THE OZONIZER AND THE "LIGHT EFFECT"

By S. Deb and (Miss) N. Ghosh

The paper first reviews the present state of our knowledge of the so-called "Light Effect" consisting of a sharp decrease of the discharge current in an ozonizer tube on exposure to light. Results of studies made by different workers on the different aspects of the effect, e.g. its dependance on the nature of the gas used, on the intensity and frequency of incident radiation, on the variation of the applied voltage on temperature, on the manner of illumination and on the surface condition of the walls of the discharge space, are collected and systematised. It is shown that for a proper understanding of the effect it is essential that the mechanism of the discharge in the ozonizer be first understood. For this purpose oscillographic records of the discharge current have been made under different conditions ; these are reproduced in the paper. The theory of the effect as originally suggested by Mitra and later developed by the authors is discussed in detail. According to this theory the origin of the effect is to be traced to the action of light on the surface charges (produced under discharge) on the walls of the annular discharge space of the ozonizer tube. Mechanism of the discharge as also that of the formation of surface charge are explained.

The theories proposed by other workers are also reviewed.

Production of ozone by the so-called silent electric discharge has been known for a long time and Siemen s ozonizer, a familiar apparatus in chemical laboratories, was introduced as early as 1858. Though so well known and so widely used for preparation of ozone, the nature of the electrical discharge passing in the ozonizer is by no means simple and has been the subject of many investigations. Unfortunately, the ordinary or even the advanced text-books on chemistry seldom explain the mechanism of the discharge and the average student is left with a vague idea about its role and nature. In recent years the study of the ozonizer discharge has come into prominence in this country because of a curious effect, generally called "A New Light Effect" first noticed by Joshi (*B. H. U. Jour.*, 1943, **8**, 99, *Proc. Indian Sci. Cong.*, 1943, Part II, 74-77). Briefly the effect is as follows :

If the ozonizer, when in action, is flooded with light (visible light including red) the current passing through it is found to decrease markedly. Under optimum condition (using chlorine gas instead of oxygen and at a pressure of a few tens of mm.) the decrease of current might be as much as 94% (Joshi and Deo, *Nature*, 1944, **153**, 434).

The effect seems strange because apparently the action of light, if any, would be to increase the current by promoting ionization. (It should be noted that under special circumstances a "positive" light effect *i.e.*, an increase of discharge current on illumination with light may also be obtained. See Sec. 2). Joshi and his co-workers have studied the various aspects of this effect and have published a large number of notes on the subject. Unfortunately, most of these are only in the form of very short Abstracts in the Proceedings of the Indian Science Congress Association. The purpose of the present paper is firstly, to make a review of the present state of our knowledge regarding the nature of the discharge, secondly, to give a connected account of the experimental

work on the "Light Effect" done so far and thirdly, to make a critical review of the
explanations of the "Light Effect" which have been given. The theory of the effect
as developed by the authors (*Science & Culture*, 1946-47, **12**, 17) of this paper from a
suggestion of Prof. S. K. Mitra is also discussed in fuller detail. It is hoped that the
paper would give a complete picture of the action of the ozonizer and of the light effect
and would thus be of help to the future investigators in the field.

1. EXPERIMENTS WITH OZONIZER : THE MECHANISM OF THE DISCHARGE

Fig. 1(a) shows the experimental arrangement for exciting the ozonizer tube. The

FIG. 1(a)   FIG. 1(b)   FIG. 2
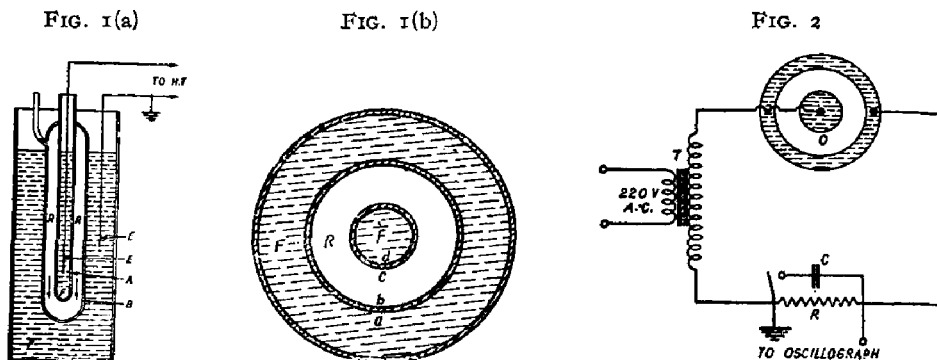

Fig. 1(a). The ozonizer tube. The high tension a. c. flows through the condenser system shown in
        Fig. 1(b). A and B are the two concentric glass electrode surfaces ; FF, the conducting liquid ;
        platinum electrodes EE serve as the leads for the applied voltage ; RR is the discharge space.

Fig. 1(b). Illustrating the condenser system in the ozonizer tube   FF is the conducting liquid plates
        of the condensers. The dielectric is partly glass (ab, cd) and partly the gas in annular space R.

Fig. 2.   Recording of the discharge current by cathode ray oscillograph. The voltage developed accross
        the resistance R is led to the oscillograph. The condenser C can be placed across R if
        desired to by-pass high frequency component of the discharge current.

tube is of the Brodie type and consists essentially of a double-walled glass tube through
which the gas to be subjected to silent discharge flows [Fig. 1(b)]. The inner tube, as
also the outer containing vessel, contain some conducting liquid (e.g. salt solution). The
two conductors are connected to the output of a high voltage transformer (20,000 volts)
capable of yielding a current of several milliamperes. It may be mentioned that the
ozonizer as introduced by Siemen's and also of common use even now employs tin foils
instead of electrolyte solution for electrical contacts.

It is obvious that the ozonizer is in effect a cylindrical condenser as depicted in
Fig. 1(b) of which the conducting elements are the eletrolytes in the inner and outer
cylinders and the dielectric in between is partly glass (ab and cd) and partly air R or
the gas which is being used. From the very nature of the apparatus it is clear that
it will work only with alternating voltage, because it is then and then only that a dis-

placement current can continually flow through the system and produce continuous electrical effect.

