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Ionization of Gases by Light

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The subject of this article, the ionization of gases by ultraviolet light, is a narrow but singularly inviting department of modern physics. The obstacles to experiment are so great that they are only now being overcome by the latest improvements in laboratory technique; nearly all the valuable data are of recent acquisition, and the period of discoveries is not yet past. Some of the results afford excellent confirmation of present atomic theory; others are still obscure and challenging.

THE subject of this article is more narrowly restricted than those of many others of the series. It is narrower even than the title might imply; for by "ionization" I mean for the present only the detachment of the most loosely bound electron of a molecule or an atom, and by "light" only the waves of the visible spectrum and that adjoining range of wavelengths to which the name of ultraviolet is customarily confined. Either of these limitations is implicit in the other; for though most molecules are fashioned with electrons bound with varying degrees of tightness, and the removal of any one thereof is an act of ionization, it is beyond the power of such light-waves to abstract any except the loosest. Perhaps it will be found instructive if for so definite and circumscribed a problem I relate the methods of experiment, the data of the experiments, the simple theory, and the artifices which have been conceived to reconcile the theory and the data, sometimes with success and at other times in vain.

Most of the really valuable data are of recent acquisition, for there are difficulties hampering the attack upon the problem, which the progress of laboratory technique is only gradually clearing away. Consider, for instance, the question of providing the light. It is desirable to be able to illuminate the gas with monochromatic light of any wavelength, photons of any energy. When ionization by electrons is being studied, one varies the energy and the wavelength at will by varying the voltage impressed on the electrons. With light, this is not within our power; one has to take the quanta as they are supplied by a luminous source.

If the spectrum of the source consists of bright lines widely separated, the ionization which any of them alone produces may be measured, and the energy of the quanta is very narrowly defined. On the curve of ionization *vs.* frequency, then, every spectrum line supplies an experimental point of which at least the abscissa is certain. But at the frequencies between the lines, there is no way of getting information; and many a published curve is traced by guesswork right across the regions of major importance where data are essential, simply because Nature left those regions vacant of lines in the spectrum of the mercury arc!

If on the other hand the source has a continuous spectrum or one crowded with bright lines, the device for resolving or filtering the light will transmit to the ionizable gas photons not of a single wavelength, but of a range of many Angstroms—dozens or scores of Angstroms, perhaps even a hundred. A single measurement may be, and usually is, plotted as if it belonged to the central wavelength of the transmitted band; but actually the ionization results from waves of all the wide range, and not even from a uniform distribution of energy across the range, but from a distribution affected by the qualities both of the source and of the resolving apparatus. With chemical filters, *i.e.* with coloured absorbing liquids, bands of transmitted light may be formed in various parts of the spectrum. They are likely to be broad and hazily bounded, and limited in number; but the liquid filters are inexpensive and easy to handle, and in tracing backward the sequence of observations on any one substance, one often finds that the very earliest were made with filters. Monochromators—which is to say, spectroscopes—form bands of which the central wavelength and the width may be varied at will. This sounds ideal; but in practice, of course, the narrower the transmitted range of wavelengths, the scantier the transmitted energy; and one must compromise as best one may between a band too narrow to produce a measurable degree of ionization, and one so broad that it is hard to apportion the credit for the effect which it produces among the frequencies which make it up. It will be evident that the ideal curve, drawn through experimental points scattered thickly all through the spectrum and each corresponding to a single wavelength, is difficult of attainment and even of approach!

As the atmosphere of the earth prevents us from observing the spectra of the stars at shorter wavelengths than some $280m\mu$, so the opacity of all terrestrial solids prevents us from projecting quanta of smaller wavelength than $125m\mu$, into an enclosure. Indeed, it is only from fluorite and only from occasional samples of fluorite that one can make windows which are transparent so far out; the next best and much the commoner substance, quartz, ceases to transmit at about $145m\mu$. We are thus almost entirely debarred from observations on the noble gases and on the common diatomic gases, which is deplorable.

