

Influence of Irradiation on Discharge Current in an Ozonizer

S. Deb, A. K. Saha, and M. Ghosh

Citation: *The Journal of Chemical Physics* **21**, 1486 (1953); doi: 10.1063/1.1699284

View online: <http://dx.doi.org/10.1063/1.1699284>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/21/9?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[Expectation of ozone generation in alternating current corona discharges](#)

Phys. Plasmas **19**, 033513 (2012); 10.1063/1.3695390

[Influence of Duration and Rate of Pulse Rise of the Applied Voltage on the Ozone Concentration in the Barrier Glow Discharge](#)

AIP Conf. Proc. **812**, 345 (2006); 10.1063/1.2168858

[Influence of Irradiation on the Low Frequency Electrodeless Discharge in Chlorine](#)

J. Chem. Phys. **19**, 514 (1951); 10.1063/1.1748276

[Ozone in Silent Electric Discharge](#)

J. Chem. Phys. **8**, 899 (1940); 10.1063/1.1750603

[Critical Voltage for the Formation of Ozone by the Alternating Current Discharge](#)

J. Chem. Phys. **3**, 529 (1935); 10.1063/1.1749718



proportionally large, as in CH_4 . Of course, the centers of polarizability need not then be chosen at the nuclear centers. For example, if the "polarizability center" for CH bonds is chosen at 0.694A (the "center of gravity" of polarizability)³⁶ from the carbon atom, and the bond polarizability³⁷ $0.6592 \times 10^{-24} \text{ cm}^3$ and ionization poten-

tial³⁸ of 14.5 eV are assumed, we obtain 1.90 kcal/mole as the heat of vaporization at the boiling point in reasonable agreement with the observed value of 2.05 kcal/mole.

Support of this work by the U. S. Office of Naval Research is gratefully acknowledged.

³⁶ See I. Nitta and S. Seki, *J. Chem. Soc. Japan* **62**, 581 (1941).

³⁷ K. Fajans and C. A. Knorr, *Ber. Deutsch. Chem. Ges.* **59**, 256 (1926).

³⁸ *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, 1951), 33rd ed.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 21, NUMBER 9 SEPTEMBER, 1953

Influence of Irradiation on Discharge Current in an Ozonizer

S. DEB, A. K. SAHA, AND M. GHOSH

Institute of Radio Physics and Electronics, University of Calcutta, Calcutta, India

(Received January 6, 1953)

The paper outlines the principal characteristics of the effects of irradiation on the discharge current in an ozonizer. The "electronic surface charge theory" of the effect developed by Deb and Ghosh, on a suggestion of Mitra, is explained and is further extended by taking into account the role played by the negative ions formed in the discharge space. It is assumed that the effect of irradiation is to decrease the charges deposited on the surface and to increase those in the volume. The former reduces the discharge current due to the neutralization of the surface charges and the latter increases the main discharge current due to the applied voltage. The net effect is generally a decrease if conditions are favorable for the capture of the electrons in the volume by neutral gas molecules, leading to the formation of negative ions. In all other conditions the effect is generally an increase. It is shown that the theory, in its extended form, is able to account for the origin and the characteristics of both the positive and the negative effects. Numerical calculations of the various rate processes involved in the proposed mechanism are also made. It is shown that the relative magnitudes of these processes are such as to support strongly the "electronic surface charge theory" of the effect.

I. INTRODUCTION

THE instantaneous decrease (or, under special conditions, increase) of the discharge current through an ozonizer tube when it is flooded with light, and its associated phenomena, have been the subject of numerous studies, especially in India where the effect was first observed.^{1,2} A number of theories have also been proposed to explain the various observed effects. Unfortunately, none of the theories proposed so far gives a satisfactory and complete explanation of the various aspects of the effect. Of the various theories proposed the "electronic surface charge theory" proposed by Deb and Ghosh^{3,4} appears to offer the most plausible explanation of the phenomena. However, this theory does not account for the "positive" effect— increase of discharge current on irradiation; this effect is obtained under special conditions. It is the purpose of the present paper to examine critically the various proposed theories including that of "electronic surface charge" which will be discussed in greater detail. It will be shown that this theory, suitably extended, is able

to explain both the "negative" and the "positive" effects, as also the other associated phenomena.

