Supplementary materials

PCCP ID: CP-ART-05-2010-000469

sm1- Glossary of symbols

AB(1ϕ)	a unimolecular photoreactions involving an initial species A and a photoproduct B (A $\rightarrow$ B).
$A_{A}^{\lambda_{irr}}(0)$	absorbance of the reaction medium at the initial time (t = 0), for the irradiation conditions.
$A_{A}^{\lambda_{irr}}(t)$	absorbance of the reaction medium at time t, for the irradiation conditions.
$A_{A}^{\lambda_{obs}}(0)$	absorbance of the reaction medium at the initial time (t = 0), for the observation conditions.
$A_{A}^{\lambda_{obs}}(t)$	absorbance of the reaction medium at time t, for the observation conditions.
$A_{A}^{\lambda_{obs}}(t_x)$	absorbance of the reaction medium at time t_x
$A_{A}^{\lambda_{obs(\lambda_i)}}$	absorbance measured at the specific wavelength λ_i.(= λ_m, λ_k or λ_x)
$\beta^{\lambda_{irr}}$	proportionality constant of the actinometer at a given λ_{irr}; $\beta^{\lambda_{irr}} = \frac{k_{AB}^{\lambda_{irr}}}{P_{\lambda_{irr}}}$
β^{λ_x}	$\beta^{\lambda_{irr}}$ value for λ_x
C_0	initial concentration.
$\varepsilon_{A}^{\lambda_{irr}}$	molar absorption coefficient of species A at an irradiation wavelength
j	number of values of radiant power ($P_{\lambda_{irr}}$).
k, m, x	indexes used for different irradiation wavelengths.
$k_{AB}^{\lambda_{irr}}$	reaction rate constant when the reaction is subjected to an irradiation beam whose wavelength is λ_{irr}
$k_{AB}^{\lambda_x}(nor)$	normalized value of the rate constant when the irradiation optical path length used for a given experiment is different from that used to develop the present actinometric method: $k_{AB}^{\lambda_x}(nor) = k_{AB}^{\lambda_x}\frac{2.1}{l_{\lambda_x}}$

$l_{\lambda_{irr}}$	the optical path length of the excitation beam inside the sample. (irradiation conditions)
$l_{\lambda_{obs}}$	the optical path length of the probing light ($l_{\lambda_{obs}} = 1\,cm$). (observation conditions).
λ_{irr}	wavelength of the irradiation beam.
λ_{obs}	wavelength of the observation (probing) light.
n	set of wavelengths used for irradiation of the sample (λ_{irr_n}).
P	radiant power.
$P_{\lambda_{irr}}$	radiant power of the monochromatic incident light at λ_{irr}
P_{λ_x}	radiant power value used in the experiment yielding $k_{AB}^{\lambda_x}$
Φ_{AB}	quantum yield of the phototransformation $A \rightarrow B$
$\Phi_{AB}^{\lambda_{irr}}$	quantum yield of the phototransformation when subjected to the irradiation beam whose wavelength is λ_{irr}
r	correlation coefficient.
RK	Runge-Kutta numerical integration method.
t_x	reaction time interval.
UV	ultraviolet spectral range.
Vis	Visible spectral range.

sm2- simulated kinetic traces of manuscript

Simulation 2 (Table 1)

