Spectroscopic Determination of Quenching Cross-Sections of Excited Mercury Atoms (6^3P_1, 6^3P_0) in Molecular Collisions

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The concentrations of Hg(6^3P_1) and (6^3P_0) atoms, [Hg_1*] and [Hg_0*], were determined from the absorptions of 4358 and 4047 Å lines in the Ar-diluted mercury vapor in the presence of several quenching molecules, under the radiation of 2537 Å emission. An apparent absorption intensity was not proportional to [Hg_1*] or [Hg_0*], and was sensitive to the ratio of the spectral half-width of the light source to that of the absorption line. Therefore, a method to correct an absorption intensity was proposed. The relation of [Hg_1*] to [Q], a concentration of quenching molecules, is explained well by the Stern-Volmer equation. The value of [Hg_0*] increases with [Q] until it reaches a maximum at a certain value of [Q], and a further increase of [Q] results in a decrease of [Hg_0*]. These findings are explained well by the following mechanism: (1) $Hg+h\nu \rightarrow Hg_1^*$, (2) $Hg_1^* \rightarrow Hg+h\nu$, (3) $Hg_1^*+Q \rightarrow Hg+Q$, (4) $Hg_1^*+Q \rightarrow Hg_0^*+Q$, (5) $Hg_0^*+Q \rightarrow Hg+Q$, (6) $Hg_0^* \rightarrow Hg$ (by collisions with a wall). The respective values of cross-sections (σ^2) of N_2, CO, and NO for process (3) are $\lesssim 0.03$, 0.60, and 20 Å^2, and those for process (4) are 0.36, 2.1 and 5 Å^2, and those for process (5) are $\lesssim 3.6 \times 10^{-4}$, 0.15 and 8.0 Å^2.

The collisional cross-section for quenching an excited mercury atom Hg (6^3P_1) has been obtained by the intensity measurement of the fluorescence from Hg (6^3P_1)[1,2] or by observing directly a lifetime of 6^3P_1 state[3]. However, the cross-section thus determined is the sum for the two quenching processes, *i.e.*, from 6^3P_1 to the ground state 6^1S_0 and to the metastable state 6^3P_0. Scheer and Fine[4] found that collisional cross-sections of CO and N_2 for quenching 6^3P_1 to 6^3P_0 were nearly the same, and concluded that CO was a more efficient quencher than N_2 for the process 6^3P_1 to 6^1S_0. Later, Callear and Williams[5] observed the time history of the absorption due to the existence of Hg(6^3P_0) after the flash excitation of mercury atoms, and concluded that all of the cross-sections of various molecules for the process 6^3P_0 to 6^1S_0 were very small compared with the 6^3P_1 quenching cross-sections. Furthermore, they could not find any systematic relation between a cross-section for quenching 6^3P_1 to 6^3P_0 and an energy discrepancy which could not be converted to the vibration of a quenching molecule. Kimbell and Le Roy[6] previously determined the stationary concentration of Hg(6^3P_0) in the system of N_2 gas with mercury vapor illuminated by the mercury resonance line assuming the Lambert-Beer rule. However, their assumption should be uncertain.

In this paper, we propose an accurate method to determine the concentrations of Hg(6^3P_1) and (6^3P_0) from the absorptions of 4358 Å (7^3S_1—6^3P_1) and 4047 Å (7^3S_1—6^3P_0) spectral lines. Based on this method, the cross-sections of N_2, CO, and NO for the quenching processes, $^3P_1 \rightarrow {}^1S_0$, $^3P_1 \rightarrow {}^3P_0$, and $^3P_0 \rightarrow {}^1S_0$ are determined.

Experimental

An outline of the apparatus in this experiment was similar to that used by Karl, Kruus, and Polanyi.[7] The reaction cell was a Vycol glass tube, 4 cm in diameter and 100 cm long, and was surrounded by four low pressure mercury lamps (Toshiba Electric Co., germicidal lamp) that were made from quartz tubes, 2.5 cm in diameter and 89.3 cm long. Each of these exciting lamps was operated by the direct current and had a power of 7.5 watt at 2537 Å radiation, and the emission intensities of other spectral lines were less than 1/30 of that of 2537 Å line. The intensity of 2537 Å radiation from the exciting lamps was monitored by a photoelectric tube (Toshiba Electric Co., PV-43), that was sensitive only to the 2537 Å line. Another low pressure mercury lamp (Ushio Co., ULO-6DQ), d.c. operated, was used as a light source for the measurement of absorption. Apparent concentrations of Hg(6^3P_1) or (6^3P_0) atoms were determined in terms of the optical density, $\log I_0/I$, at 4358 Å for 6^3P_1 atoms and 4047 Å for 6^3P_0 atoms. The light beam, 5 mm in diameter, from the ULO-6DQ lamp was modulated at 25 Hz by a chopper before entering the cell and was passed longitudinally through the cell. The intensity of the beam was measured by a grating monochrometer (Japan Spectroscopic Co., CT-1), and the out-put from the photomultiplier was filtered by a 25 Hz tuned amplifier. The spectral slit-width of the monochromator was usually about 2 cm^{-1}, so that the observed intensity was an integrated one of 4358 or 4047 Å spectral line profile.

