Light Distribution in Cylindrical Photoreactors

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Flow photoreactors are commonly (*1* to *4*) illuminated by locating the cylindrical reactor tube and the lamp at the foci of an elliptical reflector. Usual practice is to assume that all the light striking the reactor wall will be directed radially inward (Figure 1a). The intensity profile for this radial model is strongly dependent upon radius, according to the equation

$$I_\lambda(r) = I_{w,\lambda} \frac{R_1}{r} [e^{-\mu_\lambda(R_1-r)} + e^{-\mu_\lambda(R_1+r)}] \quad (1)$$

Actually, the lamp is not a line light source, so that radiation emanates from points displaced from the axis of the lamp. This situation, combined with imperfections in the elliptical reflecting surface, indicates that the intensity in the reactor tube will tend to be independent of radius near the central axis. This suggestion, originally made by Huff and Walker (*2*), was investigated by Jacob and Dranoff (*5*) who measured the intensity distribution using a small selenium-barrier photocell. They found that the intensity was nearly uniform if the reactor radius were less than 0.5 in. The relations between intensity and radius, average intensity over the whole reactor, and rates of photoreaction were developed mathematically for the extremes of diffuse and radial models in connection with studies of the photodecomposition of formic acid solutions (*6*).

In this communication, the radial distribution of intensities is derived for the more general case of partially diffuse light. The extremes of this case are the radial and diffuse models. The results are then applied to the questions of how the intensity distribution affects the rate of reaction, averaged across the reactor diameter; the light intensity at the reactor wall, as evaluated from actinometric data; and rate constants determined from kinetic data for the photoreaction.

PARTIALLY DIFFUSE-LIGHT MODEL

In the radial model, all incident rays intersect at the central axis of the reactor tube, so that the intensity approaches infinity as $r \to 0$. In the diffuse model (Figure 1c), a parallel band of rays, wider than the reactor diameter, passes through the reactor cross section from all directions with equal probability. As an intermediate case, suppose that a parallel band of rays, of width $2R_2$ which is less than the reactor diameter, passes through in such a way that the center ray of the band goes through the central axis. This partially diffuse model is shown in Figure 1b. Within the circle of radius R_2 all directions have equal probability, although only a few directions are illustrated in the figure. For all models, the incident rays lie in planes normal to the central axis. As the band width in the partially diffuse model decreases, the radial model is approached; as the band width increases, diffuse light is obtained.

In the partially diffuse model consider the inner circle of radius R_2 through which all light rays pass in all directions with equal probability. Choose a point P at a radius r from the center. The lines through P, which are tangent to the inner circle, intersect with an angle 2θ, as shown in Figure 2a. Within this angle, light rays pass through both P and the inner circle. Point A is located on the diameter through P at the reactor circumference. The tangents to the inner circle, which intersect at A, form an angle $2\theta_1$. The ratio of the number of rays which pass through the inner circle and P to the number which pass through the inner circle and A is θ/θ_1. If the intensity at A is $2I_{w,\lambda}$, the intensity at P is $2I_{w,\lambda}(\theta/\theta_1)$, if no absorption occurs. When point P reaches the inner circle, the intensity attains its maximum value of $2I_{w,\lambda}(\pi/2\theta_1)$ and retains this value within radius R_2.

If absorption takes place in the reactor, attenuation along the light path must be taken into account. Consider two rays, $\overrightarrow{DP}$ and $\overrightarrow{BP}$, on the same path but directed oppositely (Figure 2b). The angle between this path and the diameter through P is φ. By using Lambert's law, the attenuation is $e^{-\mu_\lambda x'}$ and $e^{-\mu_\lambda x''}$ for each ray, respectively, where

$$x' = -r \cos\varphi + (R_1^2 - r^2 \sin^2\varphi)^{1/2} \quad (2)$$

$$x'' = r \cos\varphi + (R_1^2 - r^2 \sin^2\varphi)^{1/2} \quad (3)$$

Among all light paths through P the probability of a path being between φ and $\varphi + d\varphi$ is $d\varphi/2\theta$. Hence, the intensity at P due to light paths between φ and $\varphi + d\varphi$ is

$$I_{w,\lambda}\left(\frac{\theta}{\theta_1}\right)\frac{d\varphi}{2\theta}(e^{-\mu_\lambda x'} + e^{-\mu_\lambda x''})$$

