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THE INFLUENCE OF THE METHOD OF EXCITATION ON TRANSITION PROBABILITIES IN SODIUM VAPOR

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Abstract

Fluorescence has been excited in sodium vapor at 180°C by illuminating with the second member of the principal series, $\lambda = 3303$A. Both the first and second members of the principal series appeared in the fluorescence, the first member being due to the atom returning to its normal state in steps. The ratio of the intensities of the two lines was determined by photographic photometry and the results compared with what might be expected on the basis of measurements by Weiss on the sodium arc. In the arc the atom returns to the normal state from the $3P$ by way of the $2S$ twenty-five times as often as the direct transition occurs whereas in fluorescence approximately the same number take each path. This is contrary to the usual assumption that the transition probabilities are independent of the method of excitation.

The intensity of any spectrum line depends on the number of atoms in the state from which the line originates and a factor, called the transition probability, which determines the fraction of this number which leave the excited state by the path corresponding to the spectrum line. These transition probabilities have been assumed to be constants. For the case of lines having the same initial level this assumption requires that the ratios of the intensities shall be independent of the method of excitation used.

In this paper we wish to present evidence based on a study of the transitions from the $3P$ level of sodium that the hypothesis that transition probabilities are independent of the method of excitation is untenable.

If sodium is excited to the $3P$ state there are three paths by which it may return to the normal ($1S$) state. The following diagram shows these different paths which are labelled for convenience in discussion as (a), (b), and (c). The fine structure of the terms is not shown. Weiss* has recently published the results of an investigation showing that the ratio of the transition probabilities of $3P \rightarrow 2S$ and $3P \rightarrow 1S$ is 25 to 1 if the radiation is excited by a low voltage arc. Since the $3P \rightarrow 2S$ transition is the first step in path (b) above, the last step of which is the emission of "D" light, we should expect on the basis of Weiss' experiments that if we had a large number of sodium atoms in the $3P$ state the ratio of the number of quanta of "D" light to the number of 3303A (the $3P-1S$ transition) should be at least 25 to 1[1]. That

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* Weiss Ann. d. Physik **1**, 565 (1929).

[1] According to a theory of Einstein's, the high intensity of the $2S$–$3P$ radiation in the arc used by Weiss would cause an induced emission which would increase the observed intensity. We have estimated the amount of this induced radiation assuming that energy density in the arc corresponded to 4000°K and found that the induced emission was only 20 percent of the total. We feel that this is a maximum value.

it should exceed this somewhat may be seen from the above diagram which shows that "*D*" light is also emitted by path (c).

No direct measurements have been made on sodium which would give the relative numbers taking the paths (b) and (c) but some idea of the magnitudes may be obtained from similar situations in other spectra. Such data are tabulated qualitatively by Grotrian[2] and show that the transitions by path (c) are apt to be equal to or less than those by path (b). This would mean that in the case under consideration the ratio of the intensity of the *D* lines to λ3303 should lie somewhere between twenty-five and fifty. Qualitatively this agrees with the observation of R. I. Strutt[3] on the fluorescence of sodium vapor excited by absorption of the 3303 line. In his first experiments only "*D*" light was observed in fluorescence but the later experiments showed both lines with the "*D*" line having much the greater intensity. On the other hand, the work of Terenin[4] indicates a considerably different result. He found that if sodium iodide is illuminated with light having a frequency sufficient to dissociate the salt and excite the sodium atom to the 3*P* state no fluorescence light was visible but both the *D* lines and the 3303 line could be photographed. No statement is made concerning the relative intensities of the two but from our own experience in photographing spectra we should say that the 3303 light would have to be comparable in intensity with the *D* light if it was to be observed with any reasonable photographic exposure. A comparison of the experimental conditions in Terenin's and Strutt's work indicated that there was considerable chance of collisions of the second kind transferring atoms from the 3*P* to the 2*P* state in Strutt's work. This would result in an increase in the *D* light at the expense of the 3303. It was decided, therefore, to repeat Strutt's work using pure

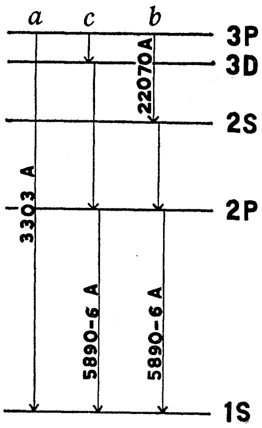

Fig. 1. Three paths by which a sodium atom in the 3*P* state may return to the normal 1*S* state.

