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Stepwise Fluorescence in Mercury-Nitrogen Mixtures

The 3650 Line

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The experiments of Wood and of Gaviola show that when mercury vapor is illuminated by light from a mercury arc, and nitrogen is added in increasing amounts, the concentration of atoms in the $^3P_2$ state passes through a minimum. No simple theory accounts for this result. An explanation involving excitation of atoms in the $^3P_1$ state by vibrating nitrogen molecules is discussed. The results obtained when a filter of bromine vapor is used indicate a transfer of excited mercury atoms from one to another ^3D state upon collision with nitrogen.

Some years ago R. W. Wood performed experiments on the optical excitation of mercury vapor. They were continued in collaboration with E. Gaviola, who wrote several papers on the theory. In this splendid series of papers[1] by these authors the principal effects were explained. Nevertheless, the theory developed by Gaviola does not adequately account for the observed changes of the intensity of the 3650 line ($2\,^3P_2-3\,^3D_3$). The purpose of the present paper is to consider the behavior of this line, point out the questions which it raises, and suggest interpretations of the results.

The 3650 Line in the Fluorescence of Pure Mercury Vapor

First, it is desirable to reconsider the behavior of the 3650 line in the fluorescence excited in pure mercury vapor by the full light of the mercury arc. Fig. 1 gives the Grotrian diagram of the levels of the mercury atom with which we are concerned. 1*a* is drawn to scale, 1*b* is schematic. On it are indicated the wave-lengths of the principal lines and their relative intensities in the arc as given by Wood (II, p. 782; III, p. 474). Wood and Gaviola interposed neutral screens between the source of exciting light and the fluorescing vapor (V). For each screen there was a factor, *f*, by which the intensities of all exciting lines were reduced. They found that the intensity of the 3650 line in the fluorescence was reduced by the factor f^3, and the intensity of the 3654 line by the factor f^2. In earlier experiments (II, p. 784) the intensities of the 5461, 4358, 4046, 3663, 3131, 3125, and 2967 lines had been found to vary in the same way as that of 3654, so these other lines must also vary in intensity as f^2. One concludes from the change of the 3650 line that the concentration of excited atoms in the $^3D_3$ state must vary with f^3, and that the concentration of the atoms in the $^3P_2$ state must vary with f^2. This is apparent from Eq. (1) for the steady state.

$$[^3P_2]a_{3650}\cdot I_{3650}\cdot f=[^3D_3]\cdot A_{3650}=J_{3650}\ (\propto f_3). \quad (1)$$

(Notation: In this equation and in the following ones, the square brackets, [ ], will be used to represent concentrations of excited atoms in the states indicated by the symbols within the brackets.

The *a*'s are effective absorption coefficients,
The *I*'s are intensities in the exciting light before modification by screens,
f is the transmission factor of the screen,
The *A*'s are Einstein emission coefficients,
The *J*'s are intensities of emitted light in fluorescence.)

These conclusions were drawn by Wood and Gaviola, of course, but the argument is repeated here for elucidation of the equations and notations which are used in this paper. In all of these equations the left side will represent the rate of formation of excited atoms (no. per cc per sec.) and the right-hand side will represent the rate of disappearance. The concentration of the variety

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[1] Henceforth these papers will be referred to by the Roman numerals given to them here. I. R. W. Wood, Proc. Roy. Soc. London, **A106**, 679 (1924); II. R. W. Wood, Phil. Mag. **50**, 774 (1925); III. Ibid. **4**, 466 (1927); IV. R. W. Wood and E. Gaviola, Phil. Mag. **6**, 271 (1928); V. **6**, 352 (1928); VI. E. Gaviola, Phil. Mag. **6**, 1154 (1928); VII. **6**, 1167 (1928); VIII. E. Gaviola and R. W. Wood, **6**, 1191 (1928).