The desired photons being successfully fired into the gas, the next problem is that of distinguishing the ionization they may cause in it from whatever other liberation of charge they may effect in striking walls, electrodes, or any of the other furniture within the tube. Light of sufficient frequency to ionize a gas will usually be able to produce an outflow of electrons from almost any metal. One takes of course the elementary precaution of designing one's tube in such a way, that the beam of light traverses it from entrance-window to exit-window without touching any electrode; but the disparity of the effects is nevertheless so great, that a modicum of scattered light may evoke more electrons from the metal than the primary beam in all its strength detaches from atoms of the gas. Some experimenters use alternatively two electrodes of very unequal size, expecting that a current due to ionization of the gas will be the same in magnitude whichever they use as cathode, while a current due to light falling on the electrodes will be greater when the larger is the cathode. Some vary the density of the gas, assuming that if the current is proportional to density it must be due to the effect which they seek; but it would also vary as the density, if instead it consisted of electrons expelled from the electrodes by light proceeding from excited atoms of the gas. Some finally have so designed their apparatus that they perceive positive ions only; this seems to be the safest way.

Like Hughes,* I will divide the data according to the character of the gases to which they refer: the common or "permanent" (chiefly diatomic) gases first, then mercury, finally the alkali metals.

The *permanent gases* can be disposed of in short order, for our knowledge in this field is scanty, though surprising. Measurements of ionization by electron-impacts, and what little has yet been deduced from spectra, agree in indicating that for all of them (with the slight exception of nitric oxide NO) the ionizing-potential is greater than 10 volts. Translating this figure into wavelengths of light, we infer that only photons of smaller wavelength than $125 m\mu$ can ionize such a molecule in a single impact. Therefore light which is able to traverse any window of solid substance should be unable to ionize any permanent gas (except NO); in other words, any such gas enclosed in a tube should be immune to ionization by any radiation entering from outside. Yet there is unimpeachable evidence that air, and oxygen and nitrogen separately, and possibly hydrogen and iodine, are ionized by light which has penetrated fluorite. The threshold for these gases must

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* A. L. Hughes, *Ionization of Gases and Vapors by Light* (Washington University Studies, 1929). I have benefited much by this article, and also by that of F. L. Mohler, *Recombination and Photoionization* (Reviews of Modern Physics **1,** 216–227 (1929)).

therefore lie on the long-wave side of $125 m\mu$. For air it is presumed to lie between this and $145 m\mu$, since a plate of quartz holds back the ionizing rays. The discrepancy between these and the expected thresholds may not seem large, but it is important. Naturally one has recourse to the idea of a two-stage ionization, occurring when two quanta in succession are absorbed by the same molecule—an idea which, we shall see, is frequently invoked in other cases. If this is valid, the ionization should increase as the square of the intensity of the light. There seem to be no data bearing on this point. To quote from Hughes, "further investigations in this field are badly needed."[1]

With *mercury* the situation is much more definite, but for those who like to have simple theories verified completely it is no more satisfactory.

The spectrum of the mercury atom is well mapped and well interpreted, and the ionizing-potential for electron-impacts has been determined over and over again. From both of these it follows that ionization by single photons should be possible only at wavelengths smaller than 1188A. However it is certain that the light of the famous resonance-line of mercury, 2537A, is able to ionize the vapor of the element whence it proceeds.[2]

This seems the natural equivalent of the well-known fact that when mercury atoms are bombarded by a sufficiently dense electron-stream, ionization begins at the resonance-potential. The quanta of the wavelength 2537A have 4.9 equivalent volts of energy. Such a photon strikes an atom, and excites it transferring if from the normal into a certain excited state, denoted by the symbol 2^3P_1; a second comes along and likewise is absorbed, bringing the energy of excitation of the atom up to twice 4.9 equivalent volts; this amount falls short of the ionizing potential by only 0.6, and a third photon more than supplies what is required. So runs the simple interpretation; but we shall see that only the first of these steps is confirmed by further experiment, and that the rest of the process must happen in some other way, though the way is far from clear.

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[1] For references to the literature I refer to Hughes (*l.c.*) Among the latest papers are those of A. L. Hughes (*Proc. Camb. Phil. Soc.*, **15**, pp. 483–491 (1910)); F. Palmer (*Phys. Rev.* **32**, pp. 1–22 (1911)); E. B. Ludlam (*Phil. Mag.* (6) **23**, pp. 757–772 (1912)); W. West, E. B. Ludlam (*Proc. Roy. Soc. Edinb.*, **45**, pp. 34–41 (1925)). Some of the early work on air was confused by what appears to have been a photoelectric effect of particles of colloid size ("nuclei" or *Kerne*) produced by the action of ultraviolet light on impurities in the air—one of the once-popular and now forgotten problems of physics.

[2] Literature: G. F. Rouse and G. W. Giddings, *Proc. Nat. Acad. Sci.*, **11**, pp. 514–517 (1925); **12**, pp. 447–448 (1926). F. G. Houtermans, *ZS. f. Phys.*, **32**, pp. 619–635 (1925). Twenty years ago W. Steubing (*Phys. ZS.*, **10**, pp. 787–793 (1909)) observed that light coming from a mercury arc and passing through quartz was able to produce a current in a tube containing mercury vapor; but his result has been impugned.