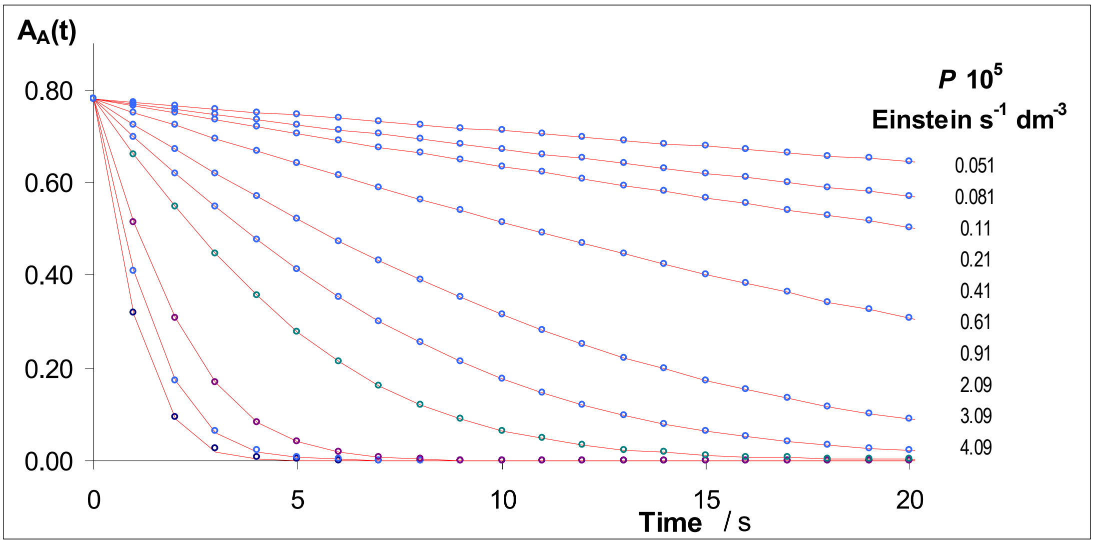

Fig. SM-01

Simulation 3 (Table 1)

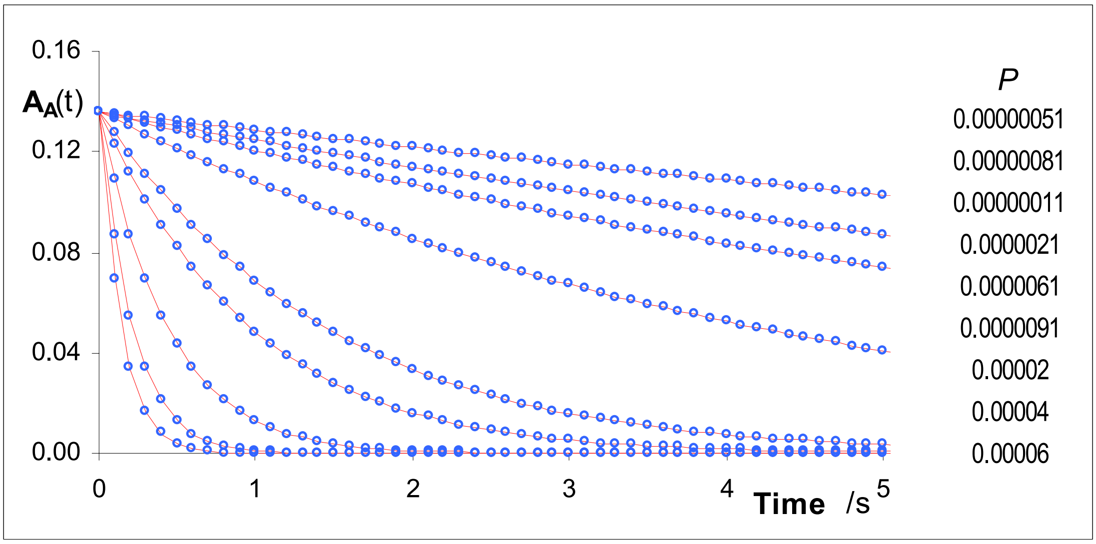

Fig. SM-02

Simulation 1 with high radiant power values (0.002 – 6 Einstein s^{-1} dm^{-3})

