Supplementary material

1. Glossary

Labelling

AB(1k,2ϕ)	bimolecular kinetic system
A	Species A (initial reactant); photochemically active
B	Species B (photoproduct); photochemically and thermally active
AB	transformation of species A into B
BA	transformation of species B into A
λ	an arbitrary wavelength
obs	observation wavelength (λ_{obs})
irr	irradiation wavelength (λ_{irr})
isos	isosbestic-point wavelength (λ_{isos})
PSS	index or argument relative to the reaction at the Photo-Stationary State
0	index or argument corresponding to time zero of the reaction
P	photochemical process
T	purely thermal process
Ω	index standing for either P or T letters
$f(\lambda_{exc})$	a function dependent on the excitation wavelength
RK	Runge-Kutta numerical integration method
α, β, δ, Γ, Δ, c_1, c_2, c_3	eight constants of the methods that are used in the bulk of the mathematical development and whose analytical expressions are defined in the text

Irradiation and observation conditions

I_0^{exc}	incident light intensity of the excitation beam at λ_{irr} (I_0^{irr}) or λ_{isos} (I_0^{isos})
λ_{exc}	an arbitrary wavelength used to irradiate the sample; for this method, it includes λ_{isos} which is the wavelength of an isosbestic point and λ_{irr} ($\neq \lambda_{isos}$) an irradiation wavelength where $\varepsilon_A^{irr} \neq \varepsilon_B^{irr}$ and both have non-zero values.

λ_{obs}	an arbitrary observation wavelength (=λ_{irr} for the spectrokinetic methods)
l_{probe}	optical path length of the monitoring light inside the sample
l_{irr}	optical path length of the irradiation light inside the sample

Concentrations

$C_i\,(t)$	concentration of species i = A or B at time t
$C_i\,(PSS)$	concentration of species i = A or B at time PSS
C_0	total concentration of the species in the reactive medium

Kinetic parameters

$\phi_i^{\lambda_{exc}}$	generic quantum yield of the transformation i when the reaction medium is subjected to an excitation beam whose wavelength is λ_{exc}
$\phi_{AB}^{\lambda_{exc}}$	quantum yield of the transformation of A into B at the excitation wavelength λ_{exc} (which may be either irr or isos)
$\phi_{BA}^{\lambda_{exc}}$	quantum yield of the transformation of B into A at the excitation wavelength λ_{exc} (which may be either irr or isos)
k_{BA}	first-order rate constant of the thermal transformation of B into A
$F^{irr}(t)$	photokinetic factor at the irradiation wavelength and time t
F_{PSS}^{irr}	(or $F^{irr}(PSS)$) constant photokinetic factor at λ_{irr} at PSS
F_0^{irr}	(or $F^{irr}(0)$) constant photokinetic factor at λ_{irr} and t = 0
F^{isos}	(or $F^{isos}(t) = F^{isos}$) constant photokinetic factor at λ_{isos}
$m_{0,\Omega}^{irr/obs}$	initial velocity of reaction Ω when irradiation has been carried out using λ_{irr} (= isos or irr) and observed at λ_{obs} (= irr)
$a_{19\Omega}$	overall first-order reaction rate for the process Ω
$a_{4\Omega}$	first-order direct reaction rate for the process Ω
$a_{5\Omega}$	first-order reverse reaction rate for the process Ω
γ_{isos}	constant factor that multiplies quantum yields when $\lambda_{exc} = \lambda_{isos}$

Spectroscopic parameters

ε_i^{λ} extinction coefficient of species *i* (A or B) at λ (= isos, irr or obs)

$M_{tot}^{\lambda_{exc}/\lambda_{obs}}$ the total absorbance of the medium measured at various excitation/observation wavelengths' combinations (e.g. $M_{tot}^{isos/isos}$, $M_{tot}^{isos/irr}$ and $M_{tot}^{irr/irr}$ respectively at isos/isos, isos/irr and irr/irr)

$M_{tot}^{F}(t)$ the total absorbance used to make up the equation of the photokinetic factor (F). Three particular values are interesting for the calculations of the method : (i) at the initial time ($M_{Tot}^{F_0^{irr}}$ for calculation of F_0^{irr}), (ii) at the isosbestic point ($M_{tot}^{F^{isos}}$ for F^{isos}), and (iii) at the PSS ($M_{tot}^{F_{PSS}^{irr}}$ for F_{PSS}^{irr})

