PHOTOELECTRICITY WITHIN CLASSICAL PHYSICS: FROM THE PHOTOCURRENTS OF EDMOND BECQUEREL TO THE FIRST MEASURE OF THE ELECTRON CHARGE

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In the literature we first find the denomination '*photoelectric effects*' as referred to the electric effects of light in relation with chemical action: these researches stemmed from the investigations on the properties of light. In 1839 Edmond Becquerel noticed that '*By the action of a beam of sun light over two different liquids, chemically interacting and carefully superposed in a glass container, an electric current was developed, as indicated by a very sensitive galvanometer connected with two platinum plates dipping in the two different solutions.*'[1] This observation was followed by other works by Becquerel himself and by others, all of them concerned with the action of light on chemical reactions, through which electrical effects could be produced. These phenomena were acknowledged as very complicated and can hardly be considered as photoelectric effects, but gave rise to a chapter of chemistry (the actino-chemistry) and to a large number of empirical results, although of very difficult interpretation. Up to the turn of the century, works of this kind were carried out without a clear understanding of the complicated phenomenology under study and without any interaction with the main stream of research on what is now called the photoelectric effect.

It was from a completely different line of research (Maxwell's electromagnetic theory) that came Hertz's discovery. In 1887 he wrote a paper '*On an effect of ultraviolet light upon the electric discharge*', observed while he was working on the effects of resonance between very rapid electric oscillations.[2] The first observation was actually fortuitous. Two electric sparks were produced simultaneously in an induction coil: when a case screened the second spark from the first one, the maximum spark length became decidely smaller. The development of the paper is logical and leads to clear conclusions:

[1]E. Becquerel, *La lumière: ses causes et ses effets*, tome second, Paris (1867), p. 122.

[2]H. Hertz, 'Über eine Anfluss des ultravioletten Lichtes auf die electrische Entladung', *Annalen der Physik und Chemie*, 31 (1887), 983-1000.

'*The light of the active spark must be regarded as the prime cause of the action... the observed phenomenon... must... be solely an effect of the ultraviolet light.*' Among other things, Hertz investigated also the effect of rarefaction, the behaviour of different materials and of different parts of the passive spark. In particular, it turned out that the action '*takes place near the poles, more especially near the negative pole.*' However, '*whether the effect is produced entirely at the cathode, or only chiefly at the cathode, I have not been able to decide with certainty.*' On this point a definite answer came one year later from Wiedemann and Ebert,[3] who recognized that the action takes place only at the negative electrode.

As a matter of fact, it must be stressed that Hertz's paper traced a full research program. The following works (by Hallwachs, Stoletow, Righi, Elster and Geitel) collected a conspicuous amount of experimental results and lead to several conclusions as far as the various properties of the effect and its dependence on several parameters were concerned. However, they lacked the methodological clarity of Hertz's paper.

We shall now review the main results obtained by these authors in the period ranging from 1888 to 1897, and we shall try to clarify the relation between the photoelectric effect and the research that was developing on the electrical discharge in gases and on cathode rays. As it is well known, this research would have lead to the discovery of the electron and to a new understanding of the structure of matter.

Righi, Hallwachs and Stoletow made contemporary experiments on the behaviour of conductors, negatively charged or neutral, exposed to ultraviolet light. From the point of view of the interpretation of the phenomenology, we can say that Hallwachs was the only one who cared about what is happening inside the metal surface: '*It seems to me as most probable ...that it takes place at the surface* [of the metal], *in some way, a separation of the electric charges*'.[4] Both Righi and Hallwachs, after having investigated the discharge of charged metals by ultraviolet light, made experiments with metals '*in the natural state*'; here the priority goes to Righi.[5].

According to all these authors, the charge carriers were negatively charged atoms or molecules of the gas, adherent or surrounding the metal surfaces. The idea that the gas molecules were the charge carriers and, consequently, a necessary component of the phenomenon observed, was so deeply rooted that

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[3]E. Wiedemann, H. Ebert, 'Über den Einfluss des Lichtes auf die electrischen Entladungen', *Annalen der Physik und Chemie*, 33 (1888), 241-264.

