Fluorescence: From Infancy to Stokes.

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Abstract: Fluorescence spectroscopy is a very emerging multidisciplinary field of research and its application covers a wide range from physical to chemical to medical sciences. This mini-review is a flash back of its development from early era up to the modern interpretation by Gabriel Stokes. This review will particularly help the undergraduates to create an interest about spectroscopy among them.

Keywords: Luminescence, Fluorescence, Phosphorescence, Incandescence, Stokes Shift, Fluorspar.

I. INTRODUCTION

Let start with the question- what is meant by the term ‘Luminescence?’. Luminescence is basically emission of light by a material without ‘heating’ the emitting material. That means it is the emission of ‘cold-light’ (opposite of incandescence). This mini-review aims to provide a brief of evolution of the discoveries of so called ‘Fluorescence’ up to the time of Stokes. Luminescent materials may be of different kinds- organic, inorganic or organo-metallic types. Emission of light occurs from an electronically excited molecule. Again, luminescence may be of various types depending upon the source of excitation, e.g., Photoluminescence, Electroluminescence, Chemiluminescence, Bioluminescence, Sono-luminescence etc.

II. PHOTOLUMINESCENCE AND FLUORESCENCE

In this article, we’ll talk about only the materials which show photoluminescence. Photoluminescence is the emission of photons from an excited species when the excitation is executed via absorption of light. Two well-known types of photoluminescence are fluorescence and phosphorescence. First reported observation of cold light emitting material came in the literature in the long back in 1565 (in fact, that is the first reported observation of fluorescence). Nicolas Monardes, a spanish physician was the first person to observe that phenomenon of fluorescence and describe the strange blue colour from a water extract of wood of plant of *Lignum Nephriticum* [1,2].

III. PHOTOLUMINESCENCE AND PHOSPHORESCENCE

Another breakthrough in the history of luminescence is the discovery of Bologna Stone by Italian Cobbler-alchemist, Vicenzo Cascariolo, in 1602. He calcinated the Bologna Stone and obtained a strange substance which glowed in the night. In fact, this was the first reported case of phosphorescence. It was later established that the phosphorescence was due to the formation of Barium Sulfide from Bologna Stone which contains Barium Sulfate.

IV. AN UNDERSTANDING OF EMISSION OF COLD LIGHT

Famous names in the 17th century like Robert Boyle (1626-1691) and Isaac Newton (1626-1727) also tried to understand the phenomenon of the origin of this type of ‘cold light’. They found that dilute solution is more apparent for exhibiting the luminescence properties (the term *Luminescenz* was introduced by Eilhardt Weidemann much later in 1888). A little progress was made in 18th century in understanding this phenomenon of strange light. But to make understand this occurrence of cold light from certain materials, one should have a detailed idea about how light interact with matter. Newton had already discovered the dispersion of light, i.e., the light is composed of seven colors and can be splitted up. Under this influence of Newtonian school, people tried to explain this peculiar color based on the scattering and dispersion of light. The work of David Brewster (1781-1868)[3]* and John Herschel (1792-1871)[4] may be recalled in this context. Brewster, in 1833, observed a red color from an alcoholic solution of green leaf (chlorophyll) and also reported a blue light from fluorspar (a mineral containing Calcium Fluoride), when exposed to white light beam. He tried to explain this effect as an outcome of scattering or dispersion of light. Herschel’s work was remarkable. He studied the solution of quinine sulphate and also performed a rough spectral analysis that time! He showed that apparent blue color of quinine sulphate is made up of three colors, viz., blue, green and a little bit yellow. *But that can be observed only when the solution of quinine sulphate can be illuminated by blue end of the spectrum of white light and not the red end.* This was indeed a wonderful observation and unfortunately, he couldn’t realize the observed light is of longer wavelength than the incident light rather he described the blue color as a form of ‘surface dispersion’. His work was very influential and Stokes used same solution for his famous experiment. Becquerel’s family had also an outstanding contribution in luminescence. Edmond becquerel (father of Henry Becquerel, inventor of radioactivity) along with his contribution in the development of photovoltaic cell, he studied the color displayed by Calcium Sulfide and was the first to report that emitted light is of *longer wavelength* than incident light in 1842[5,6]. In 1858, he also developed a phosphoroscope.

*Brewster also published a biography of Sir Isaac Newton in 1831 and examined many Newton’s work. Therefore, it was a high chance that he inclined towards Newtonian’s thought and tried to understand his findings.

Before going into Stoke’s pioneering work, it would be worth recalling the discovery of absorption and emission spectrum from the middle of 18th century up to 50s of 19th century[7]. Melville (1756)[8] observed the characteristics light from metal salts in presence of alcohol (emission). The study of James Gregory (1785) and Fraunhofer (1821) further helped to understand the dispersed spectra in more details. Wheastone (1835) also observed that the metals can be differentiated by emitted light. In the contemporary period of Stoke, many Great of nineteenth century tried to explain many experimental facts based on absorption by the materials, followed by emission. The list includes names like Foucault (1849), Angstrom (1853) etc. All these findings and theories might create a mindset of Stokes to explain the observed light from quinine sulfate solution from a different angle. Stoke's experiment was very simple. He allowed various part of the light to pass through a solution of quinine sulfate and nothing happened when visible part of the light interacted with the solution. But the 'invisible light' (ultraviolet region) made an astonishing change. The colourless solution suddenly glowed when exposed to ultraviolet light. This was practically making an 'invisible' into 'visible' and was really exciting! Stoke published all his findings in *Philosophical Transaction* in a monumental paper [9,10] in 1852. He introduced the term 'Fluorescence' and rationalized the 'Bright light' from quinine sulfate solution as an outcome of absorption of light of shorter wave-length and emission of longer wave-length. This shifting of wave-length from shorter to longer later became 'Stokes Shift'. He also explained the dependence of fluorescence on concentration and also threw light on how it could be used as an analytical tool [11]. After Stokes, the study of fluorescent materials continued to expand and a remarkable development occurred during the first half of twentieth century and in particular, the contribution of J. Perrin and F. Perrin [12] was noteworthy. The subject has now become an important multidisciplinary field and finds its application in diverse areas of Physics, Chemistry, Biology and medicine.

V. Conclusion

The development of fluorescence involved many greats from 16^{th} to 20^{th} century, particularly its development in the early days was very spectacular. Any science graduate may find this review useful as this may create an interest about spectroscopy, if they embark upon a research career.

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