As mentioned in the above, the nature of the discharge passing through the ozonizer is by no means simple. Warburg (*Verhand. Deut. Phys. Ges.*, 1903, p. 382) appears to be the first to have recognised this. He and his co-workers made extensive studies both of the physical mechanism of the ozonizer discharge and also of the nature of the chemical reactions proceeding with it. He pictured the action as follows. Assume, for simplicity, that the applied voltage instead of being sinusoidal is alternating between two sharp pulses of values $+E$ and $-E$ volt. If E (say $+E$) is sufficiently large, the insulation of the gas contained in the annular space breaks down and large numbers of positive and negative ions are formed. These are urged towards the two inner electrode surfaces and form surface charges. This gives rise to a field opposed to the externally applied voltage. When this field attains a particular value M, the external field, so far as the discharge is concerned, is neutralised and the discharge stops. Now if the external voltage is switched over to $-E$, the phenomenon is repeated in the opposite direction.

Warburg was, however, careful to point out that the above simple picture is not applicable in the case of an ozone tube operated with alternating voltage, because in that case the external voltage and the opposing voltage set up by the surface charges increase simultaneously making the problem more complicated. St. Sach (*Ann. Physik*, 1915, 47, 886), however, performed experiments with A. C. and showed that the above picture of Warburg provides a useful approach to the actual mechanism of the discharge with A. C. operating voltage.

Very early in course of his investigations Warburg (*Z. tech. Physik*, 1924, 165) discovered that the discharge current had a component, the frequency of which was very high compared to that of the applied alternating voltage. Warburg and Leithauser (*Ann. Physik*, 1903, 28, 1) measured the discharge current both by electrometer and by thermo-junction and observed that the thermo-junction always indicated a stronger current than the electrometer. They traced the origin of this discrepancy to the existence in the discharge current of high frequency components. When the electrometer was used for measurement the high frequency component was largely by-passed through the electrometer capacity as also through the self capacity of the resistance which had been inserted in the circuit for measurement of the voltage. It was, however, observed, that these high frequency currents did not contribute to the ozone formation because the rate of formation remained unaltered even when these high frequency currents were damped out by increasing the value of the resistances in the circuit. Warburg also determined the proportion of the high frequency components, using different resistances, and different amplitudes and frequencies of the applied voltage and with decreasing value of the thickness of the discharge space. The frequency component was found to be $10^5 - 10^6$ cycles/sec.

Warburg, however, did not clearly explain the mechanism of the production of the h.f. currents. This was done by Klemenc, Hintenberger and Höffer (*Z. Eelectrochem.*, 1937, 43, 708) who pointed out that the h.f. currents consist of a great many closely

packed unidirectional pulses rather than h.f. oscillations as originally thought of. These authors investigated the nature of the discharge current with the help of a cathode ray oscillograph (Fig. 2). The discharge current was made to flow through the resistance R and the voltage developed across it was applied to the deflecting plates of the cathode ray oscillograph. The trace on the oscillograph thus depicted the variation of current in the discharge circuit. It was observed that between the current and the applied voltage there was a phase difference of about $\pi/2$. The h.f. phenomena occurred about the points where the current trace on the oscillograph was a maximum that is, when voltage was at its zero value. The authors explained the discharge phenomenon as follows :

The applied A.C. voltage in course of its periodic cycle becomes large enough to produce ionization in the gas. The electrons and the positive ions, thus produced, move in opposite directions under the action of the external field and are deposited as surface charges on the opposite glass walls. These surface charges produce an opposing field in the discharge space so that the resultant field decreases steadily in intensity until it attains a value M at which the ionization and along with it the discharge stops. Now in course of time, as the applied A.C. voltage changes over to the opposite cycle, the external field is removed. The two oppositely charged layers are now free to neutralise themselves. But as the surface charges are on insulating (glass) surface, the neutralisation does not take place in one single spark but in a number of sparks between small isolated elements of surface charges. These sparks constitute the observed high frequency currents superposed on the main current. A study of the oscillograph trace also shows that the high frequency currents are obtained when the applied voltage passes through its zero value.

To test the above hypothesis Klemenc *et al* subjected the ozonizer to high D.C. voltage. No luminous discharge was observed even when the voltage was increased up to 15 Kv. On removing the voltage, however, and at the same time short circuiting the terminals, the whole of the discharge space showed luminous discharge. The explanation, as already stated, is as follows : The high applied field causes ionization in the annular space. The ions produced move in the discharge space and are deposited as surface charges. These layers of charges of opposite sign largely neutralise the applied field in the annular space. On short circuiting the electrodes the surface charges become free to neutralise themselves by sparks in the annular space and produce the observed luminosity.

2. EXPERIMENTAL STUDIES ON THE "LIGHT EFFECT"

As mentioned earlier Joshi has noticed that the discharge current decreases markedly when the ozonizer is exposed to light. A survey of the results of experimental studies on the effect made so far is made below.

Note : A convenient way of expressing the relative magnitude of the effect is to note the percentage of variation. Thus if $|\Delta i|$ be the change in current value (irrespective of sign) and i the original current, then $\dfrac{|\Delta i|}{i} \times 100$ gives the percentage value of the effect. Table I gives a typical set of "light effect" measurement.

TABLE I

Gas used.	Exciting voltage (kV).	Pressure (in mm. of Hg).	Radiation.	% Δi.	Observer.
Cl_2	11.2	596	White light (200 watt lamp).	35	Joshi & Deo (*Nature*, 1944, **153**, 434)
Air	10	8	White light (100 watt lamp).	3 54	Tawde & Gopalkrishnan (unpublished paper)
O_2	10	130	White light (200 watt lamp).	12	Deb & Ghosh (unpublished data)
Cl_2	10.7	260	X-rays	17	Joshi (*Curr. Sci.*, 1944, **13**, 278).
Cl_2	,,	,,	White light (200 watt lamp).	25	,,

(a) *Effect of the Gas used.*—It has been observed that the effect is most marked in chlorine. Under optimum condition it may be as much as 94%. Next in order come bromine, iodine, oxygen, air, nitrogen and hydrogen (Deshmukh, *J. Indian Chem. Soc.*, 1947, **24**, 211 ; Joshi, *B. H. U. Jour.*, 1943, **8**, 99 ; *Proc. Indian Sci. Cong.*, 1943, Part II, 74-77. According to earlier observations by Joshi (*loc. cit. B. H. U. Jour.*, 1943) the effect is not detectible and perhaps absent in monatomic metallic vapours like that of sodium. In a later communication, however, the effect is reported to have been obtained in alkali metals and in mercury using more sensitive detectors and under some special conditions (*Curr. Sci.*, 1947, **16**, 19). For example, a 30% effect was obtained in potassium vapour, near the threshold potential V_m below which the gas in the discharge space is not ionized. The effect has also been observed in a number of compound gases, e.g. SO_2, HCl, NO_2 (*Proc. Indian Sci. Cong.*, 1942, Part III, *Chem. Sec.*, Abs. No. 57 and 62).