It was the beautiful experiment of Rouse and Giddings which confirmed that the first of the steps is the entry of the atom into the 2^3P_1 state; for they showed that ionization of the gas occurs only when the impinging quanta have just the energy required for that transition, not when they have a little less or even a little more. This they were able to show because of the phenomenon of "self-reversal." When a luminous gas becomes dense and hot, the lines of its emission-spectrum broaden; for the atoms perturb one another, the energy-values of their stationary states are changed by various amounts, and the frequencies of many of the quanta which emerge are appreciably shifted upwards or downwards from the original or "standard" values appropriate to isolated atoms. If in addition the region of density and heat is surrounded by another where the gas is cooler and more rarefied, the atoms in this outer zone, being relatively unperturbed, will be able to absorb the quanta having the standard frequencies, but not those others of which the frequencies are shifted. In technical language, the "core" of the line is absorbed; only the "wings" pass through; the line exhibits "self-reversal." In the spectrum of the ordinary mercury-vapor lamp, the line 2537 is notably self-reversed. Cooling the lamp with flowing water or an air-blast, however, abolishes the effect; the line shrinks to its normal narrowness, the wings disappear, but the photons of the core are able to escape from the tube. Any action therefore which is performed by the light of a cooled mercury-vapor lamp, but ceases when the cooling is suspended, must be due to quanta having energies adjusted exactly to the values which are able to excite isolated atoms of mercury. Rouse and Giddings found that ionization of gaseous mercury is precisely such an action.[3]

We cannot so readily conclude that the second step in the ionization-process is the absorption of a second 4.9-volt quantum. It would be rather of an odd coincidence, if there were an excited state of the mercury atom differing in energy from the 2^3P_1 state by just so much as this latter differs from the normal state—not, however, an impossible coincidence. Another and a stronger argument is furnished by the fact that when quanta of various wavelengths shorter than 2537—including some which could transfer the atom from the 2^3P_1 into other known excited states—are projected into the gas along with 2537, the rate of ionization is not augmented. If none of these can help the electron to escape, it is not so likely that a second quantum of precisely the wavelength 2537 can achieve it. Moreover the duration of the

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[3] There was still a residual current in the irradiated tube when the cooling of the lamp was discountinued; but it depended on the size of the cathode in such a way as to suggest that it was due to light falling on that electrode (cf. page 343). Houtermans later verified this result.

2^3P_1 state is known to be so short (of the order of 10^{-7} second) that under the actual conditions of some of the experiments an atom would not often meet two quanta in such quick succession that at the advent of the second it would still be in the 2^3P_1 state into which the first had put it. In other words, the number of 2^3P_1 atoms in the gas at any moment is too small.

This last would be a serious obstacle to any theory, but for the fact that the mercury atom possesses another stationary state slightly below the 2^3P_1, the which is *metastable.* This is the 2^3P_0 state, of 4.7 equivalent volts; its mean duration may amount to something like a hundredth of a second. Now collisions of mercury atoms in the 2^3P_1 state with atoms of certain other kinds, argon notably, may cause the former to pass over into 2^3P_0. This is an instance of "collisions of the second kind." When mercury-vapor is mixed with a much larger quantity of argon and is illuminated with 2537 light, the number of 2^3P_0 atoms is at any moment much greater than the number of 2^3P_1 atoms would be, if the argon were absent; further, it is proportional to the amount of argon.

Now F. G. Houtermans found that the rate of ionization, in mercury mixed with argon and irradiated by 2537, is proportional to the amount of argon. Therefore, in one stage of its progress from a normal atom to an ion, the mercury atom must be in the 2^3P_0 state. It enters this state from the 2^3P_1 because of a collision with an argon atom. How does it leave? by absorption of a second 4.9-volt quantum? Two of the considerations of the last paragraph but one speak against this idea, and Houtermans thinks that the 2^3P_0 atom collides with another which is in the 2^3P_1 state, and there is an interaction—this would be another sort of "collision of the second kind"—in which one of them adds to its store of energy all or most of what the other possesses. So it arrives within an equivalent volt or so of the state of ionization; if one were to take over all the energy of excitation of the other, it would have $4.7 + 4.9 = 9.6$ equivalent volts, out of the 10.4 required. Still a third step seems to be essential.