Sample gases used were all commercial ones, and their nominal purities were 99.99% for Ar. 99.999% for N_2, 99.5% for CO, and 98.5% for NO. Argon and nitric oxide were purified by successive distillation at liquid nitrogen temperature, and other gases passed through a U-shaped glass tube packed with active charcoal. In order to minimize the pressure dependence of the absorption intensity, quenching gases were diluted in argon, and the total pressure in the reaction cell was kept constant, where argon could be assumed to be a very poor quencher. A quenching gas diluted in argon, from which mercury vapor was removed by passing through a spiral tube cooled to an appropriate temperature, −194.5°C or −119°C, was fed into the reaction cell *via* a mercury saturator at a constant temperature.

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[2] R. J. Cvetanović, "Progress in Reaction Kinetics," Vol. 2, Pergamon Press, London, (1964), p. 39.

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[6] G. H. Kimbell and D. J. Le Roy, *Can. J. Chem.*, **38**, 1714 (1960).

[7] G. Karl, P. Kruus, and J. C. Polanyi, *J. Chem. Phys.*, **46**, 224 (1967).

Results and Analyses

Absorption Intensity and Concentration of Excited Mercury Atom. The absorptions of 4047 and 4358 Å lines were seen, when a gaseous mixture of Ar, N_2, and Hg was irradiated by the exciting lamp. In this case, the Lambert-Beer rule cannot be applied, since it is well known in atomic absorption spectroscopy that the properties of the spectral line itself, *i.e.* (1) the hyperfine structure of the lines, (2) the ratio of the absorption and emission line widths, (3) the resonance line broadening, must be considered. To investigate this point in experiment, it was examined how the absorption intensity of 4047 Å line was dependent on the intensity of 2537 Å radiation from the exciting lamp. Two examples of the results are shown by curves A and B in Fig. 1. The optical density is not in a linear relation to the intensity of exciting radiation, though the concentration of $Hg(6^3P_0)$ in the cell should be proportional to the intensity of 2537 Å line.

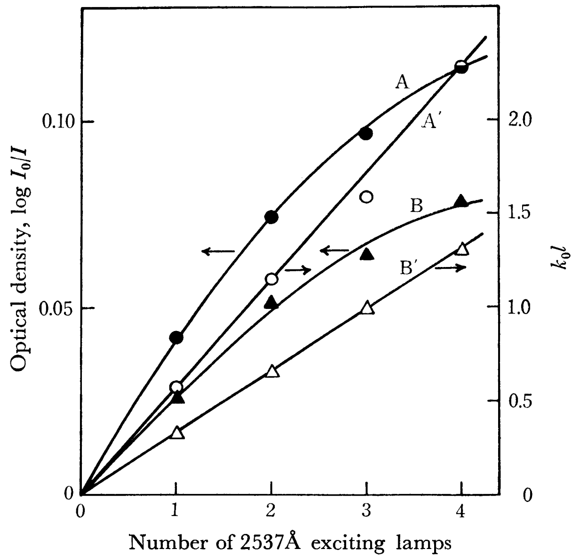

Fig. 1. Relative intensity of 2537Å radiation *vs.* the optical density at 4047Å, and relative intensity *vs.* calculated values of [Hg_0*] in k_0l unit.
A(●), A'(○): $p(N_2)=0.03$ Torr, $p(Ar)=4.97$ Torr; B(▲), B'(△): $p(N_2)=0.03$ Torr, $p(Ar)=0.97$ Torr.

To analyze this result, the profiles of the 4047 Å line from the light source and the absorption line of $Hg(6^3P_0)$ are assumed to be of Doppler broadened type. This assumption is only approximately applicable, because the spectral line profile from the discharge lamp must be dependent on many factors, *e.g.*, Doppler, collision, Stark effects, *hfs*, *etc.*, and the absorption line has a combined form of Doppler and collision broadened profiles with *hfs*. However, the purpose of the present experiment is not to clarify the spectral line profile, but to find the physical quantity proportional to the concentration of the excited mercury atoms from the optical density. Therefore, we tried to correct the curves of the absorption intensities in Fig. 1 to be linear to the intensity of 2537 Å line under the above assumption. The spectral intensity, E_ν, at a wave number ν from the light source is represented by[1)]

$$E_\nu = \text{const} \times \exp[-(\omega/\alpha)^2], \tag{1}$$

where

$$\omega = 2(\nu-\nu_0)(\ln 2)^{1/2}/\Delta\nu_D,$$

$\Delta\nu_D$, the Doppler breadth of the absorption line, and ν_0 is the wave number at the line center or peak of the profile, and α is the ratio of the emission line breadth to absorption line breadth. Equating the absorption coefficient, k_ν, to $k_0\exp(-\omega^2)$ in Doppler broadening, the absorbancy A is

