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Beyond the Beer–Lambert law: The dependence of absorbance on time in photochemistry

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ABSTRACT

The photochemical law governing chemical conversion of a photoactive species is derived and solved analytically. In the absence of solution mixing, the law predicts a remarkable symmetry in which the dependence of light intensity on distance matches the dependence of concentration on time. An exact method is described whereby a time sequence of experimental transmittance/absorbance data obtained during a light-induced chemical process can provide a value of the quantum yield for the photoreaction. It is demonstrated that this procedure is not invalidated by solution mixing.

1. Introduction

Photochemists make extensive use of a law discovered by Bouguer [1], but generally attributed to Beer [2] and Lambert [3], as a tool in investigating the mechanisms of photochemical reactions; however, they rarely probe the underlying physics. Because the Beer–Lambert law treats the concentration of the absorber as constant and uniform, the law becomes open to question whenever the light-absorbing species is changed photochemically. Nonetheless, the law is commonly invoked in interpreting the photochemistry of light-induced processes.

Herein we directly address the physics of a photochemical process. We explore from first principles how light intensity and absorber concentration evolve in space and time during constant illumination. Our findings are then used to discover a precise way of measuring the quantum yield for the chemical consumption of a photochemically active absorber.

2. The Beer–Lambert law in photometry

The most frequent chemical applications of the Beer–Lambert law are analytical [4], relying on the absorption of light in a solution (usually liquid, but sometimes solid or gaseous) to provide a measure of the uniform concentration c of a light-absorbing solute. When a sample of such a solution is confined within a cell with a path-length X, having walls that are parallel, planar, and non-absorbing at the wavelength of interest, the *traditional form* of the Beer–Lambert law asserts that

$$A \equiv \ln\left\{\frac{I(0)}{I(X)}\right\} = \varepsilon c X \tag{1}$$

Here $I(0)$ is the intensity of monochromatic light entering the solution perpendicularly to one face and $I(X)$ is the intensity of light exiting the solution through the opposite face. With an SI unit of $m^2\,mol^{-1}$, the constant ε goes by a variety of names, one of which is *molar absorptivity*. The dimensionless quantity A, termed the *absorbance*, is defined by Eq. (1) as the logarithm (sometimes decadic logarithms are used) of the ratio of the incident light intensity to the transmitted light intensity; it is automatically measured in modern photometric instrumentation. The *transmittance* T, is also provided by many instruments; the expression

$$T \equiv \frac{I(X)}{I(0)} = \exp\{-\varepsilon c X\} \tag{2}$$

gives its definition and its interpretation according to the Beer–Lambert law.

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Eqs. (1) and (2) arise by integration of the *differential Beer–Lambert law*

$$\frac{dI}{dx} = -\varepsilon c I \tag{3}$$

in which x is the dimension along which the light travels. This is a more fundamental formulation, not being anchored to any particular geometry or experiment.

With S denoting the cross-sectional area of the cell and n representing the amount (number of moles) of absorber present, yet another way of stating the Beer–Lambert law is

$$A = \ln\left\{\frac{I(0)}{I(X)}\right\} = \frac{\varepsilon n}{S} = \varepsilon X c_{\text{average}} \tag{4}$$

This equation may be shown to be valid whether or not the concentration is uniform. This is as expected because it is the number of light-absorbing molecules present that is important, rather than their distribution.

In analytical applications of photometry it is unusual to consider the effect of non-uniform absorber concentration, because such a circumstance rarely arises. The situation is different, however, if the absorber is photolabile and undergoes decomposition or other transformation during the irradiation experiment. In such a circumstance the concentration will generally become non-uniform, even though the solution was homogeneous at the onset of the experiment.

3. The Beer–Lambert law in photochemical studies

In photochemistry [5] the absorption of light leads to destruction or transformation of the species that absorbs the light. In consequence, absorption diminishes the concentration of the absorber which, in turn, changes the rate of light absorption, leading to interplay between these two properties. Time, a variable that is absent in pure photometry, enters the picture when photochemistry occurs. Both light intensity and absorber concentration vary with time as well as from point to point in solution. Under these conditions the traditional Beer–Lambert law becomes inadequate. On the other hand, there is no reason to question the validity of the differential version of the law, because that formulation describes a relationship that is obeyed at a single point in space at a single instant in time.