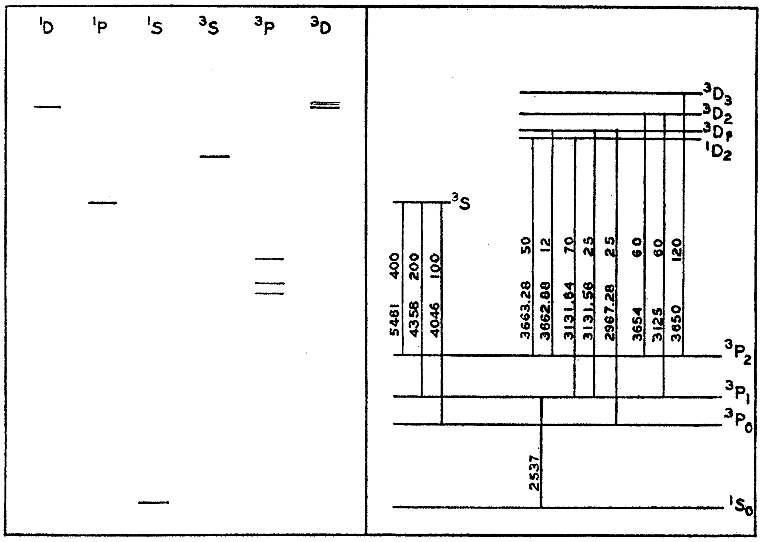
of excited atoms under consideration appears as a common factor on the right-hand side.

Next consider the equation for the balance of $^3P_2$ atoms.

$$[^3S]A_{5461}=[^3P_2](f\Sigma aI+b). \tag{2}$$

On the left-hand side of this equation there should also appear other terms corresponding to the emission of the 3663, 3654, and 3650 lines which results in the formation of atoms in the $^3P_2$ state. Since these lines are very much weaker than 5461 these terms may be neglected. The term ΣaI on the right is the sum of four separate terms, each of which represents absorption of one of the four lines just mentioned. 5461 is much the strongest line in the exciting light but its absorption is not detectable experimentally, whereas that of 3650 has been observed (VII, p. 1171). The b term includes all other processes by which $^3P_2$ atoms are removed, such as collisions with other atoms, and with the walls. Since the $^3P_2$ atoms are metastable, their mean life is large enough for such effects to be of importance. The ($^1S-{}^3P_2$) forbidden line, 2270, does not appear so that its emission need not be included. The left-hand side of Eq. (2) gives J_{5461}, the intensity of the green line in emission. It is experimentally observed to be proportional to f^2. We have just seen above that $[^3P_2]$ is also proportional to f^2. These two facts are reconcilable only if $\Sigma aI \ll b$, because of the f which multiplies into ΣaI. Thus, we must conclude that the $^3P_2$ metastable atoms are removed principally by collision and not by absorption of radiation. This is exactly opposite to the suggestion of Gaviola (VI, p. 1165). The point was one of minor importance in his considerations, so he did not make as careful an analysis of the factors involved. Since the pressure in the experimental tube could not have been much above the vapor pressure of mercury ($\sim$0.001 mm) the mean free path of these excited atoms is presumably large compared to the size of the tube. The metastable atoms can get to the walls quickly. The probability of losing energy and being reduced to $^3P_1$, $^3P_0$ or $^1S_0$ atoms at the first collision must be large, since the decrease of intensity of the 3650 line in fluorescence across the tube does not indicate an equalized, uniform distribution of $^3P_2$ atoms.

It is obvious that Eq. (2) represents an average behavior, rather than being one which takes proper account of the balance in any particular portion of the tube. Such an equation would have to include terms both for the loss and gain of $^3P_2$ atoms by thermal motion. These would contain geometrical factors and be complicated. Because of the low pressure the ordinary equations for



(a) (b)

FIG. 1. Grotrian diagram of certain levels of the mercury atom.

diffusion would not be relevant. The b of Eq. (2) puts such terms together as a net loss. The b is different for different places in the tube. Such considerations for the other excited states lead to the same conclusions as those reached by Wood and by Gaviola by substantially equivalent methods.

It should be noted that the above and the following remarks refer only to the conditions in a small region of volume of the experimental tube. It is to be thought of as close to the side where the exciting light enters, since nearly all of the experimental data cited were obtained for such places. The question of the distribution of density of the exciting atoms across the tube is a vastly more complicated one. The equations of Gaviola (VI, p. 1161) can represent only a very rough first approximation, even when diffusion is unimportant, because of his assumption of exponential absorption. The over-all absorption of an emission line can be accurately exponential only when there is the same coefficient of absorption for all parts of the line. In general, in such reversals of emission lines the variation of the absorption coefficient with frequency is more rapid than that of the intensity of the absorbed line.

