INDIRECTLY EXCITED FLUORESCENCE SPECTRA

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ABSTRACT

Fluorescence spectrum of thallium mixed with Hg vapor.—(1) *Repetition of experiments of Franck and Cario.* The illuminated end of the quartz tube containing Tl metal was placed in the hottest part of the furnace to avoid condensation. In the fluorescence spectrum all Tl lines to be expected theoretically, from $2p_1-2s$ to $2p_1-4d_1$ and $2p_1-5d_2$ were identified. This excitation shows that the life of the $2p_1$ state is for Tl atoms of the order of 10^{-6} sec. (2) *Enhancing effect of inert gases.* Series of spectrograms with the same tube confirmed the results of Donat. As the pressure of A or N_2 was increased the intensity of λλ5350, 3776 and 2768 increased rapidly reaching a maximum for 5 to 20 mm of A or 5 to 10 mm of N_2. A trace of O_2 neutralizes this enhancing effect. (3) *Experiment with Tl vapor distilling past the window.* In this case a "negative effect" was observed, the addition of a neutral gas decreasing the fluorescence. This was probably due to the interference of the inert gas on the rate of distillation and hence on the amount of Tl present near the window. (4) *Experiments with closed tubes at uniform temperature.* The enhancing effect was also obtained with these tubes, showing that it cannot be an indirect effect of the interference of the neutral gases with the distillation of the Tl vapor in Donat's experiments, but is definitely associated with the presence of the neutral gas. (More intense fluorescence was obtained with N_2 at 5 mm and Hg at 0.16 mm than with N_2 at 8 mm and Hg at 0.5 mm, the Tl being at 0.45 mm.) (5) *Conclusions regarding role of Hg atoms in the $2p_3$ state.* These results confirm the assumption of Franck and Donat as to the part the Hg atoms in the metastable $2p_3$ state take in the energy transfer to normal Tl atoms. Comparison of spectrograms at different partial pressures indicates that the metastable Hg atom may survive many collisions with normal A or N_2 molecules but easily gives up its energy when colliding with normal Tl or Hg atoms, probably more easily to Tl than to Hg.

INTRODUCTION

1. Klein and Rosseland[1] concluded from theoretical considerations, based on the application of the second law of thermodynamics to a system of atoms, electrons, and radiation, that so-called collisions of the second kind must occur between activated atoms and electrons. Due to such a collision an activated atom may return to its normal state without sending out the radiation that is connected normally with this transition, the corresponding quantum $h\nu$ being then distributed between both colliding particles in the form of kinetic energy, according to the principle of momentum.

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[1] O. Klein and S. Rosseland, Zeits. f. Phys. **4**, 46 (1921).

2. J. Franck[2] extended this idea of collision of the second kind to a system which contained besides electrons, activated atoms, and radiation, also normal atoms of a suitably chosen vapor. He then predicted that activated mercury atoms, when colliding with neutral atoms of a vapor which does not absorb the effective radiation and which has its resonance potential below 4.9 volts, may excite the atoms of the vapor, causing them to emit their fluorescence spectra. These spectra ought to contain all lines corresponding to transitions from energy levels E_2 to E_1, where $E_2 - E_1 \leqq 4.9$ volts. Experimental investigations carried out by Cario,[3] Franck and Cario,[4] Kopfermann,[5] and Donat,[6] confirmed this theoretical prediction in the case of Tl, Cd, Pb, Bi, Ag, and In. On account of the analogy of this excitation of spectral lines with the process of sensitization of photographic plates, Franck called the new phenomenon the "sensitized fluorescence."

3. A closer investigation of the spectra revealed two new facts. (1) Some lines corresponding to energy transfers $E_2 - E_1 > 4.9$ volts appeared on the plates. (2) Abnormally high intensities of some of the lines could not be accounted for by considerations of the theoretical probability of collisions with the required amount of relative energy. To account for these Franck found it necessary to assume (a) that the excitation energy of an activated Hg atom may be added to the relative kinetic energy of the colliding particles, so that the sum of both exceeds under favorable conditions the equivalent of 4.9 volts; (b) that due to collisions some of the activated Hg atoms ($2p_2$ state) may be thrown over into the lower metastable state for a time longer than the life-time in the $2p_2$ state.