The reader may have wondered that I have as yet said nothing about the dependence of ionization on intensity of light, for evidently the former should increase as the cube of the latter if the process is a three-stage one as I have sketched. The matter has been tested by experiment; the answer was unexpected, for the ionization varies as the square of the light—as though the process were of two stages.[4] We

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[4] This simple result was obtained only over certain ranges of temperature and pressure of the vapor, but these were precisely the ranges where both are low, and we should expect the result to be most reliable and least subject to confusion by secondary effects. As the pressure rises so does the exponent n in the relation *ionization* = (*intensity*)^n.

cannot suppose that the atom after its second gulp of energy picks up the remaining 0.8 volt in a collision with a fast-moving ordinary atom, for at normal temperatures such fast-moving atoms would be excessively rare. Houtermans suggests that when a 2^3P_0 and a 2^3P_1 atom collide with one another, they unite to form an ionized molecule Hg_2^+. This is far from being the only case in which a molecule is invoked as the *deus ex machina* to help out with an otherwise untenable theory.

We turn now to the alkali metals, or rather to the three heavier among them, cæsium, rubidium, and potassium. With these it is more nearly possible to get a full view of the situation. The phenomena are not confined to spectrum ranges in or beyond the remotest attainable fringes of the ultra violet. Indeed, in these four cases, even the wavelength where ionization by *single* impact should begin is well within reach, being in the nearer ultra violet; 2412A for Na, 2856 for K, 2968 for Rb and 3183 for Cs. Ionization currents are provoked by light at even greater wavelengths; this resembles the case of mercury irradiated by 2537, and is equally perplexing, indeed more so. They are however much greater, near or beyond the limiting wavelength for one-stage ionization; and there, we seem to be witnessing the simplest process of all. With cæsium, rubidium and sodium, the data in this range conform to simple theories in a gratifying way. I will consider these first, and then the most mysterious case of all, that of potassium.

The vapor pressures of the alkali metals increase with atomic number, and for rubidium and cæsium are great enough to permit the methods employed with the gases mentioned above: which is to say, that stationary vapor of known density may be illuminated by light of known intensity, and the amount of ionization be measured absolutely by drawing off all the ions. This I denote as the "absolute" method. There is another, the "method of space-charge annulment." The tube containing the vapor contains also a hot-filament cathode and some form of anode, and the filament is kept so hot, the P.D. between it and the anode kept so low, that the electron-borne current between cathode and anode is limited by its own space-charge. When positive ions are formed in the vapor, as in these experiments they are by light, a fraction of the negative space-charge is annulled, and the current increases. The change in the current is a measure of the number of positive ions formed. Nothing of the sort results if light falls on solid objects in the tube and ejects electrons, an insensitiveness which is a great advantage of the method. For positive ions it is a very sensitive method; one finds such statements as "each positive ion formed causes a million extra electrons to flow from cathode to anode," and Foote and Mohler, who were the first to apply this method to ionization by light, perceived the effect at pressures of mercury vapor as low as .002 mm. Hg. It does not permit of absolute measurements; but one may use it to make accurate measurements of the relative ionizing-power of light of any number of wavelengths, and then standardize them *en bloc* by a determination at a single wavelength with the absolute method.

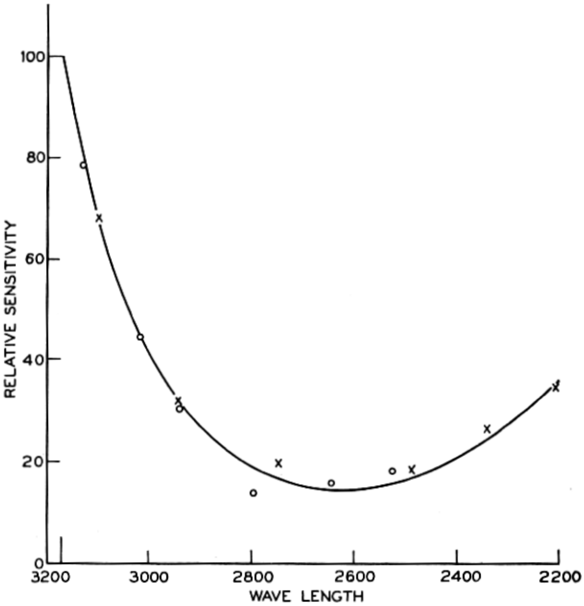

Fig. 1—Ionization by light plotted as function of wavelength for cæsium (Critical wavelength: 3184A). (F. L. Mohler, C. Boeckner).

