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Determination of the $6^3P_1 \longrightarrow 6^3P_0$ Transition Rate of Hg in CO and NO by a Modulation Technique

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In order to determine the branching ratio for Hg(6^3P_1) deactivation to the 6^3P_0 and 6^1S_0 states in CO or NO, a modulation technique was utilized. The intensity of 253.7-nm radiation was modulated at a frequency in the range from 0.1 to 20 kHz, and the resulting a.c. component of the Hg(6^3P_1 or 6^3P_0) concentration was measured by monitoring the absorption of the 435.8- or the 404.7-nm emission line from an Hg discharge lamp. The lower detection limit of excited Hg atoms was 10^7 cm^{-3} in this experimental method. On the basis of the Hg(6^3P_0) concentration relative to that of Hg(6^3P_1) in an Ar+CO or NO mixture including information on the phase delay, the $6^3P_1 \rightarrow 6^3P_0$ transition rate could be determined; the $6^3P_1 \rightarrow 6^3P_0$ cross section was found to be 22.4 Å^2 for CO and 7.1 Å^2 for NO and the $6^3P_0 \rightarrow 6^1S_0$ cross section to be 1.80 Å^2 for CO and 37 Å^2 for NO at room temperature.

A number of studies[1)] have been reported on the lifetime measurement of Hg(6^3P_1) atoms, which gives the sum of the rate constants for the collisional processes, $6^3P_1 \rightarrow 6^3P_0$ and $\rightarrow 6^1S_0$. In order to separate these two processes, it is necessary to monitor a transient or stationary concentration of Hg(6^3P_0) atoms through an energy transfer process. (Hereafter, Hg(6^3P_1), Hg (6^3P_0) and Hg(6^1S_0) will be denoted by Hg_1*, Hg_0* and Hg, respectively.) Three reports have appeared on the determination of the $Hg_1^* \rightarrow Hg_0^*$ spin-orbit relaxation rate. The method employed by Callear and McGurk[2)] is based on the fact that the Hg_0* concentration in a quenching gas relative to that in N_2 just after the flash excitation of Hg results in the quantum yield of Hg_0* (=the spin-orbit relaxation rate divided by the Hg_1* deactivation rate), since N_2 deactivates Hg_1* only to Hg_0*. In a previous experiment by Horiguchi and Tsuchiya,[3)] a stationary concentration of Hg_0* atoms yields the spin-orbit relaxation rate if the Hg_0* deactivation rate is known. Vikis *et al.*[4)] have also determined this rate by detecting the Hg_0* atoms through the amount of H_2 formed by the reaction of ethylene with Hg_0*. In these experiments, however, if the collisional transition from the 6^3P_1 state is mostly to the 6^1S_0 state or if the deactivation rate of Hg_0* is of the same order of magnitude as that of Hg_1*, the Hg_0* concentration becomes very small, and it is difficult to determine it to high accuracy. In this paper, a modulation technique is introduced in order to improve the detectivity of the Hg_0* atoms as well as to obtain information on the kinetics of excited Hg atoms.

Experimental

The apparatus was essentially the same as that described in a previous paper.[5)] A quartz cell (3 cm in diameter and 24 cm in length) containing a gaseous mixture of Ar+a quenching gas containing Hg vapor at 1.9×10^{-4} Torr was illuminated by six low-pressure Hg discharge lamps (Toshiba 10-W germicidal lamps). A 200-W oscillator (Elger, 251) with a frequency variable in the range from 0.01 to 10 kHz supplied the power for the lamps through ballast resistors. Then, the intensity of 253.7-nm radiation was modulated at twice the frequency of the power source with a waveform that was approximately triangular rather than sinusoidal. An example of the waveform is shown in Fig. 1. The waveform is composed mainly of the fundamental component, the harmonic contribution being less than 10% of the fundamentals. For the present experiment, only the fundamental component is considered. This is justified if the rate equation for Hg* deactivation is of first order with respect to [Hg*], since the harmonic components may be separated from the fundamentals.

For detection of the Hg* atoms, the 404.7- or 435.8-nm emission line from a d.c.-operated Hg discharge lamp was passed through the cell, and then into a monochromator (Spex, 1700III) equipped with a photomultiplier. The output was analyzed by a lock-in amplifier (P. A. R. 186), the reference signal of which was supplied from a photo-tube that monitored 253.7-nm radiation. A quadrature output from the lock-in amplifier divided by an in-phase output gave the tangent of the phase-shift angle for the a.c. component of the Hg* concentration. Since the absorption intensity is not proportional to the Hg* concentration at higher densities, a condition of a low Hg* concentration was chosen in order to meet the requirement that the optical density for absorption be less than 0.02. The signal-to-noise ratio was greatly improved by using a lock-in amplifier, so that absorptions with optical densities as small as 10^{-4} could be detected. This absorption corresponds to 10^7 cm^{-3} of Hg_0* or Hg_1* atoms under the present conditions. In a previous experiment,[3)] the lower detection limit of [Hg_0*] was *ca.* 10^9 cm^{-3}. This can be expected from the atomic absorption spectrometry for analyses of atoms having *f*-numbers similar to Hg_0*. Thus, the sensitivity is improved by a factor of 10^2 in the present modulation technique.

