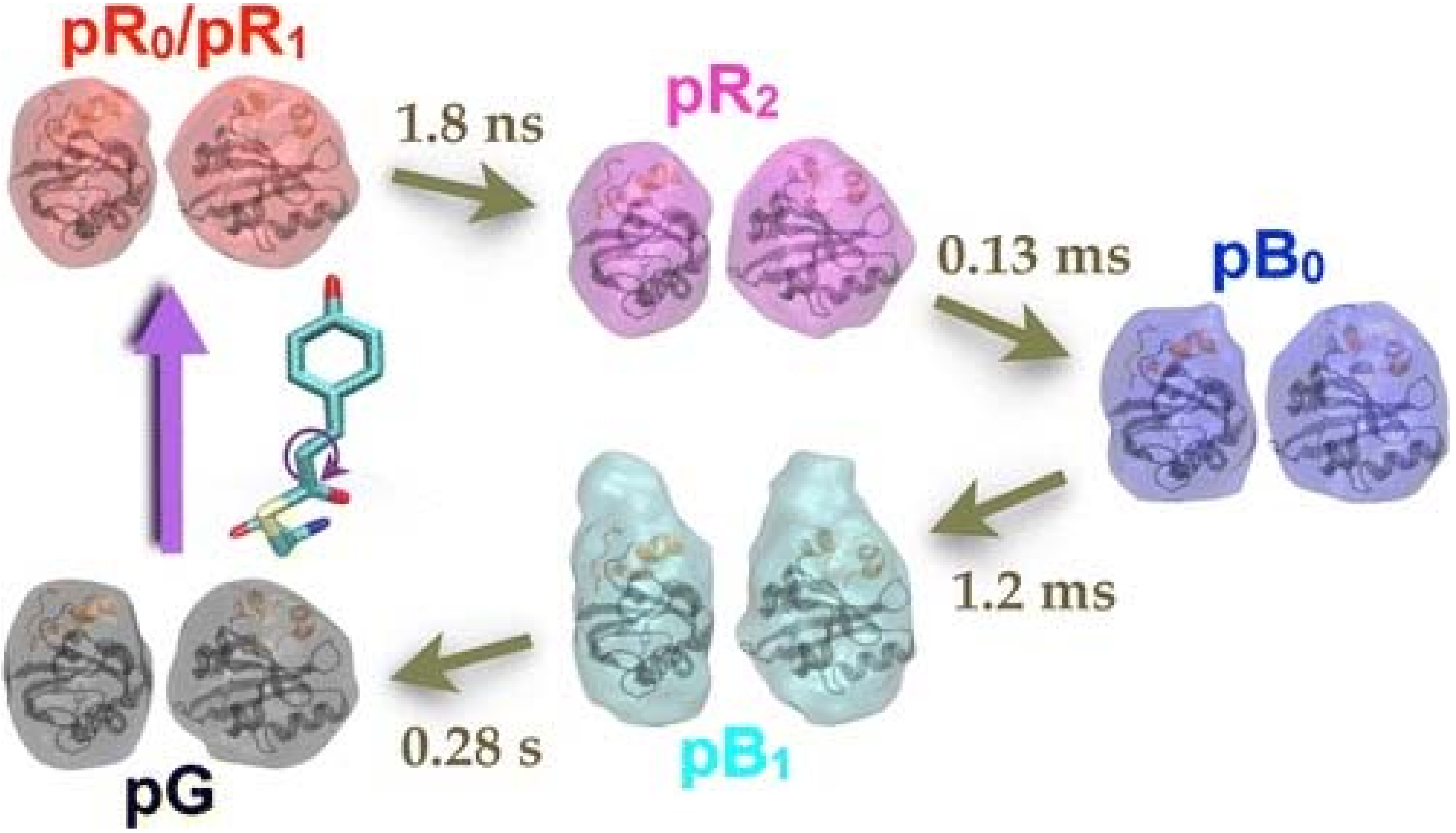
Zewail, *ChemPhysChem*, **2001**, *2*, 294



