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NUMERICAL STUDIES OF THE GROWTH AND DECAY OF RESONANCE FLUORESCENCE: TRAPPING TIME *VERSUS* ATOM CONCENTRATION FOR MERCURY, SODIUM, CADMIUM, NITROGEN, HYDROGEN AND OXYGEN RESONANCE LINES

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Summary

The ratio of trapping time T to natural lifetime τ has been calculated numerically, at atom concentrations N in the range 10^{10} to 10^{17} cm^{-3}, for the N 120.0 nm, H 121.6 nm, O 130.6 nm, Hg 184.9 nm, Cd 228.8 nm, Hg 253.7 nm, Cd 326.1 nm and Na 589.0 nm resonance lines. Allowance has been made for multiplet and hyperfine structure. Differences in the form of graphs of T/τ *versus* N between transitions having large and small f values are accounted for. For the Hg 253.7 nm line the calculated trapping times are in excellent agreement with experimental data in the literature over the entire concentration range, from very small to very large optical depths.

Introduction

Previous communications [1, 2] have given results of numerical solution of the equation

$$dU_{KL}/dt = I_{KL} - (Q + T_{KL})U_{KL} + \sum_{MN} (U_{MN} - U_{KL})G_{KLMN} \quad (1)$$

for Ar 106.7 nm and Cd 228.8 nm fluorescence. In equation (1) U_{KL} is the concentration of excited atoms in the volume element specified by indices K and L, Q is the pseudo first-order quenching rate, T_{KL} is the rate coefficient for escape of photons from element KL to the outside of the fluorescence cell, and G_{KLMN} is the rate coefficient for transfer of photons from element MN to element KL. The solution of the equation consists of tables of values of the excited atom concentration in each volume element and of the radial fluorescence intensity at three preselected distances from the beam input window, at each of several hundred time steps. The present paper gives the results of calculations for atomic resonance lines of hydrogen,

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nitrogen, oxygen, sodium, cadmium and mercury. For the Hg 253.7 nm line detailed comparison is made with experimental data in the literature.

Two complicating factors have to be considered in connection with the calculations for this group of atoms. The first is multiplet structure and the second is hyperfine structure. For multiplets which have a single lower state with well separated upper states, such as the sodium D-lines or the N 120.00, 120.02, 120.07 nm multiplet, it is sufficient to treat individual lines of the multiplet as separate cases unless some specific mechanism is known to interconvert the upper states. No such mechanism has been included in the present calculations for sodium and nitrogen. The sodium D-lines are treated as independent transitions, akin to the 253.7 nm and 184.9 nm lines of mercury, or the 326.1 nm and 228.8 nm lines of cadmium. For the H 121.6 nm line we have another simple case, because the two upper states $^2P_{1/2}$ and $^2P_{3/2}$ are almost perfectly degenerate with one another and with the $2^2S_{1/2}$ state. In most of the calculations for H it has been assumed that the ^2S and ^2P states are able to be interconverted very rapidly, for example by stray electrical fields, so that the Lyman-α line can be regarded as associated with a single upper state of degeneracy 8. A few calculations have been made with upper-state degeneracy 6 for comparison.

For the oxygen 130.4 nm triplet the situation is quite different, in that there is a single excited state with three well separated but significantly populated ground states. This case has been treated as follows: the population of oxygen atoms in each of the three sublevels of the ground ^3P_J state has been calculated at the temperatures of the lamp, filter layer and fluorescence cell. These populations are independent of time. The Voigt profile appropriate to each absorption line in each part of the system, lamp, filter and cell, has been calculated using the relevant atom population. In each volume element the rate of absorption of each exciting line from the lamp has been calculated and the contributions of the three lines have then been added together to give the total excitation rate I_{KL} of eqn. (1). Similarly, for each line the contributions to T_{KL} and G_{KLMN} have been evaluated individually, and then added together to produce the total rate coefficient. The calculations show, incidentally, that photon transfer and escape are significantly enhanced by multiplet structure of this type. The strongest line of the multiplet provides effective transfer of excitation over short distances, while the weakest line provides effective transfer and escape from the cell over long distances. Three separate matrices of $(T'_K + T''_K)$, in the notation of the previous communications, are used to calculate the contribution of volume element KL to the radial fluorescence observed at an axial position specified by the index L. The main output of the computer program which takes account of this multiplet structure comprises a single set of values of excited atom concentration and three sets of values of fluorescence intensity.