I now reproduce two of the most recently published curves of ionization vs. wavelength: Fig. 1 for cæsium, from F. L. Mohler and C. Boeckner;[5] Fig. 2 for rubidium, from E. O. Lawrence and N. E. Edlefsen.[6] It is the downward trend of these curves from the limiting wavelength towards shorter waves which interests us now. Ionization by light of a given intensity is most abundant when the quanta have just the energy required to detach the electron, and no more. The more the energy of the photon exceeds the strictly necessary value, the less it is likely to be captured and have its energy spent for ionization.

The various theories, except for one, predict a steady downward trend; one in particular, that of R. Becker, supplies the broken curve

[5] *Bur. Stand. Journ. Res.*, **3,** pp. 303–314 (1929).

[6] *Phys. Rev.*, (2) **34,** pp. 233–242 (1929).

of Lawrence and Edlefsen's figure (relative ordinates have no significance, it is only the trends of the curves which should be compared).

Mohler and Boeckner also measured the actual number of ions produced by light of known intensity in a known quantity of gas, using of course the absolute method, and expressing their results in the following way. Suppose a thin stratum of gas, of thickness dx and area A. Denote by N the number of atoms per unit volume of the gas; then $NAdx$ will stand for the number in the stratum. Denote by Q the total number of photons striking the stratum in unit time; suppose that they fall upon it perpendicularly, and are evenly distributed over its area. The number of ions formed in the stratum in unit time, I will be proportional to $NAdx$ and to Q/A. Write:

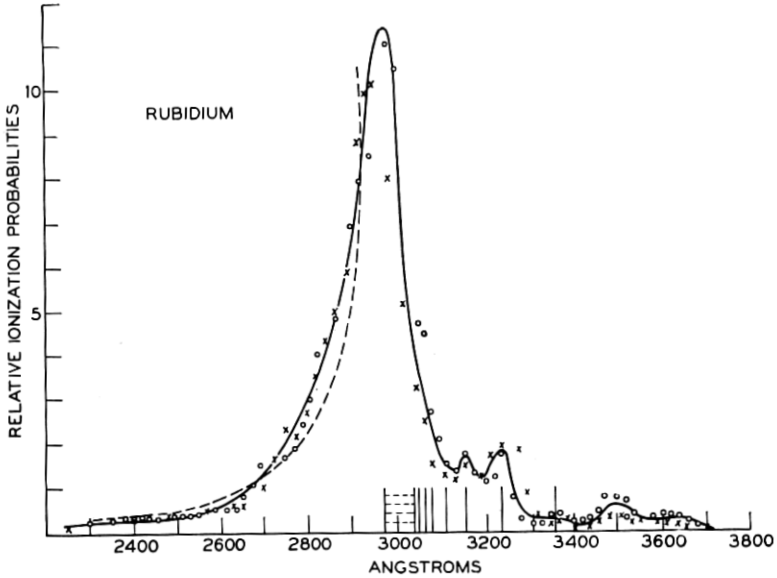

Fig. 2—Ionization by light plotted as function of wavelength for rubidium (Critical wavelength at 2968A). Circles and crosses correspond to different densities. (E. O. Lawrence, N. Edlefsen.)

$$I = kNQdx$$

the coefficient k is the quantity of which the experiments are designed to reveal the value. (We should not be entitled to expect this to be constant, if more than a small fraction of the quanta were spent in ionization; but in the practical cases we may.) The values which they give are $(2.3 \pm 0.2) \cdot 10^{-19}$ for cæsium and $1.1 \cdot 10^{-19}$ for rubidium, at the limiting frequency in each case. Earlier E. M. Little[7] had got a value two orders of magnitude lower for cæsium; this difference has not been reconciled. These values will later be compared with those to which the theories lead.

The upturn in the curve of Fig. 1 on the shortwave side of 2600A may serve[8] as an introduction to the case of *potassium.* Adjourning therefore the discussion of the righthand part of the curve of Fig. 2, I take up next this strange and singular case.

The first who plotted an ionization-vs-wavelength curve for potassium was E. O. Lawrence.[9] The vapor-pressure of potassium being low, he so designed his tube that the beam of light passed across the vertically-rising jet of gas distilling from a pool of highly-heated metal. This expedient was used by all the other physicists who worked upon potassium, and was at one time held responsible for the curious results, until finally Mohler and Boeckner confirmed the previous data by measurements on stagnant vapor. The ionization-current was collected by electrodes placed on either side of the jet and away from the light; so the method is fit to give the relative ionizing-powers of light of various wavelengths, though not an absolute measurement, the density in the jet being unknown. Lawrence's monochromator provided beams of light extending over some 80A of the spectrum.