4. The correctness of the last assumption seemed strikingly confirmed by some new results obtained by Donat. He found that when A or N_2 is added to the mixture of Hg and Tl showing the sensitized fluorescence of the latter, the intensity of all Tl lines increased remarkably, while the resonance of Hg became weaker. It has been shown that even at atmospheric pressure of A — when, as we know from investigations of Wood,[7] Cario,[3] and Stuart[8] the resonance of Hg vapor is largely reduced— the Tl lines $\lambda\lambda$5350, 3776, 3529 and others appear stronger than without A present. This relatively high intensity of the Tl lines in the presence

[2] J. Franck, Zeits. f. Phys. **9**, 259 (1922).
[3] G. Cario, Zeits. f. Phys. **10**, 185 (1922).
[4] G. Cario and J. Franck, Zeits. f. Phys. **17**, 202 (1923).
[5] H. Kopfermann, Zeits. f. Phys. **21**, 316 (1924).
[6] K. Donat, Zeits. f. Phys. **29**, 345 (1925).
[7] R. W. Wood, Phys. Zeits. **13**, 353 (1912).
[8] H. Stuart, Zeits. f. Phys. **32**, 262 (1925).

of a large number of A atoms, when the probability of a collision of an activated Hg atom with an A atom is enormously greater than the probability of its collision with a Tl atom, makes it necessary to assume that many Hg atoms may be thrown over into a metastable orbit $2p_3$ and retain their energy for a relatively long time. This explanation involves, however, a new important assumption as to the nature of the metastable $2p_3$ state of the Hg atoms.

Till now we have defined the metastable state of an atom, according to the requirements of the selection principle, as a state from which the atom cannot come back to the normal state in the ordinary way, i.e., by sending out its surplus energy in the form of radiation. We should expect such an atom to persist in the metastable state indefinitely, provided no collision with another atom and no action of external electric or magnetic fields intervene. Thus, collisions being the only possible mechanism of bringing an atom out of a metastable state, we should expect its time of existence in such a state to be completely determined by its collisions with other atoms. Hence, if we accept Franck's explanation of the increasing effect of A on the sensitized fluorescence of Tl vapor, we have to assume furthermore that the *Hg atoms in $2p_3$ state may endure very many collisions with A atoms or N_2 molecules without going over to a lower state until they happen to collide with a Tl atom*, to which they then transfer immediately the whole amount of potential energy.

It appeared desirable, on account of the peculiarity of this last assumption, to re-examine the phenomena discovered by Franck, Cario, and Donat, repeating their experiments under better defined conditions of temperature and pressure with the purpose of finding, if possible, some other explanation.

I. Indirect Excitation of Thallium Fluorescence in Mixture with Mercury Vapor

5. The experimental method used for excitation of the Tl fluorescence through collisions with activated Hg atoms was quite similar to that used by Franck and Cario.

A Cooper-Hewitt vertical mercury arc, mounted between the poles of a small electromagnet and cooled down by a strong blast of air, was used as source of illumination. A quartz lens (4 cm diameter, 7.5 cm focus) concentrated the unresolved beam of light on a flat window of a quartz tube, illuminating it from the side at about 45°. The tube was in a horizontal position, its shape and dimensions being as shown in Fig. 1 (tube *A*).[9] Within it was placed, in the position indicated by the black

[9] At first 2 mm thick plane polished quartz plates were fused on the end of the tube. It has been found, however, that such windows when heated above 300°C, are very

spot, a piece of carefully purified metallic Tl, the whole being then inserted in an electrically heated furnace with two fused quartz windows as shown. The furnace was built in such a way that the illuminated part of the tube could be kept at a temperature a little higher than the rest, in order to prevent the flat end of the tube from being covered with a thin layer of condensed metal.

The rear end of the quartz tube was connected with a diffusion pump and contained a few cc of pure mercury in a vertical side tube which was heated by another furnace. Provisions were made to keep the part of the tube between the two furnaces at a temperature higher than that of the mercury.

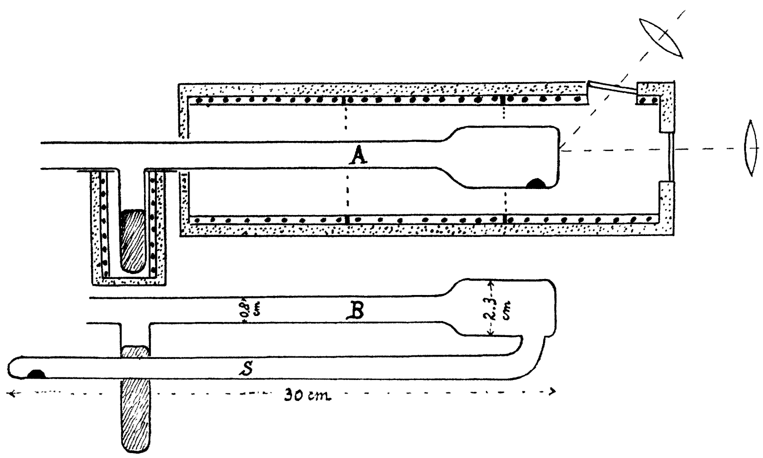

Fig. 1. Diagram of apparatus showing tube A used for repeating experiment of Franck and Cario and of Donat, also tube B in which the liquid Tl is 30 cm from the window.