II. A RESUME OF THE EFFECTS OBSERVED

The ozonizer discharge apparatus with which the phenomenon is most conveniently observed is shown diagrammatically in Fig. 1. Examination of the discharge current with a cathode-ray oscilloscope shows that a part of the current consists of numerous short duration discharge pulses (the so-called "high-frequency component") between the glass surfaces enclosing the discharge space (Fig. 2a). It is further found that it is this "high-frequency" component which is mainly affected by irradiation of the discharge tube. The effects which have been observed and which the proposed theory must explain may be summarized as follows:

(1) The main effect consists in the reduction ($-\Delta i$) of the discharge current (i) when the discharge tube is flooded with light. This is the so-called "negative light effect." (The reduction in the optimum case may be about 90 percent. The relative reduction is conveniently expressed as *percentage reduction*, i.e., $|\Delta i|/i \times 100$).

(2) Under special conditions, with low applied voltage and high pressure, there is an increase ($+\Delta i$) in-

¹ S. S. Joshi, *Nature* **154**, 147 (1944).

² S. S. Joshi and P. G. Deo, *Nature* **153**, 434 (1944).

³ S. Deb and N. Ghosh, *Science and Culture (India)* **12**, 17 (1946-47).

⁴ S. Deb and N. Ghosh, *J. Indian Chem. Soc.* **25**, 449 (1948).

stead of the more commonly observed decrease ($-\Delta i$). This may be called the "positive light effect." $-\Delta i$ is of more frequent occurrence in gases of simple diatomic molecules. In polyatomic gases, $+\Delta i$ is more prominent. $+\Delta i$ is maximum at (and prior to) striking potential V_m and inverts to $-\Delta i$ by a small increase of the voltage. $+\Delta i$ sometimes occurs at very large values of applied voltage.⁵

(3) The negative effect depends markedly on the nature of the gas used. The maximum effect is observed in chlorine. Next in order comes bromine, iodine, oxygen, air, nitrogen, and hydrogen which are in the decreasing order of electron affinity.^{5,6}

(4) The effect is pressure-dependent. Depending upon the applied voltage and the geometry of the tube, there is a pressure at which the effect is maximum.²

(5) The percentage value of the effect ($\Delta i/i_{\text{dark}} \times 100$) is maximum at a voltage slightly above the threshold voltage V_m of the discharge. It then diminishes slowly with further increase of voltage.⁷

(6) The effect depends markedly on the intensity of the incident radiation, the relative variation being more pronounced at lower values of the intensity.⁸

(7) The effect is much larger when the ozonizer tube is illuminated from the side than axially.⁹

(8) The effect decreases with increase of frequency of the applied (ac) voltage and ultimately vanishes at radio-frequencies.¹⁰

(9) The reduction in the discharge current on irradiation occurs in all parts of the spectrum—from extreme red to x-rays.⁷ It occurs both within and outside the selective absorption bands characteristic of the enclosed gas.¹¹

(10) The effect depends markedly on the condition of the wall of the discharge vessel. Thus, it depends on ageing and previous heat treatment.¹ Also, the percentage effect changes when the walls of the discharge tube are coated with different substances.^{8,12}

III. THE ELECTRONIC SURFACE CHARGE THEORY

A number of theories have been proposed to explain the observed effects. These may be broadly classified under two heads. According to one, importance is given to the electrons and negative ions in the discharge space, it being assumed that the formation of the latter is promoted by the incidence of light on the contained gas.^{13,14} According to the other, it is the deposit of the charges on the walls of the discharge space that is

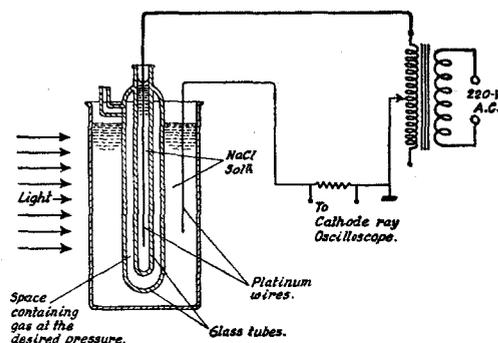


FIG. 1. The ozonizer discharge apparatus.

ultimately responsible for the effect.^{3,4,15,16} It is, however, to be noted that, except for only a few, none of the theories takes account of the fact that it is the high-frequency component of the discharge current which is mainly affected.

