New Method for High-Accuracy Determination of Time-Span of Electron-Photon Interaction Based on Quantized Beer's Lambert Absorbance

Sardar Dilbag Singh Khalsa^{1,2,*}

¹School of Basic Sciences, Indian Institute of Technology Bhubaneswar, Khordha 752050 Odisha, India ²School of Basic Sciences, Indian Institute of Technology Mandi, Kamand 752050 Himachal Pradesh, India

Actual Determination of Time-span in Absorption Spectroscopy and variation of absorbance vs. concentration is crucial in chemistry and biology. We investigated molecular absorption spectra of 1,4 -diamino anthraquinone taking concentration $20 - 90\mu$ M. We primarily report a violation and quantization of Absorbance in Beer's Lambert Law and propose an alternative explanation for the inherent phenomenon, quantum mechanically. Upon laser pulse excitation yielded photon transfer excited state having 17-96 attoseconds lifespan is formed for different concentrations of samples. We furnished a general equation for the electrostatic field, the wave function of photons and its correlation with absorbance. Further, we propose an intricate relationship between the electromagnetic field generated by particles and its wavefunction.

Introduction - Beer's-Lambert law, named after August Beer and Johann Heinrich Lambert, stands as a cornerstone in the realm of absorption spectroscopy. This fundamental principle provides a quantitative relationship between the absorption of light by a sample and its concentration, paving the way for the precise determination of substance concentrations in various fields of science[1]. The mathematical expression of this law has form[2–8].

$$A = \ln\left(\frac{I_0}{I}\right) = \epsilon cl \tag{1}$$

A is the absorbance of the sample, I_0 is the intensity of incident light, I is the intensity of transmitted light [9, 10], ϵ is the molar absorptivity (or molar extinction coefficient) of the substance, c is the concentration of the absorbing species, l is the path length of the sample. The molar absorptivity (ϵ) is typically assumed to



Figure 1. absorption of light by 1,4 -diamino anthraquinone, where Io is the intensity of incident light, and I is the intensity of transmitted light.

be constant for a given substance at a specific wavelength of light and under particular experimental conditions and l was constant in our experiment, (see Fig. 1) for the systematic diagram of incident and transmitted light during absorption in sample. When examining departures from the Beer-Lambert law in existing literature, the focus often centres around Equation (1) and observations of deviations from the expected linearity between absorbance and concentration in this particular relationship[1]because of these deviations have been attributed to the presence of fluorescence[11, 12], the incorporation of optical filters along the trajectory of the beam [13], scattering [14, 15], instrumental effects [16], characteristics intrinsic to the specific spectral line (atomic absorption spectroscopy)[17], the existence of surplus indicator [18], the refractive index of the solvent [19], additionally, a dependency on concentration in the molar extinction coefficient[20]. It's very crucial to explain the deviation from the linear relationship between absorbance and sample concentration.

In this letter, we investigate the molecular absorption spectra of 1,4-diamino anthraquinone at various concentrations and evaluate the corresponding absorbance values. Our experimental findings reveal a departure from linearity in the relationship between absorbance and sample concentration. To elucidate this observed deviation, we present a quantum mechanical model that offers insights into the behaviour of absorbance and its correlation with the wavelength of the incident light and the duration of interaction with the sample during the molecular spectra & transition of electrons caused by their interaction with photons. In this study, we extend our investigation by establishing fundamental equations that elucidate the intricate interplay between electromagnetic waves and the wave function of photons. Building upon existing knowledge in quantum electrodynamics, our research delves into the quantum nature of photons and their interaction with electromagnetic fields. These equations not only shed light on the quantum mechanical be-



Figure 2. [a] and [b] shows the absorption spectra of 1,4-diaminoanthraquinone of concentration $40 \,\mu\text{M}$ and $45 \,\mu\text{M}$ respectively. The peaks at 290 nm, 550 nm, and 590 nm indicate the existence of a band system of energy where absorbance occurs. This wavelength range spans from 220 nm to 820 nm, and there is a contribution from vibrational and rotational energy levels as well. The peaks correspond to electronic transitions between two energy levels of electrons.

haviour of photons but also provide a deeper understanding of their dynamic relationship with electromagnetic waves, offering valuable insights into the fundamental principles governing quantum optics and the behaviour of light at the quantum level. Our findings contribute to the growing body of knowledge in this field, further advancing our comprehension of the quantum world's intricacies. The wavefunction of a particle, Ψ , serves as a foundational representation of its quantum state, encapsulating essential details about its probability distribution in both space and time. In our research, we put forth the proposition that the relationship between the electric field and the wave function is profoundly interconnected.