2. α *coefficient values for Figures 1 and 2.*

These values are calculated using data of Tables 1 and 2 and Eq.6b

Table SM-01

	$m_0^{irr/irr}$	ε_A^{isos}	F^{isos}	I_0^{isos}	$m_{0,P}^{isos/irr}$	ε_A^{irr}	F_0^{irr}	I_0^{irr}	α
Fig. 1	0.00578	22558	1.463	$2x10^{-6}$	0.02338	9536	1.883	$9.1x10^{-7}$	**0.9996**
Fig. 2	-0.05017	18617	1.93	$6x10^{-6}$	-0.0673	58690	1.369	$2x10^{-6}$	**1.00011**

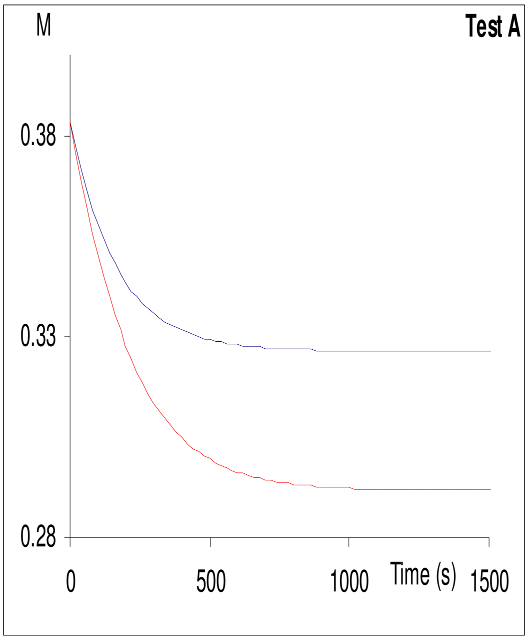
3. *Examples of AB(2ϕ,1k) kinetics : $\phi \neq f(\lambda_{exc})$; $\phi_{BA} > \phi_{AB}$; $l_{irr} \neq l_{probe}$;*

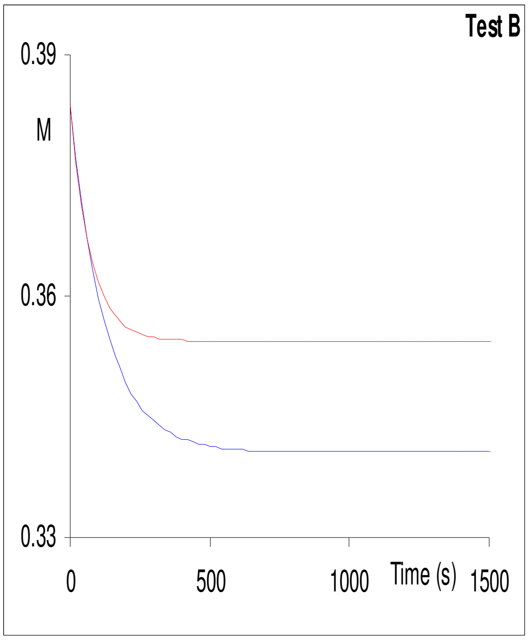
Table SM2 gives a few examples more about testing method #1. Data that should be available experimentally are shown first and are used to feed RK simulation. The elucidation method is applied to the traces obtained and the values for the unknowns are determined.

The calculations assumed that irradiation and observation path lengths are different as well that the reverse quantum yields are higher than the forward ones.