The nominal purities of the sample gases, Ar, N_2, CO, and NO, were 99.999, 99.995, 99.5, and 98.5%, respectively. The first two gases were used without further treatment.

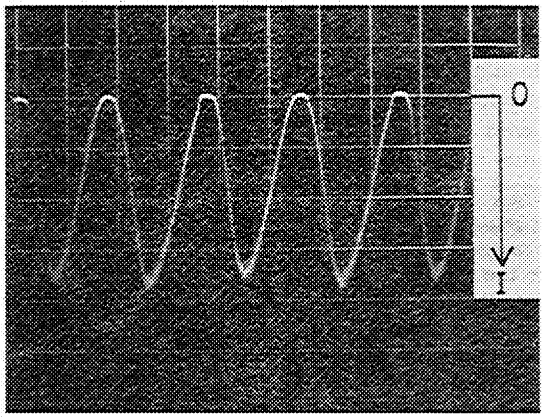

Fig. 1. Waveform of the 253.7-nm radiation intensity from an Hg discharge lamp powered by an oscillator whose frequency is 500 Hz (0.5 ms/div.).

CO was purified by repeated adsorption and desorption on molecular sieve 5A at liquid N_2 temperature, and NO was first passed through a column containing molecular sieve 5A and solidified several times for further purification. The fraction of Ar or CO in an Ar+CO mixture was determined by pressure measurement in a mixing vessel of calibrated volume. Hg vapor in the gas mixture was once removed by passing the gas through a spiral trap at 77 K, and later, the gas was fed into the cell through an Hg saturator at 0 °C. Since Hg-sensitized decomposition of NO was expected, a flow technique was adopted for measurements in an Ar+NO mixture. A capacitance manometer (M.K.S. 210) was employed for the pressure measurements; the fraction of NO in the mixture was determined from the pressure increase which was measured differentially.

Principle of the Modulation Technique

The application of the modulation technique to studies on chemical kinetics has been reviwed by Phillips.[6] Here, the modulation spectroscopy to elucidate the initial stage of Hg-photosensitized reactions will be discussed. If excited Hg atoms are formed in an Ar+CO mixture, the following energy transfer processes should be taken into account:

$$\mathrm{Hg} + h\nu(253.7\text{-nm}) \rightleftharpoons \mathrm{Hg_1^*}, \qquad (1)$$

$$\mathrm{Hg_1^*} + \mathrm{CO}(v=0) \rightleftharpoons \mathrm{Hg_0^*} + \mathrm{CO}(v=1), \qquad (2)$$

$$\mathrm{Hg_1^*} + \mathrm{CO}(v=0) \longrightarrow \mathrm{Hg} + \mathrm{CO}(v\geq 0), \qquad (3)$$

$$\mathrm{Hg_0^*} + \mathrm{CO}(v=0) \longrightarrow \mathrm{Hg} + \mathrm{CO}(v\geq 0), \qquad (4)$$

$$\mathrm{Hg_0^*} \longrightarrow \mathrm{Hg}, \qquad (5)$$

$$\mathrm{CO}(v=1) \longrightarrow \mathrm{CO}(v=0), \qquad (6)$$

of which Reaction 5 is the sum of all deactivation processes including wall collisions and those with impurity molecules, and Reaction 6 represents similar processes for the deactivation of CO(v=1). Vibrational excitation of CO in Reactions 3 and 4 has been demonstrated by the infrared emission measurements of Polanyi and coworkers.[7] However, direct experimental evidence for vibrational excitation in Reaction 2 has not yet appeared. However, since the spin-orbit relaxation in N_2 accompanies vibrational excitation of N_2,[5] it is reasonable to suppose a similar reaction for $\mathrm{Hg_1^*}$-CO collisions.