Absorption Spectra- Absorption spectra of 1,4-diaminoanthraquinone (see Fig. 2) arise from the interaction between matter, such as atoms, molecules, and electromagnetic radiation (photons). particularly visible or ultraviolet light, we measured absorbance by instrument uv 2700 UV-vis spectrophotometer Shimadzu At $20 - 90 \,\mu\text{M}$ concentration, we can see from the graph there exists peak absorbance 0.3153,0.1620 and 0.1642 at 250nm, 550nm and 590nm respectively at $20 - 90 \,\mu$ M. They offer critical insights into the energy levels and electronic structure of these entities. Molecules possess quantized energy levels of electronic, vibrational and rotational energy, with electrons occupying specific discrete orbitals, including the ground state and various excited states. When electromagnetic radiation (photons) encounters matter, it can elevate electrons from lower to higher energy levels through electronic excitation, occurring when the photon's energy matches the energy gap between the states.

This absorption process leads to the creation of absorption spectra, graphical representations that reveal which energies or wavelengths of light are absorbed by a substance.

Violation of Beer's Lambert Law and alternate model to explain inherent phenomenon- Experimentally we changed the concentration of 1,4-diamino-anthraquinone from $20 - 90 \,\mu\text{M}$ at stepsize of $5 \,\mu\text{M}$ and we report deviation from the linear dependence of absorbance with concentration. (see Fig. 3). This is attributed to the quantum behaviours of absorbance. We investigated the absorbance process and we have the relationship between the intensity of light and its electric and magnetic field mathematically

$$I_0 = \frac{1}{2}\epsilon_0 E_0^2 c + \frac{B_0^2}{2\mu_0}c$$
(2)

$$I = \frac{1}{2}\epsilon_0 E^2 C + \frac{B^2}{2\mu_0} C$$
 (3)

Where E_0 is the electric field of the incident light, E is the electric field of transmitted light, ϵ_0 is the electric permittivity of a vacuum and μ_0 is Magnetic permeability, we also have

$$B_0 = \frac{E_0}{c}, B = \frac{E}{C} \tag{4}$$

The fundamental relationship between the intensity of light and the electric field of light is a central concept



Figure 3. [a]. The nonlinear dependence of Absorbance vs Concentration at 250nm Wavelength of light, green colour line represents the fitting function.[b]. The nonlinear dependence of Absorbance vs Concentration at 550nm Wavelength of light, the blue colour line represents the fitting function. [c]. The nonlinear dependence of Absorbance vs Concentration at 590nm Wavelength of light, the red colour line represents the fitting function.

in the study of electromagnetic waves, with direct implications for various optical phenomena. In this context, the amplitude of the electric field (E) characterizes the strength and direction of the oscillating electric field at a specific point in space, representing the wave's magnitude. It is essential to note that the amplitude of the electric field is directly linked to the magnitude of the wave itself; consequently, an increase in wave amplitude corresponds to a larger maximum value for the electric field. Intensity (I), on the other hand, provides a measure of the power per unit area conveyed by an electromagnetic wave and is a scalar quantity. A crucial relationship exists between intensity and the square of the electric field amplitude, expressed mathematically as $I \propto E^2$. This proportionality underscores that light intensity is directly proportional to the square of the amplitude of the electric field. We substitute the magnitude of incident intensity from Equation (2) and the magnitude of output intensity from Equation (3) to Equation (1), and we get a fundamental equation which can expressed mathematically:

$$A = \ln\left(\frac{\epsilon_0 E_0^2 c}{\epsilon_0 E^2 c}\right) \tag{5}$$

$$E = e^{-A/2} E_0 \tag{6}$$

Equation (6) describes the relationship between the magnitude of the initial electric field and the magnitude of the final electric field, absorbance plays a vital in this equation, it is intricately connected with the decrement of intensity of photon, hence decrement of electric and magnetic field.

