ON THE CONCENTRATION OF METASTABLE MERCURY ATOMS

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Abstract

The concentration of metastable atoms in presence of 3 mm nitrogen obtained using the measurements of Stuart seems to be in contradiction with a calculation given here using observations of Wood. The contradiction disappears if the different statistical weights of the levels 2^3P_1 and 2^3P_0 are taken in account. Corrected curves for the number of metastable atoms as functions of the foreign gas pressure are given for CO, H_2O, N_2, A and He which are to replace the corresponding curves of the previous paper. It is shown that the assumption of the author that by high primary light intensities the number of metastable atoms increases only with the square root of the intensity is strikingly supported by measurements of Wood.

THIS paper is a continuation of a previous one[1] by the author "On life and concentration of metastable atoms and the quenching of mercury resonance radiation." The concentration of metastable mercury atoms produced by collisions of resonance ones optically excited with nitrogen (or other foreign gas molecules) can be calculated numerically from the well-known fact that the introduction of a few mm of nitrogen into the vessel containing the mercury vapour (illuminated by a quartz mercury lamp) produces a many-fold increase in the intensity of the visible mercury lines emitted as fluorescence by the vapour. R. W. Wood[2] observed increases of the intensity of the green line 5461 ranging from 16 to 32 times. He interpreted this increase as due to the accumulation of metastable atoms when nitrogen is present and he was able to show experimentally by means of the absorption of the line 4046 that metastable atoms actually were present in large amounts. Let us now calculate numerically how many metastable atoms were present in the experiments of Wood, repeated and extended afterwards by the author.[3]

I

The green line 5461 is emitted by the 2^3S_1 level and its intensity in fluorescence which we will call J_{5461} is equal to

$$J_{5461} = A_{5461} \cdot N_s \qquad (1)$$

if A_{5461} is the Einstein spontaneous transition probability and N_S the number of atoms in the level 2^3S_1. This level can be reached when mercury vapour alone is in the fluorescence vessel ("vacuum" case) practically only[3] through

[1] E. Gaviola, Phys. Rev. **34**, 1373 (1929).
[2] R. W. Wood, Phil. Mag. **50**, 761, 774 (1925); **4**, 466 (1927).
[3] E. Gaviola, Phil. Mag. **6**, 1167 (1928).

the absorption of the line 4358 of the arc on the part of the the resonance atoms in the level 2^3P_1, the number of which we call $N_1{}^0$. It is therefore possible to write

$$N_s(\text{vacuo}) = \frac{1}{c} N_1{}^0 \cdot I_{4358} \cdot B_{4358} \cdot \tau_s \qquad (2)$$

where I_{4358} is the intensity of the line 4358 of the primary light source, B_{4358} its Einstein absorption coefficient and τ_S the mean life of the atoms N_S.

If a few mm pressure of nitrogen gas are admitted to the vessel containing the saturated mercury vapour, many resonance atoms are brought down by collisions with nitrogen molecules to the mestastable level 2^3P_0 where owing to

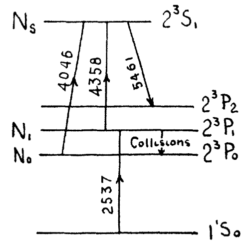

Fig. 1. Diagram of transitions.

is long life they accumulate until a concentration is obtained which, as the absorption experiments show is many times larger than the one of resonance atoms. The level 2^3S_1 is reached now practically only by the absorption of the line 4046 of the primary lamp on the part of the metastable atoms N_0 and consequently

$$N_s\,(\text{gas}) = 1/c \cdot N_0 \cdot I_{4046} \cdot B_{4046} \cdot \tau_s. \qquad (3)$$

It may be thought that the admission of nitrogen might also disturb the atoms in the level 2^3S_1 diminishing their number as a result of collisions, in which case formula (3) would give too large numbers. But according to recent results of Hanle and Richter[4] it takes at least 80 mm pressure of nitrogen to produce noticeable influence upon the level 2^3S_1. Formula (3) is therefore correct for all pressures below 80 mm and as our pressures do not exceed 10 mm we can quietly use it. Combining (1) with (2) and with (3) and dividing we obtain

$$J_{5461}\,(\text{gas})/J_{5461}\,(\text{vacuo}) = N_0/N_1{}^0 \cdot I_{4046}/I_{4358} \cdot B_{4046}/B_{4358}.$$

This ratio was photographically measured and found to be equal to 32 in Wood's earlier experiments, therefore

$$N_0/N_1{}^0 = 32 \cdot I_{4358}/I_{4046} \cdot B_{4358}/B_{4046}. \qquad (4)$$

Now, the ratio I_{4358}/I_{4046} of the intensities of the blue and violet lines of the arc has been repeatedly measured and found to be equal to 2. As both lines

[4] W. Hanle and E. F. Richter, Zeits. f. Physik **54**, 816 (1929).