[4]W. Hallwachs, 'Über den Einfluss des Lichtes auf electrostatisch geladene Körper', *Annalen der Physik und Chemie*, 33 (1888), 301-312, p. 311.

[5]A. Righi, 'Di alcuni nuovi fenomeni elettrici provocati dalle radiazioni - Nota V', *Rendiconti della Reale Accademia dei Lincei*, 4, II (1888), 16-19.

it was not dismissed, even when both Righi and Stoletow made a series of experiments in rarefied air. Stoletow went so far as saying: '*Even in extremely rarefied air the actinic current was far from being zero; I am not able to say whether this depends on the imperfection of the vacuum or on the sensitivity of my apparatus.*'[6] This strong belief may appear peculiar from our point of view; but, in line with the general knowledge of the structure of matter of those times, the only possible alternative was that put forward in 1889 by Lenard and Wolf: electrical discharges in gases were to be attributed to '*charged dust*', released from the metallic electrodes or from the glass walls of the tube. Accordingly, in photoelectric experiments, a direct action of light on the metal surface could produce the emission of '*metallic dust*'.[7] According to J. J. Thomson, '*The experiments of Lenard and Wolf do not establish which is the seat of electrification, whether the gas or the metallic dust... we have to rely on the indirect proofs given by the laws that describe the convection currents released from the illuminated surface. Apparently they show that the gas plays an important role in the discharge phenomena.*'[8] Actually, the '*dust*' hypothesis was dismissed in the main stream of investigations and the essential role played by the gas generally acknowledged.

Among the contributions between 1888 and 1897 it is important to quote some other experiments by Stoletow. Stoletow studied the dependence of the photoelectric current on the distance of the electrodes (at atmospheric pressure) and on the pressure, when the potential difference between the elctrodes is varied. In the latter case he found that, at low pressures, the intensity of the current was independent from the potential difference. As we have already mentioned, Stoletow had no doubt about the role of the gas particles and no interest in what was happening inside the metal, in spite of his admission that the effect can happen '*at the expense of radiation*' through a process of '*absortion of light*' from the negative electrode. So, the clue to the understanding of the insignificant role of the gas was neglected and the difficulties of interpretation of low pressure measuremets shifted the interest towards experiments at higher pressures: in some respect, the photoelectric effect became a tool for investigating the electrical conduction of gases.

In this context, it is interesting to see how J.J. Thomson commented Stoletow's results in a book published in 1897: '*The curves show that at very low pressure the current is independent of the intensity of the electric field;*

[6]M.A. Stoletow, 'Suite des recherches actino-électriques', *Compets Rendues*, 107 (1888), 91-92, p. 92.

[7]P. Lenard, M. Wolf, 'Zerstäuben der Körper durch das ultraviolette Licht', *Annalen der Physik und Chemie*, 37 (1889), 443-456.

[8]J.J.Thomson, *Les discharges éléctriques dans les gaz*, Paris, (1900), p. 56. The english edition is dated 1897.

therefore, it is a saturation current.'[9] The account of Thomson is somehow surprising, especially if we consider that, some chapters later, the existence of the electron is clearly recognized. Nevertheless, he writes: '*This fact* [i.e. the existence of the saturation current] *could prove that, in this case, the current carriers are either the mercure vapours of the pump or the particles removed from the metal surface.'*[10]

A large number of experiments were carried out by Elster and Geitel between 1889 and 1895; we will mention only some of them. An important investigation of these authors concerned '*The influence of a magnetic field on the photoelectric discharges in a rarefied gas*'.[11] The interpretation was in favour of an '*electrodynamic deviation of the lines of force through the gas*', and as a consequence, the authors considered more probable that the particles of the gas (and more specifically of the free gas) assume a charge during the contact with the illuminated surface, thus becoming the charge carriers. In another paper, Elster and Geitel tried to classify metals according to their '*photoelectric sensitivity*': they found that the more electropositive a metal is, the greater is its sensitivity. Therefore, they can be ordered as in Volta's series[12] (Righi too obtained similar results, not always consistent). The same authors verified the unipolarity of the effect,[13], a matter that had been for a long time controversial, especially after the works of Branly (1891-93).[14]

On the whole, it appears that experimenters faced a very complicated phenomenology and collected a huge amount of experimental results. However, the general conception of the strcuture of matter focused their attention on the gas rather than on the interaction between light and the metal surface.