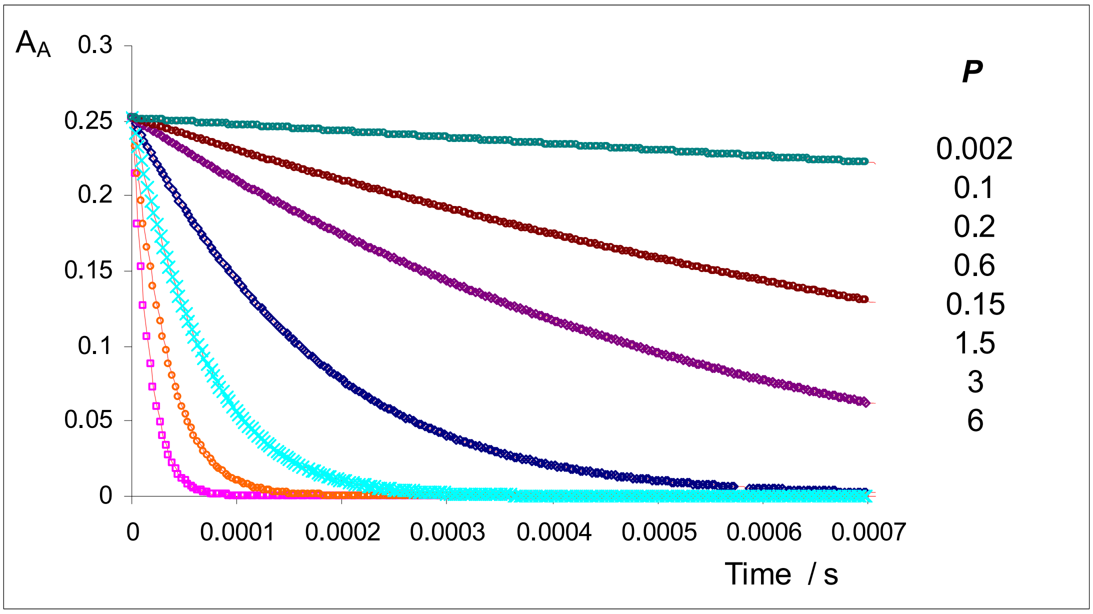

Fig. SM-03

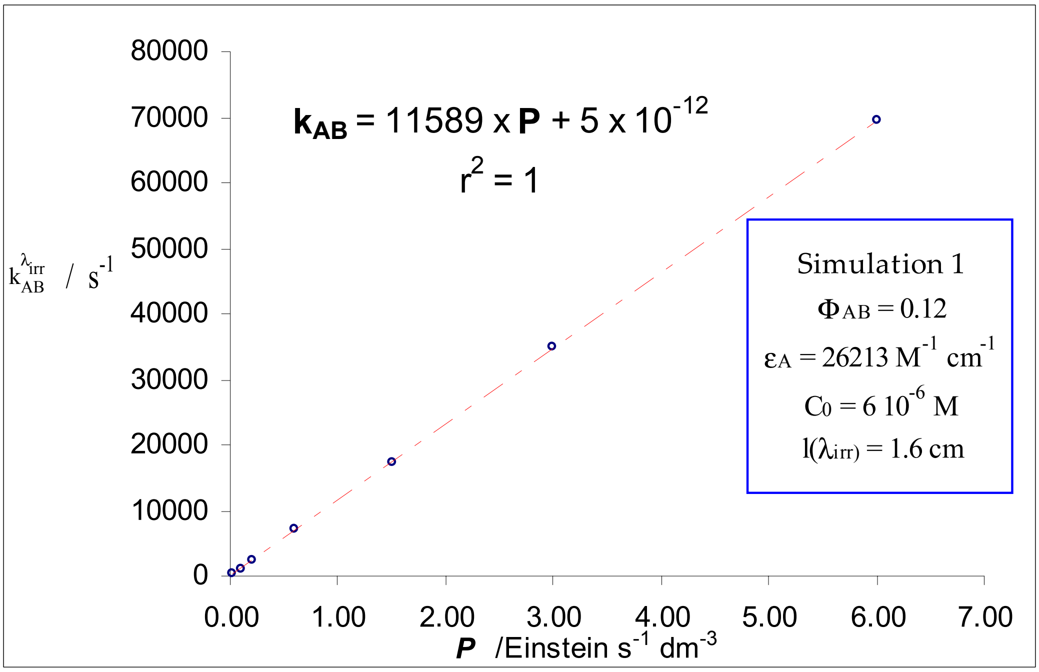

Fig. SM-04

Data used for the construction of simulation 3 in ms.