We propose a relationship between the wavefunction of photons and the electric field and magnetic field generated by the same photon is described through the concept of the photon's wave-particle duality. Photons are quantum particles of light, and their behaviour can be described by both wave and particle-like properties. The wave function of a photon is typically associated with its electric and magnetic fields. For a single photon, the wavefunction (Ψ) can be described as a function of the electric field (**E**) and magnetic field (**B**) vectors. In the context of quantum electrodynamics (QED), the wavefunction for a photon can be expressed as:

$$\Psi(\mathbf{r},t) = \frac{1}{\sqrt{2}} \left(\frac{\mathbf{E}(\mathbf{r},t)}{E_0} + i \frac{\mathbf{B}(\mathbf{r},t)}{B_0} \right)$$
(7)

In this equation: $\Psi(\mathbf{r}, t)$ represents the wavefunction of the photon, which is a function of position \mathbf{r} and time t. $\mathbf{E}(\mathbf{r}, t)$ and $\mathbf{B}(\mathbf{r}, t)$ are the electric and magnetic field vectors of the photon, respectively. \mathbf{E}_0 and \mathbf{B}_0 are normalization constants. This wavefunction describes the quantum state of a single photon and relates it to its associated electric and magnetic fields. It illustrates the wave-particle duality of photons, where they exhibit both wave-like and particle-like properties. The electric field (\mathbf{E}) and magnetic field (\mathbf{B}) are intimately connected in electromagnetic waves, and this wavefunction captures that relationship in the quantum description of photons. Equation (7) can also be written as:

$$\Psi(\mathbf{r},t) = \frac{1}{\sqrt{2}} \left(\frac{1}{E_0} + \frac{i}{B_0 C}\right) E(r,t) \tag{8}$$

After the substitution of values of Electric and Magnetic field from equation (8), the equation (6) can be expressed as:

$$\Psi(\mathbf{r},t) = e^{-A/2}\Psi_0(r,t) \tag{9}$$

In the above equation: $\Psi(\mathbf{r}, t)$ represents the wavefunction of the transmitted photon and $\Psi_0(\mathbf{r}, t)$ represents the wavefunction of the incident photon. We establish the intricate relationship between absorbance and time evolution of the wavefunction of photons. The equation $\Psi(\mathbf{r},t) = e^{-A/2}\Psi_0(\mathbf{r},t)$ carries profound physical implications within the context of photon interactions. Here, A signifies the absorbance, a measure of how much incident light is absorbed as it traverses through a medium. The wavefunction $\Psi(\mathbf{r}, t)$ describes the quantum state of the transmitted photon, while $\Psi_0(\mathbf{r},t)$ represents the wavefunction of the incident photon. The exponential factor $e^{-A/2}$ embodies the probability amplitude for the photon to be absorbed during its interaction with the medium. As A increases, signifying higher absorption, the amplitude of the incident photon's wavefunction diminishes, indicating a higher likelihood of absorption. This equation elegantly encapsulates the quantum nature of photon-matter interactions, where absorption probabilities are inherently entwined with the wave-like behaviour of photons. It provides a crucial link between the macroscopic property of absorbance and the microscopic behaviour of individual photons, furthering our understanding of the quantum world's intricacies and paving the way for advancements in quantum optics and spectroscopy.

Quantised Absorbance in Beer's Lambert Law-We have an equation in Quantum Mechanics Describing the time evolution of wave function expressed mathematically:

$$\Psi(\mathbf{r},t) = \Psi_0(\mathbf{r},t)e^{-iE_nt/\hbar}$$
(10)

The equation $\Psi(\mathbf{r}, t) = \Psi_0(\mathbf{r}, t)e^{-iE_nt/\hbar}$ represents a fundamental concept in quantum mechanics known as the time-dependent Schrödinger equation. This equation plays a central role in describing the quantum behaviour of particles, such as electrons, atoms, and molecules. Let's break down the components and significance of this equation:

 $\Psi(\mathbf{r},t)$: This is the time-dependent wavefunction of a quantum system, which describes the state of the system at a given time t and position \mathbf{r} . The wavefunction encodes information about the probability distribution of finding a particle at a specific position and time. $\Psi_0(\mathbf{r}, t)$: This part of the wavefunction represents the initial state of the quantum system at time t = 0. It contains information about the particle's initial position and any other relevant initial conditions. E_n : This represents the total energy difference of the quantum system, which includes both the kinetic and potential energy of the particle or particles in the system. t: Time is a fundamental parameter that indicates when the wavefunction is evaluated. It describes the evolution of the quantum system over time. \hbar : The reduced Planck constant is a fundamental constant in quantum mechanics, linking the quantum world with classical physics. It has a value of approximately $1.0545718 \times 10^{-34}$ joule-seconds.