Things could be made clearer only after the identification of some characteristics of cathode rays. In 1897 J. J. Thomson determined the ratio m/e for cathode rays, which was found to be about $10^{-7}\, g\, (e.m.u)^{-1}$, that is about 1000 times smaller than that of the hydrogen ion. This result, together with other properties of cathode rays, suggested to Thomson the idea that matter is composed of particles ('*corpuscules*') much smaller than atoms.[15] Thereafter, Thomsom looked for a measure of the charge of the '*corpuscle*'. He first worked

[9] J.J. Thomson, (footnote 8), p. 59-60.

[10] Ibidem.

[11] J. Elster, H. Geitel, 'Über den hemmenden Einfluss des Magnetismus auf lichtelectrische Entladungen in verdüntenn Gasen', *Annalen der Physik und Chemie*, 41 (1890), 166-176.

[12] J. Elster, H. Geitel, 'Über die durch Soonenlicht bewirkte electrische Zerstreuung von mineralischen Oberflächen', *Annalen der Physik und Chemie*, 44 (1891), 722-736.

[13] J. Elster, H. Geitel, 'Über die angebliche Zerstreuung positiver Electricität dur Licht', *Annalen der Physik und Chemie*, 57 (1895), 24-33.

[14] See for instance: E. Branly, 'Déperdition des deux électricités par les rayons très réfrangibles', *Comptes Rendues*, 114 (1892), 68-70.

[15] J.J.Thomson, 'On cathode rays', *Philosophical Magazine*, 44 (1897), 293-316.

on gases ionised by X rays;[16] then, he switched to the photoelectric effect. The property of the photoelectric charge carriers of becoming nuclei of vapour condensation allowed the measurement of e; their property of being deviated by a magnetic field assured the measure of e/m. The values were found to be in good agreement with the charge of the hydrogen ion obtained from electrolitic experiments and with the ratio e/m previously found for cathode rays.[17]

An independent investigation was carried out by Lenard who, on the basis of measurements of the ratio e/m for the photoelectric charge carriers in good vacuum, suggested that they could be slow cathode rays. Merritt and Stewart carried out similar experiments showing '*the development of cathode rays by ultra-violet light*'.[18]

The way was open to the interpretation of the photoelectric effect as emission of '*corpuscles*' (Thomson) or '*quanta of electricity*' (Lenard) from the illuminated electrode. But why only then? As we have seen, many experimental facts had been there for a long time, and some of them have been explicitly quoted by Thomson (Elster and Geitel), Lenard (Righi), Merritt and Stewart (Righi) in their conclusive papers. But in order to become readable they needed a new conception of the structure of matter, that came from the apparently different field of research of cathode rays. It was only at that point that the importance of studying separately the emission of '*corpuscles*' (photoelectric effect) and their transport through the gas (discharge process), became clear.

Thereafter, many new problems woud have arisen from the investigation of the interaction between radiation and matter; but this is a new story.

[16] J.J.Thomson, 'On the charge of electricity carried by the ions produced by Röentgen rays', *Philosophical Magazine*, 46 (1898), 528-545.

[17] J.J.Thomson, 'On the masses of the ions in a gas at low pressure', *Philosophical Magazine*, 48 (1899), 547-567.

[18] E. Merritt, O.M. Stewart, 'The development of kathode rays by ultraviolet light', *Physical Review*, 11 (1900), 230-250.