A second quartz lens enabled the image of the illuminated window to be thrown upon the slit of a large Hilger spectrograph. Cramer's isochromatic plates (very sensitive in the region of the green Tl lines) gave the most satisfactory results.

6. The first trace of λ5350 could be detected visually in the spectrum when the temperature of the main furnace was about 500°C and the temperature of Hg higher than 60°C. Photographs obtained after one hour exposure with Tl at 800°C and Hg at 100°C show almost all the

easily attacked by the vapors. They may be cleaned in an oxygen-hydrogen flame, but even then they do not last long and must be too often renewed. Far more satisfactory results could be obtained by simply blowing one end of a sealed-off tube flat. Windows of that kind can be made sufficiently even and plane, and endure many hours of exposure without showing any loss of transparency.

lines that could be expected according to Bohr's energy level scheme. The following lines were identified.

5350	$2p_1-2s$	2918	$2p_1-4d_1$
3776	$2p_2-2s$	2826	$2p_1-4s$
3529	$2p_1-3d_2$	2768	$2p_2-3d_2$
3519	$2p_1-3d_1$	2711	$2p_1-5d_2$
3230	$2p_1-3s$	2580	$2p_2-3s$
2922	$2p_1-4d_2$	2380	$2p_2-4d_2$

The existence of the lines 2711 ($2p_1-5d_2$), 2918 ($2p_1-4d_1$), 2922 ($2p_1-4d_2$) is very significant. It shows that in some Tl atoms electrons have been raised up to $4d_1$, $4d_2$, $5d_2$ levels. Energy equivalent to 4.9 volts is not sufficient to bring them to these levels from the normal $2p_2$ orbit. The energy transfer from Hg atoms must have occurred while the electrons were in $2p_1$ state, brought there by collisions with normal atoms, or more likely on their way back from higher states. The possibility of excitation of lines corresponding to such high energy levels like $4d_1$, $4d_2$, and $5d_2$ shows at any rate that the lifetime of the $2p_1$ state is for Tl atoms at least of the same order of magnitude as the time between collisions of Tl and Hg under our conditions, i.e., about 10^{-6} sec.[10]

II. The Effect of A and N_2 on the Indirect Excitation of Tl-Fluorescence

7. The experimental arrangement remained the same as before, only provisions were made for introducing gases under known pressure.

Argon supplied by the General Electric Company was guaranteed to be 99.8 percent pure, the main impurity being nitrogen. Nitrogen made from air by the ordinary process (ammonium chloride, ammonium hydroxide, and copper) had been passed through a liquid air trap and a tube with hot copper gauze.

The effect of A under different pressures up to 1 atm. is clearly shown in Fig. 2. The first spectrum shows the Franck-Cario effect in Tl without argon. All six following spectra show the Tl lines enhanced by A at

[10] This time may be computed from the well-known equation (L. Boltzmann, Vor lesungen über Gastheorie) for the number of collisions

$$\nu=\sigma^2\, p\times 2666\cdot 6\sqrt{(2\pi N/k\theta)\,(m+m_1)/mm_1}$$

where σ = the mean value of the diameters of Tl and Hg; p = the total pressure; $N=0.607\times10^{24}$; k = Boltzmann's constant 1.37×10^{-16}; θ = the temperature, 1073°K; m = the atomic weight of mercury, 200.6; m_1 = the atomic weight of thallium, 204. If we take the diameter of Hg in the normal state, i.e., $3.5.10^{-8}$ cm and the diameter of Tl obtained from the x-ray analysis of crystals, $3.4.10^{-8}$ cm we get $T=1/\nu=2\times10^{-5}$ sec. Assuming that all mercury atoms are activated and have then according to Stuart (H. Stuart, Zeits. f. Phys. **32**, 267, 1925) the diameter $3.4(3.5\times10^{-8}$ cm), we get $T=1/\nu=5.5\times10^{-6}$ sec.

different pressures. This remarkable enhancement of all Tl lines is in agreement with Donat's statement. However, the effect he obtained was different for different lines; some of them showing more or less pronounced maxima at pressures between 1 and 100 mm Hg, whereas no maxima were noticed by him for the lines 5350, 3776, 2768; he reports that their intensities increased rapidly with the pressure to a few centimeters and