λ	A_A^{obs}	ε_A	β	A_A^{irr}
300	0.097127	46251	125240.311	0.136
320	0.089116	42435.97	114909.827	0.125
340	0.068832	32777.31	88755.70357	0.096
360	0.044757	21312.7	57711.37714	0.063
370	0.033834	16111.31	43626.84393	0.047
390	0.016992	8091.612	21910.79134	0.024
400	0.011289	5375.848	14556.93596	0.016
420	0.004379	2085.405	5646.942148	0.006

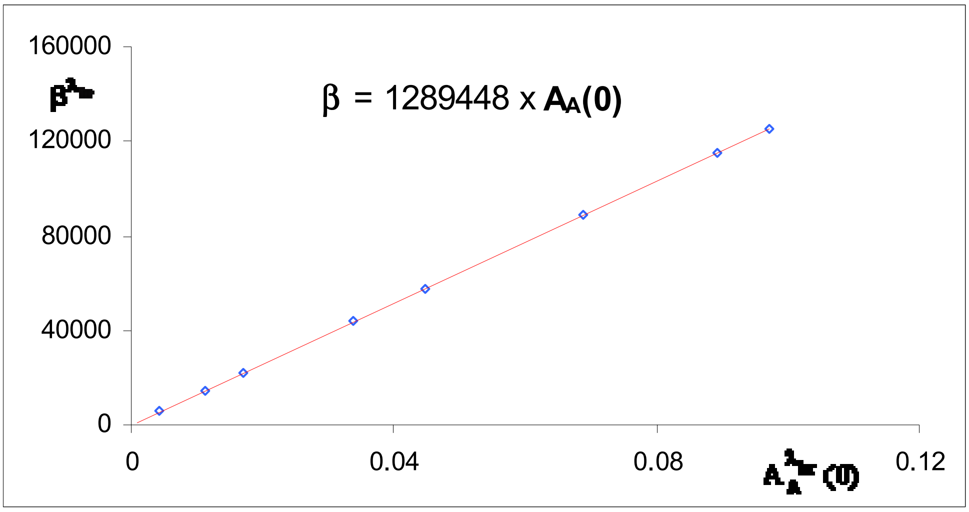

Fig. SM-05: Coefficients $\beta^{\lambda_{irr(k)}}$ *vs.* $A_A^{\lambda_{obs(k)}}(0)$ plots for simulation 3 system in Table 1, at different irradiation wavelengths (with C_0 is constant and the quantum yield is wavelength independent).

