The Detection of Hg(6^3P_1 and 6^3P_0) Atoms by an Atomic Absorption Method and Their Quenching Cross Sections

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The absorption intensities of the 435.8- and 404.7-nm lines by Hg(6^3P_1 and 6^3P_0) atoms were calculated taking into account the hyperfine structure under the assumption of a Doppler spectral line shape. The calculated values were tested by comparison with experimental absorption of the line in an Ar+N_2+Hg mixture illuminated by 253.7-nm radiation. This procedure led to the conclusion that the ratio of the spectral half-width of the 404.7-nm line from a low-pressure Hg lamp to that of the Hg(6^3P_0) absorption line should be 2.25±0.25 instead of the value of 5 determined in the previous experiment. On the basis of this value, the quenching cross sections of the excited Hg atoms reported in the previous paper were revised. The corrections are generally less than 20%, so that it is not necessary to change the previous conclusions.

In a previous paper,[1] a method was described to determine the quenching rate of excited Hg atoms for the processes $6^3P_1 \rightarrow 6^3P_0$ and $\rightarrow 6^1S_0$ from the observation of a stationary concentration of Hg(6^3P_0) atoms in a gaseous mixture of quencher +Hg vapor illuminated by 253.7-nm radiation. (Hereafter, Hg_1*, Hg_0*, and Hg stand for Hg atoms in the 6^3P_1, 6^3P_0, and 6^1S_0 states, respectively.) The Hg_0* concentration [Hg_0*], was estimated by the absorption measurement of the 404.7-nm line emitted from a low-pressure Hg discharge lamp. In this procedure, care was paid to verify that the absorption intensity was a function of [Hg_0*] as well as of the ratio of the spectral line half-width from the light source to that of the absorption line. In order to determine this ratio (denoted here by α), it was assumed that the [Hg_0*] in the mixture of Ar+N_2 is proportional to the intensity of the 253.7-nm radiation and that the 404.7-nm line is composed of a single spectral line. However, according to recent results,[2] the [Hg_0*] in the Ar+N_2 mixture is proportional to the square root of the 253.7-nm radiation intensity. Moreover, the 404.7-nm line has 9 hyperfine components resulting from the isotope shift and the nuclear-spin coupling. Therefore, the value of α reported previously must be corrected. In addition, the quenching cross sections[3] of the excited Hg atoms determined from the observed decay of the absorption at 404.7-nm must also be revised.

Experimental

The apparatus is essentially the same as that described in Ref. 1. In a quartz cell (3 cm in diameter and 24 cm in length) containing an Ar+N_2 mixture with an Hg pressure of 1.9×10^{-4} Torr, excited Hg atoms were formed by illumination with 253.7-nm radiation from 6 low-pressure Hg discharge lamps (Toshiba, 10-W germicidal lamp) surrounding the cell. The cell has an outer jacket filled with a 0.6 M $NiSO_4$ aq solution to avoid excitation of the Hg atoms to levels higher than the 6^3P_1 state. Another low-pressure Hg discharge lamp was employed as a light source for the 404.7- and 435.8-nm lines which were modulated by a chopper at 125 Hz before entering the cell. A d.c. source supplied the power for the Hg discharge lamps. A monochromator (Spex, 1700) and a lock-in amplifier (P. A. R. 186) were used to monitor the line intensity. The absorption due to [Hg_1*] was very weak, so that the 253.7-nm radiation intensity was modulated at a frequency of 0.12—3 kHz and the resulting a.c. component of the absorption at 435.8-nm was measured without the chopper; the signal obtained divided by the d.c. intensity of the 435.8-nm line from the source gives the absorbance. This procedure makes it possible to detect optical densities for absorption as small as 10^{-4}.

The rotational (=translational) temperature of the sample gas in the cell under the irradiation of 253.7-nm radiation was 292±15 K. This was estimated from the observed rotational temperature of CO, added as a tracer to the mixture.[4]

The nominal purities of the sample gases, Ar and N_2, were 99.999% and 99.99%, respectively. The method of gas handling is the same as that described previously.

