[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

PHOTOCHEMICAL STUDIES. II. THE ACTIVATION OF A MERCURY SURFACE BY LIGHT. A POSSIBLE RELATION BETWEEN PHOTOELECTRIC EFFECT AND PHOTOCHEMICAL ACTION[1]

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While many extremely accurate determinations of photoelectric currents and of the velocity of photoelectrons have been made, the theory underlying this effect, due, perhaps, to lack of definite knowledge of the state of electrons in a metal, may be considered as rather indefinite. The classical Einstein equation, $eV = h\nu - h\nu_0$, has been used by Millikan[2] to obtain a very accurate value of Planck's universal constant, h. The same author[3] points out that in case the photoelectric effects of two different metals are studied in the same photoelectric cell, the equation, $K' - K = \frac{h}{e}(\nu_0 - \nu_0')$, (where K' is the contact potential of the first metal against the metal of which the case of the photoelectric cell is made, K is the contact potential of the second metal against the metal of the case, h is Planck's universal constant, e is the charge on the electron, and ν_0 and ν_0' are the photoelectric threshold frequencies of the two metals studied) can be interpreted only in one of the following ways: (1) the energy of the electron after its escape from the atom is always equal to $h\nu$ and the absorbed energy greater than $h\nu$; (2) the same energy is required to detach an electron from all atoms (an impossible conclusion); (3) the photoelectrons are from the beginning the free electrons, rather than constituents of the atoms. De Broglie[4] has shown that photoelectrons due to X-rays come from definite energy levels in the atoms. For many metals the threshold frequency of the photoelectric effect is below the frequency of the first resonance radiation of the metal in the vapor state. This would suggest either that the electrons are really free electrons and that the term $h\nu_0$ in the Einstein equation merely represents the work necessary to remove an electron from the surface, or else that the electrons are still attached to the atoms but are in orbits or positions of higher energy level than if the atoms were in the vapor state. If we assume, in some such manner as does Knorr,[5] that there is a distinct difference

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[1] This article is an abstract of a thesis presented by Howard R. Moore to the Ogden Graduate School of Science of the University of Chicago in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Millikan, *Phys. Rev.*, **7**, 355 (1916).

[3] Millikan, *ibid.*, **7**, 26 (1916).

[4] De Broglie, *J. phys. radium*, **2**, 265 (1921).

[5] Knorr, *Z. anorg. allgem. Chem.*, **129**, 109 (1923).

between a polar and a non-polar bond, then one might expect, since the orbit or position of the valence electron of the mercury before combination bears no direct relation to the orbit or position of the electron in the compound, that an atom which has lost an electron would react more readily with oxygen than would a neutral atom, providing that electrons are available in the immediate vicinity to complete the quota of valence electrons necessary in the molecule. It was with the object of determining whether the photoelectric emission of some of these "free" or "loosely bound" electrons increased the speed of a reaction on a mercury surface, that the present research was undertaken. The results may be interpreted more easily if it is postulated that the electrons are not really free, but are associated in some way with the atoms in the metal. This would imply that the term $h\nu_0$ in the Einstein equation is really the sum of two terms one of which represents the work necessary to detach an electron from the atom when it is in this loosely bound state, and the other the work necessary to remove the electron from the surface.

It may be pointed out that Haber and Just[6] have observed electron emission during the course of certain reactions. When the alkali metals reacted with certain gases electrons were emitted, even in the dark, and the metal attained a potential of about one volt. Whether this emission was a necessary accompaniment of the reaction, or whether it was due to a secondary phenomenon, was not decided. Their experiments are of interest, however, in connection with the results herein reported.

Part I will present an approximate determination of the threshold wave length of mercury. Part II will give a brief résumé of the results together with the details of the experimental procedure. Part III will give a brief discussion of the results.

I. An Approximate Determination of the Photoelectric Threshold of Mercury

Certain authors[7] have indicated that the photoelectric effect is dependent to a large extent upon the quantity of gas adsorbed on the surface and upon other factors difficult to control. Mercury was chosen for these experiments because it is possible to obtain reproducible surfaces more easily with it than with most other metals.