The total intensity at P is obtained by integrating from $-\theta$ to θ

$$[I_\lambda(r)]_{\text{pd}} = I_{w,\lambda}\left(\frac{\theta}{\theta_1}\right)\int_{-\theta}^{\theta}(e^{-\mu_\lambda x'} + e^{-\mu_\lambda x''})\frac{d\varphi}{2\theta} \quad (4)$$

for $R_2 \leq r \leq R_1$. If P is within the inner circle, θ in Equation (4) becomes $\pi/2$, so that

$$[I_\lambda(r)]_{\text{pd}} = I_{w,\lambda}\frac{\pi/2}{\theta_1}\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}}(e^{-\mu_\lambda x'} + e^{-\mu_\lambda x''})\frac{d\varphi}{\pi} \quad (5)$$

for $0 \leq r \leq R_2$. The angles θ_1 and θ are calculated from

$$\sin\theta_1 = \frac{R_2}{R_1} \quad (6)$$

$$\sin\theta = \frac{R_2}{r} \quad (7)$$

Equations (4) and (5) give the radial distribution of intensity as a function of r and in terms of R_1, R_2, μ_λ, and $I_{w,\lambda}$.

If $R_2 \to 0$, θ and φ also approach zero. Then, from Equations (2), (3), and (4)

$$I_\lambda(r) = \lim_{\substack{\theta\to 0\\ \varphi\to 0}} [I_\lambda(r)]_{pd}$$

$$= (I_{w,\lambda}) \frac{\theta}{\theta_1} [e^{-\mu_\lambda(R_1-r)} + e^{-\mu_\lambda(R_1+r)}] \quad (8)$$

From Equations (6) and (7), as $R_2 \to 0$, $\theta_1 \to R_2/R_1$ and $\theta \to R_2/r$. Hence, Equation (8) becomes

$$[I_\lambda(r)]_{rad} = (I_{w,\lambda}) \frac{R_1}{r} [e^{-\mu_\lambda(R_1-r)} + e^{-\mu_\lambda(R_1+r)}] \quad (1)$$

which is identical with Equation (1).

If $R_2 \to R_1$ and $\theta_1 \to \pi/2$, Equation (5) is applicable for all r and becomes

$$[I_\lambda(r)]_d = \frac{I_{w,\lambda}}{\pi} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} (e^{-\mu_\lambda x'} + e^{-\mu_\lambda x''}) d\varphi \quad (9)$$

This is the intensity distribution for wholly diffuse light and is equivalent to the expression developed in (6).

If there is no light absorption, Equations (4), (5), (1), and (9) with $\mu_\lambda = 0$ give the distribution functions for each model:

$$[I_\lambda(r)]_{pd} = 2\ I_{w,\lambda} \frac{\theta}{\theta_1} \qquad R_2 \leq r \leq R_1 \quad (10)$$

$$= 2\ I_{w,\lambda} \frac{\pi}{2\theta_1} \qquad 0 \leq r \leq R_2 \quad (11)$$

$$[I_\lambda(r)]_{rad} = 2\ I_{w,\lambda} \frac{R}{r} \quad (12)$$

$$[I_\lambda(r)]_d = 2\ I_{w,\lambda} \quad (13)$$

Average light intensities over the whole reactor diameter, for conditions of negligible absorption, are obtained by integrating Equations (10) to (13). The results are

$$[\bar{I}_{\lambda,\mu=0}]_{pd} = \frac{2\ I_{w,\lambda}}{\pi R_1^2} \left[\int_{R_2}^{R_1} \frac{\theta}{\theta_1} 2\pi r dr + \pi R_2^2 \frac{\pi}{2\theta_1} \right] \quad (14)$$

$$[\bar{I}_{\lambda,\mu=0}]_{rad} = 4\ I_{w,\lambda} \quad (15)$$

$$[\bar{I}_{\lambda,\mu=0}]_d = 2\ I_{w,\lambda} \quad (16)$$

These equations show that, for the same average intensity, the intensity at the reactor wall has to be twice as large for diffuse light as for radial light.