Table SM-02

Simulation test → ----------------- Parameters ↓	**A**	**B**	**C**	**D**
C_0	9 x 10^{-6}	9 x 10^{-6}	1 x 10^{-4}	1 x 10^{-4}
Isosbestic conditions				
ε_A^{isos}	5241	5241	35241	35241
I_0^{isos}	1.5 x 10^{-6}	1.5 x 10^{-6}	1 x 10^{-5}	1 x 10^{-5}
γ_{isos}	4.37 x 10^{-2}	4.37 x 10^{-2}	0.0999	0.0999
$m_{0,P}^{isos/irr}$	-1.73 x 10^{-3}	-1.73 x 10^{-3}	6.7 x 10^{-3}	6.7 x 10^{-3}
k_{BA}	0	0.01	0	0.03
a_{19P}	-3.36 x 10^{-2}	-4.36 x 10^{-2}	-5.99 x 10^{-2}	-8.99 x 10^{-2}
l_{probe}	1	1	3	3
l_{irr}	2.8	2.8	1.5	1.5
Non-isosbestic conditions				
ε_A^{irr}	42629	42629	1011	1011
I_0^{irr}	1 x 10^{-7}	1 x 10^{-7}	3.5 x 10^{-6}	3.5 x 10^{-6}
$M_{tot}^{irr/irr}$ (PSS)	0.2916	0.3544	0.3849	0.3211
F_{PSS}^{irr}	1.0378	0.9051	1.86	1.9248
$m_0^{irr/irr}$	-4.04 x 10^{-4}	-4.04 x 10^{-4}	6.92 x 10^{-4}	6.92 x 10^{-4}
Coefficient α				
F^{isos}	1.9854	1.9854	0.1891	0.1891
F_0^{irr}	0.8524	0.8524	1.9435	1.9435
α	1	1	1	1
Results from the application of the elucidation method #1				
ε_B^{irr}	18141	18141	1756	1756
$\phi_{AB}^{\lambda_{isos}}$	0.18	0.18	0.3	0.3
ϕ_{BA}	0.59	0.59	0.3	0.3


M
Test A
0.38
0.33
0.28
0
500
1000
Time (s)
1500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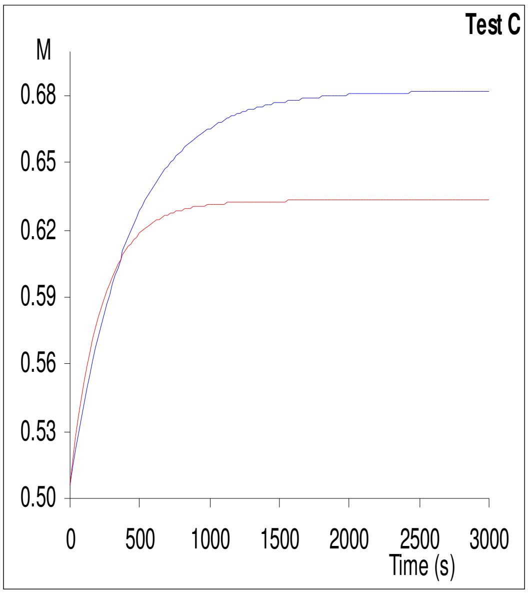
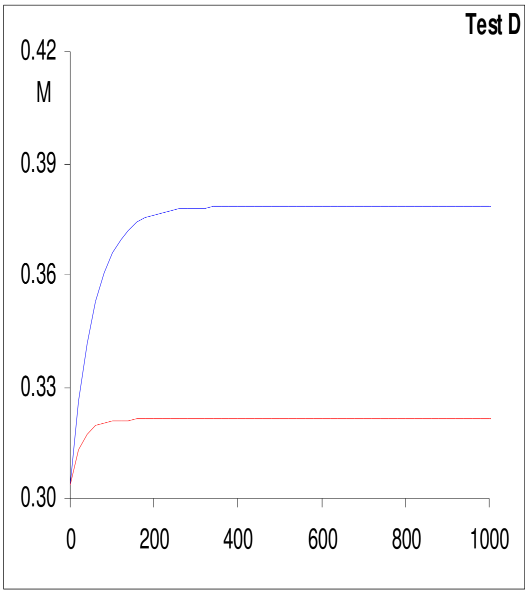
0.39
M
0.36
0.33
0
500
1000
Time (s)
1500


Test C
M
0.68
0.65
0.62
0.59
0.56
0.53
0.50
0
500
1000
1500
2000
2500
3000
Time (s)


Test D
0.42
M
0.39
0.36
0.33
0.30
0
200
400
600
800
1000

4. *Examples of AB(2ϕ,1k) kinetics : $\phi = f(\lambda_{exc})$*

The table consists of data that should be available experimentally, which are used to feed the method and subsequently determine the values of the unknowns (Table SM-03).