The mercury used in these experiments was agitated strongly for several hours with dil. nitric acid and then distilled in a vacuum. In the later work on the activation of the surface by light, various liquids and solutions were used as color filters to limit the wave lengths of light used. The object of this preliminary investigation was not so much, therefore, to determine the exact threshold wave length of mercury, as to determine

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[6] Haber and Just, *Ann. Physik*, **30**, 411 (1909); **36**, 308 (1911); *Z. Elektrochem.*, **20**, 320 (1914).

[7] See, for example, Wiedemann and Hallwachs, *Verh. deut. physik. Ges.*, **16**, 107 (1914). Millikan and Souder, *Phys. Rev.*, **8**, 310 (1916).

which filters allowed light of such wave length to pass that electrons were emitted from the metal.

To accomplish this purpose, a galvanometer having a sensitivity of 5×10^{-8} amperes per millimeter deflection was used. Since photoelectric currents are of the order of 10^{-12} ampere, this galvanometer was obviously not sensitive enough to indicate photoelectric currents directly. By admitting air to a pressure of a few tenths of a millimeter and applying a potential of 220 volts between the mercury and an electrode placed above the surface, this current is multiplied by about 10^4 due to ionization of the gas. Deflections of a few millimeters were obtained, depending upon the intensity of the light used.

It is, of course, a question whether the application of such a potential would not increase the wave length of the photoelectric threshold. This might either be occasioned by the action of the field in pulling the electrons out of the surface, or by driving positive ions formed in the gas a small distance into the metal. These results were verified for certain absorption cells (propyl alcohol and ethyl alcohol) by means of an electrometer and with a potential of 55 volts.[8] It is probable that the change in the threshold with this potential is less than the limits of error, about 200 Å.

The source of light used was a quartz mercury-arc lamp containing argon at a pressure of 8 to 10 cm. During the early stages of the experiments described, the lamp gave many lines and a faint continuous spectrum to a wave length slightly below 2000 Å. With continued use, however, the quartz crystallized somewhat and practically no lines were emitted below 2250 Å.

It was shown that the currents observed were not due to leak along the glass walls, nor (which is very improbable) to production of ions in the air by the radiation, by reversing the potential applied. No deflection was noted in any of these cases.

Various liquids were placed in quartz cells and interposed between the light and the window of the vessel containing the mercury. A quartz lens was used to concentrate the light on the surface. The absorption spectra of the liquids were then photographed with a quartz prism spectrograph,[9] using the same source of light and the same lens. Table I gives the results obtained, together with the shortest wave length transmitted in each case.

TABLE I

APPROXIMATE DETERMINATION OF THE PHOTOELECTRIC THRESHOLD OF MERCURY

Liquid in absorption cell	Wave length Å.	Result
Ethyl alcohol	2250	Positive
Glycerol	2482	Positive
Calcium nitrate (0.1 *N*)	2537	Positive
Acetic acid (glacial)	2537	Positive
Cobalt chloride (2 *N* in CH_3OH)	2650	Negative
Propyl alcohol	2750	Negative
Glass	3200	Negative

We can state as a result of these observations that the photoelectric

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[8] The authors wish to express their appreciation to Dr. T. F. Young for the use of the electrometer and for aid in this verification.

[9] We are indebted to Professor H. I. Schlesinger for the use of the spectrograph.

threshold of mercury is certainly between 2750 and 2537 Å. The line at 2650 Å. in the case of cobalt chloride dissolved in methyl alcohol is very faint, so that the statement that the threshold is between 2537 and 2650 must not be given much weight.

Since this work was completed, Kazda[10] has published a value of 2735 Å. as the photoelectric threshold of mercury. This agrees within the experimental error with the results reported above.