EFFECT OF LIGHT ATTENUATION ON DIFFERENTIAL RATES

When the objective of the flow kinetics study is a rate equation, it is advantageous to use a differential reactor. Then, the measured rate in a photoreactor is the average value over the reactor diameter. Since the concentration change is insignificant, the averaging process is with respect to the light intensity. Suppose that the rate $\Omega_\lambda(r)$ is of order m in concentration and order n with respect to light absorbed, $Ia(r)$; then

$$\Omega_\lambda(r) = k\ C^m [Ia(r)]^n = k\ C^m [\mu_\lambda I_\lambda(r)]^n \quad (17)$$

By using Equations (4) and (5) for the light distribution, the average rate is

$$[\bar{\Omega}_\lambda]_{pd} = \frac{k\ C^m}{\pi R_1^2} (\mu_\lambda^n) \left\{ \int_0^{R_2} \left[(I_{w,\lambda}) \frac{\pi}{2\theta_1} \int_{-\pi/2}^{\pi/2} (e^{-\mu_\lambda x'} + e^{-\mu_\lambda x''}) \frac{d\varphi}{\pi} \right]^n 2\pi r dr + \int_{R_2}^{R_1} \left[I_{w,\lambda} \frac{\theta}{\theta_1} \int_{-\theta}^{\theta} (e^{-\mu_\lambda x'} + e^{-\mu_\lambda x''}) \frac{d\varphi}{2\theta} \right]^n 2\pi r dr \right\} \quad (18)$$

To show the effect of attenuation, the average rate from Equation (18) should be compared with that corresponding to no attenuation, $\mu_\lambda \to 0$. This corrected rate is given by integrating the point rate across the reactor radius, with Equations (10) and (11) used for the light distribution:

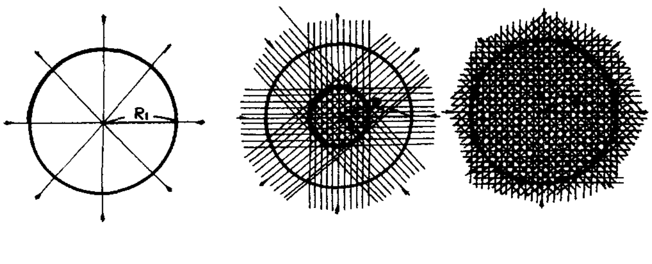
$$[\bar{\Omega}_\lambda]_{pd}^{Corr} = \frac{k\ C^m}{\pi R_1^2} \mu_\lambda^n\ I_{w,\lambda}^n \left[\left(\frac{\pi}{\theta_1}\right)^n \pi R_2^2 + \int_{R_2}^{R_1} \left(\frac{2\theta}{\theta_1}\right)^n 2\pi r dr \right] \quad (19)$$

The ratio of Equations (18) and (19) will be called the *correction factor* f:

$$f = \frac{[\bar{\Omega}_\lambda]_{pd}^{Corr}}{[\bar{\Omega}_\lambda]_{pd}} \quad (20)$$

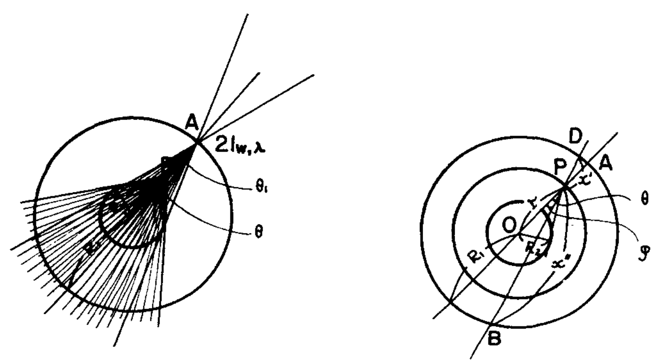
Multiplying the observed rate by f gives a rate corrected for no attentuation; f thus increases with the extent of the attenuation effect.

Equations (18) to (20) were employed to calculate f for $n = 0.5$ and 1, values most frequently encountered in photochemical rate equations. The 0.5 power is obtained for free-radical, chain reactions initiated by photon absorption and terminated by collision of two active centers. The first-power dependency corresponds to nonchain decomposition of light-activated molecules. Figure 3 gives the results for f in the range of μ_λ from 0.01 to 10. The maxi-



a. Radial b. partially Diffuse c. Diffuse

Fig. 1. Characteristics of various light models.



(a) (b)

Fig. 2. Geometry of partially diffuse light.

mum μ_λ was chosen so that f does not exceed 20, a situation where only a very thin outer layer of the cylindrical reactor would be effective for reaction. The abscissa of Figure 3 represents the extent of diffuse light across the reactor, as measured by R_2 (see Figure 1). When $R_2 = 0$, the radial model is applicable, while $R_2 = 1.0$ cm. corresponds to wholly diffuse light, since the calculations are based upon $R_1 = 1$ cm. The results show that the effect of attenuation is not influenced significantly by the light-distribution model for 0.5-order dependency. For first-order dependency of intensity, the effect of attenuation is greater for the radial-light model and becomes rather large for high μ_λ.