The starting point of the "electronic surface charge theory" of Deb and Ghosh^{3,4} (developed on a suggestion by Mitra¹⁷), is the mechanism of the production of the high-frequency part of the discharge (first hinted at by Klemenc *et al.*¹⁸). This theory explains satisfactorily the commoner negative light effect. It, however, leaves unexplained the rarer positive effect. In what follows the theory of Deb and Ghosh will be extended, leaving unaltered their basic assumptions, to include an explanation of the positive effect also.

A. The Discharge Mechanism

The first step in the ozonizer discharge phenomena is the initiation of the discharge in the usual manner by the applied field. (See in Fig. 1 the space containing the gas.) This is followed by a separation of the electrons and positive ions under the influence of the field. This is because the electrons, on account of their lighter mass, are greatly accelerated by the field towards the positive wall and are deposited on the wall. (It is to be noted that the electronic surface charge is formed not directly on the glass wall but on an adsorbed layer of the gas molecules on the surface.) The positive ions, on the other hand, because of their heavier mass, hardly move within this time and remain as volume charge. The applied field within the discharge space of the ozonizer thus becomes neutralized by the field due to the separated charges—electronic surface charge and positive ion volume charge—and the discharge stops.

It is also to be noted that some of the electrons may be left free as space charge, especially in front of the

⁵ S. S. Joshi, *Current Sci. (India)* **16**, 19 (1946).

⁶ G. S. Deshmukh, *J. Indian Chem. Soc.* **24**, 211 (1947).

⁷ S. S. Joshi and P. G. Deo, *Current Sci. (India)* **12**, 306 (1943).

⁸ S. S. Joshi, *Current Sci. (India)* **14**, 35 (1945).

⁹ N. R. Tawde and K. Gopalkrishnan, *Proc. Indian Acad. Sci.* **29A**, 171 (1949).

¹⁰ S. N. Tewari and B. Prasad, *Current Sci. (India)* **14**, 229 (1945).

¹¹ S. S. Joshi, *Current Sci. (India)* **13**, 278 (1944).

¹² S. S. Joshi, *Current Sci. (India)* **13**, 253 (1944).

¹³ S. S. Joshi, *Current Sci. (India)* **14**, 175 (1945).

¹⁴ S. S. Joshi, *Current Sci. (India)* **14**, 317 (1945).

¹⁵ W. L. Harries and A. von Engel, *Proc. Phys. Soc. (London)* **B64**, 916 (1951).

¹⁶ W. L. Harries and A. von Engel, *J. Chem. Phys.* **19**, 514 (1951).

¹⁷ S. K. Mitra, *Active Nitrogen—A New Theory* (The Indian Association for the Cultivation of Science, Jadavpur, Calcutta, 1945), p. 58.

¹⁸ Klemenc, Hintenberger, and Hoffer, *Z. Electrochem.* **43**, 708 (1937).

negatively charged surface, and some of them may also attach themselves to the neutral molecules to form negative ions, the formation being facilitated by the comparatively high gas pressure, the gas molecules providing the "third body." The proportions in which the electrons will form surface charge, will form negative ions, or will be left free, depend on a number of factors, e.g., the gas pressure, the relative surface area, the temperature, and the previous history of the glass wall.

If now the applied field is switched off, the field due to the separated charges takes hold of the discharge phenomena. From the nature of the distribution of the charges as explained above, it follows that the volume charge of positive and negative ions will be more or less at constant potential and there will be a large fall of potential within a small distance close to negatively charged surface. Hence, positive ions drawn from the volume charge will be accelerated by the intense field in front of the negatively charged surface and will arrive in torrents on the same to recombine with the electrons, the recombination being facilitated by the surface molecules acting as the "third body." Further, if there are free electrons within the region of the fall of potential mentioned above, these will be accelerated towards the positive volume charge to recombine with positive ions or to attach themselves to neutral molecules to form negative ions. The currents due, firstly, to the torrent of positive ions on to the negative surface charge and secondly, to the motions of electrons towards the positive volume charge constitute the observed high-frequency neutralizing discharge current. The former provides the major part of the current, because, the neutralizing negative surface charge had been quickly and copiously formed during the part of the discharge when the applied field was on. It is to be remembered that the positive ions, coming as they are from different distances, do not all arrive at the same instant on the neutralizing wall. Hence, the neutralization is not instantaneous.