II. The Activation of a Mercury Surface

For the reaction[11] Hg (l) + $^1/_2O_2$ (g, 1 atm.) = HgO (s), ΔF°_{298} = —13,808. This reaction is, however, immeasurably slow at ordinary temperatures. It was thought that it might be possible to obtain appreciable amounts of oxide if the mercury surface had been activated previously by light of the proper wave length. Since for the reaction,[11] Hg (l) + $^1/_3O_3$ (g, 1 atm.) = HgO (s), ΔF°_{298} = —24,608, it was desirable to reduce the possibility of ozone formation to a minimum. This was done in the first experiments by allowing the light to fall on the surface and then admitting oxygen just as the light was turned off. The source of light in these preliminary experiments was a high potential discharge in hydrogen between mercury electrodes. The discharge tube and the reaction vessel were fitted with either fluorite or quartz windows and the windows were placed in direct contact so that absorption of radiation by the air was reduced to a minimum. The oxygen was prepared by heating potassium permanganate. The reaction vessel was first evacuated with a mercury diffusion pump to a low pressure and the light was allowed to act on the surface for about an hour. Oxygen was then admitted to a pressure of about one atmosphere just as the light was turned off. Appreciable amounts of oxide could be detected on the surface. It seemed that more oxide was formed when fluorite windows were used than with quartz, but the results were very qualitative in nature.

Meyer[12] states that oxygen begins to absorb at a wave length of about 2000 Å. This wave length is not transmitted by Pyrex glass. In the next series of experiments a continuous stream of oxygen was allowed to pass over the mercury surface. It was led down to about a millimeter from the surface in a Pyrex tube and issued in a fine jet at the point where the light was incident on the surface. In this manner the ozone formed would be rapidly carried away by the stream of gas. On examination of the surface with a lens the formation of small amounts of oxide at the point where the oxygen encountered the surface could be noted. Oxide was formed when glycerol and cobalt chloride dissolved in methyl alcohol were used as color filters and none when a plate of glass was used. When 220

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[10] Kazda, *Phys. Rev.*, **22**, 523 (1923).

[11] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., **1923**, p. 607.

[12] Meyer, *Ann. Physik*, **12**, 849 (1903).

volts was applied in such a manner as to hinder the escape of electrons from the surface, no formation of oxide could be detected.

The last experiment with oxygen consisted in allowing the light to fall continuously on a mercury surface in the presence of oxygen at a pressure of one atmosphere. Color filters were used which cut out those wave lengths that cause ozone formation. Results similar to the above were obtained and small retarding potentials considerably reduced the amount of oxide formed.

It is well known that nitrogen dioxide reacts readily with mercury. This reaction probably takes place according to the equation,[13] $4Hg\ (l) + 2NO_2\ (g) = 4HgO\ (s) + N_2\ (g)$; $\Delta F^{\circ}_{298} = -79{,}072$. When nitrogen dioxide is admitted, the mercury surface to all appearances remains nearly unchanged for some time. At a fairly definite point, however, the film of oxide "sets," that is, becomes thick enough so that wrinkles may be seen on the surface. This can best be noted by looking at the surface with reflected light. It was thought that a fairly quantitative measure of the speed of the reaction could be obtained by determining the time of formation of this film.

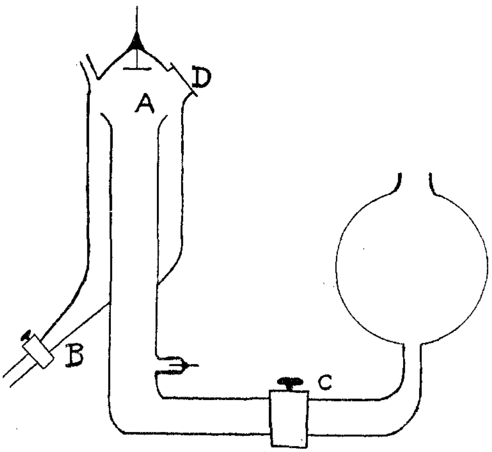

Fig. 1.

Fig. 1 shows the type of reaction vessel used. The vessel was evacuated to a pressure of about 0.1 mm. and mercury admitted through the stopcock, C, until it reached the top of the inner tube at A. D is a quartz window so arranged that light could be focussed on the mercury surface. After each experiment the apparatus was flushed out with nitrogen, and the surface renewed by allowing more mercury to enter through C. The excess of mercury was drawn off through B. The nitrogen dioxide was prepared by heating lead nitrate and contained, therefore, some oxygen. The first few runs took more time for the formation of the film than later ones and were not consistent among themselves. This retardation was probably due to traces of moisture, present in spite of passage of the gas through two long tubes of phosphorus pentoxide. The presence of a field alone, without the action of light, did not affect the time of formation of the film. Fig. 2, Curve I, gives an idea of the reproducibility of the results without light.