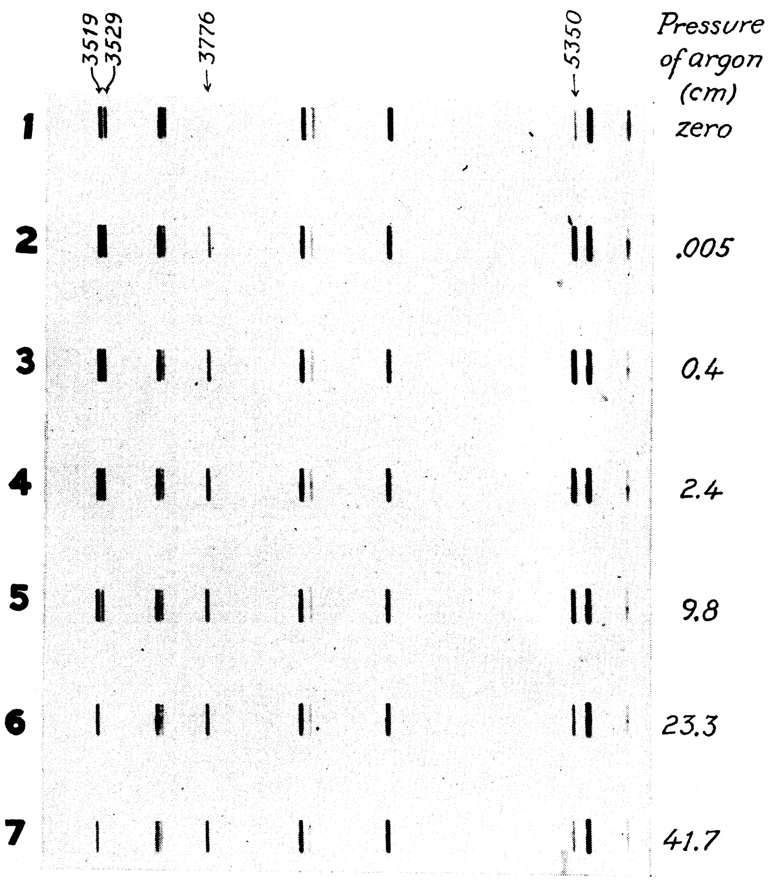

Fig. 2. Spectrograms of fluorescence in mixtures of Tl and Hg vapors, with an inert gas argon also present at various pressures as indicated. The time of exposure in each case was 32 min; the Tl was at 680°C, the Hg at 100°C.

then remained constant up to atmospheric pressure. The results of the present investigation show that a maximum in the effect of A on the intensity of the Tl spectrum appears *on all the lines without exception, but at different pressures*. As may be seen in Fig. 2, the lines 5350, 3776, and 2768 decrease in intensity when the pressure exceeds 2 cm, the optimum being for 5350 between 5 and 20 mm.

The decrease of intensity is naturally explained by the fact that at higher pressures collisions of the second kind must occur as well between argon and excited Tl atoms as between argon and mercury atoms. The maximum is very flat and may not show up as distinctly on photographs taken with longer exposures. This might account for the apparent equal intensity of blackening on Donat's plates.

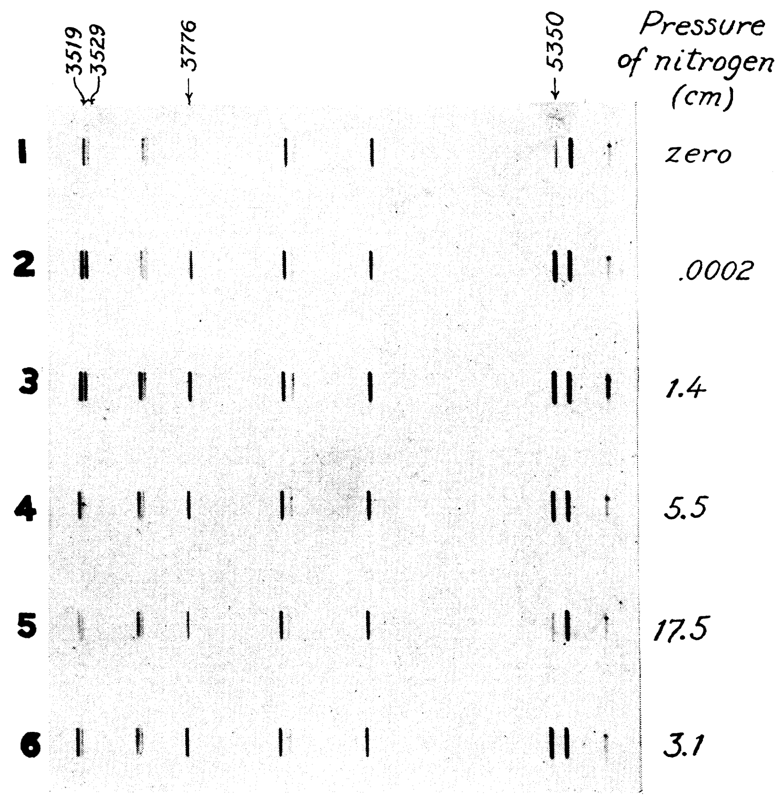

Fig. 3. Fluorescence spectra of Tl and Hg with N_2 present. Exposure 32 min. Tl at 640°C, Hg at 100°C.