The existence of the high-frequency "pulse discharge," in a direction opposite to that of the initial discharge, has been verified experimentally by Klemenc *et al.*¹⁸ by suddenly switching off the applied steady field and also by Deb and Ghosh¹⁹ by using for the external field short-duration voltage pulses.

In the above, we have considered the case when a steady field is applied and when the same is removed. A little consideration shows that if, instead of steady field, we have a field increasing with time (as during one half-cycle of an alternating field) the starting and stopping of the discharge will occur a number of times but the phenomenon will essentially be the same as described above (Fig. 3a). (The case is fully discussed with photographic illustrations of the discharge current in the paper of Deb and Ghosh cited above.)

B. Effects of Irradiation

Next, let the experiment be performed when the discharge tube is flooded with light (say, visible white light). Since the electron affinity of the glass walls (i.e., of the layer of adsorbed molecules) is quite small, there will be photodetachment of electrons from the surface. The negative charge density on the surface will, therefore, be less when the light is acting, the detached electrons forming space charge in front of the cathode. The internal field, opposing the external field and stopping the discharge, will thus be that due to the positive volume charge (as before) separated from the electronic charges residing partly in the volume close to cathode surface and partly on the surface itself. Depending upon the pressure in the discharge tube, a proportion of the electrons will also attach themselves to the neutral gas molecules producing negative ions.

We can now make the two following postulates regarding the immediate effects of flooding the ozonizer with light on the neutralizing high-frequency "pulse" discharge currents when the applied field is removed:

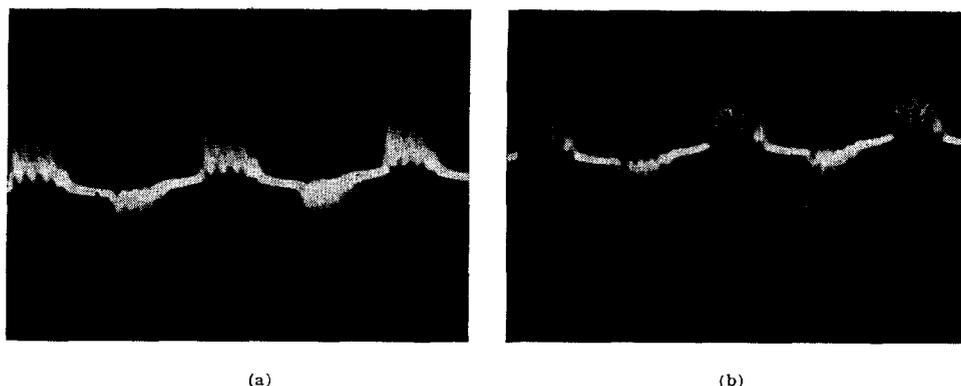


FIG. 2. Oscillographic pictures of discharge current; (a) in darkness, (b) in light. The discharge current consists of a series of low-frequency pulses and a larger number of high-frequency pulses (for interpretation see Sec. III). The effect of irradiation is to reduce the high-frequency pulse component of the discharge current.

¹⁹ S. Deb and N. Ghosh, *Science and Culture, India* 14, 39 (1948-49).