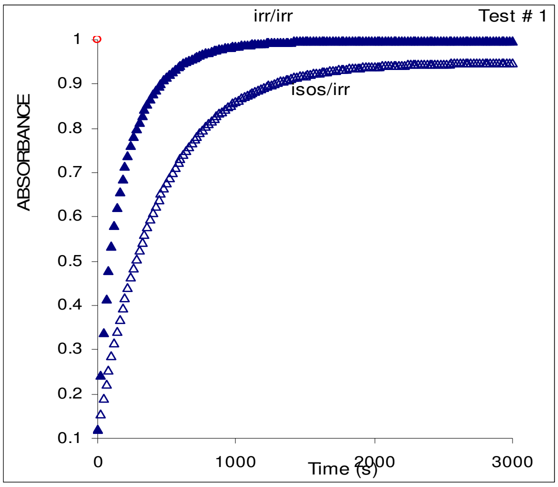
The latter are given below with the error (in %) to those original values used to generate the simulated kinetic traces.

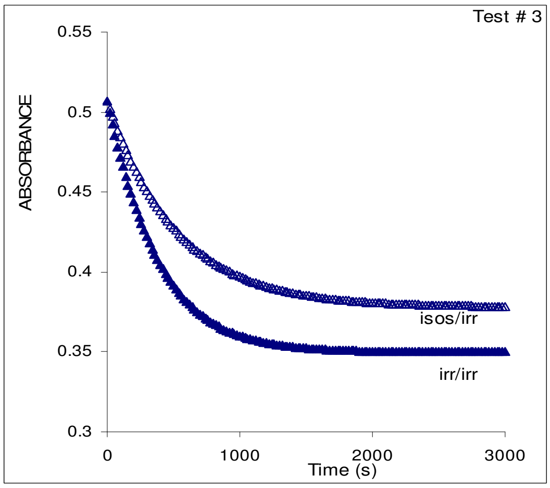
The calculations assumed that irradiation and observation path lengths are equal.

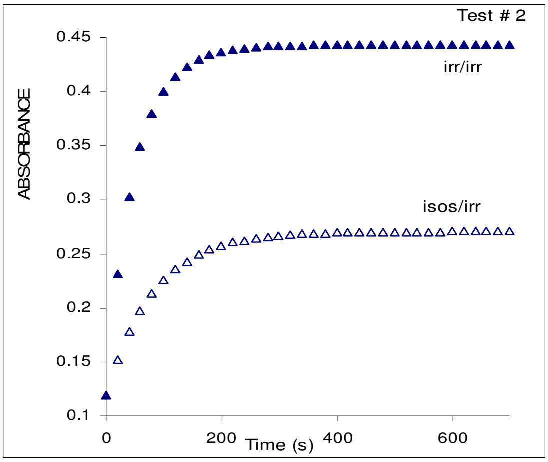
The traces presented concern the light induced photochemical reactions (each one is labelled by the number of the corresponding test example).