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[13] Watt's, "Dictionary of Chemistry," Longmans, Green and Co., **1894**, vol. III, p. 566.

Curve II, Fig. 2, shows a series of points taken as follows. The quartz mercury arc lamp described above was used without any light filter; 220 volts was applied during the time the light was allowed to act on the surface, in such a way as to aid the removal of electrons from the surface. The gas was admitted a fraction of a second before the light was turned off; the field was turned off at the same time and the electrodes shorted. If the field was left on after the gas was admitted the results were erratic. In general, however, the time required for the formation of the film was nearly the same as without the action of light.

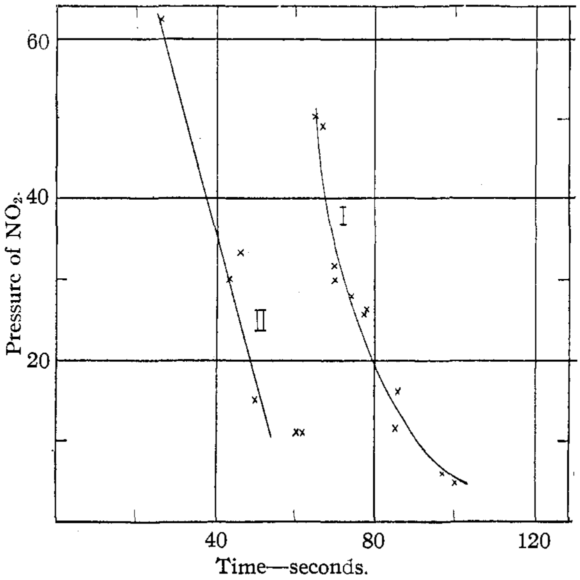

Fig. 2.

Fig. 3 shows two curves at constant pressure of nitrogen dioxide (30 cm.) with various applied voltages. In these experiments the field was left applied after the gas was admitted. For high voltages (above six volts) the time required is the same as without light, 70 seconds. For voltages below six volts the time becomes shorter and passes through a minimum at about 1 volt. The minimum was obtained at 1.0 volt in four different runs. In one run it was found to be 1.1 volts and in one other 1.5 volts approximately. The other curve, $\lambda > 2650$, was obtained by interposing a solution of cobalt chloride in methyl alcohol. One other curve (not shown) was obtained by interposing glycerol. The optimum voltage was also at 1 volt in this case.

Fig. 4 shows the effect of wave length at constant pressure of nitrogen dioxide and 1 volt applied continuously. The differences between A, B and C are due, probably, to the intensity of the light transmitted by the various filters. D and E gave the same results as without light, namely 70 seconds.

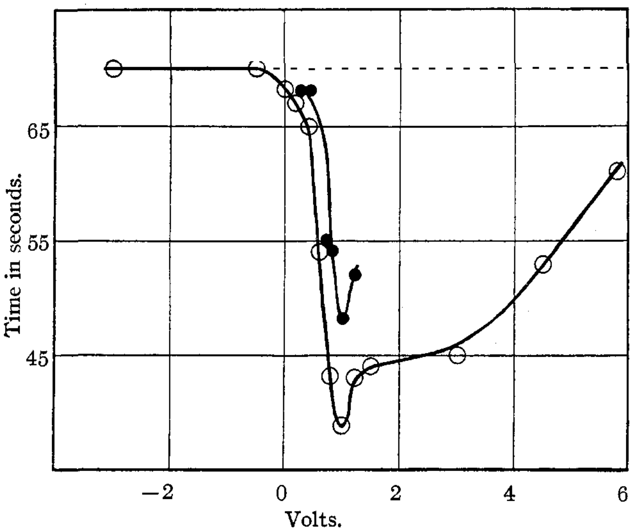

Fig. 3.—Upper curve, $\lambda > 2650$. Lower curve, $\lambda > 2250$.