Few data can have been more unexpected, indeed more positively unwelcome, than those which he obtained; for what they intimated was, that ionization begins, or at least *the sharp increase of ionization occurs, at a wavelength definitely too small.* It seems as though a photon could not ionize a potassium atom without having definitely *more* than the necessary energy; a conclusion which would be in disaccord with fundamental theory, and with the (subsequent) experiments upon rubidium and cæsium.

New experiments upon potassium gave comfort to the theory, but also demonstrated the anomaly which Lawrence had discovered.[10] The

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[7] *Phys. Rev.*, (2) **30**, pp. 109–118, pp. 963–964 (1927).

[8] However it does not appear in the corresponding curve obtained by Lawrence and Edlefsen.

[9] *Phil. Mag.*, **50**, pp. 345–359 (1925). There had been four precursors: S. H. Anderson, L. A. Gilbreath, R. C. Williamson, R. Samuel (for the references, see Hughes, *l.c.*). The earliest two reported ionization at wavelengths where it now seems unlikely that true ionization of the vapor would have been perceptible; the others used chemical filters and so were unable to plot a curve, but seem to have observed the weak ionization produced between 2800 and 3100A.

[10] Such a proof would relieve us from one of the greater difficulties of the "molecule" hypothesis—the necessity of assuming that ionization of a K_2 molecule by light is an event thousands of times as probable as that of a K atom, for in potassium vapor under the actual conditions free atoms are believed to be a thousand times more abundant than molecules, and yet the ions which we are ascribing to the latter are much more plentiful. R. W. Ditchburn and F. L. Arnot (*Proc. Roy. Soc.*, **123**, pp. 516–536 (1929)) found nothing but K^+ ions in the ionized vapor, thus disposing of the notion that the process might consist in the detachment of an electron from a thenceforward stable K_2 particle.

curve which I display as Fig. 3 is taken from the latest paper,[11] but the marked points comprise those of Lawrence's first article (large circles) and those obtained in the interim by R. C. Williamson.[12] The monochromators used in these late researches gave narrower wavelength-bands than those used formerly, and so revealed the small peak at the proper limiting-frequency which had eluded Lawrence at the outset. The much more prominent peak at shorter waves remains outstanding. The data, be it mentioned, are here reduced to equal intensities of light for the various wavelengths.

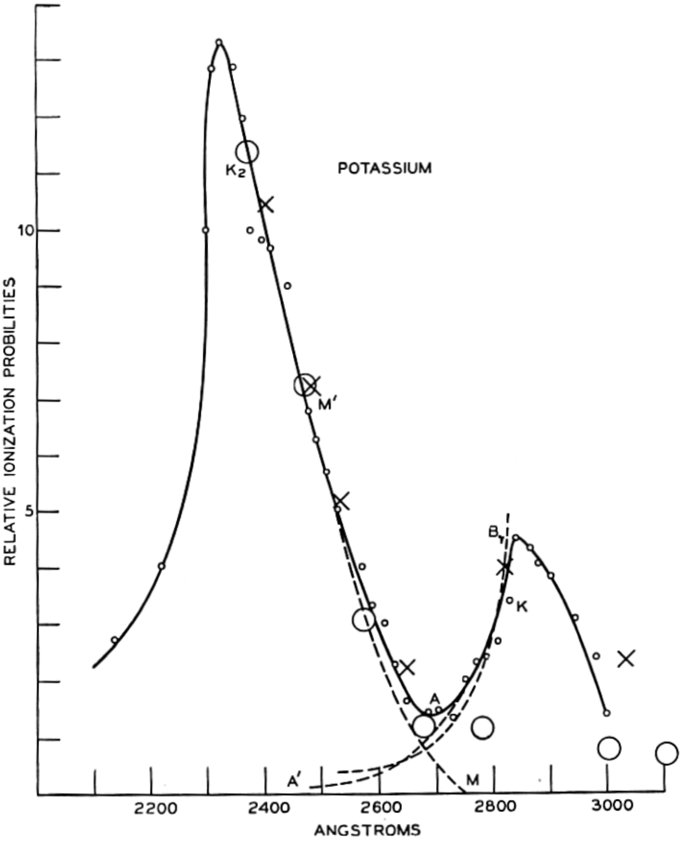

Fig. 3—Ionization by light plotted as function of wavelength for potassium (Critical wavelength: 2856Å). Circlets, crosses and large circles correspond to different sets of observations by Lawrence & Edlefsen, Williamson & Lawrence. (E. O. Lawrence, N. Edlefsen.)