The problem of hyperfine structure is significant in connection with the heavier atoms mercury and cadmium. For the lighter elements, where hyperfine splittings are much less than the Doppler width, hyperfine structure has been neglected. For mercury the 253.7 nm line consists of five component

groups of approximately equal intensity, each group being separated from the next by about five times the Doppler width. There is good theoretical [3] and experimental [4] justification for treating this case by simply dividing the k_0 value (the peak, Doppler-only absorption coefficient) by the number of hyperfine components. The same treatment has been adopted for the Hg 184.9 nm line, for which the upper state has the same J and F values. With cadmium the hyperfine splittings are smaller, the separation between component groups of transitions being comparable with the Doppler width. Breckenridge and coworkers [5], who have calculated trapping times for Cd 326.1 nm fluorescence at low cadmium concentrations, have divided the k_0 value by 3 on the grounds that the components form three fairly well separated groups. For want of a better procedure the same method has been used in the present calculations for the 326.1 nm and 228.8 nm lines. However, it must be pointed out that, because the three groups of lines are not all of the same intensity (Breckenridge *et al.* estimate the intensity ratios to be 1:7:2), and the most intense group derives from one set of isotopes (the even isotopes) while the weaker groups derive from a different set of (odd) isotopes, one would expect to have two distinct sets of excited atoms whose populations decay at different rates. Thus in general the decay of cadmium fluorescence should not follow a single exponential. Where the present calculations can be compared with those of Breckenridge *et al.* the agreement is very good.

Results and discussion

The growth and decay of resonance fluorescence has been calculated for a cylindrical fluorescence cell of length 3.5 cm and diameter 3.0 cm, with an axial exciting beam of diameter 1.6 cm. Trapping times have been determined from the rate of exponential decay of the fluorescence immediately after the exciting beam was turned off, and from the phase shift between the excitation and fluorescence waveforms [2]. The light source consisted of a thin layer of 'lamp' gas at a high temperature, T_{lamp} plus a 2 cm thick 'filter' layer at an intermediate temperature, T_{filter}. The concentration of ground-state atoms in lamp and filter was taken as 4.5×10^{13} atom/cm^3 for all fluorescers except oxygen, for which the concentration was 1×10^{14} cm^{-3}. The temperatures assumed for lamp, filter and fluorescence cell, and the concentrations of helium buffer gas in lamp, filter and cell were as given in Table 1, which also gives other relevant parameters. The Lorentz cross-section of helium [3] was taken as 5×10^{-15} cm^2 throughout; the Holtsmark cross-section of the emitting atom was calculated from the formula of Weisskopf as given by Mitchell and Zemansky [3]. The results to be discussed here refer to fluorescence observed immediately opposite the middle of the fluorescence cell, at a distance of 1.750 cm from the beam input window. Typical results are given in Table 2 to show the size of the variation in trapping time between the centre of the cell and points close to the beam input and exit windows.

TABLE 1

Parameters used in trapping-time calculations; g_1 and g_2 are the degeneracies of the lower state and the excited state, respectively; N is the number of fluorescent atoms per cm^3; M is the number of helium atoms per cm^3; f values are from refs. [3] and [6].

Atom	λ/nm	g_1	g_2	A/s^{-1}	f values	$N_{filter,lamp} \times 10^{-13}$	$M^*_{filter,lamp} \times 10^{-16}$	M_{cell}	T_{lamp}/K	T_{filter}/K	T_{cell}/K
H	121.6	2	8	4.70×10^8	0.4162	4.5	4	4×10^{16}	600	400	300
N	120.0	4	6	5.49×10^8	0.14	4.5	4	4×10^{16}	600	400	300
O	130.6	1	3	1.3×10^8	0.032	10.0	4	4×10^{16}	600	400	300
Hg	184.9	1	3	7.69×10^8	1.19	4.5	4	zero	600	500	450
Hg	253.7	1	3	8.8×10^6	0.0278	4.5	4	zero	600	500	450
Cd	228.8	1	3	5.0×10^8	1.20	4.5	4	zero	650	620	600
Cd	326.1	1	3	4.35×10^5	0.00175	4.5	4	zero	650	620	600
Na	589.0	2	4	6.76×10^7	0.67	4.5	4	zero	650	620	600

*M = Helium; Lorentz broadening cross-section assumed = 5×10^{-15} cm^2.