According to Joshi (*Curr. Sci.*, 1947, **16**, 19) the magnitude of the effect varies in the same order as the electron affinities of the gases.

(b) *Effect of Change of Pressure.*— Starting from atmospheric pressure and gradually decreasing the same the effect first appears at a particular pressure. It then reaches a maximum value at a particular value of the pressure and then diminishes on further reduction of pressure and ultimately vanishes at about a mm or so. The maximum effect ordinarily occurs at about the middle range of pressures. With chlorine Joshi obtained the optimum effect at 46.5 cm. of pressure (*Nature*, 1944, **153**, 434). The optimum pressure, however, varies with the applied voltage and with the geometry of the tube. The authors of the present note obtained the same with oxygen at about 15 cm. of pressure at 10 Kv.

(c) *Effect of the Applied Voltage and Change of Frequency.*—It has been found that the effect does not appear below the striking potential V_m of the gas. V_m is also called by Joshi (*Curr. Sci.*, 1946, **15**, 281) as the threshold potential. On increasing the voltage beyond V_m both the discharge current and (Δi) increase. The percentage value of the effect, however, does not continue to increase (Joshi and Deo, *Curr. Sci.*, 1943, **12**, 306). It first increases, reaches a maximum value at a voltage slightly in

excess of V_m and then diminishes with further increase of voltage. It has also been found that the proportion of the h. f. current in the discharge (which is the component of the discharge current affected by light) diminishes as the applied voltage is increased (Warburg *Z. tech. Physik*, 1924, 165: Joshi, *Proc. Ind. Acad. Sci.*, 1945, **22 A**, 389 ; Prosad and Jain, *ibid.*, 1947, **25 A**, 515).

The effect also varies when the frequency of the applied voltage is altered (Tewari, *Proc. Indian Sci, Cong.* 1946, Part III, *Phys. Sec.*, Abs. No. 34). Unfortunately there has not been sufficient observations in this connection. From the limited data available, it appears that the effect decreases with increase in frequency and ultimately vanishes at radio frequencies (Tewari and Prasad, *Curr. Sci.*, 1945, **14**, 229 ; Das-Gupta, *Science & Culture*, 1946, **11**, 318). Studies with the latter frequencies, however, is only for very small voltages at which there was no appreciable discharge. Joshi and Lad (*Proc. Ind. Acad. Sci.*, 1946, **22 A**, 293) for instance, obtained a 18% effect at 50 cycles and a 12% effect with 500 cycles in chlorine. 17 kV was used. No effect was observed with 0.94 volt at 5-10 mc/s.

Joshi (*Proc. Ind. Acad. Sci.*, 1945, **22 A**, 389) observed an appreciable effect with uni-directional pulsating voltage, *i. e.*, rectified unsmoothed A.C. voltage.

(*d*) *Effect of Change of Wave-length of the Incident Radiation.*—The effect has been studied with wavelengths ranging from that of ordinary red light to that of the X-rays. (Joshi and Deo, *Curr. Sci.*, 1943, **12**, 306 ; Joshi, *ibid.* 1944, **13**, 278). In the ultraviolet (Joshi, *ibid.*, 1945, **14**, 317) and the visible range the effect generally increases with the lowering of the wavelength of the exciting light. Tawde and Gopalkrishnan (unpublished paper) obtained a linear variation of the percentage value of the effect within the range 6536.7Å-5350.1Å. A threshold value of the wave length at 8021Å was obtained therefrom by extrapolation.

With X-rays a lower value (17%, the corresponding value for white light being 25%) was obtained (Joshi, *Curr. Sci.*, 1944, **13**, 278). However, the two values cannot be compared as nothing is definitely stated about the relative intensities of X-rays and white light. On continuous exposure for half an hour, the decrease became permanent, *i. e.*, the discharge current did not regain its original value when the X-ray tube was switched off. No such permanent effect has been obtained with ordinary light in spite of exposure of several hours for days together.

(*e*) *Effect of Varying the Intensity of the Incident Light.*—Studies with chlorine, iodine and oxygen have shown that the effect depends markedly on the intensity of the incident beam, the variations being more pronounced at lower values of the intensity (Joshi, *Curr. Sci.*, 1945, **14**, 35). The result has been confirmed quantitatively by Tawde and Gopalkrishnan (unpublished paper) for a number of wave-lengths and at different pressures. From a study of the nature of the curves obtained these authors proposed the following relation for the variation of %Δi with the frequency and the intensity of the incident beam :

$$\%\Delta i = A I^{0 \cdot 4} (v - v_0)$$

where A = a constant depending on pressure, nature of the surface of the ozonizer and applied voltage.

ν = wave number of the light used.

ν_0 = threshold frequency (in wave number) below which no effect is obtained

I = intensity of the incident light in lumens.

(f) *Effect of Ageing.*—It has been observed that the production of light effect requires some amount of ageing of the discharge vessel (Goyal, *J. Indian Chem. Soc.*, 1947, **24**, 203). Thus Mohanty and Kamath (*Proc. Indian Sci. Cong.*, 1647, Part III, *Phys. Sec.*, Abs. No. 15) studying with oxygen have observed that the effect is small in a freshly made ozonizer and reaches a constant maximum only after sometime. The authors of the present paper have also observed a similar effect in chlorine and oxygen. It appears that the positive light effect [Sec. 2 (j)] is also affected by ageing, though the results obtained are not yet very clear. Thus Sarma (*Proc. Indian Sci. Cong.*, 1947, Part III, *Phys. Sec.*, Abs. No. 20) reports that the positive effect in iodine obtained by working at low voltage diminishes on prolonged ageing under discharge. But, according to Ranga Raja Rao (*ibid.*, 1947, Part III, *Phys. Sec.*, Abs. No. 18) a reverse effect is obtained in iodine when the wall is coated with KI and I_2 in acetone. Again according to Joshi and Bhatt (*ibid.*, 1942, Part III, *Chem. Sec.* Abs. No. 69) there are three stages $A \rightarrow B \rightarrow C$ in the variation of discharge current with time in iodine vapour. A shows discontinuities ; during B the current fluctuates rapidly and the conductivity increases ; in C the ageing effect is minimum. The transition from A to C depends upon temperature.