The modulated intensity of 253.7-nm radiation may be represented as

$$I = \bar{I} + I_0 e^{i\omega t}, \qquad (7)$$

where ω is the angular frequency of modulation. Corresponding to the above equation, the excited species formed make a cycle of appearance and dissipation, *i.e.*,

$$\begin{aligned} x_0 &= [\mathrm{Hg}] = \bar{x}, \\ x_1 &= [\mathrm{Hg_1^*}] = \bar{x}_1 + \boldsymbol{x}_1 e^{i\omega t}, \\ x_2 &= [\mathrm{Hg_0^*}] = \bar{x}_2 + \boldsymbol{x}_2 e^{i\omega t}, \\ y_0 &= [\mathrm{CO}(v=0)] = \bar{y}_0, \\ y_1 &= [\mathrm{CO}(v=1)] = \bar{y}_1 + \boldsymbol{y}_1 e^{i\omega t}, \end{aligned}$$

where the first term of the right-hand side in each case represents the d.c. component of the respective concentration and the second term the a.c. component, except for ground-state atoms or molecules whose a.c. components are disregarded since they are much more abundant than the excited species. The amplitude of the a.c. component must be a complex number since a phase delay is expected.

On the basis of the mechanism involving Reactions 1—6, the rate equations can be written as

$$\mathrm{d}x_1/\mathrm{d}t = k_1 I_0 x_0 - k_{-1}x_1 - k_2 y_0 x_1 - k_3 y_0 x_1 + k_{-2} x_2 y_1, \qquad (8)$$

and

$$\mathrm{d}x_2/\mathrm{d}t = k_2 x_1 y_0 - k_{-2} x_2 y_1 - k_4 x_2 y_0 - k_5 x_2, \qquad (9)$$

where the rate constant for Reaction j is denoted by k_j and the reverse reaction rate by k_{-j}. If the a.c. parts of these equations are separated, the following equations can be derived:

$$i\omega \boldsymbol{x}_1 = k_1 I_0 \bar{x}_0 - (k_{-1} + k_2\bar{y}_0 + k_3\bar{y}_0)\boldsymbol{x}_1 + k_{-2}\bar{y}_1\boldsymbol{x}_2, \qquad (10)$$

and

$$i\omega \boldsymbol{x}_2 = k_2\bar{y}_0\boldsymbol{x}_1 - (k_{-2}\bar{y}_1 + k_4\bar{y}_0 + k_5)\boldsymbol{x}_2. \qquad (11)$$

In these equations, it is assumed that $\bar{y}_1 \gg |\boldsymbol{y}_1|$, since the lifetime of CO(v=1) is much longer than ω^{-1}, which is less than 1.3 ms. The imaginary part of Eq. 10 results in the equation,

$$\begin{aligned} -\boldsymbol{x}_1^{\mathrm{i}}/\boldsymbol{x}_1^{\mathrm{r}} &= \tan\phi_1 \\ &= [1/(k_{-1} + k_2\bar{y}_0 + k_3\bar{y}_0)][\omega + k_{-2}\bar{y}_1(-\boldsymbol{x}_2^{\mathrm{i}}/\boldsymbol{x}_1^{\mathrm{r}})]. \end{aligned} \qquad (12)$$

The corresponding equation derived from Eq. 11 is

$$\begin{aligned} -\boldsymbol{x}_2^{\mathrm{i}}/\boldsymbol{x}_2^{\mathrm{r}} &= \tan\phi_2 \\ &= [1/(k_{-2}\bar{y}_1 + k_4\bar{y}_0 + k_5)][\omega + k_2\bar{y}_0(-\boldsymbol{x}_1^{\mathrm{i}}/\boldsymbol{x}_2^{\mathrm{r}})]. \end{aligned} \qquad (13)$$

Here, ϕ_1 and ϕ_2 are defined as phase delay angles for the a.c. components of $[\mathrm{Hg_1^*}]$ and $[\mathrm{Hg_0^*}]$, respectively, and $\boldsymbol{x}_j^{\mathrm{r}}$ and $\boldsymbol{x}_j^{\mathrm{i}}$ are the real and imaginary parts, respectively, of $\boldsymbol{x}_j$. The real part may be obtained from the in-phase signal of the absorption and the imaginary from the quadrature.

The reciprocal radiative lifetime of $\mathrm{Hg_1^*}$ is estimated to be $3.5\times10^6\ \mathrm{s^{-1}}$ which is calculated according to the Milne-Samson equation[8] for the correction of radiation imprisonment effect. This value is much larger than the angular frequency of modulation in this experiment. Therefore, the phase delay for the $\mathrm{Hg_1^*}$ concentration may not be of detectable magnitude, *i.e.*, $\tan\phi_1 \fallingdotseq 0$. Hence, Eq. 13 can be approximated by

$$\tan\phi_2 = \omega/(k_{-2}\bar{y}_1 + k_4\bar{y}_0 + k_5). \qquad (13')$$

In addition, the real part of Eq. 11 results in the relation,

$$k_2 y_0 = \omega(\boldsymbol{x}_2^{\mathrm{r}}/\boldsymbol{x}_1^{\mathrm{r}})(\tan\phi_2 + \cot\phi_2). \qquad (14)$$

Thus, the spin-orbit relaxation rate of $\mathrm{Hg_1^*}\rightarrow\mathrm{Hg_0^*}$ can be determined if the phase-delay angle and the a.c. component of the $\mathrm{Hg_0^*}$ concentration relative to that of $\mathrm{Hg_1^*}$ are measured.