TABLE 2

Comparison of trapping times T at different distances from the beam input window. N = fluorescent atoms per cm^3. Distances from input window in parentheses.

	N	O	Hg
λ/nm	120.0	130.2	253.7
N	10^{14}	10^{15}	3×10^{14}
T(0.239 cm)	174 ns	92.0 ns	7.32 μs
T(0.755 cm)	247 ns	162 ns	13.2 μs
T(1.750 cm)	288 ns	205 ns	18.6 μs
T(2.745 cm)	265 ns	183 ns	16.6 μs
T(3.261 cm)	206 ns	150 ns	12.8 μs

Results for the whole series of transitions studied are summarized in Fig. 1 in the form of graphs of log (T/τ) *versus* N, where T is the trapping time for decay from the steady state fluorescence, τ the natural lifetime, and N the concentration of ground-state atoms. For most of the points shown there was less than 5% difference between the 'average' phase-shift trapping time and the exponential decay rate of the initial transient. The initial decay is the quantity that is plotted. Successive curves are displaced upwards by one unit for clarity. There is an interesting gradation in form between the curves for transitions of large f number, such as Cd 228.8 or Hg 184.9, and those for transitions of small f number, such as Hg 253.7. Where the f number is large the range of N over which T varies approximately linearly with N is quite short, and is succeeded by a range in which T varies approximately as $N^{1/2}$. The knee in the curve of log T/τ *versus* N appears to correspond to the concentration at which the Doppler core of the absorption line ceases to be a major contributor to the T and G integrals. When there is a range at large N in which T is almost independent of N, this is the range in which Holtsmark broadening prevents the absorption coefficient from increasing in proportion to N. There is also a difference in form between the radial concentration profiles of excited atoms in the two extreme cases, as shown in Figs. 2 and 3. The Hg($^1P_1$) concentration profiles at short times in Fig. 2 show a sharper distinction between the regions inside and outside the exciting beam than do the corresponding profiles for Cd($^3P_1$) in Fig. 3. Thus the difference in behaviour of T/τ with increasing N can be associated with a difference in the relative magnitudes of internal radiative transfer, via the G_{KLMN} terms, and escape of radiation via the T_{KL} term. To take a definite example, consider the Cd 326.1 nm line in the range 10^{14} to 10^{15} atom/cm^3, and the Cd 228.8 nm line in the range 10^{13} to 10^{14} atom/cm^3. The ratio of the transmission integral $T(y)$ to the transfer integral $G(y)$ at a distance y = 0.6 cm ($\sim r_{cell} - r_{beam}$) goes from 1.50 to 0.48 for the 326.1 nm line and from 0.61 to 1.42 for the 228.8 nm line in their respective ranges of N.

The results in Tables 3, 4 and 5 show the expected effect of upper-state degeneracy on trapping time. In each of these Tables results are given for three distances from the input window. In Table 3 the two sodium D-lines are compared, and in Table 4 the three components of the nitrogen triplet. (Both sodium transitions were assigned the same lifetime; the nitrogen lifetimes were as given in ref. [6].) In Table 5 it is shown that the trapping time for Lyman-α radiation is not greatly affected by whether or not the 2 $^2S_{1/2}$ state is assumed to be rapidly interconverted with the ^2P_J states, because the change in degeneracy from 6 to 8 is not very drastic.