$$A = \int_{-\infty}^{+\infty}[\exp-(\omega/\alpha)^2]\{1-\exp[-k_0l(\exp-\omega^2)]\}d\omega \Big/ \int_{-\infty}^{+\infty}\exp-(\omega/\alpha)^2 d\omega, \tag{2}$$

where l is the length of the reaction cell, and k_0 is the absorption coefficient at the peak, that can be related to the oscillator strength f as

$$k_0 = 2(\ln 2/\pi)^{1/2}(\pi e^2 fN/mc\Delta\nu_D), \tag{3}$$

where e and m are electron's charge and mass, respectively, c, the light velocity, and N, the concentration of absorbing atoms per unit volume. Using the theoretical value of f,[8)] k_0 for Hg (6^3P_1) and (6^3P_0) are 6.21×10^{-12} N and 5.90×10^{-12} N cm^{-1}, respectively. The absorbancy can be developed as[1)]

$$A = \sum_n(-1)^n(k_0l)^n/n!(1+n\alpha^2)^{1/2}, \tag{4}$$

and this value is calculated by the HITAC 5010 computer with various values of α and k_0l, where l is 100 cm in this study. Some of the calculated results from Eq. (4) are shown graphically in Fig. 2, where the optical density, derived from the calculated value of $A(=(I_0-I)/I_0)$, is used. It is seen from this figure that the optical density is strongly dependent on the value

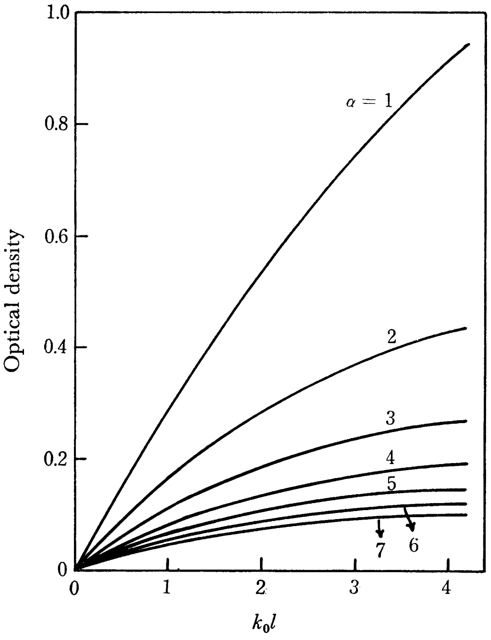

Fig. 2. Relation of the calculated optical density to k_0l with various values of α.

[8)] N. P. Penkin, *J. Quant. Spectrosc. Radiat. Transfer*, **4**, 74 (1964).

of α, that is, when the half-width of the spectral line from the light source is larger than that of the absorption line, the absorption intensity becomes small though the concentration of absorbing atoms is constant.

The experimental curves in Fig. 1 should be represented by one of the theoretical curves in Fig. 2. When the scale of the abscissae in Figs. 1 and 2 is converted to the logarithmic one, one can seek a theoretical curve that agrees with the experimental one in the range of 0.04—0.06 of the optical density. The values of α thus obtained are 5.2 for 1 Torr of the total pressure, and 5.0 for 5 and 10 Torr. A small dependence of α on the total pressure is due to the fact that the half-width of the collision-broadened line is about 1/10 that of the Doppler broadened one at 10 Torr if the optical collision cross-section of Ar or N_2 is 100 Å^2. By the use of the theoretical curves in Fig. 2 and the obtained value of α, a value of k_0l, in other words, a concentration of Hg(6^3P_0) can be determined from an absorption intensity. The curves A′ and B′ in Fig. 1 are thus obtained, and show that the concentration of Hg(6^3P_0) is proportional to the intensity of 2537 Å radiation from the exciting lamp. It is also seen from Fig. 1 that the absorption intensity for 5 Torr of the total pressure is larger than that for 1 Torr even if the partial pressure of N_2 is the same. This is due to the fact that the deactivation of Hg(6^3P_0) is governed by the collision with the wall of the reaction vessel. The collisional frequency with the wall is much dependent on the total pressure (see later).

In conclusion, the simple application of the Lambert-Beer rule is inappropriate in the present experimental condition, and the total pressure must be kept constant to avoid the collision broadening effect and the influence of wall collisions. In the following experiment, it is assumed that argon and quenching molecules have the same optical collision cross-section, and that the 4358 Å line profile from the light source has the same line-width as the 4047 Å line. The latter assumption may be open to question, but an apparent optical density is nearly proportional to the concentration of Hg(6^3P_1), which is very small compared with that of Hg(6^3P_0).