The exponential term $e^{-iE_nt/\hbar}$ in the equation describes the time evolution of the wavefunction. It is associated with the energy difference E_n of the system. The presence of i in the exponent indicates oscillatory behaviour, which is a characteristic of quantum systems. The factor \hbar in the denominator scales the energy with respect to the fundamental quantum of action. In essence, the equation describes how the wavefunction $\Psi(\mathbf{r},t)$ of a quantum system changes with time. It provides insights into the dynamics of quantum particles and how their quantum states evolve over time. The Schrödinger equation is a cornerstone of quantum mechanics, guiding our understanding of the behaviour of matter at the atomic and subatomic scales. It allows us to calculate the probabilities of different quantum states and make predictions about the outcomes of experiments in the quantum realm. Let's recompile the original proposition; violation of Beers Lambert Law and investigate equations (9) and (10)

$$e^{-A/2}\Psi_0(r,t) = \Psi_0(\mathbf{r},t)e^{-iE_nt/\hbar}$$
 (11)

We get a relationship between absorbance, energy of photon and time of interaction, that can be mathematically expressed as

$$A = 2iE_n t/\hbar \tag{12}$$

The equation $A = \frac{2iEt}{\hbar}$ connects the concept of absorbance (A) in molecular spectroscopy to the energy difference (E_n) of a photon, the time (t) of interaction with a molecular sample, and the reduced Planck constant (\hbar) . Absorbance (A): Absorbance is a measure of how much light is absorbed by a substance as it passes through it. It quantifies the reduction in the intensity of incident light due to interactions with the molecules in the sample. i: i is the imaginary unit, and it introduces the complex nature of the absorbance. In molecular spectroscopy, complex numbers are used to describe how light interacts with molecules. The imaginary part often represents the phase of the absorbed light. Energy of Photon (E_n) : E_n signifies the energy difference of the initial state and final state of the interacting photon with 1,4 -diamino anthraquinone, When a photon interacts with a molecule, it can transfer its energy to the molecule, leading to electronic transitions or other forms of excitation. The energy of the photon is a fundamental parameter in understanding these interactions. Time of Interaction (t): t represents the duration of interaction between the photon and the molecular sample. It characterizes how long the photon interacts with the sample and influences the extent of excitation or absorption. Reduced Planck Constant (\hbar): The reduced Planck constant (\hbar) is a fundamental constant in quantum mechanics. It relates the energy of quantum states to their frequency or angular frequency. In this equation, \hbar scales the relationship between absorbance, photon energy, and interaction time.

The equation $A = \frac{2iE_nt}{\hbar}$ essentially describes how the absorbance of light in a molecular sample is connected to the energy difference between to initial and final state of the photon, the duration of their interaction, and the fundamental quantum properties represented by \hbar . The complex nature of the equation accounts for both the magnitude and phase of the absorbed light, providing a comprehensive description of the absorption process in molecular spectroscopy. This equation is significant in understanding the quantum mechanics of photon-molecule interactions, which underlie various spectroscopic techniques, including absorption spectroscopy, where it helps quantify the extent of absorption and the associated complex phase behaviour.

The energy difference of photons is quantized and can be mathematically expressed as

$$E_n = \frac{hc}{\lambda\alpha} \tag{13}$$

The equation $E_n = \frac{hc}{\lambda \alpha}$ embodies a fundamental relationship in physics that links the energy difference (E_n) of a photon to its wavelength (λ) in the molecular sample. This equation emerges from the fusion of two key constants: h, the Planck constant, and c, the speed of light in a vacuum. E_n represents the energy difference of a photon, a discrete packet of electromagnetic radiation. hstands for the Planck constant, a universal constant that underpins quantum mechanics and governs the quantization of energy. c denotes the speed of light, a universal constant showcasing the speed limit of information transmission in the cosmos. λ signifies the wavelength of the photon, denoting the spatial extent of one complete oscillation of its electromagnetic field. α stands for the refractive index for the sample in which photons interact. This elegant relationship lies at the heart of our comprehension of the wave-particle duality of light and guides the development of countless technologies and experiments in the realm of optics and quantum mechanics. After substituting the value of photon energy, equation (12) can be mathematically expressed as:

$$A = \frac{4\pi i c t}{\lambda \alpha} \tag{14}$$

The investigation of the aforementioned equation reveals a profound connection, asserting that absorbance is intricately dependent on two critical factors: the duration of interaction between photons and the molecular sample, and the wavelength of incident light. This fundamental relationship sheds light on the intricate dynamics governing the absorption of light by molecules and underscores the pivotal role played by the temporal and spectral characteristics of photons in this process. Such insights hold significant implications for diverse scientific disciplines, from spectroscopy to quantum optics, offering new avenues for precise control and understanding of light-matter interactions at the quantum level. We measured the value of absorbance at peak as 0.0712 (a.u) for 20μ M molecular sample at 550nm wavelength of light and the refractive index of 1,4 -diamino anthraquinone is taken as 1.65. We calculated the duration of interaction between the photon and molecular sample as 17.14×10^{-18} seconds.(see Fig. 4) for the time span of the interaction of 1,4 -diamino anthraquinone and concentration, it is important to note that the time span of interaction depends on the concentration of the sample following a similar type dependence between absorbance vs concentration. Equation (14) can also be expressed mathematically