(g) *Effect of the Mode of Illumination.*—The light effect depends markedly on the manner in which the discharge tube is illuminated. The effect is found to be definitely higher if the ozonizer tube is illuminated from a side than when axially (Prasad, *ibid.*, 1947, Part III, *Phys. Sec.*, Abs. No. 17). As a matter of fact, it has been reported that with strictly axial illumination the effect is almost absent (Tawde and Gopalkrishnan, unpublished paper). These results are in accordance with the theory that the light effect is a surface phenomenon and does not depend on the volume of the gas brought under the influence of light. For instance, by covering up portions of the discharge tube by means of black paper and also by varying the inclination of the discharge tube to horizontal plane it is found that the effect is directly proportional to the effective area of the electrodes exposed to light.

(h) *Effect of Temperature Variation.*—It is possible that the light effect is affected by a change in the temperature of the discharge tube. The results obtained so far are, however, inconclusive. For instance, Joshi and Kuppuswamy (*ibid.*, 1941, Part III, *Chem. Sec.*, Abs. No. 35) report that the light effect increases with decrease of temperature in the range 7°-75°. But Joshi and Deshmukh (*ibid.*, 1942, Part III, *Phys. Sec.*, Abs. No. 38) report an opposite result. The latter result has been confirmed by Joshi and Kane (*ibid.*, 1942, Part III, *Chem. Sec.*, Abs. No. 60) in bromine and iodine.

(*i*) *Effect of Surface Condition.*—The discharge current, as also the percentage of light effect, is strongly modified when the annular walls of the discharge tube are coated with different substances. Results obtained so far with different wall-coatings and gases in the discharge space are shown below in a tabular form.

TABLE II

Coating material.	Gas used.	Effect.	Observer.
Mixture of KI, I_2 and KCl	Iodine vapour	Positive effect; a marked increase of the discharge current'	Joshi and Murthy (*Proc. Indian Sci. Cong.*, 1942, *Chem. Sec.*, Ab. No. 67)
Solution of KI, I_2 in acetone	Iodine vapour	Negative effect; which decreases with time. After 30 hours' exposure positive effect was observed.	Ranga Raja Rao (*ibid.*, 1947, *Phys. Sec.*, Ab. No. 18).
Solution of I_2 in ether and iodoform deposited on the wall by evaporation.	Chlorine and iodine.	No effect.	Do.
Solution of I_2 in benzene	Chlorine	15% Negative effect.	Ranga Raja Rao (*loc. cit.*) *ibid.*
Solution of I_2 in alcohol	Chlorine	27% Negative effect.	Do.
KI and alcohol	Chlorine	38% Negative effect.	Do.
Iodoform film	Iodine vapour	Negative effect increased from 28% to 30% when iodoform film was decomposed by heating.	Do.
KI with a trace of alcohol	Iodine vapour	1250% increase of current on illumination at *low voltage.* When the voltage was increased a transition to normal negative effect was obtained.	Sarma (*ibid.*, 1947, *Phys. Sec.*, Ab. No. 20).
Coatings of stable alkali chlorides		Current increases but corresponding light effect diminishes.	Cherian (*ibid.*, 1945, *Phys. Sec.*, Ab. No. 17).

(*j*) *Positive Light Effect.*—Under certain experimental conditions the discharge current shows an increase on illumination. The phenomenon is much less general than the negative effect. From observations made on many gases it has been found that the positive effect is generally obtained when the pressure in the discharge tube is comparatively high and the applied voltage comparatively low. The gases studied and the conditions under which a positive light effect has been found is shown in a tabular form below.

TABLE III

Gas used.	Pressure (in mm of Hg).	Exciting voltage.	Observer.
Air	Higher than 16.2	—	Joshi and Rao (*Proc. Indian Sci. Cong.*, 1942, *Chem. Sec.*, Ab. No. 55).
Oxygen	Higher than 22	300—3000 volts (r. m. s.)	Joshi and Cherian. (*ibid.* Ab No. 56).
Iodine	—	150—820 volts	Joshi and Bhatt. (*ibid.*, Ab. No. 61).
Bromine	50	—	Joshi and Raghavan (*ibid.*, Ab. No. 65).
Chlorine	—	—	Do.

Conditions under which a positive light effect is obtained when the walls are coated with different materials are shown in Table II.

(k) *Other Characteristics of the Effect.*—It has been observed that the time lag, if any, between the instant of illumination and the diminution of the current is extremely small (Joshi, *Curr. Sci.*, 1944, 13, 253). The current also ordinarily regains its original value as soon as the light is cut off. The case of X-rays is perhaps an exception to this.

The effect is not potential reversible, *i. e.*, under otherwise identical conditions the effect at a particular voltage is found to depend somewhat on whether the value is established from a higher or from a lower voltage (Joshi and Murthy, *Proc. Indian Sci. Cong.*, 1942, Part III *Chem. Sec.*, Abs. No. 67; Joshi and Raghavan, *ibid.*, Abs. No. 64).

If the pressure is gradually decreased keeping the exciting voltage constant, it is found that at the breakdown point the discharge current is markedly unsteady. If now the tube is exposed to light, the discharge becomes steady. The steadying effect is also perceptible at much lower value of pressure though the current strength is greatly reduced at the same time.

(l) *A Note on the Effect of using different kinds of Indicating Instruments.*—Since the discharge current contains a h. f. component, it is evident that the intensity of the detected current would depend on the type of the indicator employed. It may be recalled that the indicating instrument for recording the voltage is generally placed across a high resistance R (Fig. 2) put in series with the discharge circuit. The indicating instrument used may be electrometer, valve voltmeter, metal rectifier, etc. Thermo-junction in series with the discharge circuit may also be used to measure the discharge current directly. Now, since the discharge current has a h. f. component, it is obvious that the current value as obtained from the instrument will be less if the indicating instrument has appreciable self-capacity through which the h. f. is by-passed. Warburg (*Z. tech. Physik*, 1948, 165) in his original experiment noticed the difference between the readings of an electrometer and a thermo-junction and hence concluded that there was a h. f. component of the discharge current. In recent years unfortunately this simple fact has not been recognised and there has been much confusion in the interpretation of the experimental results. Joshi and his collaborators have in fact experimented with different types of indicators, e. g. vacuo-junctions, valve voltmeters (using diodes, triodes and pentodes) and metal oxide type of rectifiers with the object of determining the effect of the different types of rectifiers and indicators on the light effect. The results obtained by these workers can all be explained if the capacities, inherent or stray, of the indicating instrument and the associated apparatus are taken into account. For instance, it is reported that thermo-junctions indicate a higher discharge current as also higher percentage Δi, while the metal oxide rectifiers show a smaller effect. The result is as expected. The metal oxide rectifiers have much larger associated capacity than the thermo-junctions which by-pass a large proportion of the h. f. current. Again, it has been found that other conditions remaining the same, the light effect obtained by using 6H6 valve, triode and pentode as detectors, were 47%, 80% and 97% respectively. Here also the input capacities of the three thermionic tubes decrease in the order mentioned. It has also been observed that if the resistance is replaced by an inductance and

the indicating instrument, e. g. valve voltmeter, is inductively coupled to it a much higher value of the percentage effect is obtained, This also is easily explained, because in this case there is much less chance of h. f. leakage.