The results in Table 6 show that the trapping times for the three components of the O 130.4 nm triplet are almost identical with one another, as was to be expected because the three lines arise from the same upper state. Such differences as do occur result from differences in the transparency of the system for the three lines, which cause the fluorescence signals to probe slightly different regions of the excited atom distribution within

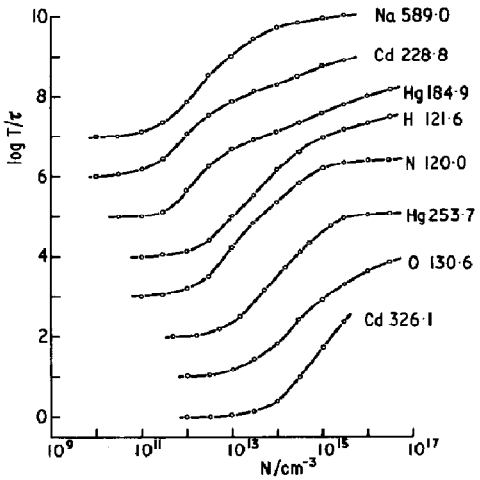
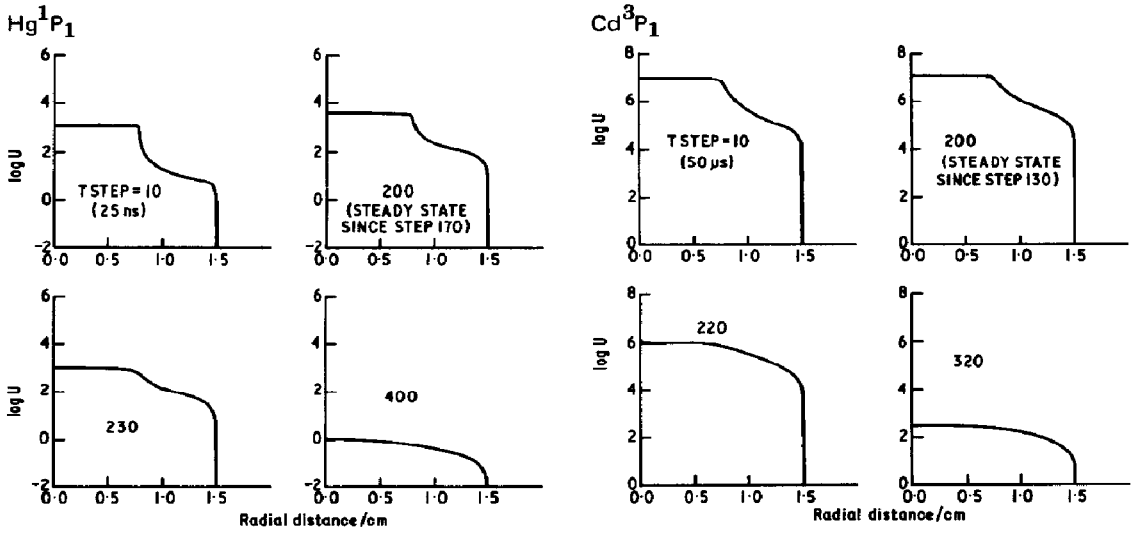


Fig. 1. Calculated values of T/τ, the ratio of trapping time to natural lifetime, for Na 589.0, H 121.6, N 120.0, Cd 228.8, Hg 184.9, Hg 253.7, Cd 326.1 and O 130.6 nm fluorescence. Fluorescence observed opposite mid-point of 1.5 cm radius cell; conditions as listed in Table 1. Successive curves have been displaced upwards by one unit for clarity.



Fib. 2. Radial concentration profiles for $Hg(^1P_1)$ after various numbers of integration steps. [Hg] = 5×10^{13} cm^{-3}. Exciting beam turned off at step 200.

Fig. 3. Radial concentration profiles for $Cd(^3P_1)$ after various numbers of integration steps. [Cd] = 9×10^{14} cm^{-3}. Exciting beam turned off at time-step 200.

the cell. The relative steady-state fluorescence intensities of the three lines have been measured by Bemand and Clyne [7] at oxygen atom concentrations up to 2×10^{14} cm^{-3}. The calculated steady-state intensities in Fig. 4 are in good agreement with the experimental data given in their Fig. 3a.

For the Hg 253.7 nm line there is a considerable body of experimental data with which to compare theoretical trapping times. Michael and Yeh [8] have compared their own experimental values with those of Yang [9], and

TABLE 3

Comparison of trapping times for Na 589.0 and 589.6 nm lines. (Upper state degeneracies 4 and 2 respectively.)