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[2] Grotrian, Graphische Darstellung der Spektren, V. II, Springer, 1928.

[3] R. I. Strutt, Proc. Roy. Soc. (London) **A91**, 511 (1915); ibid. **A96**, 272 (1920).

[4] Terenin, Zeits. f. Physik **37**, 98 (1926).

sodium vapor at low pressures so as to eliminate the effects of collisions of the second kind.

EXPERIMENTAL

The fluorescence experiment was carried out with an apparatus assembly shown diagrammatically in Fig. 2. The letters in the figure indicate the following: (*s*) the source of exciting radiation, a sodium arc of the type described by the authors;[5] (*l*), quartz lens; (*f*), filter to extinguish the *D* light from the exciting radiation; (*o*), opening to the furnace into which a jet of hot air was continuously blown so that sodium did not condense on the windows of the fluorescence tube; (*r*), fluorescence tube entirely of quartz; (*sp*), slit of Hilger quartz spectrograph. After testing a number of filters, the "Corex A, Red Purple" filter of Corning Glass was found the most suitable. No *D* light was registered on a panchromatic plate after 10 minutes exposure with the full intensity of the arc. A transmission of the 2537A mercury line is allowed by this filter, hence there was no fear of a large decrease of energy of the 3303A exciting line. The cone of exciting light was brought as near as possible (1 or 2 mm) to the side of the fluorescence bulb from which the fluorescent cone was observed, so that re-absorption of the fluorescence light would be a minimum. The entire system, exclusive of the filter, was of quartz, and the number of parts through which the light must pass was reduced to a minimum so that as little energy as possible was lost by reflection. The furnace was thermostatically controlled to within 5°C of any predetermined temperature. For the investigation the temperature ranged from 170° to 220°C. A temperature lower than this gave a vapor pressure of sodium too low for photographic observation of the 3303A fluorescence, and a temperature higher than this caused the flask to be "browned" by the sodium vapor so that it became opaque to the ultraviolet. In most of the work a temperature of about 180°C was maintained. At this temperature the fluorescence energy was sufficient so that a suitable

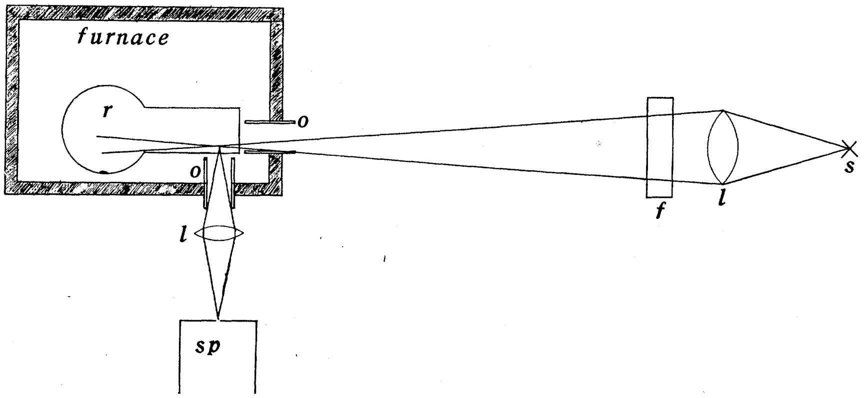

Fig. 2. Diagrammatic sketch of apparatus.

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[5] Christensen and Rollefson, Phys. Rev. **34**, 1154 (1929).

photographic blackening for photometry was obtained in three hours; the vapor pressure was also low enough so that the fluorescent cone of light extended with very little diminution throughout the length of the fluorescence bulb. If the excitation is by *D* light, at this pressure, the light cone also extends throughout the bulb and is fairly sharp, looked at from the window to the spectrograph. This gives evidence of the fact that there is little absorption of the fluorescence light before it leaves the bulb in the direction of the spectrograph.