Quenching Mechanism and Rates. The following processes are considered as a quenching mechanism in the present system,

$$\text{(i)}\quad \mathrm{Hg}(6^1S_0) + h\nu \xrightarrow{k_1} \mathrm{Hg}(6^3P_1),$$

$$\text{(ii)}\quad \mathrm{Hg}(6^3P_1) \xrightarrow{k_2} \mathrm{Hg}(6^1S_0) + h\nu,$$

$$\text{(iii)}\quad \mathrm{Hg}(6^3P_1) + Q \xrightarrow{k_3} \mathrm{Hg}(6^1S_0) + Q,$$

$$\text{(iv)}\quad \mathrm{Hg}(6^3P_1) + Q \xrightarrow{k_4} \mathrm{Hg}(6^3P_0) + Q,$$

$$\text{(v)}\quad \mathrm{Hg}(6^3P_0) + Q \xrightarrow{k_5} \mathrm{Hg}(6^1S_0) + Q,$$

$$\text{(vi)}\quad \mathrm{Hg}(6^3P_0) \xrightarrow{k_6} \mathrm{Hg}(6^1S_0),$$

where Q represents a quenching molecule, and the concentration of Hg(6^3P_1) will be denoted by [Hg$_1$*], and that of Hg(6^3P_0) by [Hg$_0$*], and that of Hg(6^1S_0) by [Hg]. McAlduff and Le Roy[9] have proposed further processes including the collision between an excited mercury atom and a ground state atom;

$$\text{(vii)}\quad \mathrm{Hg}(6^3P_1) + \mathrm{Hg}(6^1S_0) \longrightarrow \mathrm{Hg_2}^*,$$

$$\text{(viii)}\quad \mathrm{Hg_2}^* \longrightarrow \mathrm{Hg}(6^3P_0) + \mathrm{Hg}(6^1S_0),$$

$$\text{(ix)}\quad \mathrm{Hg_2}^* + Q \longrightarrow \mathrm{Hg_2} + Q.$$

If these processes take place besides the reactions (i)—(vi), the concentration of Hg(6^3P_0) produced in the system of Ar, N_2, and Hg mixture, must not have a simple linear relation to the pressure of mercury vapor. This is not the case in the present experiment, since [Hg$_0$*] has been found proportional to a pressure of mercury vapor in the range of 2×10^{-5}—1.9×10^{-4} Torr. Here, the pressure of mercury vapor was ordinarily 1.9×10^{-4} Torr, that is the saturated one at 0°C, and the effective collision frequency of an excited mercury atom with ground state atoms is very small compared with that of quenching by N_2 molecules, even if the collision cross-section of an excited mercury atom with a ground state atom is supposed about 100 Å^2.

From the reactions (i)—(vi), the stationary concentration of Hg(6^3P_1) is expressed by

$$[\mathrm{Hg_1}^*] = k_1I[\mathrm{Hg}]/\{k_2+(k_3+k_4)[Q]\}, \tag{5}$$

where I is an intensity of 2537 Å radiation. If [Hg$_1$*] without quenching molecules is denoted by [Hg$_1$*]$_0$, Eq. (5) reduces to the Stern-Volmer relation,

$$[\mathrm{Hg_1}^*]_0/[\mathrm{Hg_1}^*] = 1 + [(k_3+k_4)/k_2][Q]. \tag{5'}$$

The concentration of Hg(6^3P_0) can be formulated as

$$[\mathrm{Hg_0}^*] = k_2k_4[\mathrm{Hg_1}^*]_0[Q]/\{(k_3+k_4)k_5[Q]^2 + [k_2k_5+(k_3+k_4)k_6][Q]+k_2k_6\}. \tag{6}$$

The value of [Hg$_0$*] increases with increasing [Q] untill [Q] reaches [Q]$_{\max}$,

$$[Q]_{\max} = [k_2k_6/(k_3+k_4)k_5]^{1/2}. \tag{7}$$

With this value of [Q], [Hg$_0$*] has a maximum value. Further increase of [Q] results in a decrease of [Hg$_0$*], and finally [Hg$_0$*] reduces to zero with very large amount of quenching molecules. Eq. (6) can be rewritten as

$$[\mathrm{Hg_0}^*] = (k_4/k_6)[\mathrm{Hg_1}^*]_0[Q]/\{([Q]/[Q]_{\max})^2 + [(k_5/k_6)+(k_3+k_4)/k_2][Q]+1\}. \tag{6'}$$

The observed relation of [Hg$_1$*] or [Hg$_0$*] against [Q] is explained well by the above equations, and $(k_3+k_4)/k_2$, k_4/k_6, and k_5/k_6 can be determined.