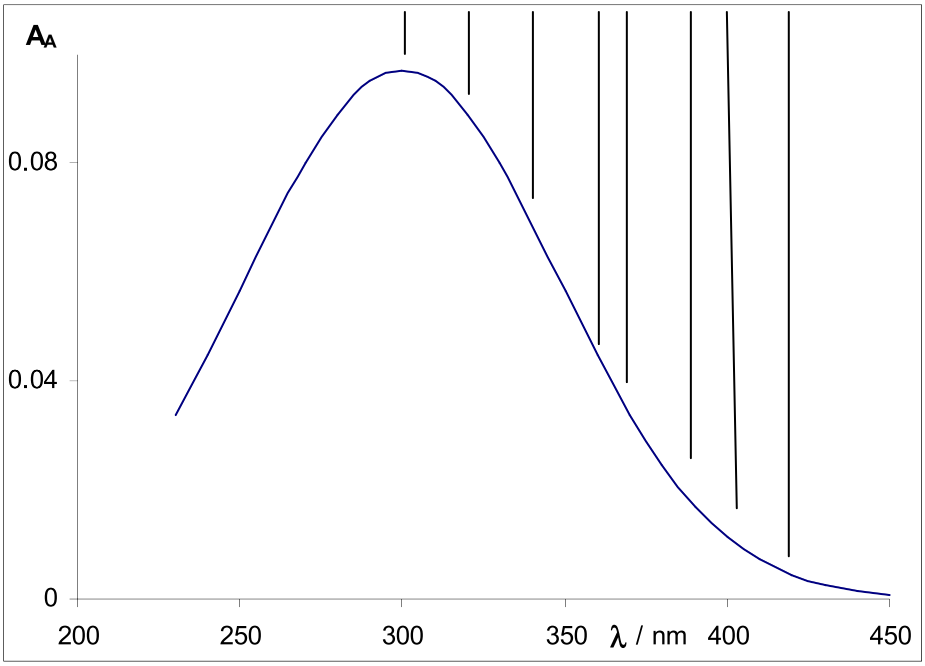

Fig. SM-06: Simulated spectrum used as the basis for Figure SM-05. (The bars indicate the selected irradiation wavelengths used for the determination of β values. The calculation is performed under the assumption that only species A absorbs in this spectral region.

Sm3- Extra example of simulated kinetics

Data feeding RK calculation

Φ_{AB}	0.9
ε_A^{irr}	32231
C_0	1.90 10^{-5}
P	**10^{-5} to 10^{-7}**
l_{irr}	1
$A_A(0)$	6.12 10^{-1}
k_{AB}	6.68 10^{-1}

Kinetic traces at various P values

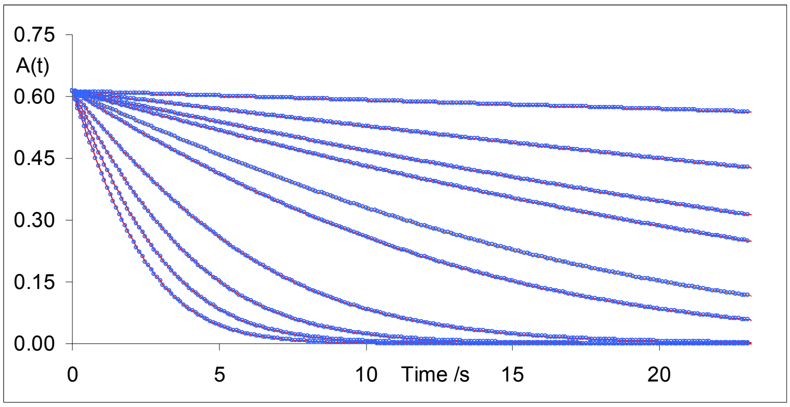

Fig. SM-07

P	***k_{AB}***
1.00E-05	6.68E-01
8.00E-06	5.34E-01
6.00E-06	4.01E-01
4.00E-06	2.67E-01
2.00E-06	1.34E-01
9.00E-07	6.01E-02
7.00E-07	4.68E-02
4.00E-07	2.67E-02
1.00E-07	6.68E-03
1.00E-06	6.68E-02
1.50E-06	1.00E-01

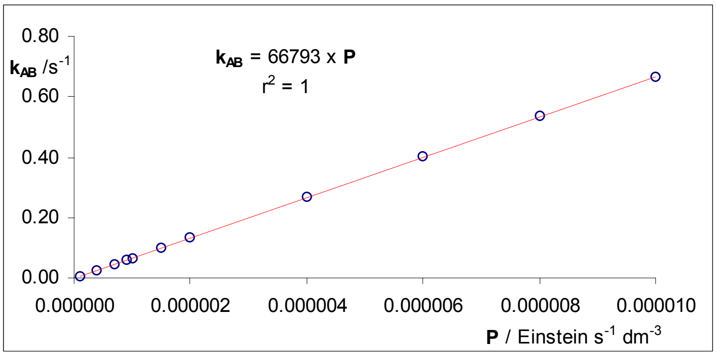

Fig. SM-08

Sm4- Examples of experimental results not shown in ms

Traces for 524/524: dots (experimental points) ; line (model Eq.1)

The initial absorbances (initial concentrations) are different.