EFFECTS OF ADDED NITROGEN ON THE 3650 LINE

Wood found that the addition of nitrogen to the tube gave rise to marked changes in the intensities of the different lines in fluorescence. Most of them become stronger. The 3650 line was first markedly diminished in intensity by small amounts of nitrogen and then augmented by larger amounts. As is well known, many of the effects are the result of a great increase of the concentration of atoms in the $^3P_0$ state. The absorption of 4047 by such excited atoms was directly observed and accounts for the great enhancement of 5461, 4358 and 4047.

This great enhancement of 5461 would lead one to expect a corresponding increase of 3650, since $^3P_2$ atoms are being produced by emission of 5461. The contrary result must mean that the $^3P_2$ atoms are destroyed upon collision with N_2 molecules. Gaviola presents a theory based on this hypothesis (VII, p. 1173) which is in good accord with the experiments as far as the principal effect of a diminution of intensity is concerned. Unfortunately it does not lead to the observed result that the intensity again increases at higher pressures. In order to explain this discrepancy one might be tempted to suggest production of $^3D_3$ atoms by some process other than the absorption of the 3650 line by the $^3P_2$ atoms (as in the last section of this paper). This will not suffice, however, since the more direct experiments on the absorption of the 3650 line show slight absorption at zero pressure of nitrogen, no absorption at intermediate pressures, and increased absorption again at higher pressures (VII, p. 1171). The concentration of $^3P_2$ atoms evidently goes through a minimum, and this is reflected in the intensity of the 3650 line in fluorescence.

The difficulty of understanding this behavior can be seen by consideration of the equation for the steady state of the $^3P_2$ atoms. It is

$$[^3S]A_{5461}=[^3P_2]\{\Sigma aI+K_2+k_2p+\Delta/p\}. \quad (3)$$

As above, the production of $^3P_2$ atoms by emission of lines other than 5461 is negligible. Further, the term representing absorption of light, ΣaI, is undoubtedly even less important here than above, where it was negligible. K_2 takes care of any manner of disappearance of $^3P_2$ atoms which is independent of the pressure of the nitrogen. Collisions with nitrogen molecules and with impurities in the nitrogen used are represented by the k_2p term, p being the pressure of the nitrogen. The Δ/p term is of the form which has been found suitable for taking account of the decreased rate of diffusion to the walls at higher pressures.[2]

The experimentally observed fivefold decrease in the intensity of the 3650 line produced by the addition of 0.05 mm of nitrogen can mean only that the k_2p term far outweighs the Δ/p term, which latter tends to give an initial change in the opposite direction. The right-hand side of (3) can thus be represented to a fair approximation by a term of the form K_2+k_2p. This is essentially the same as Gaviola's theory. Noting that the left-hand side of (3) is proportional to

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[2] E. W. Samson, Phys. Rev. **40**, 940 (1932); Klumb and P. Pringsheim, Zeits. f. Physik **52**, 610 (1929). Obviously this is incorrect for very low pressures since it goes to infinity for zero pressure. $\Delta/(p+p_0)$ would be a better form. See E. Gaviola, Phys. Rev. **34**, 1373 (1929).

TABLE I. *Ratio of intensities as a function of pressure.*

P (mm)	0	0.05	0.1	0.2	0.43	1.25	2	4	11
J_{5461}/J_{3650}	1	7.5	8	8	6	12	7.5	4.3	12.7

J_{5461}, and taking the intensity of 3650 as proportional to $[^3P_2]$ (3) becomes

$$K_2+k_2p=CJ_{5461}/J_{3650}, \tag{4}$$

C being a constant of proportionality. The values of the ratio J_{5461}/J_{3650} are given in Table I. These ratios in Table I are computed from Wood's provisional values of the relative intensities (III, p. 485). Although they do not lie on a smooth curve the approximate constancy of the ratio at higher pressures is apparent. This requires that k_2 be much less than K_2, which leaves unaccounted for the marked change produced by a change from a pressure of 0 to one of 0.05 mm. Eqs. (3) and (4) are completely inadequate for representing the facts.