The experimental values of [Hg$_1$*]$_0$/[Hg$_1$*] are plotted in Fig. 3 against the partial pressure of N_2, CO, or NO as a quencher. The linear slope of the curve in Fig. 3 gives a value of $(k_3+k_4)/k_2$. As is mentioned, the line broadening effect by the existence of argon atoms causes an increase of [Hg$_1$*], because the absorption of 2537 Å radiation becomes more effective. Here, [Hg$_1$*]$_0$ is 4.8×10^7 atoms cc^{-1} with 5 Torr of argon pressure, and 3.5×10^7 with 1 Torr.

Figure 4(a) shows that [Hg$_0$*]/[Hg$_1$*]$_0$ increases monotonously with increasing pressure of N_2, and that [Hg$_0$*]/[Hg$_1$*]$_0$ at 5 Torr of the total pressure is larger than that at 1 Torr. The former fact means that the value of [Q]$_{\max}$ is far from the present experimental

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[9] J. E. McAlduff and D. J. Le Roy, *Can. J. Chem.*, **43**, 2279 (1965).

range, *i.e.*, k_5 is very small. The later experimental finding is to be explained by the fact that a value of k_6 becomes larger as a total pressure decreases. This shows that the deactivation of Hg(6^3P_0) is not due to a radiative process, but to collisions with the wall of the cell. Very long radiative lifetime of Hg(6^3P_0), *i.e.*, 5.6 sec,10) supports this explanation. Under the condition, $[Q] \ll [Q]_{max}$, Eq. (6′) can be approximated to,

$$[Hg_1^*]_0/[Hg_0^*] = (k_6/k_4)(1/[Q]) + (k_5/k_4) + [(k_3+k_4)k_6/k_2k_4]. \qquad (8)$$

The values of $[Hg_1^*]_0/[Hg_0^*]$ are plotted *vs.* $1/[Q]$ in Fig. 4(b), using the data in Fig. 4(a), and a value of k_6/k_4 is obtained from a slope of a straight line in Fig. 4(b).

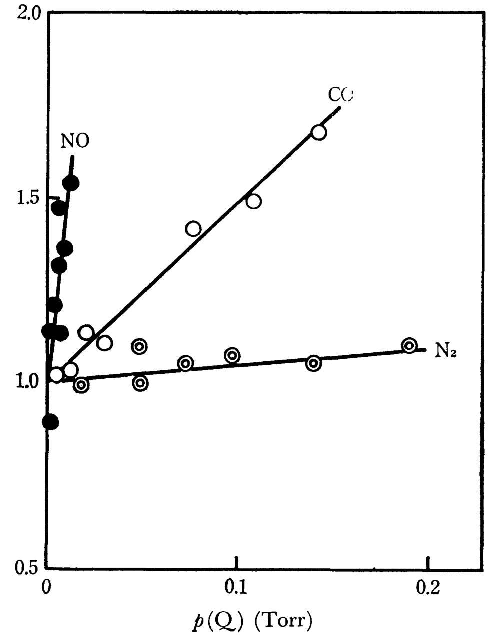

Fig. 3. Plots of $[Hg_1^*]_0/[Hg_1^*]$ *vs.* partial pressure of quencher. Total pressure in the cell is 5 Torr, and a partial pressure of Hg vapor is 1.9×10^{-4} Torr. N₂: ◎, CO: ○, NO: ●

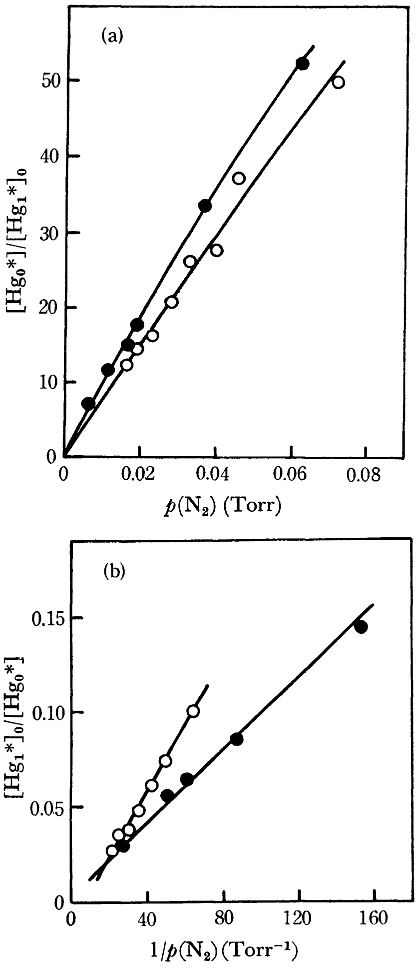

Fig. 4. (a) Plots of $[Hg_0^*]/[Hg_1^*]_0$ *vs.* partial pressure of N₂. Total pressure in the cell is 5 Torr (●) and 1 Torr (○), and a partial pressure of Hg vapor is 1.9×10^{-4} Torr.
(b) Plots of $[Hg_1^*]_0/[Hg_0^*]$ *vs.* $1/p(N_2)$.