Results and Discussion

Calculation of the Absorption Intensities of Excited Atoms. Taking the hyperfine splitting of 404.7- and 435.8-nm lines into account, the intensities for absorption by Hg_0* and Hg_1* atoms were calculated. For the calculation, the fine structure of the Hg lines observed by Schüler and Keyston[5] were adopted; the 404.7- and 435.8-nm lines are composed of 9 and 15 hyperfine components, respectively. It can be assumed that the line profile of each component of the 404.7- and 435.8-nm absorption lines is Doppler broadened with a common F. W. H. M. denoted by $\Delta\nu_D$. Though the line profile for radiation from a discharge lamp is dependent on many factors such as Doppler and collisional broadening, the Stark effect, *etc.*, it can be approximated by a Doppler-broadened line with a F. W. H. M. of α times that of the absorption line, *i.e.*, $\alpha\Delta\nu_D$. Thus, the spectral profile of the i-th component of the line from an Hg discharge lamp is given by

$$E^{(i)}(\nu) = E_0{}^{(i)}\exp\{-(\ln 2)[2(\nu-\nu_0{}^{(i)})/\alpha\Delta\nu_D]^2\}, \quad (1)$$

where $\nu_0{}^{(i)}$ is the frequency at the line center of the i-th component and $E_0{}^{(i)}$ is the peak intensity at $\nu_0{}^{(i)}$. Similarly, the absorption coefficient of the i-th component is

$$k^{(i)}(\nu) = k_0{}^{(i)}\exp\{-(\ln 2)[2(\nu-\nu_0{}^{(i)})/\Delta\nu_D]^2\}. \quad (2)$$

Since the absorbance A is defined as 1−(transmitted radiation, I)/(incident radiation, I_0), the observed absorption which should be the sum of those for the individual hyperfine components is described as

$$A = \int\sum_i E^{(i)}(\nu)[1-\exp(-k^{(i)}(\nu)l)]\mathrm{d}\nu \Big/ \int\sum_i E^{(i)}(\nu)\mathrm{d}\nu, \quad (3)$$

where l is the absorption length. The Hg discharge

lamp emits spectral lines under optically-thin conditions, so that the relative intensity of each hyperfine component is equal to that for the absorption coefficient;

$$k_0^{(i)}/k_0 = E_0^{(i)}/E_0,$$

where $E_0=\sum_i E_0^{(i)}$ and $k_0=\sum_i k_0^{(i)}$. This last quantity is described as

$$k_0 = (2/\Delta\nu_D)(\ln 2/\pi)^{1/2}(\pi e^2/mc)fN,$$

where e and m are the charge and mass of electron, respectively, and c is the velocity of light, f the f-number, and N the number density of excited atoms; $k_0=5.905\times10^{-12}N\,\mathrm{cm}^{-1}$ for Hg_0^* and $6.207\times10^{-12}N\,\mathrm{cm}^{-1}$ for Hg_1^* atoms.

Numerical integration of Eq. 3 was carried out for various α and k_0l values. In Figs. 1 and 2, the calculated values of $\log(1-A)^{-1}$ which is equal to $\log(I_0/I)$ are plotted as a function of k_0l. It is obvious that the optical density calculated with the hyperfine splittings is smaller than that calculated assuming a single line. In the region of small optical densities (<0.1) the calculation assuming a single line for the 404.7-nm line gives 4.6 times the value with the hyperfine splittings for $\alpha=1$ and decreases to 3.4 for $\alpha=2$ and 2.7 for $\alpha=3$. This may be interpreted to a very rough approximation as a 404.7-nm line having 3 to 4 lines with equal intensities; a large α causes a dense overlapping of hyperfine lines resulting in a reduction in the effective number of lines.

Determination of the Ratio of the Emission Line Width to the Absorption Line Width. Previously, it was assumed that the $[Hg_0^*]$ in an $Ar+N_2$ mixture is proportional to the intensity of 253.7-nm radiation. This is based on the processes for the Hg_0^* production:

$$Hg + h\nu \rightarrow Hg_1^*, \quad \text{(i)}$$

$$Hg_1^* \rightarrow Hg + h\nu, \quad \text{(ii)}$$

$$Hg_1^* + N_2 \rightarrow Hg_0^* + N_2, \quad \text{(iii)}$$

$$Hg_0^* \rightarrow Hg. \quad \text{(iv)}$$

However, the recent measurement[2] of the Hg_0^* lifetime indicates that the above processes cannot explain the formation and deactivation of Hg_0^*, and that reaction (iii) must be replaced by

$$Hg_1^* + N_2(v=0) \rightarrow Hg_0^* + N_2(v=1), \quad \text{(v)}$$

where $N_2(v=1)$ is vibrationally-excited N_2. Moreover, the inverse of this reaction and the deactivation of N_2 $(v=1)$ must be added:

$$Hg_0^* + N_2(v=1) \rightarrow Hg_1^* + N_2(v=0), \quad \text{(vi)}$$

and

$$N_2(v=1) \rightarrow N_2(v=0). \quad \text{(vii)}$$

A steady-state analysis of reactions (i)—(vii), excepting (iii), leads to the relation

$$[Hg_0^*] = \frac{k_7}{2k_6}\left\{\left[\left(\frac{k_5}{k_2}[N_2]+1\right)^2+4\frac{k_1k_5k_6}{k_2k_4k_7}I[Hg][N_2]\right]^{1/2} - \left(\frac{k_5}{k_2}[N_2]+1\right)\right\}, \quad (4)$$

where I is the intensity of the 253.7-nm radiation and k_i is the rate constant for reaction (i). Equation 4 may be simplified to a good approximation as