Nobel prize in chemistry: 1999

Watching a Signaling Protein Function in Real Time by X-ray Scattering

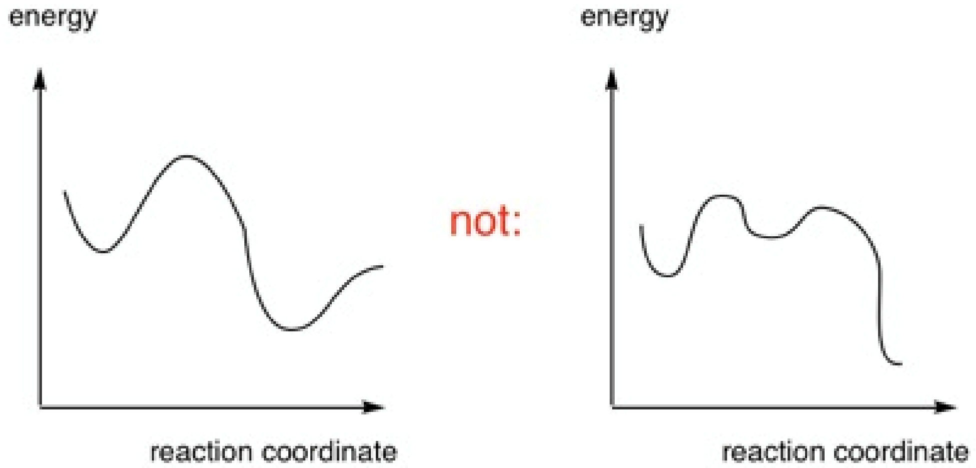
P. A. Anfinrud, *JACS*, **2016**, *138*, 8815



Photosynthetic bacterium that swims away from blue light. The protein responsible for this response is believed to be photoactive yellow protein PYP, whose chromophore isomerizes in the presence of blue light.

Reaction mechanisms, differential rate laws

An elementary reaction (ER) is a reaction of molecular species (atoms molecules, ions,…) that cannot be further separated into individual reaction steps. This is always a working hypothesis.



The differential rate law of an ER always has the form:

$$v = k_f \prod_{i=1}^{m} c_i^{-\nu_i} - k_b \prod_{i=m+1}^{n} c_i^{\nu_i}$$

A reaction mechanis corresponds to the observed overall reaction (hypothesis)

Notes

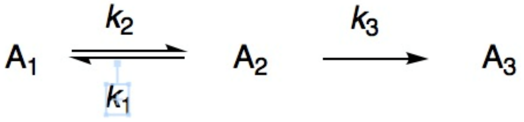
- Reaction rate constants are independent of time and chemical composition, but they do depend on temperature, solvent, ionic strength, …
- Reactions are said to be "irreversible", when the terms for the forward reaction greatly exceed those of the back reaction.
- Distinguish clearly between the "microscopic" rate constants k_f and k_b, which refer to ERs in one direction, and empirical reaction rate constants k_obs, which refer to observed net reactions. Unfortunately, in the literature the same symbol is used for both without subscripts such as f, b, or obs.
- The reaction order is defined as the sum of the exponents v_i, when the rate law has the simple form $v = kc_1^{v_1}c_2^{v_2}$….
  E.g., a reaction is second order, if $v_\mathrm{obs} = k_\mathrm{obs}c_1c_2$ and first order with respect to the components 1 and 2.
- Units: First-order rate constant: $[{}^1k] = \mathrm{s}^{-1}$.
  Second-order rate constant: $[{}^2k] = \mathrm{M}^{-1}\,\mathrm{s}^{-1}$.

Principle of microscopic reversibility

Corresponding to every individual ER there is a reverse ER, and in a state of equilibrium the average rate of every ER is equal to the average rate of its reverse. When a complex, reversible reaction (i.e., one consisting of several ERs) has reached equilibrium, then all elementary reaction steps are at equilibrium.

- If a certain combination of ERs represents the mechanism of a forward reaction, the mechanism of the reverse reaction (under the same conditions) is given by the same steps traversed backwards. (**Note:** The phrase "under the same conditions" means that this applies only to thermal reactions, not photochemical ones.)
- The sequence of transition states and reactive intermediates in the mechanism of a reversible reaction must be the same, but in reverse order, for the backward reaction as for the forward reaction.
- If the mechanism in one direction is known, then the mechanism in the opposite direction is known.
- The lowest-energy pathway in the forward direction will be the lowest-energy pathway in the reverse direction.

Exercises

1. The acid-catalyzed bromination of acetone to bromoacetone does not depend on the concentration of bromine. Explain.
2. The time-of-flight of ions in a mass spectrometer is on the order of 100 microseconds. Why can a sub-picosecond time resolution nevertheless be achieved?
3. In a reversible reaction (such as esterification of a carboxylic acid), how can you achieve complete conversion?
4. Construct a perpetuum mobile using the equilibration reaction between the isomers A, B, and C, assuming that the principle of microscopic reversibility does not hold.
5. Why is the Guldberg–Waage derivation of the law of mass action not general and not quite correct?
6. Given that the mechanism 

   $$A_1 \underset{k_1}{\overset{k_2}{\rightleftharpoons}} A_2 \xrightarrow{k_3} A_3$$

   represents a set of ER’s, write the coupled system of differential rate laws for the time-dependent concentrations $c_i(t)$ of compounds A_1 to A_3.
7. Discuss what restricts the time resolution of kinetic and spectrographic flash photolysis.