One way to approach the problem is to inquire what changes in Eqs. (3) and (4) would be necessary to get a better agreement with experiment. There seems to be no reasonable way to modify the right-hand side of Eq. (3). Collisions with the nitrogen molecules are clearly very effective in removing the $^3P_2$ atoms. It is hard to see how this effect could be other than proportional to the pressure of the nitrogen. The experimental results can be taken to indicate that there is some process of production of $^3P_2$ atoms which increases with pressure, in addition to their production by radiation of the 5461 line. If we add such a term, $C'p$, to the left-hand side of (3) and eliminate the same terms on the right as before we get

$$[^3P_2]=\frac{[^3S]A_{5461}+C'p}{K_2+k_2p}=\frac{J_{5461}+C'p}{K_2+k_2p}. \tag{5}$$

Wood's relative values of J_{5461} can be represented approximately by an empirical formula of the form

$$J_{5461}=1+ap-bp^2,$$

in which a and b are positive. This merely expresses the finding that J_{5461} grows less rapidly at higher pressures. It is perhaps better to use the more general form

$$J_{5461}=1+ap-(bp^2+cp^3+\cdots).$$

Putting this expression in (5) we get

$$[^3P_2]=\frac{1}{K_2}\cdot\frac{1+(a+C')p-(bp^2+cp^3+\cdots)}{1+pk_2/K_2}. \tag{6}$$

Inspection of Eq. (6) shows that if $[^3P_2]$ is to decrease with rising pressure, at low pressures, k_2/K_2 must be greater than $(a+c')$. If this be so there can be no minimum for $^3P_2$. Because of the negative term $-(bp^2+cp^3+\cdots)$ this concentration will decrease even faster at higher pressures. Thus we are led to the conclusion that no process which supplies $^3P_2$ atoms at a rate proportional to the pressure of nitrogen will suffice to give the observed minimum. It is necessary that there be some process of supplying $^3P_2$ atoms which is proportional to p^2, or some higher power of p, large enough to outweigh the term $-(bp^2+cp^3+\cdots)$. This conclusion seems to be a necessary one on the basis of the experimental evidence. It does not depend on the exact values of J_{5461}, which are given by Wood as being merely provisional, but on the general experimental evidence that the concentration of $^3P_2$ atoms passes through a minimum.

A process of the sort required is suggested by consideration of the sensitivity of the $^3P_2$ atoms to collision with nitrogen. These excited atoms must give up some energy to become one of three other kinds of excited atoms, either $^3P_1$, $^3P_0$, or $^1S_0$. The energy difference between $^1S_0$ and $^3P_2$ is 5.43 volts. There is no known or expected electronic difference of this magnitude in the nitrogen molecule and it is unlikely, by the Frank-Condon principle, that such large vibrational transitions should occur. Presumably $^3P_2$ atoms lose their energy to become $^1S_0$ atoms only very infrequently upon collision with nitrogen molecules. The energies involved in the changes $^3P_2\rightarrow{}^3P_1$ and $^3P_2\rightarrow{}^3P_0$ are 0.571 and 0.789 volts, respectively. Compare these with the energies of the nitrogen molecule in its $v''=0$, 1, 2, and 3 vibrational states, which are 0, 0.287, 0.570, and 0.850 volts.[3] The very close agreement between the energy of the $^3P_2\rightarrow{}^3P_1$ change and the $v''=2\rightarrow v''=0$ change leads one to suspect that the process which makes the $^3P_2$ atoms sensitive to nitrogen is the excitation

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[3] Computed from the $a\leftrightarrow X$ bands of Birge and Hopfield, Astrophys. J. **68**, 257 (1928).

of normal nitrogen molecules to the $v''=2$ state, the mercury atoms becoming $^3P_1$ atoms. Probably the better way to put it is the following: The complex unstable triatomic molecule formed by the union of a $^3P_2$ atom of mercury and a normal molecule of nitrogen can break up either into these original constituent parts or into a $^3P_1$ atom and a vibrating nitrogen molecule having $v''=2$, the energies being practically the same.