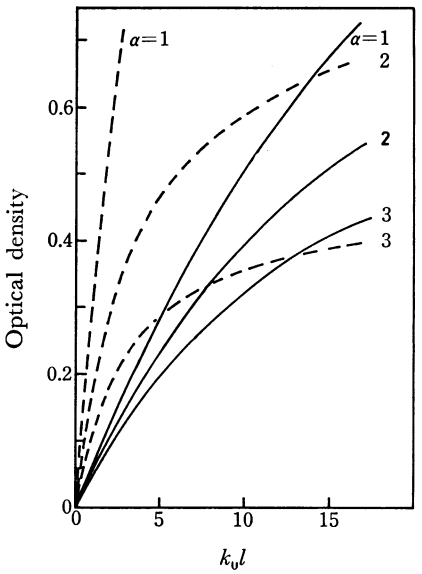

Fig. 1. Absorption intensity of the 404.7-nm line by $Hg(6^3P_0)$ atoms as a function of α; solid line: calculation with the hyperfine line structure, broken line: calculation assuming a single line.

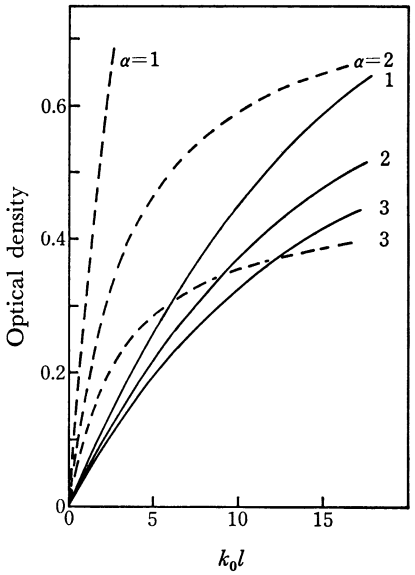

Fig. 2. Absorption intensity of the 435.8-nm line by $Hg(6^3P_1)$ atoms as a function of α; solid line: calculation with the hyperfine line structure, broken line: calculation assuming a single line.

$$[Hg_0^*] = (k_1k_5k_7[Hg][N_2]/k_2k_4k_6)^{1/2} \quad (5)$$

under the condition that $k_2>k_5[N_2]\gg k_4$. This condition is satisfied if the N_2 pressure is in the range from 1 to 30 Torr.

In order to determine α, the optical density of the 404.7-nm absorption was measured as a function of the relative intensity of the 253.7-nm radiation, as well as of the N_2 partial pressure. The intensity was estimated from the absorption of the 435.8-nm line caused by the formation of Hg_1^* in pure Ar, *i.e.*,

$$[Hg_1^*]_0 = k_1I[Hg]/k_2. \quad (6)$$

Substituting this equation into Eq. 5, the relation

TABLE 1. THE CROSS SECTIONS ($\pi\sigma^2$ IN Å^2) FOR THE QUENCHING OF Hg (6^3P_1 AND 6^3P_0) BY VARIOUS MOLECULES[a)]

Quencher	$6^3P_1 \rightarrow 6^3P_0$, $^1S_0$	$6^3P_1 \rightarrow 6^3P_0$			$6^3P_0 \rightarrow 6^1S_0$		
		This work	CM[b)]	VTL[c)]	This work	FECP[d)]	CM[e)]
N_2O	53.6[k)]	<6	<7		35(44)	14	26.7
O_2	60.5[f)]	<6	<6		35(50)	57	37.7
C_2H_4	151[g)]	<16	<15		129		82.5
C_3H_6	179[j)]	<16			135(157)		
C_2H_2	135[j)]	<13			91(113)		
H_2	24.6[f)]	<0.3	<0.7		6.0(6.6)	5.1	3.0
D_2	22.7[f)]	<0.3			8.5(9.1)		
C_3H_8	6.9[g)]	3.0(3.7)	1.4	0.87	0.15(0.23)		0.105
n-C_4H_{10}	18[h)]	11		2.2	2.0(2.9)		
i-C_4H_{10}	29[i)]	19(14)		1.06	4.2(4.4)		
$C(CH_3)_4$	6.0[g)]	5.7(5.0)		3.8	0.30(0.35)		
CO	21.7[f)]	22(12)	19.5	16.1	1.8(2.2)	7.8	2.06
NO	71.6[k)]	7.1(16)	<11		37(25)	41	50.1
NH_3	12.7[h)]	3.5(4.1)	8.1	14.2	0.038(0.05)	0.05	0.049
CO_2	10.2[f)]	0.19(0.06)	0.2	0.12	0.093(0.1)		0.104
CH_4	0.25[h)]	0.016(0.03)	0.03		4.1×10^{-4} (4.4×10^{-4})		9.0×10^{-4}
C_2H_6	1.8[h)]	0.66(0.53)	1.2	0.29	5.3×10^{-3} (6.3×10^{-3})	0.091	0.018
N_2	0.73[f)]	0.77			$<1\times10^{-3}$		