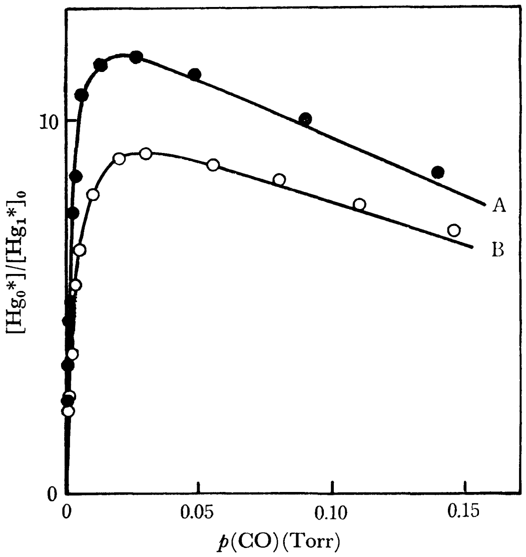

Fig. 5. Plots of $[Hg_0^*]/[Hg_1^*]_0$ *vs.* partial pressure of CO. Total pressure in the cell is 5 Torr (●) and 1 Torr (○), and a partial pressure of Hg vapor is 1.9×10^{-4}Torr. The curves, A and B, show the calculated values of $[Hg_0^*]/[Hg_1^*]_0$ from Eq. (6′) with the following values, $(k_3+k_4)/k_2 = 1.50 \times 10^{-16}$ cc·molecules⁻¹, $k_4/k_6 = 2.25 \times 10^{-13}$ (the curve A), $= 8.47 \times 10^{-14}$ (the curve B) cc·molecules⁻¹ and $k_5/k_6 = 1.61 \times 10^{-14}$ (A), $= 7.14 \times 10^{-15}$ (B) cc·molecules⁻¹.

The experimental relation between $[Hg_0^*]/[Hg_1^*]_0$ and [CO] is shown in Fig. 5, and is explained well by Eq. (6). The larger value of $[Hg_0^*]/[Hg_1^*]_0$ at 5 Torr of the total pressure than that at 1 Torr arises from the longer lifetime of Hg (6^3P_0) at 5 Torr than at 1 Torr, and this also causes an decrease in a value of $[Q]_{max}$ at higher pressure. In the pressure range of CO that is very small compared with $[Q]_{max}$, the same procedure as the case of N₂ can be applied for the determination of k_4/k_6. By the use of this value of k_4/k_6, $[Q]_{max}$ can be found by fitting the experimental values of $[Hg_0^*]/[Hg_1^*]_0$ with the curve calculated by Eq. (6′). Then, a value of k_5/k_6 can be obtained by substituting the value of $k_2/(k_3+k_4)$ into Eq. (7). In the case of quenching by NO, the experimental curve of $[Hg_0^*]/[Hg_1^*]_0$ *vs.* partial pressure of NO could not be observed accurately owing to a very small

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10) R. H. Garstang, *J. Opt. Soc. Amer.*, **52**, 845 (1962).

concentration of $Hg(6^3P_0)$, that is caused by an efficient quenching of the 6^3P_1 state to 6^1S_0 or 6^3P_0 to 6^1S_0. This also explains the fact that Callear and Williams[5] have not been able to detect the $Hg(6^3P_0)$ atoms by the flash excitation of Hg in NO or other polyatomic gases. The observed value of $[Hg_0{}^*]/[Hg_1{}^*]_0$ was 0.11 when a partial pressure of NO was 3.65×10^{-4} Torr at 10 Torr of the total pressure. By the direct measurement (see next) of the lifetime of $Hg(6\,^3P_0)$ in the same experimental condition, k_5 and k_6 were found to be 1.24×10^{-10} cc molecules^{-1} sec^{-1} and 1.0×10^2 sec^{-1}, respectively. Substituting these rate constants into Eqs. (7) and (6′), 3.7×10^{-4} Torr of $[Q]_{max}$ and 5.3 Å^2 of k_4 are obtained.

TABLE 1. OBSERVED VALUES OF QUENCHING RATES (CC·MOLECULES^{-1}) OF Hg (6^3P_1) AND Hg (6^3P_0)

Quencher	$(k_3+k_4)/k_2$	k_4/k_6	k_5/k_6
N_2	2.2×10^{-17}	3.2×10^{-14}	$\leq1\times10^{-17}$
CO	1.5×10^{-16}	2.2×10^{-13}	1.6×10^{-14}
NO	1.4×10^{-15}	5.5×10^{-13}	8.3×10^{-13}

These data are obtained at a total pressure of 5 Torr and a partial pressure of Hg of 1.9×10^{-4} Torr.