One series of experiments was tried in which the intensity of the light was varied by increasing the distance of the light from the lens. We can

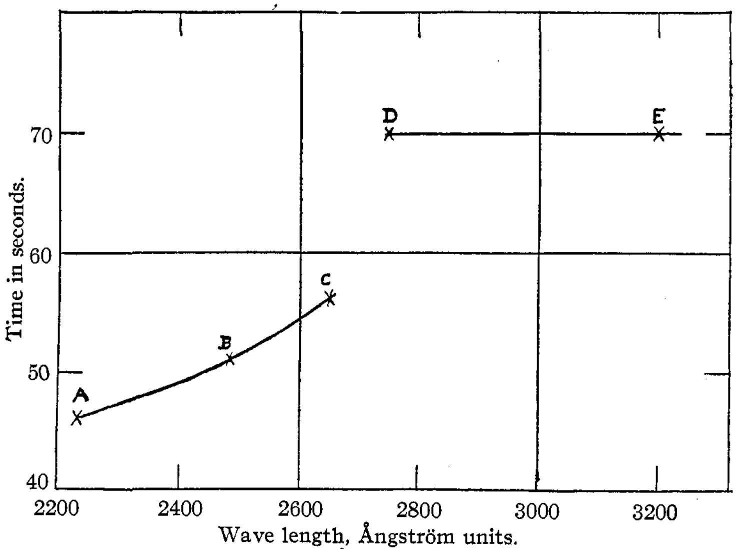

Fig. 4.—A, ethyl alcohol (2250 Å.). B, glycerol (2482 Å.). C, $CoCl_2$ in methyl alcohol (2650 Å.). D, propyl alcohol (2750 Å.). E, glass (approx. 3200 Å.).

say qualitatively that decrease in the intensity of the light leads to an increase in the time necessary for the formation of the film.

III. Discussion of Results

It is impossible to draw any wide generalizations from these experiments, but we may point out certain things which seem of interest and demand further study.

1. High voltages, if left applied, even in such a manner as to accelerate the electrons away from the surface, cause a sort of "deactivation." The deciding factor would seem, therefore, not to be the emission of the electrons alone. There is the possible explanation that the high potential aids in the replacement of those electrons which have been emitted from the surface.

2. The contact difference of potential between iron and mercury is given as 0.5 volt.[14] This can be taken as only approximating the contact potential between mercury and iron in our experiments. This contact potential acts in such a way as to diminish the potential applied. The maximum speed of the electrons emitted by the light without filter is between 0.9 and 1.0 volt. While the accuracy of our experiments is not sufficient for deciding the point definitely, it is interesting to note that the time becomes normal, that is, 70 seconds, at a negative potential of about 1 volt, if due allowance is made for the contact potential. The curve made with the cobalt chloride filter (the electrons would have smaller maximum velocities in this case) tends toward the 70-second line at a slightly higher voltage.

3. The wave length of light necessary to produce increased rate of formation of the film must be below the threshold wave length of the photoelectric effect, within our experimental error. There is, of course, the possibility of activating the nitrogen dioxide in the short interval of time before the light is turned off. Since nitrogen dioxide absorbs light in the visible spectrum, one would expect, if this were the case, to obtain an increased rate of reaction with radiation transmitted by glass. This is not found to occur.

4. The voltage for maximum rate of reaction is, within the experimental error, the same for the wave lengths employed.

5. Decrease in the intensity of the light decreases the rate of reaction.

Only a rough interpretation of these results is possible. The recent work of Cario and Franck[15] on the dissociation of hydrogen by mercury vapor under the influence of ultraviolet light of wave length 2537 Å. suggests a possible explanation, namely, that the oxygen or nitrogen dioxide is activated through contact with the mercury surface and in turn reacts with the mercury. This explanation is improbable in view of the

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[14] Pellat, *Ann. chim. phys.*, [5] **24**, 5 (1881). van der Bijl ("Thermionic Vacuum Tube," McGraw-Hill Book Co., **1920**, p. 29) gives 0.7 volt.

[15] Cario and Franck, *Z. Physik*, **11**, 161 (1922).

fact that oxide seemed to be formed only at the point where the jet of oxygen was incident on the surface (preliminary experiments, Part II). As indicated by Gibson and Noyes,[16] nitrogen dioxide may take up electrons, forming negative ions. These would, however, be accelerated away from the surface with the potentials used.