It is of course obvious that the applied voltage at which the maximum effect appears should not be affected by the indicator used, the effect of the h. f. leakage is only to make the apparatus less sensitive. This, in fact, is what has been observed.

Joshi (*Proc. Indi. Acad. Sci.*, 1945, 22A, 225) and also Prasad and Jain (*ibid.*, 1947, 26A, 515) used another method of detecting the h. f. component in which they noticed a large percentage effect. In this method the h. f. part of the discharge current is picked up by a loop aerial and is measured by means of a suitable meter, a thermo-junction for instance (Fig 3). The higher percentage effect obtained is, as expected, because the aerial picked up mainly the h. f. components of discharge current which is the chief seat of origin of the effect (Narayanswami, *Proc. Indian Sci. Cong.*, 1946, Part III, *Phys. Sec.*, Abs. No. 28 ; Das Gupta, *ibid.*, Abs. No. 31).

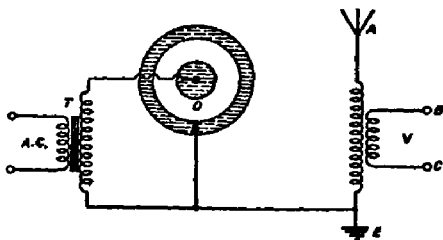FIG. 3   FIG. 4
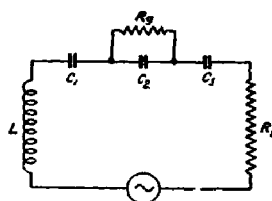

Fig. 3.   Illustrating the method of studying the high frequency components by aerial pick up.
Fig. 4.   Illustrating the equivalent circuit for the ozonizer discharge current. C_1 and C_3 are the capacities due to glass electrodes ab, bc ; C_2 is the capacity of the gas space R. L is the combined stray and transformer leakage inductance in the circuit ; R, is the total resistance including the losses and the resistance of Fig. 2. Rg represents the effective resistance due to the ionization in the gas space when there is discharge.

3. MECHANISM OF THE DISCHARGE : ORIGIN OF LIGHT EFFECT

We shall now discuss the origin of the light effect as originally suggested by Mitra and later developed by the authors of this paper (Deb and Ghosh, *Science & Culture* 1964-47, 12, 17). To understand this hypothesis it is, however, essential that we first understand clearly the mechanism of the discharge phenomena in the ozonizer. This has already been broadly indicated after Warburg (*vide supra*). For understanding the details, however, it is necessary to closely examine the oscillographic records of the discharge current under different conditions. Such records have been made by us and are reproduced in Plate I.

For taking the pictures the circuit diagram shown in Fig. 2 was used. The dimensions and the characteristics of the ozonizer tube were as follows :

Radius of the inner electrode	...	1 cm.
Radius of the outer electrode	...	2 cm
Length of the tube	...	20 cm.
Voltage	...	10 kv at 50 c. p. s.
Resistance in series (R)	...	15000 ohms.

Records were taken with air at pressure 34 cm. to 1 cm. For each pressure two pictures were taken, one with a condenser C suitably placed so as to by-pass the h.f. current and the other without the condenser. Figures. 1-8 in series (a) are for different pressures without any condenser. The corresponding figures 1-8 in series (b) in the Plate are for the same pressures but with a condenser for by-passing the h.f. current.

A close scrutiny of the oscillographic pictures reveals that in general the current through the ozonizer tube has the following components.

(i) There is an approximately sinusoidal current of the same frequency as that of the applied voltage. This is clearly distinguishable as a sinusoidal trace and is particularly noticeable when the pressure is high.

(ii) Traces of current pulses shooting up (or down) from the sinusoidal trace. These current pulses can be grouped under two heads :

(a) Groups occuring during part of a half cycle in which the individual pulses are separately observable. These we call low frequency pulses. These are clearly seen in pictures in series (b) in which the h.f. component has been by-passed.

(b) Groups in which the pulses are densely packed and run into one another. These we call h.f. pulses and are seen on and around (a).

(iii) There is a set of highly damped oscillations. These are clear in pictures (1-4) for high pressure.

We further note the very interesting fact that the discharge characteristics are not the same for the two half cycles. There is a strong asymmetry which is more marked for high pressure.

(i) *Sinusoidal current.*—This is the main A. C. current through the circuit (Fig. 4) driven by the applied voltage and needs no further consideration.

(iia) *Low Frequency Pulses.*—An examination of these pulses shows (remembering that the voltage across the discharge tube is a minimum at the peak of the sinusoidal trace) that their commencement marks the beginning of the discharge. This occurs obviously when the voltage V is equal to the breakdown voltage V_m. One should expect V_m to diminish as the pressure is decreased. This is what actually happens and is clearly seen in the series of pictures (1-8). For (1) the pressure is 34 cm ; the striking voltage V_m is high and the point of commencement of the low frequency discharge is farthest removed from the peak of the sinusoidal trace. As the pressure is lowered the point of commencement gradually moves towards the peak, the region of the lowest voltage. The origin of these pulses is as follows :