The observed values of $(k_3+k_4)/k_2$, k_4/k_6, and k_5/k_6 are summarized in Table 1. The lifetimes of $Hg(6^3P_1)$ and $Hg(6^3P_0)$, *i.e.*, k_2 and k_6, cannot be determined in the present experiment. The value of k_2 should be $1/\tau$, where τ is a radiative lifetime of $Hg(6^3P_1)$, 1.0×10^{-7} sec. However, the peak absorption coefficient, k_0 for 2537 Å line is 4.0 cm^{-1} in the present experimental condition, and the imprisonment effect of the radiation must be considered. Here, the effective radiative lifetime τ' given by Milne[11] is adopted. In his calculation, τ' for the case of infinite slab is,

$$\tau'/\tau = 1 + (k_0 l/\lambda)^2, \tag{10}$$

where $\lambda\tan\lambda = k_0 l$. Kibble, Copley, and Krause[12] ascertained that the observed radiative lifetime of Na (3^2P) was in good agreement with the value calculated by Eq. (10). In our case, τ' is 3.52×10^{-6} sec, from which we can calculate the total quenching cross-section of $Hg(6^3P_1)$ as shown in Table 2.

To determine the rate of deactivation of $Hg(6^3P_0)$, the time history of the absorption of 4047 Å after the excitation radiation was suddenly turned off, was observed in the system of $Ar+N_2+Hg$ mixture, where N_2 molecules could be assumed as very inefficient quenchers of $Hg(6^3P_0)$ atoms. The result shows that a lifetime of $Hg(6^3P_0)$ is 2.8 msec at 1 Torr of the total pressure, 6.7 msec at 5 Torr, and 10 msec at 10 Torr, and is independent of a pressure of Hg atoms. This shows that the deactivation of $Hg(6^3P_0)$ is mainly caused by collisions with the wall of the reaction vessel as already pointed out. The details of this experiment will be reported in near future. Thus, the cross-sections for the processes, $6^3P_1\rightarrow6^3P_0$ and $6^3P_0\rightarrow6\,^1S_0$, can be calculated, and are shown in Table 2. The uncertainty in a value of k_2 produces a somewhat unaccuracy in an absolute value of the total quenching cross-section for $6^3P_1\rightarrow6^3P_0$, 6^1S_0. Hence, the calculated cross-section for the process $6^3P_1\rightarrow6^1S_0$ as the difference of $\sigma^2(6^3P_1\rightarrow6^1S_0, 6^3P_0)$ and $\sigma^2(6^3P_1\rightarrow6^3P_0)$ is most unreliable in the present results. However the present finding that the cross-section of N_2 for $6^3P_1\rightarrow6^1S_0$, 6^3P_0 is very close to that for $6^3P_1\rightarrow6^3P_0$, is consistent with the experimental result of Samson.[13] This is also supported by the later experiment of Matland,[3] who has found that the temperature dependence of the quenching cross-section of $Hg(6^3P_1)$ is nearly explained by $\exp(-\Delta E/\boldsymbol{k}T)$, where ΔE is 0.07 eV. This value of the ΔE is necessary for a N_2 molecule as a kinetic energy if the energy difference between the 6^3P_1 and 6^3P_0 states is transferred to the vibration of N_2 molecule. Therefore, the result of Matland shows that the quenching of $Hg(6^3P_1)$ is mainly to the 6^3P_0 state and scarcely to the 6^1S_0 state. Thus, the estimated value of k_2 is not very different from the true one, and the cross-sections for the process 6^3P_1—6^1S_0 in Table 2 are reliable at least in an order of magnitude except that of N_2, whose cross-section for this process might be hidden in errors of the observed ones for the processes $6^3P_1\rightarrow6^3P_0$ and $6^3P_1\rightarrow6^1S_0$, 6^3P_0.

TABLE 2. CROSS-SECTIONS (σ^2 IN Å^2) FOR QUENCHING $Hg(6^3P_1)$ AND $Hg(6^3P_0)$

Quencher		$^3P_1\rightarrow{}^1S_0$	$^3P_1\rightarrow{}^3P_0$	$^3P_0\rightarrow{}^1S_0$	$^3P_1\rightarrow{}^3P_0$, $^1S_0$
N_2	this work	≤0.03	0.36	$\leq3.6\times10^{-4}$	0.39
	others	0.02[a]	0.31[a]	$\leq2\times10^{-6}$[a], 9.0×10^{-6}[b]	0.33[a], 0.13[c], 0.27[d]
CO	this work	0.60	2.1	0.15	2.7
	others	—	—	0.028[b], 0.08–0.5[e]	5.8[d]
NO	this work	20	5	8.0[h]	25
	others	—	—	0.34[b], >0.38[f]	35.3[d], 24.7[g]

a) E.W. Samson,[13]
b) A.B. Callear and G.J. Williams,[5]
c) C.G. Matland,[3]
d) A.C.G. Mitchell and M.W. Zemansky,[1]
e) G. Karl, P. Kruus and J. C. Polanyi,[7]
f) G. Karl, P. Kruus, J. C. Polanyi, and I.W.M. Smith,[16]
g) J.R. Bates,[17]
h) This value is obtained by the measurement of the lifetime of $Hg(6^3P_0)$ in the mixture of $Ar+N_2+NO+Hg$.