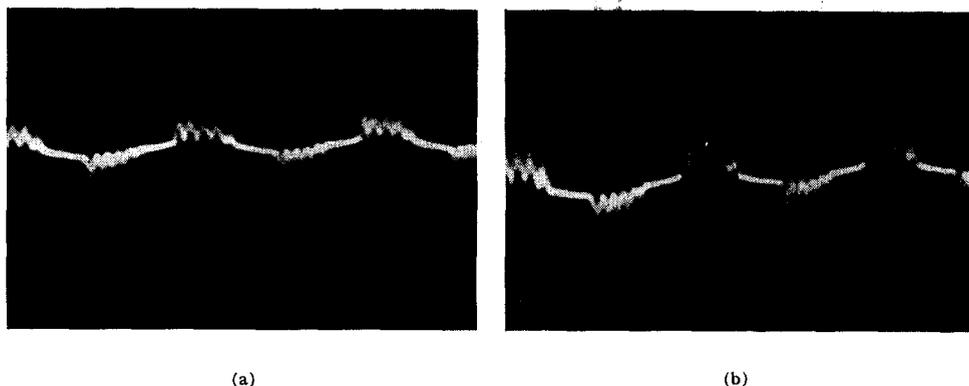


FIG. 3. Oscillographic pictures of discharge current, with the high-frequency components by-passed through a $0.0003\text{-}\mu\text{f}$ condenser, showing pulses due to the alternate starting and stopping of discharge under the combined influence of the externally applied field and the field due to the surface charges; (a) in darkness, (b) in light. The stopping of the discharge current is not complete when the ozonizer is flooded with light. Further, the height of the pulses is increased. This is because a large number of electrons are now available for the initiation of the discharge, increasing thereby the stability of the discharge.

(1) Because of the decrease in the density of the negative surface charge, the part of the high-frequency current due to the torrent of positive ions neutralizing on the negative surface charge will decrease (Fig. 2b). (This we shall call effect No. 1.)

(2) Because of the increase in the concentration of electrons in the volume in front of the cathode surface (see above), the part of the high-frequency current resulting from the electrons being accelerated away from the cathode (due to the cathode fall of potential) will increase. The discharge current will also increase as more electrons are now available for the initiation and the stability of the discharge (Fig. 3b). (These we shall call effect No. 2.)

Let us now see how these postulates can explain the observed "light effects" and the associated phenomena.

(a) When the pressure is low—so low that the probability of negative ion formation is comparatively small—the electrons detached by the incidence of light will mostly remain free. Hence, the decrease in the high-frequency discharge current due to effect No. 1 will be amply compensated by the increase due to effect No. 2. In other words, there will be little or no effect of light on the discharge current.

When the pressure is higher, the electrons released from the surface (by the incidence of light) have higher probability of forming negative ions. As the ions have low mobility, effect No. 2 will be of less importance and effect No. 1 only will be mainly operative. Hence, there will be a sharp decrease in the neutralizing high-frequency discharge current. The commonly observed negative light effect is thus explained. (It is to be noted that the light will also release electrons from negative ions in the volume. But the proportionate number made free is much less at higher pressure on account of the enhanced probability of negative ion formation at such pressures.)

(b) Next, let the gas pressure be relatively high—so

high that for the applied voltage, the discharge passes with difficulty. The electrons, produced by the intermittent discharge, are now prevented, by frequent collisions, from reaching the positive wall and hence the density of the electronic surface charge will be small. Under such conditions the few electrons that are released by irradiation help to increase the discharge current and hence stabilize the discharge. In such cases effect No. 1 is more than compensated by effect No. 2. There is thus a net increase in the discharge current. This is the less commonly observed positive light effect prominent when the applied field is just below that required for establishing a stable discharge.

(c) It is obvious that, other conditions remaining the same, the effect will be more pronounced in gases having high electronic affinity. This is because in such gases the electronic surface charge will be more copiously formed (it being recalled that the electrons are deposited not directly on the glass surface but on a layer of adsorbed molecules of the enclosed gas on the same) and the number of free electrons (as are detached from the surface) will be decreased due to the quick formation of negative ions. Effect No. 1 will thus increase and, at the same time, effect No. 2 will decrease.

(d) The magnitude and nature of the "light effect" will depend on the pressure of the gas in the discharge space as explained under (a) and (b).

(e) An increase in the applied voltage beyond the striking value will result in an increase in the direct discharge current, that is, in increased production of ions and electrons. The surface density of the electronic charge will not, however, increase proportionately because of the tendency for it to attain saturation value. The volume density of the ions, on the other hand, will go on increasing with the applied voltage. Hence, while effect No. 2 will go on increasing, effect No. 1 will not do so proportionately. The magnitude of the negative "light effect" will, therefore, increase less

relatively to the increase of the applied voltage. It will tend to a steady value and then decrease with the increase of the applied voltage.

(f) If the intensity of the light be increased, effect No. 1 will increase. But there will be proportionately more increase in effect No. 2, so that there is a net reduction in the magnitude of the negative "light effect."

(g) If the discharge tube is illuminated axially, avoiding the walls, then there will, obviously, be no negative "light effect" because effect No. 1 is absent.