$[Na]/cm^{-3}$	z/cm	$T(589.0)/\mu s$	$T(589.6)/\mu s$
1×10^{13}	0.2395	2.72	1.49
1×10^{13}	1.7500	4.23	2.49
1×10^{13}	3.2605	2.79	1.56
1×10^{15}	0.2395	10.6	9.56
1×10^{15}	1.7500	17.0	14.7
1×10^{15}	3.2605	13.5	11.9

TABLE 4

Trapping of N 120.00, 120.02 and 120.07 nm fluorescence. (Upper state degeneracies 6, 4 and 2, respectively.)

$[N]/cm^{-3}$	z/cm	$T(120.00)$	$T(120.02)$	$T(120.07)$
3×10^{13}	0.2395	64.7 ns	41.5 ns	18.8 ns
3×10^{13}	1.7500	107.7 ns	70.0 ns	29.7 ns
3×10^{13}	3.2605	72.2 ns	47.4 ns	22.2 ns
3×10^{15}	0.2395	0.970 μs	0.879 μs	0.646 μs
3×10^{15}	1.7500	1.49 μs	1.30 μs	0.951 μs
3×10^{15}	3.2605	1.24 μs	1.08 μs	0.780 μs

TABLE 5

Trapping of H 121.6 nm fluorescence, effect of upper state degeneracy. (If interconversion of $2\ ^2S_{1/2}$ and $2\ ^2P$ is effective the upper state degeneracy is 8.)

$[H]/cm^{-3}$	z/cm	$T(g_2 = 8)$	$T(g_2 = 6)$
3×10^{13}	0.2395	50.4 ns	35.3 ns
3×10^{13}	1.7500	85.9 ns	60.7 ns
3×10^{13}	3.2605	58.2 ns	41.2 ns
1×10^{16}	0.2395	3.09 μs	2.93 μs
1×10^{16}	1.7500	4.60 μs	4.29 μs
1×10^{16}	3.2605	3.71 μs	3.46 μs

Thomas and Gwinn [10], at low optical depths, and with the theoretical predictions of Holstein [11], Milne [12] and Samson [13]. Somewhat similar comparisons have been made by Hong and Mains [14]. At low optical depths the theory of Samson gives good agreement with experiment. Holstein's predictions were previously shown to agree with the experimental data of Alpert *et al.* [15] at intermediate optical depths, while at large

TABLE 6

Comparison of trapping times for the three components of the oxygen triplet at 130.4 nm. (τ = 2.63 ns)

[O]/cm^3	z/cm	T(130.6)/ns	T(130.5)/ns	T(130.2)/ns
10^{12}	0.2395	2.695	2.695	2.695
10^{12}	1.7500	2.758	2.758	2.759
10^{12}	3.2605	2.695	2.696	2.696
10^{13}	0.2395	3.412	3.414	3.430
10^{13}	1.7500	3.998	4.001	4.025
10^{13}	3.2605	3.452	3.454	3.472
10^{14}	0.2395	11.47	11.87	12.47
10^{14}	1.7500	17.35	18.27	19.57
10^{14}	3.2605	13.35	14.01	15.03
10^{15}	0.2395	93.99	93.80	93.80
10^{15}	1.7500	213.0	212.3	200.5
10^{15}	3.2605	154.6	155.5	148.8
10^{16}	0.2395	658.0	647.9	644.8
10^{16}	1.7500	1129	1069	1051
10^{16}	3.2605	820.6	774.2	758.1

optical depths the Holstein theory, as modified by Walsh [16] also accounts satisfactorily for the region in which T is essentially independent of N.