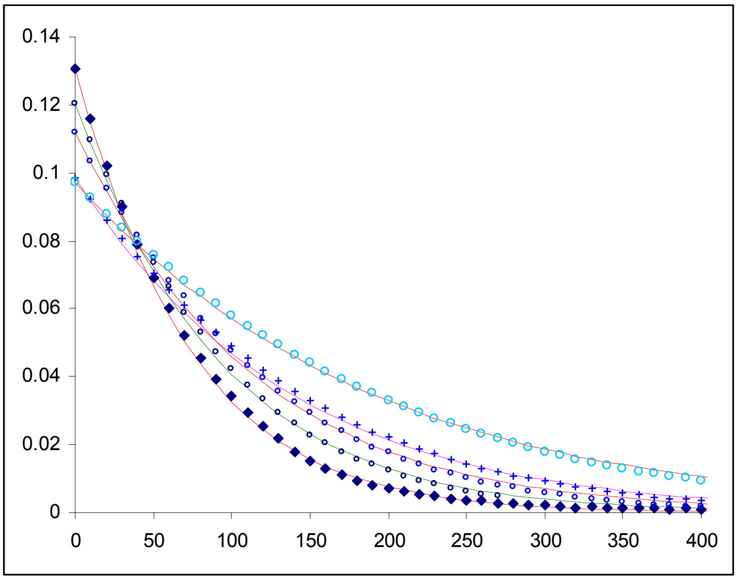

Fig. SM-09

correlation actinometry

P	k_{AB}
1.21843E-06	0.0092
9.37082E-07	0.0071
7.55565E-07	0.0057
5.21861E-07	0.0041
4.42448E-07	0.0033

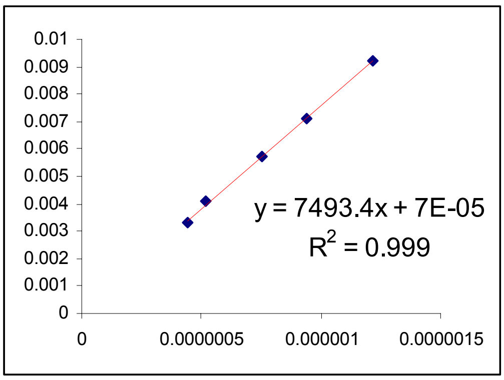

Fig. SM-10

Normalized curves of the preceding traces 524/524 (a unique initial absorbance)

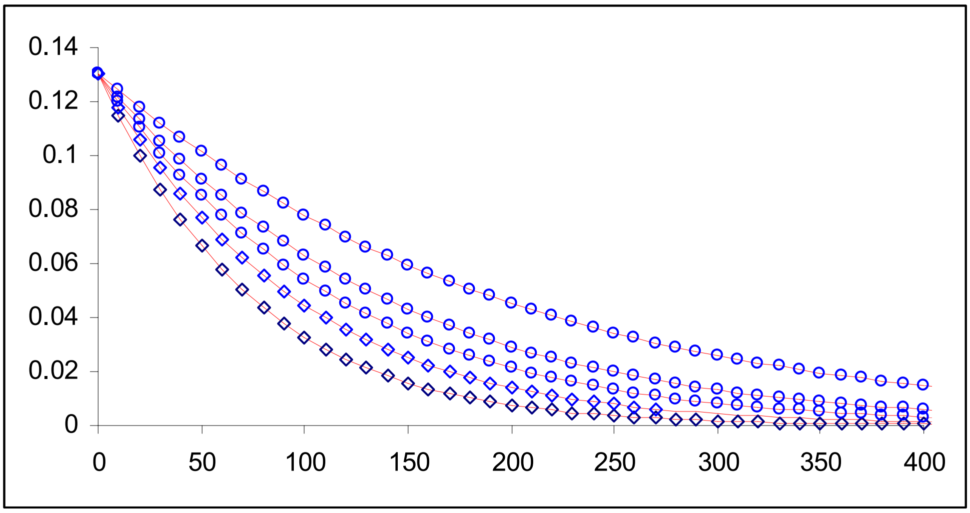

Fig. SM-11

570/570: dots (experimental points)