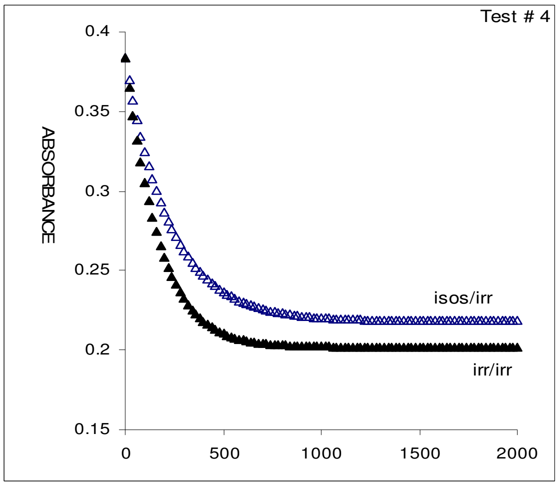
Table SM-03

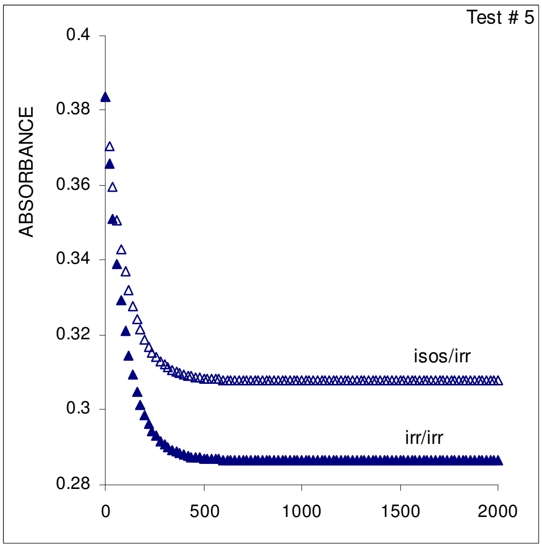
Simulation test ----------------- Parameters ↓	**1**	**2**	**3**	**4**	**5**
C_0	2×10^{-5}	2×10^{-5}	1.6×10^{-5}	5×10^{-6}	5×10^{-6}
Isosbestic conditions					
ε_A^{isos}	9165	9165	14265	21666	21666
I_0^{isos}	1.3×10^{-6}	1.3×10^{-6}	1×10^{-7}	8×10^{-8}	8×10^{-8}
$M_{tot}^{isos/irr}$ (PSS)	0.9478	0.2706	0.37807	0.21837	0.3079
F^{isos}	1.4476	1.4476	1.9749	1.855	1.855
$m_{0,P}^{isos/irr}$	1.86×10^{-3}	1.86×10^{-3}	-2.47×10^{-4}	-7.27×10^{-4}	-7.27×10^{-4}
a_{19P}	-2.24×10^{-3}	-1.22×10^{-2}	-1.91×10^{-3}	-4.40×10^{-3}	-9.60×10^{-3}
k_{BA}	0	0.01	0	0	0.0052
l_{probe}	2.4	2.4	0.6	1.8	1.8
l_{irr}	2.4	2.4	0.6	1.8	1.8
Non-isosbestic conditions					
ε_A^{irr}	2478	2478	52821	42629	42629
I_0^{irr}	8.8×10^{-7}	8.8×10^{-7}	1.5×10^{-7}	1×10^{-7}	1×10^{-7}
$M_{tot}^{irr/irr}$ (PSS)	0.99846	0.44306	0.35	0.20194	0.2866
F_0^{irr}	2.01419	2.01419	1.3585	1.5290	1.5290
F_{PSS}^{irr}	0.90103	1.4433	1.5809	1.8414	1.6856
$m_0^{irr/irr}$	7.16×10^{-3}	7.16×10^{-3}	-3.91×10^{-4}	-9.83×10^{-4}	-9.83×10^{-4}
Results from the application of the elucidation method #2					
α	15.16	15.16	0.4147	0.667	0.667
$\phi_{AB}^{\lambda_{irr}}$	0.4712 (0.25 %)	0.469 (0.083 %)	0.169 (0.17 %)	0.569 (0.1 %)	0.57 (0.034 %)
$\phi_{AB}^{\lambda_{isos}}$	0.031 (0.24 %)	0.03097 (0.094 %)	0.4096 (0.1 %)	0.378 (0.5 %)	0.38 (0.024 %)
ϕ_{BA}	0.0229 (0.37 %)	0.023 (0.089 %)	0.7203 (0.05 %)	0.19 (0.43 %)	0.19 (0.024 %)
ε_B^{irr}	32481.71 (0.35 %)	32624.11 (0.083 %)	15746.98 (0.11 %)	18108.93 (0.18 %)	18144.46 (0.019 %)


Test # 1
irr/irr
isos/irr
ABSORBANCE
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1000
2000
3000
Time (s)


Test # 3
ABSORBANCE
0.55
0.5
0.45
0.4
0.35
0.3
isos/irr
irr/irr
0
1000
2000
3000
Time (s)


Test # 2
ABSORBANCE
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
irr/irr
isos/irr
0
200
400
600
Time (s)


Test # 4
ABSORBANCE
0.4
0.35
0.3
0.25
0.2
0.15
isos/irr
irr/irr
0
500
1000
1500
2000


Test # 5
ABSORBANCE
0.4
0.38
0.36
0.34
0.32
0.3
0.28
isos/irr
irr/irr
0
500
1000
1500
2000