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Discussion

The quenching cross-section of 6^3P_0 to 6^1S_0 obtained by us show a marked difference from those by Callear and Williams.5) In their flash experiment, the half-width of flash duration reaches 51 μsec, and the production of Hg(6^3P_0) from Hg(6^3P_1) may not be neglected about 100—150 μsec after a flash excitation. Hence, there might be a possibility to underestimate a value of k_5. For the quenching process $6^3P_1 \rightarrow 6^3P_0$, Scheer and Fine4) obtained k_4(for CO)/k_4(for N_2) to be about 1, while its value was 5.8 in our result. However, absorption of 2537 Å radiation might become smaller as the total pressure in the cell decreased, owing to the pressure dependency of α, as we already discussed. In their experimental condition, the pressure of CO in the cell was lower than that of N_2 by one order of magnitude, and this might cause that the absorption of 2537 Å line for the case of CO in the cell is smaller than that for the case of N_2, and that the apparent value of k_4(for CO)/k_4(for N_2) become large compared with the true value.

Callear and Oldman14) assumed that collisional transitions between spin-orbit splitting levels of various atoms are due to the electronic-to-vibrational energy transfer, and found the systematic relations of cross-sections to energy discrepancies between spin-orbit splittings and vibrational quanta of colliding molecules. In the present case, the ratio of cross-sections for $6^3P_1 \rightarrow 6^3P_0$ is,

$$\sigma^2(N_2):\sigma^2(CO):\sigma^2(NO) = 1:5.8:14.$$

Dickens, Linnett, and Sovers15) calculated this ratio, assuming that the repulsive potential of exponential type, $\exp(-\alpha\mathbf{r})$, where $\mathbf{r}$ means the distance between an atom and a molecule, made a perturbation to the nuclear motion of molecule and the electronic one in Hg(6^3P_1) atom at an instance of collision. Their calculated ratio is 1:9.8:250 in the case of $\alpha = 5$ Å^{-1}. Therefore, the quenching process $6^3P_1 \rightarrow 6^3P_0$ of N_2 or CO may be explained by a small perturbation due to the repulsive potential between Hg atom and N_2 or CO molecule, but the mechanism for Hg(6^3P_1)—NO collision is far from this explanation. Since NO molecule has an unpaired electron, its collisional process with Hg(6^3P_1) atom must be a strongly non-adiabatic one. This is perhaps a reason why the quenching cross-section of NO for 6^3P_1—6^1S_0 is much larger than that of N_2 or CO.

Conclusion

Conclusions derived in this work are following. (1) The concentration of Hg(6^3P_1) and Hg(6^3P_0) atoms can be determined from the absorption intensity of 4358 and 4047 Å lines emitted from a mercury discharge lamp. Here, the Lambert-Beer rule is not applicable since the spectral half-width of the 4358 or 4047 Å line is five times of the absorption line, *i.e.*, a Doppler half-width at 300°K. (2) The energy transfer mechanism in the system of Ar+Quencher+Hg illuminated with the 2537 Å radiation is: (i) $Hg + h\nu \rightarrow Hg_1^*$, (ii) $Hg_1^* \rightarrow Hg + h\nu$, (iii) $Hg_1^* + Q \rightarrow Hg + Q$, (iv) $Hg_1^* + Q \rightarrow Hg_0^* + Q$, (v) $Hg_0^* + Q \rightarrow Hg + Q$, (vi) $Hg_0^* \rightarrow Hg$ (by collisions with a wall). The cross-sections for the processes, $6^3P_1 \rightarrow 6^1S_0$, $6^3P_1 \rightarrow 6^3P_0$, and $6^3P_0 \rightarrow 6^1S_0$ can be determined as shown in Table 2. (3) Most of the quenching process of Hg(6^3P_1) by a collision with N_2 or CO is $6^3P_1 \rightarrow 6^3P_0$, while the process is mainly $6^3P_1 \rightarrow 6^1S_0$ in a quenching collision with NO. (4) The cross-section for quenching 6^3P_1 to 6^1S_0 is larger by several-fold than that for quenching 6^3P_0 to 6^1S_0. The latter value is not very small except for N_2. (5) A systematic relation of cross-sections for $6^3P_1 \rightarrow 6^3P_0$ to vibrational frequencies can not be found.

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Note added in proof: It has been reported by Callear and McGurk (*Chem. Phys. Letters.*, **6**, 417 (1970)) with a new flash device that $\sigma^2(^3P_0 \rightarrow {}^1S_0)$ of NO, CO_2, and H_2 are 16.2, 0.033, and 0.95 Å^2 and that these values are much greater than previous estimates by Callear and Williams5) with the standard flash technique.