8. Donat found that pure nitrogen influences the Tl spectrum in the same way as A, the effect being, however, much weaker. A careful investigation of this effect at *very low pressures* shows, however, that the effect of N_2 may be even much stronger than that of A, provided the optimum pressure of the gas is used. *It is enough to introduce into the tube a small fraction of a millimeter of carefully purified* N_2 *(about* 2×10^{-3} *mm) to* make the whole window shine with vivid, very bright soft green light. The phenomenon is especially interesting when observed through a

spectroscope. The line 5350 flashes out suddenly and, although it had been much weaker than 5461 of Hg, becomes now many times stronger. The sharp maximum may be clearly seen in Fig. 3. Visual observations have shown that the optimum pressure of N_2 is between 5 and 10 mm. It has been noticed also that when nitrogen at this pressure is brought into the tube the intensity of 5461 of Hg increases remarkably. This

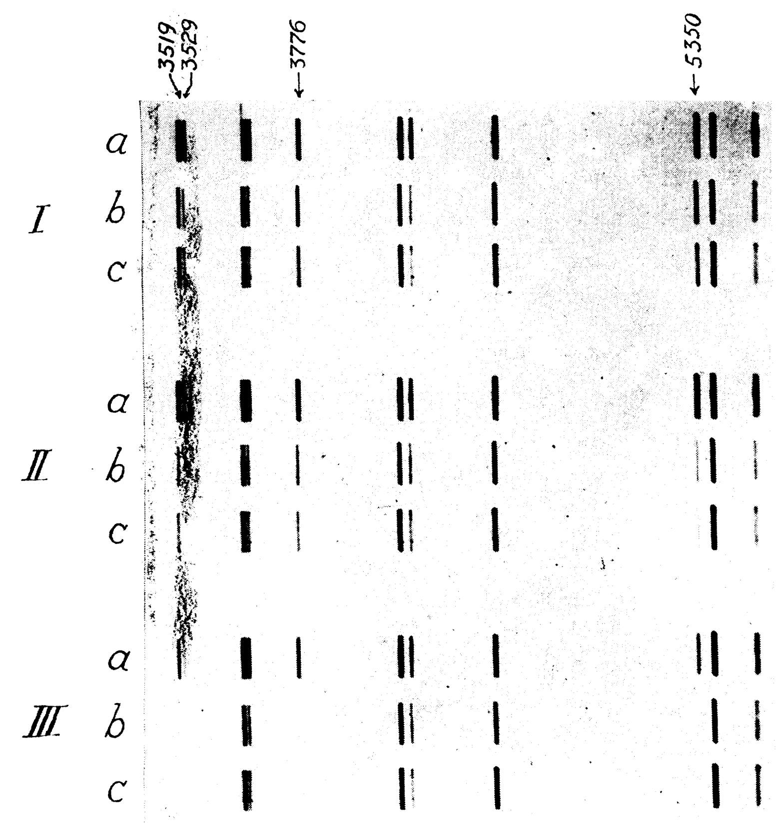

Fig. 4. Fluorescence spectra of sealed off tubes *a*, *b* and *c*.
The temperature was 680°C for group I, 590°C for group II and 490°C for group III.
Tube *a*: Tl saturated; Hg at pressure <0.16 mm; N_2 at 5 mm.
Tube *b*: Tl saturated; Hg at 0.5 mm; N_2 at 8 mm.
Tube *c*: Tl saturated; Hg at 0.5 mm; no inert gas.

observation is in close agreement with the results obtained by Wood in his investigation of the changes in the intensity distribution of the Hg spectrum due to the presence of nitrogen.[11] The effects of N_2 and A

[11] R. W. Wood, Proc. Roy. Soc. **106**, 689 (1924).

on the Tl fluorescence seem to be very sensitive to small traces of impurities, *the most destructive being oxygen.*[12] Nitrogen made from air in the way described above, but not passed over hot copper, extinguished the green Tl line entirely. Also, argon containing a minute amount of air as impurity, weakened the Tl fluorescence remarkably.

9. So far the results of the present investigation are in general agreement with what has been found by Donat.

However, the explanation suggested by him as to the accumulation of energy in the metastable $2p_3$ state of mercury atoms is, nevertheless, open to serious objections. The conditions under which the new phenomenon has been observed, are not at all defined. One part of the tube *A*, Fig. 1, containing Tl is kept at 800°C, the other with mercury being at 100°C. The saturation pressure of Tl at 800°C is about 2 mm;[13] the saturation pressure of Hg is 0.3 mm.[13] The fluorescence is a surface phenomenon, the whole process of excitation taking place on the illuminated window.

As long as no gas is present in the tube, the thallium vapor diffuses rapidly away towards the colder part of the tube. Its pressure changes from 2 down to 0.02 mm. Moreover, due to the steep gradient of temperature (from 800°C to 100°C in a distance of 30 cm) the stream of Tl vapor condenses on the way and may pump out mercury from the front part of the tube, decreasing its density below 0.3 mm. These processes evidently tend to decrease the intensity of the fluorescence.