The photographic plate chosen for the photometry was the Wratten and Wainwright Panchromatic, although photographs were also obtained on the Eastman Orthochromatic and Astronomical Green plates. The spectral photometry was accomplished by enlarging the image on the photographic plate with a well corrected lens and moving the image across a narrow slit in front of a photoelectric cell. Since only the lines 3303A and *D* appeared on the plate, the slit of the spectrograph was well opened, allowing a rather broad band to appear on the photographic plate where each line was located. These broad bands made the photometry an easy problem. The photoelectric cell was tested for energy response which was found to be linear. The light screens used in the photometry were calibrated with a thermopile and checked with a photoelectric cell. They were also tested and found to be neutral in the spectral regions of interest in this investigation.

The sodium for the fluorescence bulb was carefully purified by repeated fractional distillation in the highest attainable vacuum. When the sodium was finally introduced into the well baked-out fluorescence bulb, it was distilled from one side to the other as long as the pumping continued. The bulb was never sealed off until a vacuum of about 10^{-6}mm of mercury had been maintained for some time. By this procedure it is believed a high purity of sodium was obtained in the fluorescence bulb. The entire fluorescence bulb except the windows was well blackened with lamp black to reduce to a minimum the effect of any stray light. The inside of the whole furnace was likewise blackened. That there was no stray radiation present of appreciable amount is shown by the fact that several 3-hour exposures while the fluorescence bulb was cold failed to cause any photographic blackening, even though the full radiation of the exciting lamp was used.

Experimental Procedure and Results

A series of photographs of the fluorescence under 3303A excitation was obtained, the temperature of the fluorescence bulb ranging from 170°C to 220°C.[6] In all of the exposures made, the 3303A radiation appeared photographically much more intense than the *D* radiation.

Because of the long exposure-time necessary to obtain photographic plates usable for photographic photometry, it appeared almost a hopeless

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[6] That the 3303A radiation alone was causing the excitation was clearly shown by placing in the exciting beam of light a piece of ordinary clear window glass. This transmits all the incident radiation to about 3600A. When this was done the radiation from the fluorescence bulb entirely disappeared.

task to obtain on one plate all the necessary data for an accurate measurement of the relative transition probabilities of the transitions giving rise to the two radiations. We were forced, therefore, to standardize the photographic procedure and use a number of plates from the same emulsion. Also as far as possible, plates from the same box were used for the most important exposures. A stable hydrochinon developer was made up, put in small bottles with the tops paraffined, and placed in a cool dark place until needed. A standard temperature and time were chosen for the development, fixing and washing. During development the plates were continuously brushed with a wide camel hair brush to decrease uneven development.[7] By this procedure, fogging and unevenness of development were held within a 5 percent limit. In all cases where a check was possible, the variation of the same subject photographed and photometered on different plates agreed within about 10 percent.

To obtain the standard blackening[8]-energy curve of the plates, in the two spectral regions of interest, a direct current helium discharge was used. This has strong lines at 5875A and 3187A. Harrison[9] in his work in spectral photometry finds calibration of the plates in the visible at 25A intervals and in the ultra-violet at 300A intervals sufficient for a 2 percent accuracy anywhere in the spectrum. Thus it is evident that taking these helium lines as standard our error will not be large. It was possible to control the current in the helium discharge very closely; and the intensity ratio of the two lines was checked at the beginning and end of its use.

To obtain the energy ratio of the two lines in the helium discharge a photographic method was also necessary, a thermopile of sufficient sensitivity not being available to measure directly the energy of the two lines. This procedure was as follows: A tungsten filament electric lamp in a thin soda-glass bulb will emit a rather large amount of ultra-violet radiation extending to almost 2900A. A lamp with a straight, tightly coiled filament was selected. The normal operating current of this was 7.5 amperes. To obtain a maximum of ultra-violet, it was forced to burn at from 9.5 to 10 amperes and the image of the filament focused, with a quartz lens, on the slit of a Hilger quartz monochromator. The energy from a narrow spectral region of this source was measured on a thermopile. The thermopile was then removed and the energy allowed to fall on the slit of the quartz spectrograph used throughout the entire experiment. A series of 1-second exposures was then made, the energy being successively decreased by inserting the calibrating screens in the illuminating beam of light. The spectral energy in the *D* region was suitably adjusted so that about equivalent blackening was obtained in the two spectral regions investigated, 5890A and 3303A. In this manner three different plates were exposed, each with a series of calibration exposures in the two spectral regions. The energy coming from the mono-

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[7] Photographic Photometry; Dobson, Griffith, Harrison, p. 76.