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[11] Lawrence & Edlefsen, *Phys. Rev.*, (2) **34,** pp. 1056–1060 (1929).

[12] *Proc. Nat. Acad. Sci.*, **14,** pp. 793–799 (1928).

The molecule was invoked at once as the *deus ex machina;* the ionization beginning beyond the proper wavelengths was supposed to be ionization of molecules, with or without dissociation. So long as the threshold was thought to be near 2600 or 2550, this idea was fortified by the following calculation. Suppose that a photon of wavelength 2555A has just the energy required to split a K_2 molecule into a K atom, a K^+ ion, and a free electron; and that a photon of 2856A has just the energy required to split a K atom into a K^+ ion and a free electron. One easily sees that then the difference between the energies of these two photons would be just the energy required to split a K molecule into two neutral K atoms. The difference amounts to 0.5 equivalent volt. This figure agrees [13] with independent estimates of the value of the latter quantity, which is the heat of dissociation of K_2. The force of this agreement has just been weakened by the curve of Fig. 3, showing as it does that the ionization in question begins near 2700A—weakened, but not destroyed, for the ions produced by waves shorter than 2555 might be explained in a way which the reader will easily imagine after the next two paragraphs. The other alternative is, to hope that quantum mechanics will presently prove that the ionization-vs-frequency curve for the potassium atom ought to display both the maxima which are found.

Return now to the curve of Fig. 2 for rubidium. On the long-wave side of the limiting-frequency there is a series of peaks; they lie at the frequencies of the various members of the principal series of lines in the Rb spectrum. Even more striking peaks of this sort were earlier obtained with cæsium by Foote, Mohler, and R. L. Chenault; [14] the relevant part of one of their curves is shown as Fig. 4.

Palpably these are phenomena of the same sort as one meets when mercury is irradiated by 2537; and they signify an ionizing-process of two or more stages, the first of which is excitation by the absorption of a photon. There is probably no need to suppose more than two stages; the energy received by the atom from the photon is always much more than half of what is required to ionize. It is supposed by those who have obtained the data that the process is completed by an impact of fast-moving atom, one of those which by virtue of Maxwell's distribution have the necessary excess of energy over the relatively modest mean value corresponding to the actual temperature. The relative heights of the peaks would then be determined partly by the relative abundance of atoms having the necessary energies, and partly by the relative probabilities of the corresponding types of excitation, which

[13] R. W. Ditchburn, *Proc. Camb. Phil. Soc.*, **24,** pp. 320–327 (1928).
[14] *Phys. Rev.*, (2) **26,** pp. 195–207 (1925); **27,** pp. 37–50 (1926).

are quantities with which the theories deal. According to Foote, Mohler and Chenault, these relative heights are in fair accordance with the theories. The actual heights, however, depend on the mean duration of the excited states. I do not know whether it has been proved that these last long enough to permit the explanation.

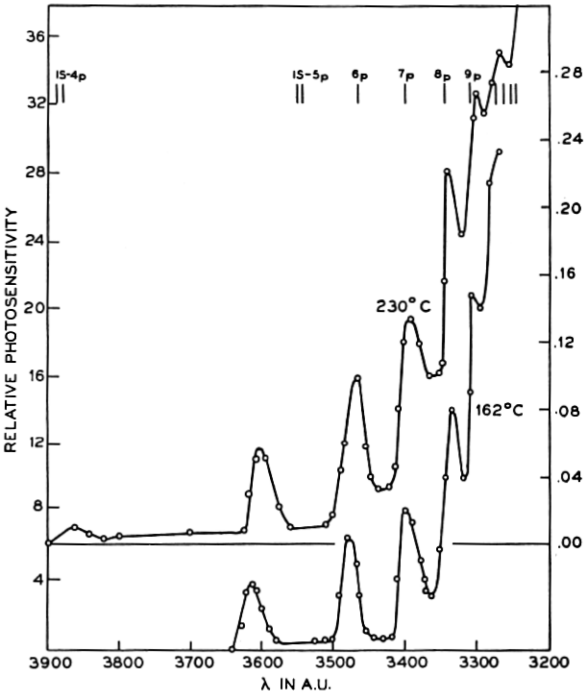

Fig. 4—Ionization of cæsium vapor by light, at wavelengths greater than the critical (3184A). (Mohler, Foote & Chenault.)