If the ionization potential of nitrogen is taken as 16.9 volts[17] and the current in the experiments on the determination of the photoelectric threshold as 10^{-7} ampere, then the photoelectric current without ionization of the gas is approximately 10^{-11} ampere. This is equivalent to about 10^8 electrons per second. The mercury surface used had an area of about 6 sq. cm. If the light acts on a layer one atom in thickness, there would be approximately 10^{16} atoms of mercury on the surface. It was found that the time of formation of the film did not vary appreciably with change in the time of exposure for times of one minute or more. On the other hand, if between one and two seconds are allowed to elapse after the light is turned off, before the gas is admitted, the time required for the formation of the film is the same as though the surface had not been activated. The duration of the activation is extremely short, probably very much less than a second. Since this is the case, approximately 10^8 molecules of mercuric oxide are formed for each atom of Hg in the active state, assuming that the film to be visible must be one molecule thick. Even if the duration of the activation were as long as one second, and if the number of molecules formed as a result of the activation is given by the expression,

$$\frac{\text{(Time of formation without light)} - \text{(time of formation with light)}}{\text{(Time of formation without light)}} \times$$

(Number of atoms on the surface), we should still have to account for the activation of an extremely large number of atoms for each electron emitted. Effects of this order of magnitude have been observed for other photochemical reactions.[18] The first explanation that comes to mind is that an atom which has lost an electron due to photoelectric emission is more reactive and tends to react with an oxygen molecule. In order to complete the outer shells of the two atoms in the mercuric oxide molecule, an electron is taken from a nearby mercury atom. This atom in turn is capable of going through the same process. This may continue until the chain comes to an accidental end. If this explanation is at all valid, it seems more logical to assume that the electrons involved are not really free, but are bound by loose constraints to the atoms in the metal.

If it is assumed that the electrons are really "free" electrons, there might be an equilibrium in the metal which is disturbed by the photoelectric emission of some of them. To restore the equilibrium a certain number

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[16] Gibson and Noyes, THIS JOURNAL, **43**, 1255 (1921).

[17] Smyth, *Nature*, **111**, 810 (1923).

[18] See, for example, Bodenstein and Dux, *Z. physik. Chem.*, **85**, 297 (1913).

of atoms would have to give up their electrons, thereby increasing the number in the active state. If this is the case, a metal placed in a strong electrostatic field should be more reactive on the side turned toward the negative pole of the field. In our experiments this was found not to be the case with potentials of 220 volts, but these would probably not be sufficient for the purpose mentioned. There still remains the difficulty of accounting for the large amount of mercuric oxide formed.

The effect of 220 volts in "deactivating" the surface is possibly due to the fact that electrons emitted are more rapidly replaced by electrons from below the surface. In this case one atom of mercury might be activated for each electron emitted, but the effect would be too small to be noticed by our method of measurement.

If it were possible to study some reaction for which the free-energy change is not negative, it could perhaps be shown that the number of atoms activated was equal to the number of electrons emitted. Such a chain action as that described above would not be possible in this case.

The conclusion that the mercury surface has been activated by the emission of electrons seems to be more plausible in view of the experiments described. The alternative explanation that the gas molecules have taken up electrons and therefore react more readily with the mercury surface should not be considered as impossible. It would be much easier to explain the effect of high voltages in reducing the rate of reaction on this basis. The kinetic energy of a molecule at room temperature corresponds to about $^1/_{30}$ of a volt, and the potential required for the maximum rate of reaction (one volt) would probably be sufficient to keep any negative ions from reaching the surface. This would seem to indicate that the effects described were due to the activation of the surface. The apparent "deactivation" by higher voltages is hard to explain without more knowledge than we possess at present of the motion of electrons in metals.

Summary

1. A rough determination of the photoelectric threshold of mercury is given.

2. The reactions of oxygen and of nitrogen dioxide are accelerated if the surface has been activated by wave lengths below the photoelectric threshold.

3. A possible theory of the activation is discussed.

4. The duration of the activation is less than one second.

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