These conditions are totally changed when gas is introduced into the tube. The gas brings in fresh mercury vapor, it slows down the diffusion of Tl vapor and it prevents the mercury from being pumped out by the condensing Tl. These changes tend to increase the intensity of Tl fluorescence. It seems, therefore, not improbable that the effect observed might be partially or even totally explained in the foregoing simple way.

Very instructive in this respect were the results obtained in experiments made with the tube *B* shown on Fig. 1. Metallic Tl placed at a distance of 30 cm from the window was heated by a special furnace and allowed to diffuse along the whole tube, the stream of vapor being carried through the illuminated portion. The green line of Tl λ5350 appeared at about 700°C. Nitrogen of 5 mm pressure *extinguished* the fluorescence instantaneously; the line *appeared again* in the absence of N_2. Analogous experiments with A gave similar results. Increase of

[12] H. Stuart found that oxygen is most effective in extinguishing the resonance radiation of mercury.

[13] Landolt-Börnstein, Tabellen.

pressure from 3.5 up to 52 mm caused an increasing *decay* of fluorescence, while the spectrum *brightened up remarkably as soon as the gas was removed.* This "negative" effect could be obtained over and over again with *gases of the same purity* as those which gave "positive" effects in the simpler tube. It has been noticed, however, that the "negative" effect became less pronounced with time, especially after the tube *was allowed to cool down frequently.* Evidently, the metallic thallium distilled slowly over into the main part of the tube bringing it automatically to the same conditions that existed in tubes used before; and, in fact, when the metal was then transferred in vacuum into the main part of the tube, and the side-tube *s* was sealed off, only the regular "positive" effect appeared again. It is evident, therefore, that as long as we work with "open," not uniformly heated tubes, we actually know nothing about the pressures of the components of the metallic mixture. All assumptions as to the nature of the elementary mechanism of energy transfer with or without the co-operation of atoms in the metastable $2p_3$ state will then necessarily retain a considerable degree of uncertainty.

10. Preliminary experiments had shown that it is not difficult to obtain the sensitized fluorescence of Tl in a *closed tube, heated uniformly* in a furnace. This discovery opened the possibility of a comparison of the intensity of Tl fluorescence in two sealed-off and uniformly heated tubes, one of them containing merely Tl and Hg, the other the same metals in an atmosphere of the gas under known pressure. The pressure of Tl vapor being then determined by the temperature of the furnace, it was only necessary to introduce into the tube a known amount of mercury vapor. It must be emphasized, however, that, according to what has been said before about the processes going on in an "open" tube, while the enhanced fluorescence appears, the pressure of mercury vapor cannot be regarded as known. It was, therefore, necessary to seal off *three* tubes prepared as follows:

The tube *a* connected with the pump and the gas container in the same way as before, was heated up to 680°C, the temperature of the side-tube with mercury being kept at 90°C. Pure N_2 of 5 mm pressure was then introduced into the tube. *While a very strong effect appeared on the green line 5350, the tube was sealed off from the pumps.*

The tubes *b* and *c* were at first connected together and to the pump and put side by side into the furnace. By shifting the illuminating lens a little one could observe the Franck-Cario effect alternatively in each of them in the same way as before. Under the influence of N_2 at 8 mm pressure the green fluorescence appeared exceedingly strong. *The tubes were then allowed to cool down to a temperature of 130°C, and were kept at* *this temperature for two hours, the temperature of the mercury being only 110°C.* After two hours one of the tubes *b* was sealed off. The other tube *c* was then pumped out and kept under highest vacuum at 130°C for another two hours and then sealed off from the pumps. The temperature of mercury was all the time kept constant at about 110°C.

Each tube was then examined in a uniformly heated furnace. Visual observations made on the green line λ5350 gave the following results.

Tube a containing Tl vapor at saturation pressure, N_2 at 5 mm, mercury vapor at the pressure $\leqq 0.16$ mm. The Tl line appears at the temperature of 360°C, increases rapidly in intensity with increasing density of the vapor and is at 700°C much stronger than 5461 (always present due to reflection and scattering). There is no difference whatever between the appearance and intensity of the spectrum in this sealed-off tube and the phenomenon observed before in an "open" tube under the same conditions.

Tube b containing Tl at saturation pressure, N_2 at 8 mm, and Hg at 0.5 mm. The line appears at about 410°C, increases in intensity with increasing density of the vapor, but does not reach the same brightness at 700°C as in the tube (a).

Tube c containing Tl at saturation pressure, Hg at 0.5 mm, and no gas. The line does not appear until about 510°C is reached, is remarkably weaker than in *a* and noticeably weaker than in *b*. The appearance and intensity of the spectrum are the same as in open tubes, without gas.