The electrons and ions which are produced by the discharge are urged towards the electrode walls b and c respectively of the discharge tube [see Fig. 1(b)]. If these electrodes were metallic, as in ordinary discharge tube, then the electrons and ions would have delivered their charges to the electrodes and in the equilibrium state as many ions would have been produced per second as absorbed by the metal electrodes. The electrodes b and c, however, being non-conductive, produce complications. Electrons and ions produced by the discharge are urged towards the electrodes but they are unable to produce continuous current and are partly deposited as surface charges on b and c and partly remain as polarized space charge. The surface charge and the space charge together neutralise the externally applied field and the discharge stops. Which of the

two, surface charge or space charge is primarily determinative of the stoppage depends of course on their relative densities. But as the applied A. C. voltage increases in course of its cycle, the breakdown voltage is again reached overcoming the neutralising effect of the surface and the space charges. There is again ionization and again deposition of surface charge and increase of space charge ; the effect of the applied external field is again neutralised and the discharge again stops. The phenomenon may thus be repeated a number of times and continue till the rate of increase of the external field becomes slower than the rate of neutralisation of the same by the increase of the surface and the space charges. This starting and stopping of discharge give rise to the low frequency pulses. The frequency of the pulses depends on several factors. Increase of mobility of the electrons and ions will quicken the deposition and thus decrease the interval between the starting and the stopping. The density of the ionization produced will also have an effect. At higher densities the rate of deposition of the charge will also increase and will shorten the interval. It will also depend upon the rate of increase of the external voltage. If the voltage rises rapidly then also the interval between the starting and the stopping of the discharge will decrease. All these factors contribute to make the spacings of the pulses different for different pressures.

A very important point to be noticed is that the surface charges are deposited not directly on the surface of the glass but rather on the adsorbed mono-molecular layer of the contained gas which is formed on the glass surface.

Formation of such a layer of the contained gas on the walls of the discharge vessel has been known for a long time. The adsorbed layer may profoundly influence the character of the discharge phenomenon. Kaplan (*Phys. Rev.*, 1932, **42**, 807) for instance has been able to produce spectra resembling those of the night sky and the aurora by specially "conditioning" the walls of the discharge tube by prolonged running. That an adsorbed layer in the ozone tube may be determinant of the light effect was also suggested by Joshi (*Curr. Sci.*, 1945, **14**, 175).

(*iib*) *High Frequency Pulses.*—These pulses, it will be noticed, were weaker for lower pressure but are more numerous and extended over a wider region for low pressure. The origin of these pulses is as follows :

The low frequency pulses discussed above leave the glass electrode surfaces strongly charged. When the external voltage begins to subside, the field due to these inner charges remains and if this field is strong enough, discharge takes place. But, as explained in Sec. 1, since the charges are on insulating surfaces, neutralisation proceeds in small isolated sparks in which small elements of surface charge recombine separately. These give rise to the observed h. f. pulses. When the pressure is high, the sparking potential is also high. The formation of surface charge is also rather incomplete. Neutralisation will therefore be effected in a few strong sparks producing in the discharge current a few strong pulses of extremely short duration. When the pressure is low, the sparking potential is small and also the formation of surface charge is more complete. The neutralisation in this case is brought about through a very large number of small sparks closely packed together.

To test the correctness of the above theory of the h. f. pulses pictures 1 and 2 in series (*d*) in the Plate were taken. In these pictures the excitation of the ozonizer was by

sharp voltage pulses, instead of by ordinary sinusoidal voltage*. In picture 1 (d) of the Plate there was no discharge and we record only the exciting pulses at right angles to the time base. In picture 2 (d) there was discharge. It will be seen that there appears now two modifications. Firstly, the exciting pulses are greatly lengthened. This is because the exciting pulses are followed by discharge and the discharge current is superimposed on them. Secondly, between the pulses there are innumerable traces of current pulses in the opposite direction. These are the h. f. pulses produced, as already explained, by the discharge of the surface charge brought about by the deposition of the electrons and ions produced by the primary pulse discharge. The fact that the h. f. current pulses are in the opposite direction is significant and is as it should be. This is because the surface charges produce voltage in the opposite direction neutralising the applied field.

A further confirmatory test for the mechanism of the discharge is furnished by pictures 1 (c), 2 (c) and 3 (c) in the Plate. These are for the case where the ozonizer had conducting (silver) coating of the inner surfaces b and c. The dimensions of the ozonizer and its other characteristics were the same as used for the series (a) and (b) of the Plate. For 1 (c) the pressure was 40 cm. For 2(c) the pressure was 20 cm. and for 3(c) the pressure was 1 cm. It will be seen that there is no dense closely spaced h. f. pulses as in pictures 1-8 in series (a). Instead, there are a comparatively few fat pulses only. This is because the surface charges being formed on conducting surfaces, the discharge of the same occurs by a few big flashes only instead of by innumerable h. f. pulses as in the case of non-conducting glass surfaces.

Asymmetry in the discharge phenomena.—The asymmetry in the different stages of the discharge is to be traced to the asymmetry of the electrode system and may be explained as follows :

For the asymmetry in the l. f. pulses which mark the main discharge due to the applied external voltage we note the following. It has been shown by Townsend (Whitehead, 'Dielectric Phenomena in Gases', 1927) that the sparking potential is different for positive and negative discharges. (Note : Discharge is said to be positive when the inner electrode is positive with respect to the outer and *vice versa*). When the pressure is high, positive discharge takes place at a voltage lower than the negative discharge. As the pressure is reduced the two sparking potential values approach each

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* The pulses were obtained in the following way. Radio frequency pulses as used for ionospheric exploration were picked up and rectified by a suitable circuit. Adjustments were made so that the input coil ·L of the rectifier tube together with its stray capacities presented an anti-resonance circuit to the incoming radio frequency. The rectifier output was freed from radio frequency components by means of a combination of by-pass condenser C and r. f. filter and was applied across the two terminals of the ozone tube. The dimensions of the ozonizer used and its other characteristics were as follows :

Radius of the inner electrode	...	...	...	4 mm.
Radius of the outer electrode	...	...	...	10 mm.
Length of the tube ...	...	...	...	15 cm.
Magnitude of the voltage pulse	...	...	...	2500 volts.
Circuit resistance ...	...	...	...	50,000 ohms

other and become equal for $\frac{\chi}{p} \backsimeq 150$ (χ = applied field in volts per cm., p = pressure in mm of Hg.) With further reduction in pressure the state of affairs is reversed and negative discharge takes place for a lower voltage. The above observation of Townsend are, of course, for metallic electrodes. We may, however, assume that the remark also holds, qualitatively at least, in the case of the ozonizer in which the inner and the outer electrodes are insulators. Asymmetry in the discharge which produces the l. f. pulses is thus expected.