INTENSITY CALCULATIONS BY ACTINOMETRY

In kinetic studies in flow photoreactors, rate constants are normally evaluated by a two-stage process. First, the intensity at the reactor wall is obtained by measuring the rate of an actinometric reaction. Second, the rate of the desired reaction is measured in the same equipment.

In the first stage, the intensity level is usually varied by introducing filters or filter solutions in the light path before the rays reach the reactor. It is convenient to introduce a hypothetical intensity $I_{b,\lambda}$ which would exist at the reactor wall if no filters were employed. The total value for all wavelengths, $I_{b,\text{tot}}$ is related to $I_{b,\lambda}$ by the normalized energy output of the lamp:

$$I_{b,\lambda} = I_{b,\text{tot}} \left(\frac{F_\lambda}{F_{\text{tot}}} \right) \tag{21}$$

Then, the wall intensity with filters of transmission T_λ is given by

$$I_{\lambda,w} = I_{b,\text{tot}} \left(\frac{F_\lambda}{F_{\text{tot}}} \right) T_\lambda \tag{22}$$

The problem in the first stage of the process is how does the light distribution effect the value of $I_{b,\text{tot}}$. The solution method based upon the partially diffuse model can be illustrated by using the uranyl-ion, activated decomposition of oxalic acid as the actinometer. This reaction is chosen because it is widely used and because the quantum yield φ_a (rate constant) and absorptivity α are well established (7). In a restricted range of concentrations, the rate is given by

$$\mathbf{r}_\lambda = (\varphi_a)_\lambda \; \mu_\lambda \; I_\lambda(r) = (\varphi_a)_\lambda \; C_a \; \alpha_\lambda \; I_\lambda(r) \tag{23}$$

For differential reactor operation, C_a is nearly constant. Integration across the reactor gives the average rate. Following the same procedure as employed to develop Equation (18), and summing for all wavelengths, we get

$$\bar{\mathbf{r}} = \frac{I_{b,\text{tot}}}{\pi R_1^2} C_a \sum_\lambda (\varphi_a)_\lambda \; \alpha_\lambda \; \frac{F_\lambda}{F_{\text{tot}}} \; T_\lambda \int_0^{R_1} g(r) \; 2\pi r dr \tag{24}$$

where $g(r)$ is $[I_\lambda(r)]_{\text{pd}}/I_{w,\lambda}$, as given by Equations (4) and (5). $I_{b,\text{tot}}$ can be evaluated from Equation (24) from the measured $\bar{\mathbf{r}}$. To illustrate the results, the ratio $I_{b,\text{tot}}/\bar{\mathbf{r}}$ was evaluated for the common actinometer condition, $C_a = 0.001$ g. mole/liter of uranyl sulfate, and for a Hanovia high pressure mercury lamp (LL, 189A10, 1,200 w.) for which the energy distribution in the 2,000 to 3,500Å. is known (8). The ratio is plotted in Figure 4 vs. R_2, for $R_1 = 1.0$ cm. While the curve is nearly flat in the region of predominantly radial light, it increases sharply as diffuse light is approached. If the light in the reactor were wholly diffuse ($R_2 = 1.0$), a 70% error would result if the radial model were used to evaluate $I_{b,\text{tot}}$ from the measured actinometer rate.