Recognize that in photochemistry both the concentration and the light intensity will generally be functions of distance and of time, so that $c(x, t)$ and $I(x, t)$ become appropriate symbols. In these terms, the differential Beer–Lambert law (3) becomes

$$\frac{\partial I(x,t)}{\partial x} = -\varepsilon I(x,t) c(x,t) \tag{5}$$

In contrast to Eq. (3), the notation of the partial differential calculus has been adopted on recognition that light intensity and absorber concentration are now functions of two independent variables.

Hitherto, because it has occurred only as a ratio, it has been unnecessary to specify exactly what is meant by light "intensity". Now we stipulate $I(x,t)$ to be the photon flux density across the plane at x at time t. This quantity is often named *irradiance*. However, because the same name is also given to the quantity of radiant energy (in $\mathrm{W\,m^{-2}}$) falling on a surface, we adopt the more specific name *photon irradiance*. Its SI unit is $\mathrm{ein\,m^{-2}\,s^{-1}}$, in which "ein" abbreviates *einstein*, one einstein being one Avogadro's number of photons.

Suppose that the sole mechanism leading to the attenuation of the light is capture of photons by the absorbing species but that only a fraction, the quantum yield $\phi(\mathrm{mol\,ein^{-1}})$, of these photons successfully removes absorber molecules. The quantum yield is regarded as a constant for any specific absorber at a particular irradiation wavelength and chemical environment. Quantum yields provide vital information in many branches of science, technology and environmental issues [6–12]. The differential Beer–Lambert law informs us that the attenuation in photon irradiance during the passage of light through a narrow wafer of solution of thickness dx is $\varepsilon I(x,t)c(x,t)dx$, and therefore the rate of destruction of photons (in $\mathrm{ein\,s^{-1}}$) within the wafer is $S\varepsilon I(x,t)c(x,t)dx$. The rate of destruction of absorber moles is ϕ times this quantity and so the number of destroyed moles is $\phi S\varepsilon I(x,t)c(x,t)dxdt$ in the time interval dt and, because the volume of the wafer is Sdx, the decrease in concentration is $\phi\varepsilon I(x,t)c(x,t)dt$. That is

$$\frac{\partial}{\partial t}c(x,t) = -\phi\varepsilon I(x,t)c(x,t) \tag{6}$$

This important result has its basis in the Beer–Lambert law and in the stoichiometry of the photochemical reaction.

Incorporated into Eq. (6) is the assumption that the kinetics of the light-absorbing reaction is first order in both the chemical absorber concentration and in photon irradiance, without any inter-absorber interactions. Also assumed is that the product(s) of the reaction do not themselves absorb or reemit radiation.

4. Insight through undimensioning

In experimental practice, the concentration of absorber is invariably uniform throughout the photochemical cell when the experiment starts; this constant value will be given the succinct symbol c_0:

$$c(x,0) = c_0 \tag{7}$$

Moreover, the photon irradiance impinging on the front surface of the cell is generally kept constant in photochemical experiments; we designate I_0 to represent this unchanging value:

$$I(0,t) = I_0 \tag{8}$$

Time and linear distance are the two independent variables in our system, but it is felicitous to replace t and x by dimensionless substitutes defined by

$$\hat{t} \equiv \phi\varepsilon I_0 t \tag{9}$$

and

$$\hat{x} \equiv \varepsilon c_0 x \tag{10}$$

The undimensioned distance scale has strict limits imposed by the cell width:

$$0 \le \hat{x} \le \hat{X} = \varepsilon c_0 X \tag{11}$$

The upper limit to the dimensionless time scale, on the other hand, depends only on the discretion, or patience, of the experimenter:

$$0 \le \hat{t} \le \hat{t}_{\max} = \phi\varepsilon I_0 t_{\max} \tag{12}$$

$t_{\max}$ being the duration of the irradiation experiment.

The two dependent variables – photon irradiance and absorber concentration – also benefit from undimensioning through the definitions

$$\hat{I}(\hat{x},\hat{t}) \equiv \frac{I(x,t)}{I_0} \tag{13}$$

and

$$\hat{c}(\hat{x},\hat{t}) \equiv \frac{c(x,t)}{c_0} \tag{14}$$

Each of this latter pair of dimensionless quantities is constrained to adopt values between zero and unity.