correlation actinometry

P	k_{AB}
1.66868E-06	0.015
1.29323E-06	0.0118
1.0179E-06	0.0097
8.76058E-07	0.0081
6.25756E-07	0.0058

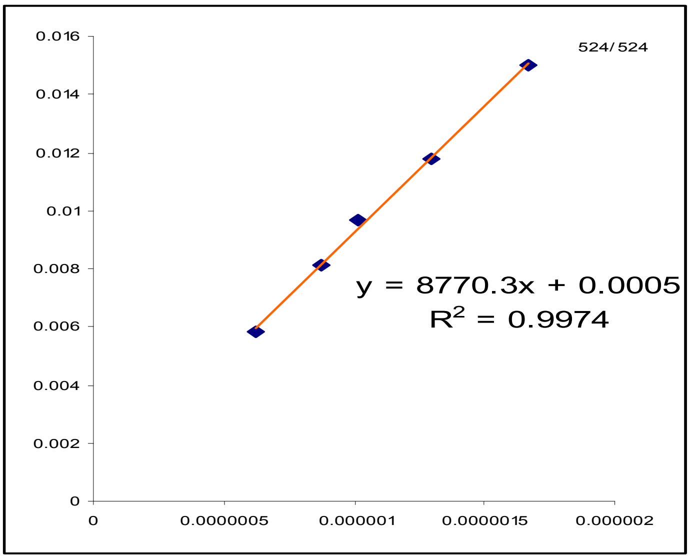

Fig. SM-12

Traces for 480/480: dots (experimental points) ; line (model Eq.1)