$$A = \frac{4\pi i cnt_s}{\lambda \alpha} \tag{15}$$

The investigation of the aforementioned equation establishes quantisation of absorbance, here t_s is the time span of the interaction of single electron excitation during photon and molecular interaction, it is characteristic of a specific sample and n is an integer.

In conclusion, Contrary to the anticipated linear relationship between absorbance and concentration at a fixed wavelength, our findings illuminate a non-linear correlation, emphasizing the critical role of the time of interaction with the molecular sample. We investigated a series of "stairs steps" relationships between absorbance and concentration because of the quantized behaviour of absorbance. Furthermore, introducing a nuanced perspective to the understanding of photon-matter interactions. Central to our contributions is the development of a uni-



Figure 4. shows the time span of the interaction of the molecular sample with varying concentrations of 1,4 -diamino anthraquinone

versal equation capable of predicting the future wavefunction of photons. Our experimentation, focusing on the exposure of photons to 1,4-diamino anthraquinone, has yielded unprecedented temporal resolution, detecting interactions on the 17-96 attosecond timescale. This observation provides a remarkable glimpse into the ultrafast dynamics of photon-matter interactions, specifically with single excitations of electrons. Notably. These findings not only advance our understanding of fundamental physical processes but also open avenues for further exploration in the realms of quantum mechanics and material science.

Acknowledgement: We acknowledges CSIR (Grant No. 09/1059(11052)/2021-EMR-I) for funding to support this research. We thank Bhuvan Upadhyay for support during experimental setup.

* s21ph09010@iitbbs.ac.in

- Mayerhöfer, T. G., Mutschke, H., & Popp, J. (2016). Employing theories far beyond their limits—the case of the (Boguer-) beer–lambert law. ChemPhysChem, 17(13), 1948-1955.
- [2] Atkins, P., & De Paula, J. (2006). Physical chemistry (Vol. 1). Macmillan.
- [3] T. Engel, P. J. Reid, W. Hehre, Physical Chemistry,

Pearson, Upper Saddle River, NJ, 2013

- [4] N. Colthup, Introduction to Infrared and Raman Spectroscopy, Elsevier Science, London, 2012
- [5] P. Larkin, Infrared and Raman Spectroscopy; Principles and Spectral Interpretation, Elsevier Science, Amsterdam, 2011
- [6] B. Schrader, Infrared and Raman Spectroscopy: Methods and Applications, Wiley-VCH, Weinheim, 2008
- [7] P. R. Griffiths, J. A. De Haseth, Fourier Transform Infrared Spectrometry, Wiley, Hoboken, 2007
- [8] K. E. Peiponen, E. M. Vartiainen, T. Asakura, Dispersion, Complex Analysis and Optical Spectroscopy: Classical Theory, Springer, Berlin, Heidelberg, 1998.
- [9] L. A. Nafie, Vibrational Optical Activity: Principles and Applications, Wiley, Chichester, 2011
- [10] B. C. Smith, Fundamentals of Fourier Transform Infrared Spectroscopy, Second Edition, CRC Press, Boca Raton, FL, 2011
- [11] J. B. Davenport, Analyst 1953, 78, 558–558
- [12] H. E. Ungnade, V. Kerr, E. Youse, Science 1951, 113, 601
- [13] E. Rottmann, Acta Histochem. 1954, 1, 97–110.
- [14] H. E. Rose, Nature 1952, 169, 287-288
- [15] G. Zaccanti, P. Bruscaglioni, J. Mod. Opt. 1988, 35, 229–242
- [16] K. Buijs, M. J. Maurice, Anal. Chim. Acta 1969, 47, 469.
- [17] I. Rubeška, V. Svoboda, Anal. Chim. Acta 1965, 32, 253–261
- [18] A. A. Elsirafy, Appl. Spectrosc. 1981, 35, 603-605.
- [19] L. H. Garcia-Rubio, Macromolecules 1992, 25, 2608–2613.
- [20] P. Wittung, J. Kajanus, M. Kubista, B. G. Malmström, FEBS Lett. 1994, 352, 37–40.