[8] The blackening value as used in this work was calculated in the manner set forth by Dorgelo; Phys. Zeits. **26**, 756 (1925).

[9] Harrison, J. Optical Soc. Am. **17**, 397 (1928).

chromator was measured with the thermopile before each series of photographs. To obtain the relative energy falling on unit area of the photographic plate, the energy as given by the thermopile was corrected for the dispersions of the two instruments, though the sum of these corrections was small, it being apparent that the corrections from the two instruments would tend to cancel each other. Stray light from the monochromator was unavoidable, and correction for this was also made. The resulting blackening-energy curves were accurately parallel though they were displaced from each other somewhat.[10] It is evident that by this procedure correction for the instrument loss in the quartz spectrograph is automatic, since the energy was measured as it was thrown on the slit of the spectrograph.

Plates were now exposed for 1 second to the helium discharge operated under the selected standard conditions,[11] and the relative energies of the two lines, 3187A and 5875A, determined from the standard blackening curves, obtained in the manner just described. The following table expresses the result, giving the ratio of the energy of these two lines.

TABLE I. *Ratio of the energy of* λ*5875 to that of* λ*3187.*

Plate	Exposure	Referred to		
		Standard Plate 1	Standard Plate 2	Standard Plate 3
1	1	12.2	9.8	10.0
1	2	11.3	8.9	9.2
1	3	12.3	9.7	9.9
1	4	11.7	9.2	9.6
1	5	12.1	9.4	9.9
1	6	11.7	9.1	9.6
2	1	13.1	9.7	11.6
2	2	13.1	9.7	11.6
2	3	13.0	10.0	11.6
2	4	13.5	10.0	11.6
2	5	13.2	10.3	11.5
		Average, E(5875A)/E(3187A) = 10.9		

In the table, E(5875A)/E(3187A) is the ratio of the energy of the 5875A line to the 3187A line when the discharge operates under the standard conditions. The values for the ratio given in the three columns are the values as obtained from the standard blackening curves given by standard plates 1, 2, and 3. The values from all three plates are used in the determination of the final average value of the ratio, 10.9.

To obtain the standard three-hour energy-blackening curves, a small-intensity helium discharge was used.[12] The energy-blackening curves for

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[10] These plates will be referred to as "standard plates" 1, 2, and 3, respectively.

[11] This discharge was operated directly from a 600-volt storage battery, suitable resistance being placed in the circuit to limit the current to 60 milliamperes. The current was not allowed to vary more than 2 percent.

[12] This was deemed necessary, since the standardized helium discharge was so intense that the screens necessary to diminish the light intensity to a suitable value for 3-hour exposures were so dense that accurate calibration of them was very difficult and subject to great error. We feel sure the error of the experiment as carried out is less than it would have been by the method of dense screens. This small helium discharge was energized by a direct current of 0.2 milliamperes. The current was controlled to 2 percent by the use of a thermionic "current limiter."

this discharge were first constructed in arbitrary units the full energy of each radiation being assigned the value 100. The units for the 3187 radiation were then evaluated in terms of the units assigned to the 5875 radiation. This was done by reducing the intensity of the standard helium discharge with screens so that three-hour exposures were practical. Since the ratio of the intensities of the radiations from this discharge has been determined the 3187 curve from the small discharge can be placed in its proper position relative to the 5875 curve.

Figure 3 gives the final blackening-energy curve for the 3-hour exposure; from this the relative energy of the 3303A and *D* light obtained from fluorescence was measured. The curves were checked from three plates. The crosses give the position of the 3187A curve relative to the 5875A curve as determined from the standard helium discharge. These points were determined from three exposures on as many different plates.