The reverse process should also occur. Some $^3P_1$ atoms should be raised to the $^3P_2$ state upon collision with vibrating nitrogen molecules. The concentration of atoms in the $^3P_1$ state is nearly constant regardless of the pressure of the nitrogen. (Collisions negligible in comparison with radiation for the balance in the $^3P_1$ state.) If there be a sufficient concentration of nitrogen molecules with two quanta of vibrational energy, and if this concentration be proportional to the square of the pressure, this process of excitation can account for the increase in the $^3P_2$ concentration at higher pressures.

Let us assume that the $^3P_2$ atoms are removed by the production of molecules of nitrogen having two quanta of vibrational energy and consider the fate of the latter. They may collide with normal nitrogen atoms, with the walls of the tube, with normal mercury atoms, with $^3P_0$ and $^3P_1$ atoms, and with each other. In which of these collisions can they be expected to lose the vibrational energy?

The collisions with normal molecules of nitrogen will be the most frequent. According to the work of Zener,[4] and of Jackson and Mott[5] it is very improbable that such a vibrating molecule will give its energy of excitation to another nitrogen molecule. Such an exchange would still leave a molecule in the $v''=2$ state and be of no significance for our consideration. It is even less probable that two molecules in the $v''=1$ state should be produced at collision. Further, collisions with normal mercury atoms, and both kinds of metastable mercury atoms should be ineffective since there are no other states into which these atoms will be put by the 0.570 or 0.283 volts which the nitrogen molecule can give without large changes of kinetic energy. One has left only the excitation of the $^3P_1$ atom to the $^3P_2$ state and collisions with the walls. The nearly exact agreement of energy is favorable for the former process. Presumably, because of the excited electron of the mercury atom, the excited atoms and vibrating nitrogen molecule will make a temporary triatomic molecule more closely bound than those resulting from the collision of a vibrating molecule with an atom in the ^1S state, or another molecule in the $^1\Sigma$ state. The effectiveness of collisions with the walls is problematical. No theory of such collisions has been developed, so far as I am aware. One might expect that the wall of the tube, on which water molecules are adsorbed, might show a sort of "stickiness" which would favor interchange of energy with the nitrogen molecules.

If we assume that the two processes mentioned are the ones responsible for the removal of the energy of the vibrating nitrogen molecules the equation for the steady state is

$$k_2'[^3P_2]p=[N_2'(2)]\{\Delta_2/p+k_1'[^3P_1]\}. \quad (7)$$

The term on the left gives the rate of formation of vibrating nitrogen molecules. Their concentration is represented by $[N_2'(2)]$. (In pure nitrogen k_2' will equal k_2 of Eq. (3)). The Δ_2/p gives the rate of loss by collision at the walls as modified by diffusion, and the $k_1'[^3P_1]$ term the rate of loss by formation of $^3P_2$ atoms. Thus we get a term $[N_2'(2)]k_1'[^3P_1]$ to be added to the left-hand side of Eq. (3). From (7)

$$[N_2'(2)]k_1'[^3P_1]=\frac{k_1'[^3P_1]k_2'[^3P_2]p}{\Delta_2/p+k_1'[^3P_1]}. \quad (8)$$

As long as $\Delta_2/p \gg k_1'[^3P_1]$ this new term is proportional to $[^3P_2]p^2$. It will appear in the denominator of the proper modification of Eq. (6) with a negative sign and will lead to a minimum for the expression just as a positive p^2 term in the numerator would do. This is fairly involved, but all that it amounts to is that in effect at the higher pressures of nitrogen the $^3P_2$ atoms lost by collision are not all irrevocably lost.

This explanation of the experimental results is, to be sure, somewhat *ad hoc*. Other explanations which have been suggested do not seem even remotely plausible.

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[4] C. Zener, Phys. Rev. **37**, 556 (1931).

[5] J. M. Jackson and N. F. Mott, Proc. Roy. Soc. **A137**, 703 (1932).