11. Fig. 4 shows the lines 5350, 3776, 3529, 3519, in all three tubes at different temperatures. The comparison of the intensities of the spectra excited in the tubes *a* and *c* shows conclusively that (1) the effect of N_2 on the intensity of sensitized fluorescence of Tl *persists in uniformly heated sealed-off tubes*; (2) it cannot be explained as due to differences in pressure of Tl or Hg, caused by diffusion and condensation in a not uniformly heated "open" tube.

The comparison of the phenomenon in tubes *b* and *c* shows that the effect is due *entirely to the presence of the gas*, thus confirming Franck's hypothesis as to the part the metastable $2p_3$ atoms must take in the elementary act of energy transfer.

Finally, comparing the intensities of the spectra excited in the tubes *a* and *b*, we see that the phenomenon observed for the first time by Donat is very strong when the pressure of mercury vapor is lower (0.16 mm) than that of Tl (0.45 mm), and less pronounced when the pressures of mercury (0.5 mm) and Tl are nearly equal. This seems to indicate that the metastable $2p_3$ atoms *while enduring very many collisions with* N_2 *molecules or A atoms may not as easily retain their energy in a collision* *with normal mercury atoms.* It is, however, possible that the probability of an energy transfer from $2p_3$ atoms to normal mercury atoms is yet much smaller than the probability of a transfer from $2p_3$ atoms to Tl atoms. This is indicated by the fact that the enhancing effect of N_2 could be observed accidentally in a tube containing a minute amount of Tl as impurity.

An attempt has been made to excite the sensitized fluorescence of Ga, but no Ga lines could be detected on the plates after one hour exposure at 960°C. The saturation pressure of Ga being still very low at this temperature it was expected that the presence of N_2 might perhaps sufficiently enlarge the amount of energy available for excitation. The plate obtained after one hour exposure at a temperature of about 960°C with 5 mm N_2 present in the tube did not show any Ga lines, but very weak traces of λλ5350, 3776, 3529, 3519 of Tl appeared distinctly. The tube had been used previously for experiments with Tl and although cleaned very thoroughly before Ga was put in evidently still contained enough thallium as impurity. It must be emphasized that the Tl lines were just detectable *only when* nitrogen was present, and were not to be found in the spectrum obtained with the same tube without gas.

This observation is valuable for two reasons: (1) It confirms the results previously obtained under conditions that exclude the possibility of the effect investigated being due to diffusion or condensation processes. (2) It indicates that the probability of an energy transfer through collisions from $2p_3$ atoms to Tl atoms is very much larger than the probability of such a transfer from $2p_3$ to normal Hg atoms.

The writer wishes to express his best thanks to Professor R. A. Millikan for the opportunity of carrying out experimental research in the Norman Bridge Laboratory, and for his stimulating interest throughout this investigation. He is also indebted to Dr. I. S. Bowen for his valuable assistance in the photographic part of the work.

Norman Bridge Laboratory of Physics,
Pasadena, California
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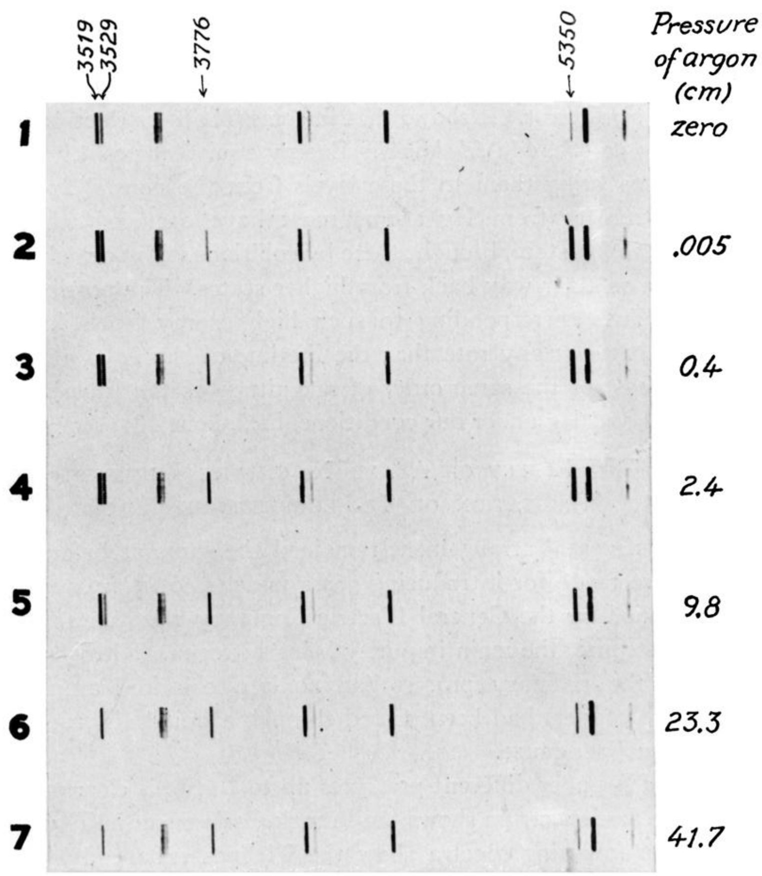