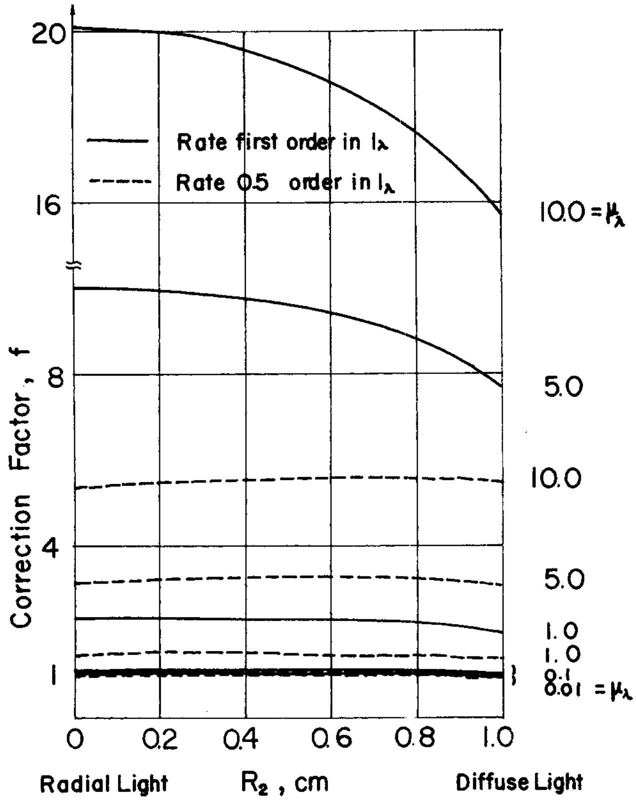


Fig. 3. Effect of light distribution on correction factor f for reactor radius (R_1) of 1.0 cm.

EFFECT OF LIGHT DISTRIBUTION ON RATE CONSTANTS

The rate constant k for the photoreaction is related to the observed rate $[\bar{\Omega}_\lambda]_{\text{pd}}$ and f by Equations (19) and (20). $I_{w,\lambda}$ is given in terms of $I_{b,\text{tot}}$ by Equation (22), and $I_{b,\text{tot}}$ is related to the measured actinometer rate $\bar{\mathbf{r}}$ by Equation (24). These equations can be combined and solved for k to give

$$k = A \frac{f \; \pi R_1^2}{\left[\left(\frac{\pi}{\theta_1}\right)^n \pi R^2{}_2 + \int_{R_2}^{R_1} \left(\frac{2\theta}{\theta_1}\right)^n 2\pi r dr \right] \left(\frac{I_{b,\text{tot}}}{\bar{\mathbf{r}}} \right)^n} \tag{25}$$

where

$$A = [\bar{\Omega}_\lambda]_{\text{pd}} \frac{1/(\bar{\mathbf{r}})^n}{C^m \; \mu^n{}_\lambda \left(\frac{F_\lambda}{F_{\text{tot}}} \right)^n (T_\lambda)^n} \tag{26}$$

Since $\bar{\Omega}_\lambda$ and $\bar{\mathbf{r}}$ are experimental quantities, A does not change with the light-distribution function used; that is, A is independent of R_2.

Equation (25) can be used to evaluate k for various light models. The correction factor f and the ratio $I_{b,\text{tot}}/\bar{\mathbf{r}}$ are available from Figures 3 and 4. The ratio of k for the partially diffuse and radial models is given in Table 1 for $0 \leq R_2 \leq 1.0$, for $0.01 \leq \mu_\lambda \leq 10$, and for rate expressions 0.5 order and first order in light intensity. These ratios seldom deviate more than 5% for the 0.5-order case. When the rate is first order in intensity, the light distribution effect on k is larger but reaches significant values (up to 19%) only when we compare the extremes of radial and diffuse light ($k_{\text{pd}}/k_{\text{rad}}$ for $R_2 = 1.0$).

It is concluded that the rate constants can be evaluated within 5%, in most cases, by using the simple radial-light model, even though the actual light pattern is partially diffuse. This result supposes that the wall intensity is obtained from actinometry in the same apparatus, and that the effect of intensity upon the rate is first order or less. For the extreme case of using a radial model when the light pattern is wholly diffuse, larger errors may result, particularly for the first-order case.

The low errors in k occur, in part, because the light model is used twice, once for interpreting the actinometric data and again in interpreting rates for the photoreaction. In contrast, large errors can occur in using the radial model to calculate the wall intensity (from actinometer data) when the light is diffuse.

ACKNOWLEDGMENT

The financial assistance of the Federal Water Pollution Control Administration, through Grant WP-00952, is gratefully acknowledged.