(h) If the interval between the switchings on and off of the applied field be smaller than the time required for the electrons to travel up to the positive wall and form the surface charge, then the "light effect" will diminish. This, in other words, means that with the increase in the frequency of the exciting ac voltage the "light effect" will decrease.

(i) Radiations of all wavelengths, the energy of which is sufficient to detach electrons from the surface charge and from the negative ions, will be able to produce the "light effect." The effect will be the highest for wavelengths whose energy is only slightly greater than the detachment energy. Obviously, the wavelength of the radiation has no relation with the wavelength of the selective absorption bands of gas under discharge.

IV. NUMERICAL ESTIMATES OF THE VARIOUS RATE PROCESSES

In the preceding section we had to introduce, in connection with the development of the "electronic surface charge theory," various electronic processes and their rates, e.g., deposit of electrons on the glass walls, detachment of electrons from the same, negative ion formation, detachment of electrons from negative ions, etc. It is desirable that some quantitative estimates—even if they be very rough ones—be made of the rates of these processes, to check that there is no contradiction in the sequence of the various stages that have been proposed in the theory to explain the positive and the negative effects.

A. Rate of Formation of the Neutralizing Surface Charge

We first make estimate of the density of the electronic surface charge that would be necessary to stop the discharge. It is reasonable to assume that the saturation density of the surface charge is reached when one electron is deposited per one surface atom. This will correspond to about 10^{14} electrons per unit area of the wall. For the typical case of an ozonizer, whose inner and outer electrodes have diameters of the order of 1 cm and 3 cm, respectively, the capacity per unit length is about $1 \mu\text{mf}$. Hence the potential developed by the surface charge of this density is

$$v = (10^{14} \times 1.6 \times 10^{-19}) / 10^{-12} = 10^7 \text{ volts.}$$

This is many orders higher than the externally applied voltage. It follows, therefore, that the opposing field due to the surface charges will be able to stop the discharge even when a very small fraction of the surface atoms hold one electron each.

Now, under usual conditions of operation, the extinction potential for the discharge system is of the order of a few hundred volts only. In order that the surface charge is able to build up an opposing potential to reduce the net potential difference to this amount, the surface density of charge should be of the order

$$\frac{10^{14}}{10^7} \times (10^3 \text{ to } 10^4) = 10^{10} \text{ to } 10^{11} \text{ electrons cm}^{-2}.$$

This may be taken as the maximum value of the surface charge built up in course of discharge in the system under consideration.

For estimating the rate of formation of the surface charge, we assume that the discharge current is almost wholly due to electrons derived from the discharge—the positive ions contributing only a negligible fraction. Since the discharge current in an ozonizer tube ranges from one-hundredth to one milliampere, we take the average value of the discharge current as 0.1 ma. The average rate of deposition of electrons on the wall surface is, therefore,

$$\frac{\text{current}}{\text{electronic charge}} = \frac{10^{-4}}{1.6 \times 10^{-19}} \approx 10^{15} \text{ sec}^{-1}.$$

Or, if the length of the ozonizer tube is taken as 10 cm, the rate is $10^{13} \text{ cm}^{-2} \text{ sec}^{-1}$. Thus, the time required to build up a surface charge density of 10^{10} to 10^{11} electrons per sq cm is 10^{-4} to 10^{-3} sec. This is the interval between the starting and the stopping of discharge giving the low-frequency pulses (Fig. 3).

B. Rate of Photodetachment of Electrons

For estimating the rate of photodetachment of electrons from the charged wall surface, we require a knowledge of its photosensitivity. Unfortunately, no experimental data on photoemissions from a composite surface consisting of electrons held by adsorbed gas molecules on glass is known. We may, however, try to make a rough estimate by examining the results obtained for composite layers on metals, such as silver-sodium oxide-sodium, etc. Under properly treated conditions these surfaces may have a sensitivity of $50 \mu\text{a}$ per lumen. For the surface under consideration a reasonable value may, therefore, be taken as about $10 \mu\text{a}$ per lumen.