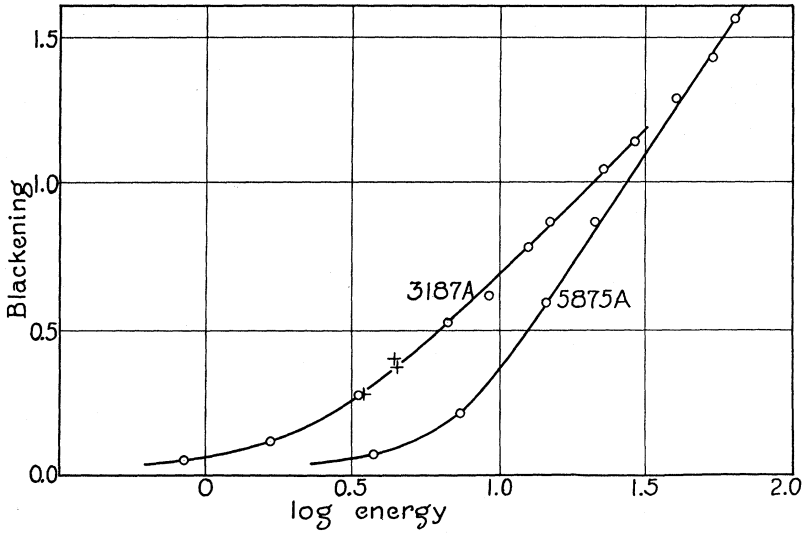

Fig. 3. Final blackening-energy curve for λ3187 and λ5875A.

Results of Measurement of Fluorescence

From three plates the mean of the energy ratio (designated by *R*) of the two radiations from the fluorescence tube reaching the slit of the spectrograph was

$$R = \frac{E(5890-6A)}{E(3303A)} = 0.64$$

For the determination of this ratio the temperature of the fluorescent sodium was 180°C. The cone of exciting light was as close as possible to the window toward the spectrograph, the center of the cone being about 3 millimeters distant. Photographs were now obtained of the fluorescence and the energy ratio of the two radiations determined when the center of the exciting cone of light was 9 millimeters distant from the window. The temperature of the sodium remained the same, 180°C. In this case the energy ratio was observed to be

$$R = 0.30$$

It is evident that the reabsorption must be corrected for, the D radiation being relatively more absorbed than the 3303A radiation.

If we assume, as a first approximation, the decrease of radiation energy is proportional to the average absorbing layer,[13] then we can write

$$-dE = kEdl$$

where E is the energy of a particular radiation and l is the absorbing layer. By integration this leads to the following expression,

$$E = E_0 e^{-kl}$$

Now if E, the energy of the 5890–6A radiation, is measured in terms of the energy of 3303A radiation, E', then

$$R = \frac{E}{E'} = \frac{E_0}{E_0'} e^{l(k'-k)} \tag{1}$$

We have determined this ratio R at two different values of l; comparing these two values of R, we get

$$R_1/R_2 = e^{((k'-k)(l_1-l_2)}$$

where the subscripts 1 and 2 refer respectively to the values obtained at 3 and 9 millimeters. Substituting in the last expression the appropriate experimental values,we obtain

$$(k'-k) = -0.127.$$

This value can be used now for determining the true energy ratio ($R_t = E_0/E_0'$) of the two lines. From equation (1) above, we get

$$R_t = Re^{-l(k'-k)} = Re^{0.127l}.$$

Substituting in this expression the values of R and l, we get

$$R_t = 0.94.$$

Thus we find that the relative energy of the D radiation to 3303A radiation will be 0.94, when these radiations have their origin from the $3P$ level of sodium excited by resonance radiation 3303A.

To obtain the relative transition probabilities, this ratio of energies must be changed to one of quanta. If N is the number of quanta and the other terms have their usual meaning, then

$$E = N(h\nu) = Nch/\lambda.$$

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[13] This seems justified in this case since we are observing resonance radiation and since there is still considerable energy in both lines when coming from the 9 millimeter depth. While we realize this assumption cannot be strictly accurate, still we feel certain it will give a correct value of the energy ratio which will be well within our other experimental errors.

Using this expression we obtain for R

$$R=\frac{N_D ch/\lambda_D}{N_{3303}ch/\lambda_{3303}}=\frac{N_D}{N_{3303}}\ \frac{\lambda_{3303}}{\lambda_D}$$

$$\therefore \frac{N_D}{N_{3303}} = R\frac{\lambda_D}{\lambda_{3303}}$$

where N_D/N_{3303} is the relative number of quanta measured in the two radiations, which is also the ratio of the probabilities of paths (a) to $(b)+(c)$. From the value of R determined in this experiment, we find

$$N_D/N_{3303}=5890/3300\times 0.94=1.7$$

Although this value was obtained from measurements on a single fluorescence bulb, still the qualitative observations of photographs taken from other fluorescence tubes confirm this value.