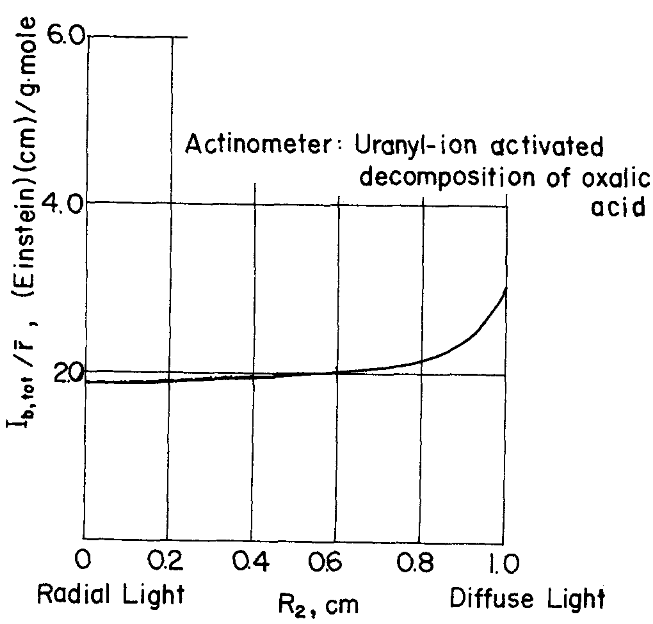


Fig. 4. Effect of light distribution on actinometer results (R_1 = 1.0 cm.).

NOTATION

- A = function of experimental quantities, defined by Equation (26)
- C = concentration, g. moles/cc.; C_A refers to oxalic acid
- f = correction factor defined by Equation (20)
- F_{tot} = total energy output of lamp; Einstein/sec.
- F_λ = energy output of lamp at wavelength λ, Einstein/sec.
- I_b = light intensity at reactor wall without filters
- I_w = light intensity at reactor wall with filters
- I_λ = light intensity at wavelength λ, Einsteins/(sq.cm.)(sec.)
- $\bar{I}_\lambda$ = average light intensity over reactor cross-sectional area
- Ia = absorbed light intensity, Einsteins/(cc.)(sec.)
- k = reaction rate constant, (cm.)(g.)/sec.
- m = order of reaction with respect to reactant concentration
- n = order of reaction with respect to absorbed light intensity
- r = radial distance from center of reactor tube, cm.
- $\mathbf{r}_\lambda$ = rate of oxalic acid decomposition at wavelength λ, g. mole/(cc.)(sec.); $\bar{\mathbf{r}}$ = average (or measured) rate over reaction cross section
- R_1 = reactor radius, cm.
- R_2 = radius within which light is diffuse, cm.
- T_λ = fraction of light of wavelength λ transmitted through all filter solutions
- x' = length defined by Equation (2), cm.
- x'' = length defined by Equation (3), cm.

Greek Letters

- α_λ = absorptivity of uranyl sulfate, sq.cm./g. mole, based upon log to base e
- μ_λ = attenuation coefficient of reactant, cm.$^{-1}$
- $\Omega_\lambda(r)$ = rate of decomposition of reactant induced by monochromatic light of wavelength λ, g. mole/(cc.)(sec.)
- $\bar{\Omega}_\lambda$ = average rate over reactor cross section, g. mole/(cc.)(sec.)
- $[\bar{\Omega}_\lambda]^{\mathrm{Corr}}$ = average rate corrected to zero absorptivity, g. mole/(cc.)(sec.)
- φ = angle between light path and diameter, Figure 2b, rad.
- $(\varphi_a)_\lambda$ = quantum yield of oxalic acid decomposition, g. moles/Einstein
- θ = angle defined by Equation (7), Figure 2a, rad.
- θ_1 = angle defined by Equation (6), Figure 2a, rad.

Subscripts

- d = diffuse-light model
- pd = partially diffuse-light model
- rad = radial-light model

Table 1. Effect of Light Distribution on Reaction Rate Constants

	R_2, cm.	μ_λ, cm.$^{-1}$ 0.01	0.1	1.0	5.0	10.0
		Ratio k_{pd}/k_{rad}				
	0.0	1.0	1.0	1.0	1.0	1.0
0.5 order in intensity	0.2	0.992	0.992	0.992	1.005	1.007
	0.4	0.984	0.983	0.980	1.007	1.017
	0.6	0.978	0.975	0.967	1.008	1.020
	0.8	0.995	0.991	0.972	1.032	1.082
	1.0	1.034	1.028	0.997	1.053	1.072
	0.0	1.0	1.0	1.0	1.0	1.0
First order in intensity	0.2	0.982	0.982	0.980	0.982	0.991
	0.4	0.981	0.980	0.970	0.973	0.973
	0.6	1.006	1.000	0.957	0.945	0.945
	0.8	1.099	1.089	1.012	0.982	0.982
	1.0	1.190	1.173	1.057	0.954	0.946

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