are emitted by the same upper level, the ratio of their intensities gives at the same time the relation of the values of their corresponding Einstein emission coefficients A_{4358} and A_{4046} if that value is not falsified by absorption or reversal of the lines before they leave the mercury lamp. As that ratio is the same for the lines of the primary lamp when the discharge is magnetically deflected against the wall of the tube as for the secondary fluorescence light in the case of "vacuo" when practically no reabsorption can take place, one can write with confidence

$$A_{4358}/A_{4046} = 2 = I_{4358}/I_{4046}. \tag{5}$$

Between the coefficients A and B there is a relation

$$A = B \cdot 2h\nu^3/c^2 \cdot q_1/q_2 \tag{6}$$

where q_1 and q_2 are the statistical weights of the lower and upper levels respectively. The statistical weights of the levels 2^3P_0, 2^3P_1 and 2^3S_1 are 1, 3 and 3, therefore for 4358 $q_1/q_2=1$ and for 4046 $q_1/q_2=1/3$. We can then write

$$A_{4358}/A_{4046} = 2 = B_{4358}/B_{4046} \cdot (\nu_{4358}/\nu_{4046})^3 \cdot \tfrac{1}{3}$$

and since $(\nu_{4358}/\nu_{4046})^3=0.8$ we obtain

$$B_{4358}/B_{4046} = 7.5.$$

Introducing the now known numerical values in formula (4) we have finally

$$N_0/N_1{}^0 = 32 \times 2 \times 7.5 = 480. \tag{7}$$

That means that when a few mm of nitrogen are present in the tube the number of metastable atoms is 480 times larger than the number of resonance atoms when no nitrogen is present. This last number can be easily obtained numerically if the intensity of the primary line 2537.5 is known. $N_1{}^0$ is for instance equal to one if 10^7 light quants are absorbed per second in the volume element considered (since the life of 2^3P_1 is 10^{-7} sec.).

II

In a former paper of mine on the same subject[1] I have made a numerical calculation of the ratio $N_0/N_1{}^0$ as a function of the foreign gas pressure for different gases (and among them for nitrogen) using the measurements of Stuart for the quenching of resonance radiation and some other experimental data. Now, Fig. 5 of that paper indicates that for a pressure of about 3 mm of nitrogen (which was the pressure used by Wood to obtain a 32 fold increase of the green line) the ratio $N_0/N_1{}^0$ ought to be about 1200. This number is nearly three times larger than the one obtained above. It is therefore necessary to solve this contradiction. This we shall here do. The values of my former paper were all calculated neglecting the fact of the different statistical weights of the levels 2^3P_1 and 2^3P_0.[5] If we take this fact into account, none of the previous formulas is changed but the value α which

[5] Dr. H. Beutler kindly called my attention to this point.

indicates the ratio N_0/N_1 for the case of thermal equilibrium and is given by the formula

$$\alpha = q_0/q_1 \cdot e^{w/kT} \tag{8}$$

where q_0 and q_1 are the statistical weights of the levels 2^3P_0 and 2^3P_1 respectively and w their energy difference, this value α becomes three times smaller than it was assumed to be in the previous paper because $q_0/q_1 = 1/3$. For the same reason the constants b and E_0 of Table I of that paper are three times too small. If we recalculate now the curves for N_0/N_1^0 as a function of

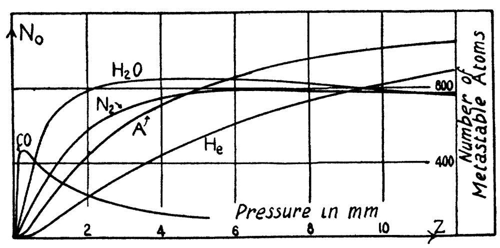

Fig. 2. Number of metastable atoms as a function of the foreign gas pressure if 10^7 quanta are absorbed per second.

the pressure of foreign gases using three times larger values for b and E_0 and a three times smaller α we obtain the curves reproduced in Figs. 2 and 3 which are to take the place of Figs. 5 and 6 of the previous paper. We see in Fig. 2 that the number N_0/N_1^0 for about 3 mm nitrogen pressure has reduced itself to about 700. This number is still larger than the one obtained independently in the first part of this paper but we have to remember that the number 480 corresponds to the experimental conditions of Wood while the number 700

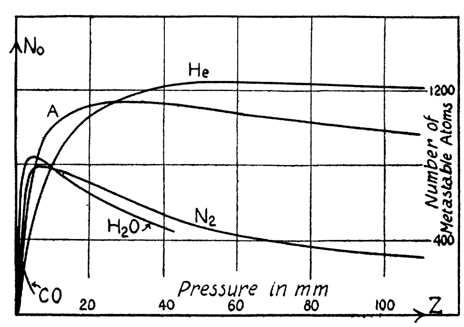

Fig. 3. Number of metastable atoms as a function of the foreign gas pressure for $N_1^0 = 1$ (10^7 quanta absorbed per second).

to those of Stuart. The main difference between the experimental conditions of both observers was that Wood used a considerably larger primary light intensity. As I have shown in the previous paper N_0 increases for large primary light intensities not proportional to the intensity itself but to the square root of it, while $N_1{}^0$ grows on linearly. The relation $N_0/N_1{}^0$ must therefore become smaller for large intensities, as in the case of Wood. An interesting confirmation of this result is given by the measurements of Wood himself. In his earlier experiments[6] he obtained as said above a 32 fold increase of the green line by the admission of nitrogen. After that he increased his primary light intensity considerably by pressing the arc discharge against the wall with a magnetic field. The increase of the green line was now at best only 15 fold.[7] The ratio $N_0/N_1{}^0$ had decreased therefore (compare formulas (4) and (7)) to 225. Since the decrease of $N_0/N_1{}^0$ for large intensities is due to collisions between two metastable atoms which destroy both of them (one is excited to a higher level, the other becomes normal) the above result is a striking hint at the fact that the probabity of such collisions (collision-section) must be rather large.

[6] R. W. Wood, Phil. Mag. **50**, 761 (1925).
[7] R. W. Wood, Phil. Mag. **4**, 485 (1927).