Error of the Measurement

From the data (Table 1) used to determine the relative intensity of the two lines in the standard helium discharge, variations as large as 24 percent from the average occur. It is probably correct to say this ratio was determined to within 25 percent. The error in placing and determining the relative positions of the two energy-blackening curves in Fig. 3 is not more than 10 percent, assuming the ratio for the standard helium lamp as correct. The error involved in determining the correct photographic blackening caused by the fluorescence radiation is 10 percent. The method of correcting for reabsorption is certainly not more than15 percent in error. The sum of all these errors gives 60 percent. One other factor must be considered, the possibility of quenching. No method was available to measure the pressure of foreign gases in the fluorescence bulb under operating conditions. Since every precaution was taken, however, to get the sodium of great purity, it is believed the error cannot be large. However, the error would undoubtedly favor an increase in the relative energy of D light.

Taking all the errors into consideration we feel that the net error in the ratio of the intensities of the two radiations does not exceed 25 or 30 percent.

Discussion of Results

If we designate the probability of return by paths (a), (b), and (c) as P_a, P_b, P_c respectively, then the result we have obtained may be expressed as

$$\frac{P_b+P_c}{P_a}=1.7$$

From this it is apparent that P_b/P_a is less than 1.7 and probably about equal to one. This value is totally different from that obtained by Weiss in the arc. The difference is far too large to be explained as due to experimental errors, therefore we are forced to conclude that the relative probabilities of the transitions $1S$–$3P$ and $2S$–$3P$ depend upon the method of excitation of the $3P$ state.

The values for the ratio of the intensities of the two radiations calculated from theoretical considerations do not agree with either of the experimental values. Bartels,[14] using the correspondence principle, obtained a value of four for the ratio. A value based on the wave mechanics can be obtained from the work of Kupper.[15]

The approximation involved in the derivation of his equations cause considerable errors for low values of n, the principal quantum number. However, if we calculate the ratio $(2S-mP/1S-mP)$ for large values of n and observe the trend as we go to low values we find that the ratio $(2S-3P)/(1S-3P)$ must be greater than 0.05.

A comparison of Trumpy's absorption measurements on sodium vapor[16] with the theoretical values shows that for low values of n the observed intensities are higher than the calculated ones, the deviation increasing as n decreases. From this it is to be expected that the deviation for the $2S-3P$ transition would be greater than that for the $1S-3P$ and therefore the experimentally determined ratio of the two should be greater than the calculated value, as is actually the case.

Very little is to be found in the literature concerning the relative intensities of lines originating in the same energy level under different conditions of excitation. Crozier[17] has studied the intensities of some mercury lines when excited by electrons of various velocities. In the case of the transitions $2^3P_1-3^3D_1$ and $2^3P_0-3^3D_1$ he obtained quite different curves but for $2^3P_1-2^3S$ and $2^3P_2-2^3S$ the curves were practically identical. To account for his results he suggests the possibility that under different conditions different fine structure levels are excited. The work of Collins[18] on the fine structure of some mercury lines under different conditions of excitation indicates that different fine-structure levels are excited by altering the method of excitation. This might be of value in explaining differences when there is a difference in the l or j of the final level but it can scarcely account for the case we are considering in sodium where the only difference between the two final levels is one of principal quantum number. It is possible that collisions may affect the transition probabilities in an arc but would have no effect in a fluorescence experiment such as we have described in this paper since the pressure was so low that the time between collisions was much greater than the mean life of the excited atom.

Further experiments have been planned which it is hoped will cast some light on the behavior of atoms in excited states. For the present, all we can say is that the future of an atom in one of its higher quantum states depends to a very marked degree either on its past or its surroundings or possibly both. Future work in this field must separate these two factors.

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[14] Bartels, Zeits. f. Physik **32**, 415 (1925).

[15] Kupper, Ann. d. Physik **86**, 511 (1928).

[16] Trumpy, Zeits. f. Physik **44**, 575 (1927).

[17] Crozier, Phys. Rev. **31**, 800 (1928).

[18] Collins, Phys. Rev. **32**, 753 (1928).