The asymmetry in the h. f. pulses is also a consequence of the asymmetry of the electrodes. It is easy to see that the density of the surface charge on the inner electrode will, on account of its smaller area, be higher than that on the outer electrode. Also, we recall that owing to the higher mobility of the electrons the surface charges are mostly electronic *i.e.* negative. It therefore follows that when the inner electrode is negative, the h. f. pulses will be stronger but since the surface area is smaller, they will be spread over a smaller part of the cycle. When the outer electrode is negative, the h. f. pulses will be less intense but on account of greater surface area will be spread over a larger part of the cycle. This is as actually observed.

An interesting consequence, which is borne out by observations, follows from the above considerations. When the pressure is high, the sparking potential is also high and the breakdown voltage may be attained only during the half cycles when the inner electrode is positive. In such case the l. f. pulses will be confined to one half-cycle only. The h. f. component, however, since it is caused by the discharge of the surface charges, will be spread over a part of the rest of the cycle. When the pressure is low there is full display of the high frequency pulses in both half cycles.

(*iii*) *Damped Low Frequency Oscillation.*—The frequency of these oscillations is related to the circuit constants L, C, R. (Fig. 4). They are produced in the process of recombination of the polarised space charge.

Origin of the Light Effect.—The origin of the light effect is now easily understood. When the electrode surface is irradiated there is electron emission from the surface charge and its density is considerably reduced. The density of the high frequency pulses, which are caused by sparking between the surface charges of opposite signs of the two walls of glass electrodes, is thus also considerably reduced. This causes reduction in the total current flowing through the ozonizer and produces the main characteristic of the light effect. The other prominent features of the light effect, e.g., its dependence (a) on the nature of the gas used, (b) on the frequency and the intensity of the incident radiation and (c) on the magnitude and the frequency of the applied potential are also satisfactorily explained on the above hypothesis.

To explain how the percentage effect depends on the nature of the gas used, we recall that the surface charge which controls the discharge phenomena is formed on the adsorbed layer of molecules on the glass surface. The surface charge will therefore be quickly and more completely formed if the electron affinity of the gas molecules is high. Hence, the greater the electron affinity of the gas used, the greater will be the proportion of the h.f. component (produced by the discharge of the surface charges) in the total current and the greater the percentage reduction of the total current on irradiation. That this is so is confirmed by the experimental results. It is well known that for the

series-chlorine, bromine, iodine and oxygen the readiness with which an adsorbed layer is formed, as also the electron affinity decrease progressively from chlorine to oxygen. The percentage light effect for these gases also decreases in the same order (Joshi, *B. H. U. Jour.*, 1943, **8**, 99).

It is found that the percentage effect increases when the intensity and the frequency of the incident radiation are increased. That this will be so is obvious on the above hypothesis, because an increase of intensity and of the frequency of the incident radiation will cause increased reduction of the surface charge density and such reduction will be followed by a reduction in the h.f. current. It is, however, difficult to predict the exact nature of relationship with the frequency of the incident radiation due to our limited knowledge of the nature of the surface forces. It may follow different laws in different ranges of wave-length.

The decrease of the percentage effect with the increase of the applied voltage is caused by the diminution of the proportion of the h.f. current in the discharge (Warburg, *loc. cit.*, Prasad and Jain, *loc. cit.*). The origin of the latter can be understood from the following rough consideration.

As already explained, the surface charges the neutralisation of which produces the h.f. pulses are also responsible for stopping the main discharge (l.f. pulses). Now if M be the extinction voltage (*i.e.*, the net voltage across the discharge space at the critical instant when the discharge stops), then the opposing voltage, set up by the surface charges, may be put equal to $KV_o - M$. (Here V_o is the peak value of the potential and K is a constant depending on the capacity system in the ozone tube and is less than 1). The density of the surface charge is thus proportional to $KV_o - M$, while the strength of the total current is proportional to $V_o - V_m$ where V_m is the threshold value of the applied voltage at which the discharge begins. The percentage of h.f. in the discharge will therefore be proportional to

$$\frac{KV_o - M}{V_o - V} = f \text{ (say)}$$

therefore,
$$\frac{df}{dV_o} = \frac{M - KV_m}{(V_o - V_m)^2}$$

Now, KV_m being the value of the starting potential is greater than M, the extinction potential. Hence, the numerator is a negative quantity. df/dV_o is also therefore a negative quantity which means the ratio f which is proportional to the percentage effect would decrease with the increase of the applied voltage. The slight increase that is observed in the range of voltage slightly in excess of V_m is due to the unstable nature of the discharge in that range.

To explain the effect of frequency we note that as the frequency of the applied voltage is increased the pulsation time becomes equal to and finally less than the time required for the full deposition of the charge. Increase of frequency therefore causes a decrease in the density of the surface charge. Hence the h.f. component of the discharge as also the light effect decrease as the frequency is increased.

Other features of the light effect such as the effect of ageing, of the mode of illumination, and of surface condition are also easily explained on the basis of the proposed

hypothesis. That a freshly made ozonizer requires some time for the display of the full effect is due to the fact that the formation of adsorbed layer of gas molecules requires some time. The almost negligible light effect when the ozonizer is illuminated longitudonally is simply because in this case the electrode surfaces are ill illuminated. That the surface condition should affect the light effect is obvious. Because, as is well known, adsorption of a gas on a surface is strongly dependent on its physical and other condition such as freedom from contamination.

In fact all the above and other characteristic features of the light effect lend support to the correctness of the proposed hypothesis.

4. OTHER SUGGESTIONS ON THE ORIGIN OF THE "LIGHT EFFECT"

It would be interesting to discuss some of the suggestions made from time to time by other workers in the field to explain the origin of the light effect. This will show how futile it is to attempt any explanation without first understanding the peculiar mechanism of the discharge phenomena in an ozonizer.

1. Joshi has offered three different suggestions, not related in any way to each other, on three occasions. These are as follows :

(i) The *ad hoc* assumption is made that an increase of the threshold potential V_m on irradiation is responsible for the origin of the light effect (Joshi, *Proc. Ind. Acad-Sci.*, 1945, **22A**, 389). The explanation is based on the observed fact that the discharge current increase as $V-V_m$ increases, where V is the applied potential. No reason is, however, given why V_m should increase on irradiation (as indeed there is none). Apart from this, the observations of Warburg (*loc. cit.*) and also of Prasad and Jain, (*loc. cit.*), that the proportion of high frequency current diminishes with increase of applied voltage go against the explanation. This is because as already indicated, it is the high frequency component of the current which is affected (generally decreased) on exposure to light and is determinative of the light effect. If irradiation increases V_m, *i.e.*, decreases $(V-V_m)$ then the proportion of high frequency current would also increase. In other words, the effect of light would be to increase the h.f. component of the discharge current. This is just the reverse of what is actually observed.