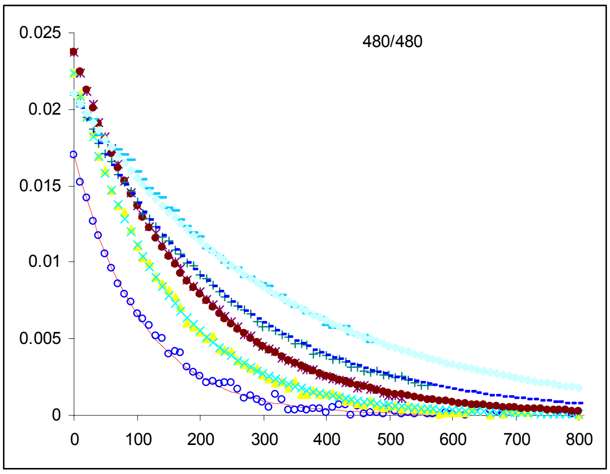

Fig. SM-13

correlation actinometry

P	k_{AB}
1.80562E-06	0.0096
1.32603E-06	0.0071
1.02223E-06	0.0056
7.48996E-07	0.00423
6.11426E-07	0.0031

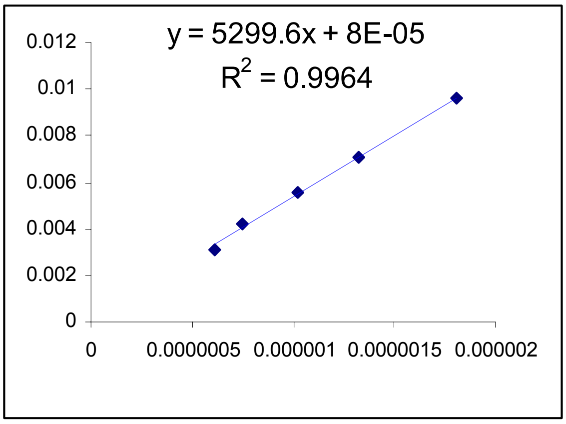

Fig. SM-14

Normalized curves

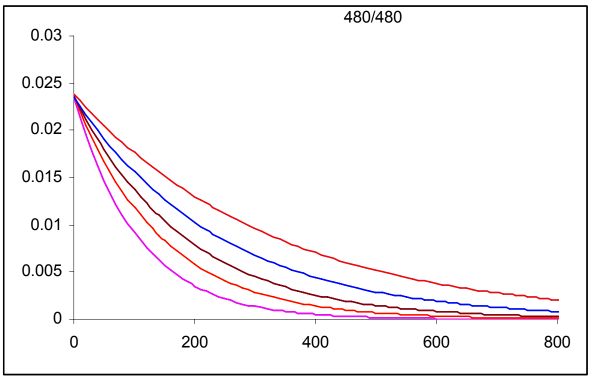

Fig. SM-15

Sm5-Experimental data for the steady state measurements of *P* (Fig.7 in MS)

λ	β	*A*(0)	*A*(t_x)	t_0	t_x	Cld. *P*	Exp. *P*	%Err
540	7775.64	0.078489	0.07218	562	572	1.29E-06	1.42E-06	10.34
540	7775.64	0.078489	0.065537	562	582	1.3727E-06	1.42E-06	3.35
540	7775.64	0.078489	0.060676	562	592	1.2985E-06	1.42E-06	9.26
540	7775.64	0.078489	0.055194	562	602	1.3229E-06	1.42E-06	7.24
540	7775.64	0.078489	0.05108	562	612	1.2842E-06	1.42E-06	10.47
540	7775.64	0.078489	0.046697	562	622	1.2861E-06	1.42E-06	10.31
540	7775.64	0.078489	0.04282	562	632	1.2795E-06	1.42E-06	10.88
500	6407	0.071621	0.066439	222	232	1.2846E-06	1.36E-06	5.87
500	6407	0.071621	0.062223	222	242	1.1989E-06	1.36E-06	13.44
500	6407	0.071621	0.055553	222	262	1.1681E-06	1.36E-06	16.43
454	4833.064	0.022797	0.015522	40	129.9	9.2575E-07	8.855E-07	4.54
454	4833.064	0.017597	0.012676	10	80	1.0052E-06		
454	4833.064	0.01683	0.011848	20	100	9.3933E-07	8.855E-07	6.07
454	4833.064	0.02675	0.02097	0	60	8.8862E-07	9.759E-07	8.94
454	4833.064	0.024784	0.019347	20	80	9.0019E-07	9.759E-07	7.75
437	4251.392	0.03786	0.02599	10	80	1.363E-06	1.2925E-06	5.45
437	4251.392	0.029925	0.02323	10	100	7.0508E-07	6.9755E-07	1.08
437	4251.392	0.02845	0.024506	10	80	5.3417E-07	5.914E-07	9.67
405	3156.48	0.04521	0.03619	0	50	1.5527E-06	1.70127E-06	8.73
405	3156.48	0.02523	0.022913	0	60	5.3878E-07	5.2882E-07	1.88
480	5722.68	0.015476	0.007972	10	80	1.7017E-06	1.8056E-06	5.75
480	5722.68	0.022082	0.013567	10	80	1.2681E-06	0.000001326	4.36
480	5722.68	0.022426	0.015279	10	80	1.0017E-06	1.0222E-06	2.00
480	5722.68	0.022611	0.016927	10	80	7.5761E-07	7.48996E-07	1.14
480	5722.68	0.023166	0.018743	10	80	5.5603E-07	6.11426E-07	9.05
570	8802.12	0.03575	0.019705	10	80	1.0311E-06	1.2184E-06	15.36
570	8802.12	0.038488	0.026479	10	80	6.5534E-07	7.556E-07	13.26
570	8802.12	0.038328	0.029321	10	80	4.7107E-07	5.2186E-07	9.73
570	8802.12	0.037127	0.029639	10	80	3.9576E-07	4.42448E-07	10.55
524	7228.184	0.084	0.0645	0	60	7.2428E-07	6.25756E-07	15.74