In Fig. 5 the results of the present calculations at low optical depth are compared with the experimental trapping times of Michael and Yeh. The horizontal axis is the mercury concentration multiplied by the radius of the fluorescence cell. For this comparison the mercury concentrations of the present work were multiplied by $(300/450)^{1/2}$, to convert from 450 to 300 K, since the horizontal axis should really be k_0 multiplied by r. The choice of the radius as a critical dimension derives from the infinite-cylinder model which is used by the analytical (as opposed to numerical) theories. The calculated results in Fig. 5 (and also in Figs. 1 and 6) refer to the fluorescence emitted at the middle of the cell, where escape of radiation via the end windows is relatively unimportant, so the good agreement with the infinite-cylinder model is not too surprising. In Fig. 6 the present calculations are compared with experimental data of Phelps and McCoubrey [17], Alpert *et al.* [15] and Thomas and Gwinn [10]. The experimental [Hg]r values have been converted to a temperature of 450 K, except for those of Alpert *et al.*, where the temperature varied from point to point during the experiments, and which have been left unchanged. Again the agreement between theory and experiment is excellent. It is noteworthy that the calculated limiting value of T at high mercury concentrations is in very good agreement with the experimental value, which is perhaps more than one would have expected in view of the considerable difference between the model used in the calculations and the side-illuminated cell of the experiments. This agreement is destroyed if no allowance is made for hyperfine structure, because it depends on the outcome of the delicately balanced competition

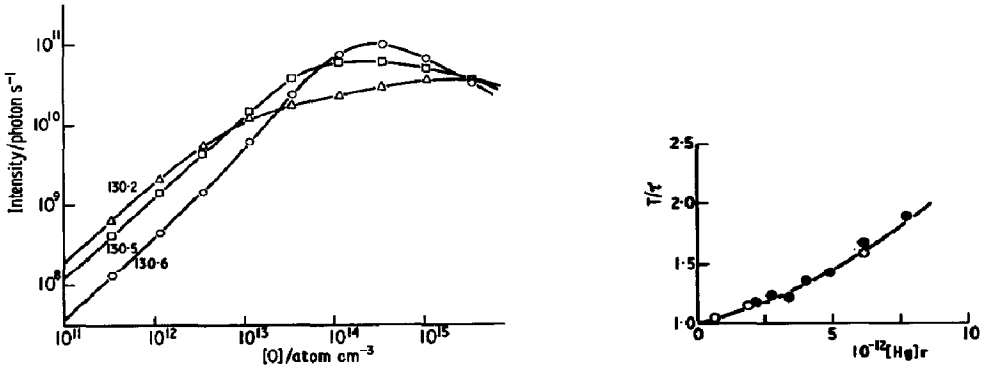


Fig. 4. Calculated steady-state fluorescence intensity *versus* atom concentration for the three components of the oxygen triplet at 130.4 nm. Fluorescence observed opposite the mid-point of the cell.

Fig. 5. Comparison of calculated and experimental values of T/τ for 253.7 nm fluorescence at low mercury pressures. [Hg]r is the product of mercury atom concentration and cell radius. Calculated values have [Hg[r multiplied by 0.816 to convert from 450 K to 300 K. ○, calculated values; ●, experimental values of Michael and Yeh.

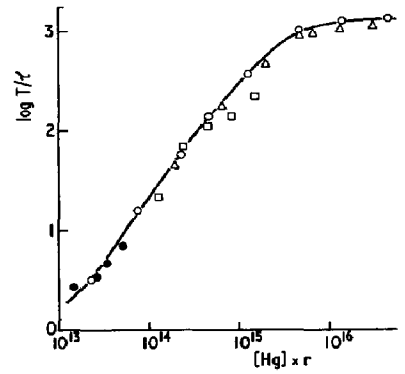


Fig. 6. Comparison of calculated and experimental values of T/τ for 253.7 nm fluorescence at high mercury pressures. ○, calculated values at 450 K; ●, experimental values of Thomas and Gwynn, [Hg]r adjusted to 450 K; □, experimental values of Phelps and McCoubrey, adjusted to 450 K; △, experimental data of Alpert *et al.*

between Holtsmark broadening and the increase of absorption coefficient with increasing N. In the absence of hyperfine structure the maximum calculated value of T at 450 K is 294 μs; with k_0 reduced by a factor of 5 the corresponding value is 120 μs. The single-isotope experiments of ref. [4] unfortunately do not provide a test of the limiting value in the absence of hyperfine splitting, because at high mercury pressures the measured decay time was limited by collisional energy transfer to isotopes which were present at low abundance, with correspondingly short trapping times.

In conclusion it can be said that the present numerical treatment of radiation trapping constitutes an advance over the theories of Samson and

Holstein mainly in that the single computer program can provide trapping times times which are in satisfactory (~10%) agreement with experiment over the whole range of atom concentration, from very low optical depth to the region of strong pressure-broadening.

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