(ii) Joshi (*Proc. Indian Sci. Cong.*, 1946, Part III, *Phys. Sec.*, Abs. No. 26) also suggests that "under discharge an activated layer is formed on the electrodes and it is in dynamical equilibrium with the gas phase ; as a primary step photo-emission occurs from the active layer and the photo-electrons thus emitted are captured by the highly electro-negative element present in the vessel to produce negative ions. These negative ions account for the effect. Further, they produce an opposing electro-static field which finally cuts off photo-electric emission. On shutting out incident light these electrons producing the electrostatic field return to the electrodes and thus produce an instantaneous reverse effect". (See also *Curr. Sci.*, 1945, **14**, 175). [In some later communication Joshi (*Curr. Sci.*, 1945, **14**, 317 ; *1947, **16**, 19), makes the further suggestion that the production of negative ions is facilitated by the fact that

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* In this paper Joshi gives an expression (Equation No. 1) for the discharge current as function of the circuit constants and applied voltage   But unfortunately the expression is wholly wrong.

the molecules are excited and that according to Frank such molecules have greater electron affinities.] The explanation, as will be noticed, is at best a complicated one and invokes quite a number of steps : Formation of an "activated layer" ; photo-emission from the same ; formation of negative ions ; production of an opposing electric field which cuts off the photo-electric emission. Perhaps, of all the steps suggested, the first, namely, the formation of an "activated layer" is the fundamental one. No reason, is however, assigned for its formation nor it is mentioned anywhere what the "activated layer" consists of—electrons or gas molecules. Further, the word "activated" has been used loosely without proper appreciation of its significance. We know of cases of activated adsorption at relatively high temperatures in which unlike the case of ordinary adsorption the binding energy of adsorbed atoms is extremely high. Thus, for instance H_2 in contact with glass shows activated adsorption at about $400°$. In this case, the heat of adsorption is of the order of 30,000 calories as compared with a few hundred calories for ordinary adsorption. Binding energy for chlorine is much higher than this. For it is well known, that chlorine, bromine, etc. are adsorbable to a far greater extent than oxygen, hydrogen or nitrogen. If by "activated layer" is meant a layer formed by activated adsorption, the binding energy of the gas molecules, i.e., the heat of adsorption would be of the order of 10 eV corresponding to radiation of wave-length less than 1250Å. But the light effect is observed even with red radiation. It is difficult to see how an "activated" adsorbed layer would be disturbed by light of such colour unless of course something else is meant by "activated layer". This, however, has not been explained and has been left vague.

. Joshi further argues that photo-electrons liberated by the incident light from the "activated layer" thus formed are captured by the gas molecules ; hence there is a reduction in ionic mobility and a consequent reduction in the current. It is difficult to follow the reasoning. Firstly, the ionization potential of the electro-negative gas used is very high. Hence, there can be no photo-emission from a layer of molecules of such gas by the light of wave-length used. Secondly, before irradiation the discharge space contains electrons and excited molecules. According to Joshi the excited molecules will capture the electrons and reduce ionic mobility. Thus the reduction effect, if any, will already be there. The first electrons liberated by the incident light will tend to increase the current and even accepting Joshi's arguments, the capture of these electrons will at best check this tendency to increase. One fails to see why it will cause a decrease of the total current.

(iii) Joshi's *Curr. Sci.*, 1946, **16**, 19) third suggestion is that the "activated layer" being formed on a dielectric surface might contain ions of both signs. "The electrostatic and inductive influence on the ions and electrons in the gas phase, modifies the annular capacity distinctive of normal gas. A photo-electric emission from the layer entails a capacitive change (and therefore a phase shift) leading to the effect".

Unfortunately, it is not explained how exactly the surface layer exerts "electrostatic and inductive influence on the ions and electrons in the gas phase" or how it "modifies the annular capacity distinctive of the normal gas" or how "the capacitive change (and therefore a phase shift)" following upon photo-electric emission should lead to the light effect. It is well known that presence of electrons and ions in an ionized gas

reduces its dielectric constant. But this reduction in the case under consideration, even granting that it may have something to do with the light effect, is negligibly small.

2. Prasad (*Nature*, 1945, 155, 362) applies Kramer's quantum mechanical dispersion formula and imagines ionization to be an extreme case of photo-excitation and tries to show that the reduction in dielectric constant of the gas in the discharge space due to optical excitation might be responsible for the observed change in discharge current. According to the author this suggests that the effect should be confined to the dielectric part of the current.

Without going into the merits of the hypothesis, it might be mentioned that the light effect is a surface effect (Sec. 3). But according to the authors hypothesis the magnitude of the effect should depend on the volume of the excited gas. Further, experimental results of Das Gupta (*Science & Culture*, 1946, 11, 318) and of Tewari and Prasad (*Curr. Sci.*, 1945, 14, 229) contradict the hypothesis. These authors while experimenting with radio frequency voltage, when the current was entirely of displacement type, observed that the light effect is negligible, if not absent.

3. Sahay (*Curr. Sci.*, 1945, 14, 122) has suggested that the effect of illumination is to produce excited atoms in the discharge space. These suffer a large number of collisions of the second type, with the electrons thereby reducing the mobility of the latter. Since the coefficient of recombination is large for slower electrons, a large number of them will disappear through recombination causing a diminution of the discharge current.

Here again, like the hypothesis of Prasad, a volume effect is presumed. Also it might be said that according to the mechanism assumed ordinary D. C. discharge tube should also show the light effect. But as already stressed the light effect is peculiar to the ozonizer tube only.

5. CONCLUDING REMARKS.

The sharp decrease in the discharge current of an ozonizer on exposure to light provides a spectacular demonstration, on the one hand, of the formation of surface charge on the glass walls of a discharge tube and on the other, of the instantaneous action of light on the same. That the so-called "light effect" is a peculiarity of the ozonizer discharge on account of the peculiar nature (insulated) and disposition of the electrodes had not been properly realised. Incidentally, it shows how vague had been our knowledge of the discharge mechanism in the ozonizer—a familiar apparatus in a chemical laboratory. The phenomenon deserves wider attention and ought to find a place in text books.

The fact that the origin of the light effect may be traced to the action of light on electronic surface charges formed on the glass electrode surface of the ozonizer was suggested to us by Prof. S. K. Mitra.

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