a) Previous values are given in parentheses if corrected. b) Calculated from quantum yields of Hg_0* determined by Callear and McGurk.[7)] c) Vikis, Torrie and LeRoy.[8)] d) Freeman, McEwan, Claridge, and Phillips.[9)] e) Callear and McGurk.[7)] f) Deech, Pitre and Krause.[10)] g) Kang Yang.[11)] h) The data of Zemansky[12)] multiplied by 1.379 a correction factor which is explained in Ref. 3. i) The value calculated from $\sigma^2(i\text{-}C_4H_{10})/\sigma^2(n\text{-}C_4H_{10})$ determined by Darwent.[13)] j) The data of Darwent[14)] multiplied by a correction factor of 1.85. k) the data of Michael and Suess[15)] multiplied by a correction factor of 0.805.

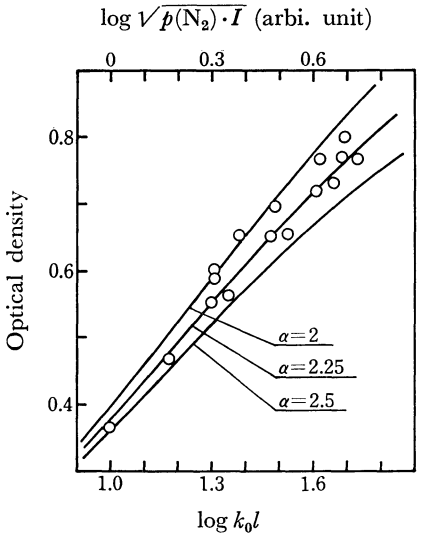

Fig. 3. Comparison of the calculated absorption intensities (solid line) of the 404.7-nm line with the experimental ones(circle) as a function of the N_2 partial pressure and the 253.7-nm radiation intensity.

$$[Hg_0^*] = [(k_5[N_2]/k_4)[Hg_1^*]_0(k_7/k_6)]^{1/2} \quad (5')$$

is obtained. Here, the absorption at 435.8-nm is so weak that the optical density can be assumed to be proportional to $[Hg_1^*]$ for any value of α. In Fig. 3, the optical density of the 404.7-nm absoption is plotted against $\log([N_2]I)^{1/2}$, together with the theoretical optical density, as a function of $\log k_0l$. The best fit to the experimental points is obtained for

$$\alpha = 2.25 \pm 0.25.$$

With this value of α, the optical density of the absorption at 404.7-nm gives the absolute magnitude of k_0l or $[Hg_0^*]$. The same value of α is assumed for the 435.8-nm line in the absence of experimental evidence. However, only a very weak absorption appears at 435.8-nm in the Hg* quenching experiment, so that the error caused by this assumption is rather small as can be understood from Fig. 2, in which the optical density is seen to be almost proportional to k_0l.

Quenching Cross Sections of Hg(6^3P_1 and 6^3P_0). The decay of the 404.7-nm absorption after a short pulse of 253.7-nm radiation was measured to estimate the Hg_0* quenching cross section as well as the spin-orbit relaxation rate of $Hg_1^* \rightarrow Hg_0^*$.[3)] The new value of α, which is 2.25 instead of 5, as found previously, changes the conversion from the optical density to the $[Hg_0^*]$. Thus, the reported quenching cross sections are revised to new values as summarized in Table 1, in which the data for collision partners of CO and NO are given from the new measurement employing a phase-shift method.[6)] There are minor changes in the cross sections: most of the Hg_0* deactivation cross sections are smaller by 10—20% than the previous values. This is due to the fact that the deactivation rate is deduced from the normalized quantity, $[Hg_0^*]/[Hg_1^*]_0$, which is not very sensitive to the value of α, especially for cases of weak absorption intensity. Thus, it is not necessary to change the conclusion derived in Ref. 3.

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