EXCITATION BY LIGHT FILTERED BY BROMINE VAPOR

In the light of the discussion in the preceding section Wood's results obtained when a bromine filter was used are most astonishing (III, p. 473). The bromine filter removes the 4047 and 4358 lines so that these lines and the 5461 line do not appear in the fluorescence at all. The concentration of atoms in the $^3S_1$ state is zero. As with no filter, the absorption of 2537 gives a considerable concentration of $^3P_1$ atoms. With no added gas the further excitation is presumably the result of the absorption of the 3125 and 3131 lines to form $^3D_1$ and $^3D_2$ atoms. By the emission of the 3663 and 3654 lines $^3P_2$ atoms are formed. The process of removal of these atoms by collision at the walls is the same as before. Because of the weakness of all of these lines compared to the 4047, 4358 and 5461 lines the concentration of $^3P_2$ atoms would be expected to be slight. The 3650 line should be exceedingly weak in fluorescence, as is found to be the case.

On the admission of 0.25 mm of nitrogen the intensity of the 3663 line (unresolved pair) is doubled and that of the 3654 line remains unchanged. Since it is principally the emission of these lines which results in the formation of the $^3P_2$ atoms the rate of formation is evidently no more than doubled. At the same pressure, with no bromine filter, the intensity of the 5461 line and proportional rate of formation is quadrupled. The removal of $^3P_2$ atoms by collision must be just as effective in both cases so that we expect less than half the concentration of $^3P_2$ atoms when the bromine filter is used. In spite of that, the intensity of the 3650 line is *increased* to twice its original value instead of being decreased to half of its original value as it is with no filter. Thus, the 3650 line is more than four times as intense as we should expect it to be from the result obtained with no filter.

There seems to be little possibility of doubt that the concentration of atoms in the $^3P_2$ state is markedly less in the presence of 0.25 mm of nitrogen. The observed increase of the intensity of the 3650 line must mean that atoms are put into the $^3D_3$ state by some process other than the absorption of 3650 light by $^3P_2$ atoms.

One possible process is the transfer of atoms from the lower $^3D_1$ and $^3D_2$ states to the slightly higher $^3D_3$ state upon collision. Undoubtedly such transfers can go in both directions, as they do among the ^3P states, but the very low concentration of atoms in the $^3D_3$ state would lead to a preponderance of upward transfers to it over downward transfers away from it. The number of such upward transfers should be proportional to the product of the concentration of the atoms in the $^3D_2$ state and to the pressure (neglecting the less likely transfers from the lower $^3D_1$ state). A rough test of this theory of the enhancement of the intensity of the 3650 line can be obtained as follows. The intensities of the 3654 and 3125 lines are proportional to the concentration of atoms in the $^3D_2$ state. At pressures of nitrogen of 4 and 0.25 mm their intensities relative to the values for zero pressure are 2 and 1, respectively. The concentration of $^3D_2$ atoms must therefore be in a ratio of 2 to 1 at these two pressures. The concentration times pressure products are 2×4 and 1×0.25, respectively, in a ratio of 32 to 1. The ratio of the corresponding intensities of the 3650 line is 30 to 2. Of the intensity of 2 at the lower pressure 0.5 is to be attributed to 3650 light absorbed by $^3P_2$ atoms. The proper ratio is thus 30 to 1.5 or 20 to 1. The agreement with the prediction of 32 to 1 is unimpressive, but not too bad in view of the difficulties of the photometry of the very weak 3650 line and neglect of transfers in the opposite direction.

As Wood pointed out (III, p. 479) the changes of relative intensity of the yellow lines gives evidence for similar transfer of atoms from the $^3D_2$ state to the very close $^1D_2$ state.

Such transfers must also contribute to the enhancement of the 3650 line at higher nitrogen pressures in the experiments without the bromine filter, discussed in the first part of this paper. They could not account for the observed changes in the concentration of atoms in the $^3P_2$ state.

The lifetime of the ^3D atoms is presumably of the order of 10^{-8} sec. It is apparent that the cross section of collisions for such transfers must be large compared to ordinary kinetic theory cross sections in order that an appreciable effect should appear at pressures as low as 2 to 4 millimeters of nitrogen.