The "light effect" is generally observed by flooding the ozonizer tube by means of light from electric bulbs of power, say, 100 to 500 watts (backed by suitable reflector) and placed some 50 cm away from the discharge tube. The efficiency of a 200-watt bulb may be taken

as 15 lumens per watt. Taking into account the inverse square fall of intensity, the luminous flux at a point 50 cm away from the bulb would be about 1 lumen. But, considering the presence of the reflector a more reasonable estimate would be 10 lumens. The rate of photodetachment comes out to be of the order

$$\frac{10 \times 10^{-6} \times 10}{1.6 \times 10^{-19}} = 10^{16} \text{ electrons cm}^{-2} \text{ sec}^{-1}.$$

This is of the same order as that of the rate of deposition of electrons.

C. Rate of Formation of Negative Ions

If ν be the collisional frequency of electrons with gas molecules and n the fraction of collisions which results in the formation of negative ions, then the rate of formation of negative ions = $N_e n \nu$, where N_e is the number density of electrons in the discharge space.

At a pressure of 10 cm of mercury, which is typical of the pressure at which the "light effect" is observed,

$$\nu = 10^{11} \text{ sec}^{-1}.$$

According to experimental results of Cravath,²⁰

for chlorine $n > 10^{-3}$,

for oxygen $n \simeq 10^{-5}$.

Therefore, the rate of formation of negative chlorine ions $\simeq 10^8 N_e \text{ sec}^{-1}$, and the rate of formation of negative oxygen ions $\simeq 10^6 N_e \text{ sec}^{-1}$. If the discharge current be 0.1 ma and the field 100 v/cm then, $N_e = 10^7 \text{ cm}^{-3}$. Hence, for this value of electron concentration, the rate of formation of negative chlorine ions $\simeq 10^{15} \text{ cm}^{-3} \text{ sec}^{-1}$, and the rate of formation of negative oxygen ions $\simeq 10^{13} \text{ cm}^{-3} \text{ sec}^{-1}$. These are of the same order as the rate of electron detachment from the surface.

D. Rate of Removal of Negative Ions: Electron Detachment and Mutual Neutralization

Electrons from the negative ions may be removed by several processes, namely, photodetachment, detachment by collisions with neutral gas molecules, and removal by mutual neutralization of negative and positive ions. Now for chlorine, electron affinity is such that ordinary visible radiation will be unable to effect any appreciable detachment. Further, if the pressure is high and the field strength low, then the charged particles will not be able to acquire sufficient energy within the distance of the mean free path and, hence, collisional detachment will remain small. However, for moderate pressure and high-field strength this process is likely to play a dominant role. The rate of removal by collisional detachment is given by

$$\alpha N^- N,$$

²⁰ A. M. Cravath, Phys. Rev. 33, 603 (1929).

where α = the coefficient of collisional detachment²¹ = 10^{-16} , N^- = number density of negative ions, and N = number density of neutral molecules.

Supposing that the formation of negative ions proceeds for a time 10^{-4} sec which is the duration of discharge for each initiation, the maximum concentration that the negative ions can attain is, from Sec. IV, C above, $10^{16} \times 10^{-4} = 10^{11} \text{ cm}^{-3}$. A more reasonable value may be 10^9 cm^{-3} . Hence, since the value of N at a pressure of 10 cm of Hg is of the order of 10^{19} , the rate of collisional detachment is $10^{12} \text{ sec}^{-1} \text{ cm}^{-3}$.

At 10-cm pressure and ordinary field strength, negative ions will be removed largely through mutual neutralization of positive and negative ions. The rate at which negative ions disappear through this process is given by

$$\beta [N^-]^2,$$

where β , the coefficient of mutual neutralization, is of the order 10^{-8} .²² With $N^- = 10^9$, the initial rate of removal through mutual neutralization = $10^{10} \text{ cm}^{-3} \text{ sec}^{-1}$.

Comparing the above with the results obtained in Sec. IV C, we find that ordinarily—when collisional detachment is unimportant—the rate of removal of negative ions will be very small compared to the rate of formation. If, however, the pressure is reduced, or the field strength is increased keeping the pressure high, so that collisional detachment becomes operative, the rate of removal of negative ions may be comparable to the rate of formation. According to Cravath²⁰ collisional detachment comes into play if

$$N/p \geq 100,$$

where N is the field across the discharge space in volts/cm and p is the pressure in mm. Thus at a pressure of 10 cm, collisional detachment will be appreciable if the field across the discharge space is increased beyond 10^4 volts cm^{-1} .