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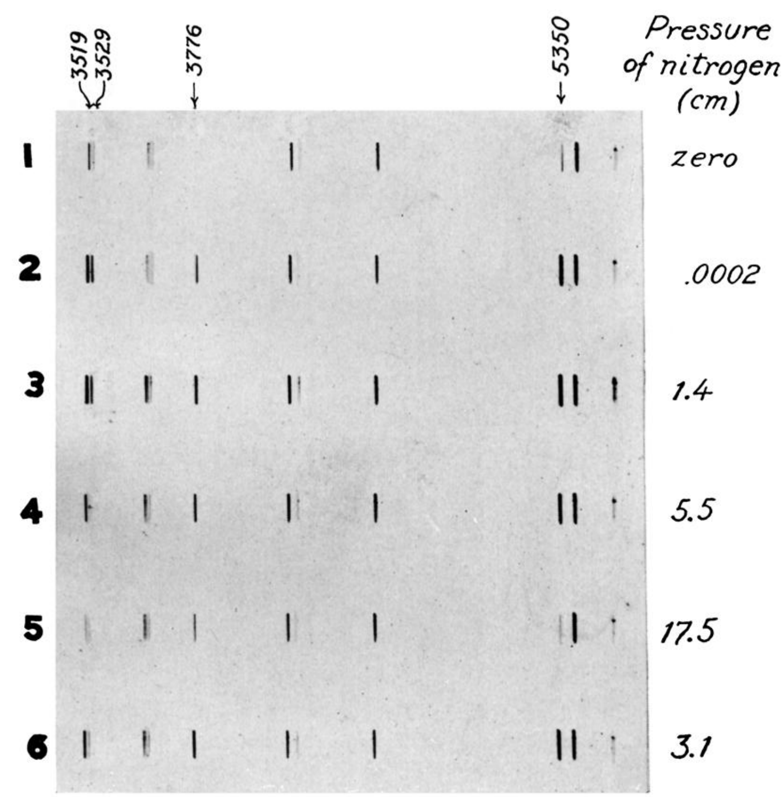
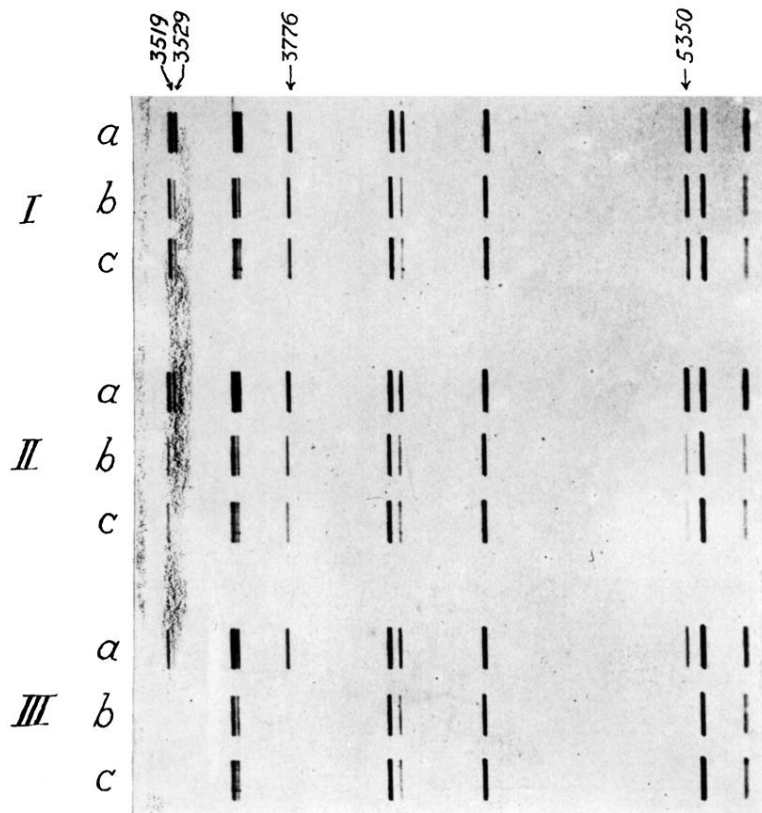


Fig. 3. Fluorescence spectra of Tl and Hg with N_2 present. Exposure 32 min. Tl at 640°C, Hg at 100°C.



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