Since the quanta spent in ionization vanish from the light, the transmitted beam when spread into a spectrum reveals absorption at their frequencies. These absorption-spectra supply all that is known as yet about the process of ionization by light in sodium and in atomic hydrogen and valuable additions to the data for the three heavier alkali metals.

It will be remembered that the lines of a line-series in an absorption-spectrum occur because the photons of the corresponding frequencies can be absorbed by atoms in a particular initial state (normal or excited) which thereupon pass over into higher states of excitation; that as the lines converge upon the limit of the series, the corresponding terminal states approach that of ionization; that the limiting or convergence-frequency itself, multiplied by h, give the energy required to ionize an atom from that initial state which is common to the entire series.

Thus photons having the convergence-frequency of any series are *just* able to detach an electron from an atom in the corresponding state. Consequently photons having any greater frequency have energy sufficient to detach an electron, and give it some kinetic energy in addition. Now we are not aware of any "quantum" limitations on the amount of energy which a freed electron may receive. We thus infer that light of any frequency superior to a convergence-frequency will be able to ionize atoms and to be absorbed in doing so, and that there will be a continuous region of absorption in the spectrum extending upwards from the limit of each series. For such a region I will use the terms *continuous band* and *continuum.*

Bohr drew this inference in the first of his epoch-making papers on the interpretation of spectra. He was able then to point to only one example; a continuum beyond the limit of the principal series of sodium, observed by R. W. Wood.[15] Afterwards J. Hartmann[16] searched the spectrograms of the stars, and in those of the so-called "hydrogen stars" he found a continuous band beyond the limit of the Balmer series. This, be it noted, is the sign of ionization of hydrogen atoms initially not in the normal, but in a certain excited state. The continua beyond the principal series of the alkali metals, however, are due to ionization of normal atoms. Those of sodium and potassium were studied by Holtsmark;[17] those of cæsium and rubidium have been discerned (Harrison, *l.c. infra*); and the former two were measured, that is to say the variation of absorption-coefficient with frequency was measured, for sodium by G. R. Harrison[18] and B. Trumpy,[19] and for potassium by R. W. Ditchburn.[20]

Obviously if the fundamental theory is correct, absorption is proportional to ionization, and the curves representing the two as functions of wavelength should coincide everywhere if scaled to coincide at any one point; and measurements of either should make the other nugatory. Unfortunately it is difficult to measure the absorption properly, perhaps impossible to do it with anything like the precision feasible with the other measurement.[21] Harrison managed to get smooth absorption-

[15] *Phil. Mag.*, (6) **18,** pp. 530–534 (1909).
[16] *Phys. ZS.*, **18,** pp. 429–432 (1917).
[17] *Phys. Rev.*, **20,** pp. 88–92 (1919).
[18] *Phys. Rev.*, (2) **24,** pp. 466–477 (1924).
[19] *ZS. f. Phys.*, **47,** pp. 804–813 (1928).
[20] *Proc. Roy. Soc.*, **117,** pp. 486–508 (1928).
[21] Mohler and his colleagues state that with an amount of ionization tenfold greater than that which is observed with cæsium at the series-limit, a stratum of the gas at 230° would have to be *nine metres* deep to give a 50 per cent absorption.

curves (obtained of course by applying the densitometer to the spectrogram) with sodium. On the other hand, the experiences of Ditchburn with potassium are not encouraging. Not only did he have to shoot a jet of rapidly-distilling vapor across the beam of light, but he was obliged to swamp it in a vast excess of nitrogen—partly to keep the metal from boiling away in a rush, partly it seems to prevent the vapor from attacking the quartz windows. The curves are very crinkly, and it is difficult to tell what share of the absorption should be credited to molecules and what to atoms.

Nevertheless Ditchburn was able to deduce a value of the coefficient k having the same order of magnitude—10^{-19}—as those which Mohler and Boeckner had obtained with cæsium and with rubidium when they were measuring, not the disappearance of photons from the beam, but the advent of ions in the gas. Mohler and Boeckner themselves observed the absorption of light in cæsium, and they found for k the value $4 \cdot 10^{-19}$,—a good agreement, but they qualify it with the words "subject to great uncertainty because of the low value of the total absorption." Let it be pointed out in closing, that agreements such as these are proof that in this region of the spectrum, photons ionize when they are absorbed, and absorption is due to ionization. To physicists familiar with the new atomic theories, this seems self-evident, and scarcely worth the proving; but it is not self-evident, and there was a time, not many years ago, when such a proof would have been a sensational event.