V. DISCUSSION AND CONCLUDING REMARKS

Let us now discuss the bearings of the results of the numerical estimates made in the last section on the theory of the electronic surface charge developed in Sec. III.

We have found that the electronic surface charge necessary for producing the requisite opposing field to stop the discharge is many orders less than the maximum capacity of the surface to hold the electrons. Further, what is more important, the time required for building up the surface charge is of the order 10^{-4} to 10^{-3} sec which is small compared to the period (1/50 sec) of the ac voltage applied for observing the effect. The phenomenon of starting and stopping of discharge (the low-frequency pulses) will, therefore, occur, a number of times in course of one half-cycle. This agrees with

²¹ A. P. Mitra, J. Geophys. Research 56, 373 (1951).

²² D. R. Bates and H. S. W. Massey, Proc. Roy. Soc. (London) A189, 261 (1946).

observation. Also, in conformity with this, the duration of the low-frequency pulses as observed experimentally is of the order 10^{-4} sec. It also at once follows that if the frequency of the applied ac field is raised to the order of 10 kilocycles sec^{-1} , the effect would disappear. This again agrees with observation.

The calculations also show that under average working condition the rate of photodetachment of electrons from the surface ($10^{15} \text{ cm}^{-2} \text{ sec}^{-1}$) is about as rapid as the rate of deposition of electrons. Because of this, the process of photodetachment becomes fully effective in a fraction of the interval between the starting and the stopping of the discharge. The instantaneous character of the effect of light is thus explained.

The rate of capture of electrons to form negative ions has been found to be as rapid as the rate of detachment from the surface due to irradiation. This shows why the negative effect is ordinarily the more dominant one.

The theory demands that for the wavelength and for the intensities of illumination usually employed, the rate of photodetachment of electrons from the negative ions should be much less than both the photodetachment from the surface and the rate of formation of negative ions by attachment. The calculated results show that this is actually the case.

It has been found that the detachment of negative ions by mutual collisions may become quite high if the field strength is high. This possibly explains why the negative effect changes over to a positive effect when the applied potential is increased to a sufficiently high value. For example, for pressure of about 10 cm of Hg a transition from negative to positive effect will occur when the voltage is raised to the order 10^4 volts. This is in reasonably good agreement with what is actually observed.

According to the theory, the positive effect is expected to occur under conditions which favor a low rate of formation of negative ions and a high rate of detachment of electrons from the same. Both these conditions are satisfied if the electron affinity of the gas used is small, the frequency of the light used is high, and the applied field strength is large. This is also in complete agreement with experimental results.

Again, according to the theory, if by means of an external field the electrons are deflected from their straight and shortest paths towards the electrode surface, two opposing effects will be expected to occur. On the one hand, there will be a diminution of the discharge current due to the restriction in the formation of the surface charge and, on the other, there will be an increase in the same due to greater chance of ionization resulting from the longer paths traversed by the electrons. Experiments performed by Bhiday, Bhide, and Asolkar²³ confirm these predictions. These authors placed the ozonizer tube in a magnetic field and found, that depending upon the pressure and the magnetic field, the strength of the discharge current sometimes showed an increase and sometimes a decrease.

From the discussion given above one is justified in concluding that the "electronic surface charge theory" as developed in Sec. III is able to account for all the principal features of the effect, both positive and negative. The two effects are always present and are controlled, firstly, by the electronic surface charge formation and the liberation of the electrons from the same by the incident light, and, secondly by the liberated electrons being captured by the neutral molecules in the volume. If the capture rate is high, we have the negative effect. If the capture rate is low, we have the positive effect. It is to be noted that, as mentioned in Sec. III A, the possibility of the formation of negative ions had also been suggested by Joshi. But the role played by these has not been interpreted correctly. The interpretation suggested earlier by Deb and Ghosh and developed further in this paper clarify the many puzzling and apparently conflicting experimental observations. The numerical calculations carried out in Sec. IV are, no doubt, based on many uncertain factors. Nevertheless, the degree of qualitative agreement obtained is quite satisfactory.

ACKNOWLEDGMENT

It is a pleasure to thank Professor S. K. Mitra for suggesting the work to us, and for his constant guidance and help in the course of preparation of the paper.

²³ Bhiday, Bhide, Asolkar, *Nature* **168**, 1006 (1951).