Results and Discussion

In Fig. 2, the observed phase-delay angle, ϕ_2, for the a.c. component of the $\mathrm{Hg_0^*}$ concentration in an Ar+CO mixture is plotted as a function of the modulation frequency. The results are in good agreement with the relation

$$\tan\phi_2 = \omega\tau, \qquad (15)$$

where τ is the lifetime of $\mathrm{Hg_0^*}$ and is defined by Eq. 13′ as

$$\tau = (k_{-2}\bar{y}_1 + k_4\bar{y}_0 + k_5)^{-1}. \qquad (16)$$

This equation shows that the lifetime is dependent on the concentration of vibrationally excited CO as well as on that of ground-state CO. If the spin-orbit relaxation accompanies the vibrational excitation, an excess amount of CO(v=1) is formed. Hence, it is expected that strong 253.7-nm radiation causes an ac-

TABLE 1. THE RECIPROCAL LIFETIME OF $Hg(6^3P_0)$ IN AN Ar+CO MIXTURE AT 10 Torr AS A FUNCTION OF THE 253.7-nm PHOTON INTENSITY

p(CO) (Torr)	253.7-nm photon intensity (photon $cm^{-3}\,s^{-1}$)				
	3.85×10^{15}	2.70×10^{15}	1.33×10^{15}	6.65×10^{14}	3.40×10^{13}
0.20	6.42	6.28	5.76	6.28	$6.22\times10^4\,s^{-1}$
0.01	5.03	5.46	4.83	4.70	$4.79\times10^3\,s^{-1}$

TABLE 2. A PART OF THE EXPERIMENTAL RESULTS FOR DETERMINATION OF $Hg_1^* \rightarrow Hg_0^*$ AND $Hg_0^* \rightarrow Hg$ TRANSITION RATES

p(CO) (Torr)	f (Hz)	x_2^r/x_1^r	tan ϕ_2	k_2y_0 (s^{-1})	$k_4y_0+k_5$ (s^{-1})
a) Data for Ar+CO mixtures at 10 Torr.					
0.045	2×10^3	6.71	0.923	1.69×10^5	1.36×10^4
0.106	2	9.47	0.401	3.44	3.13
	4	7.03	0.865	3.57	2.90
	8	4.12	1.679	4.71	2.99
0.20	1	11.7	0.106	7.01	5.93
	2	9.82	0.196	6.54	6.41
	4	9.45	0.434	6.50	5.79
0.37	2	13.3	0.118	14.4	10.65
				$k_2=(1.13\pm0.04)\times10^{-10}\,cm^3\,s^{-1}$	$k_4=(8.89\pm0.27)\times10^{-12}\,cm^3\,s^{-1}$
b) Data for Ar+NO mixtures at 1 Torr.					
2.20×10^{-4}	200	0.116	0.36	351	3490
2.34	600	0.173	0.74	399	5090
4.00	200	0.071	0.33	241	3810
5.60	200	0.089	0.21	509	5980
5.88	600	0.084	0.43	596	8710
10.2	200	0.111	0.15	909	8380
				$k_2=(3.5\pm0.9)\times10^{-11}\,cm^3\,s^{-1}$	$k_4=(1.8\pm0.5)\times10^{-10}\,cm^3\,s^{-1}$

cumulation of vibrationally excited CO which shortens the Hg_0^* lifetime through Reaction 2 in the reverse direction. This has been confirmed in the lifetime measurements of Hg_0^* in Ar+N_2 mixtures.[5] However, in an Ar+CO mixture, the lifetime of Hg_0^* does not depend on the intensity of 253.7-nm radiation, as is shown in Table 1, which lists the observed lifetimes as a function of the 253.7-nm photon intensity entering the cell. The latter quantity was varied by changing the number of illuminating lamps and their distance from the cell; the intensity was estimated from the observed value of Hg_1^* concentration in pure Ar, since Ar does not deactivate Hg_1^* and its concentration is given by $x_1=k_1I_0x_0/k_{-1}$. The results in Table 1 leads to the conclusion that there is no accumulation of CO ($v=1$) in the present system, which is probably due to the relatively short lifetime of CO($v=1$). Thus, the vibrational temperature of CO must be room temperature and the reverse of Reaction 2 may be disregarded. This estimate should be valid for other quenching gases, since these gases have relaxation times shorter than those of CO and N_2.

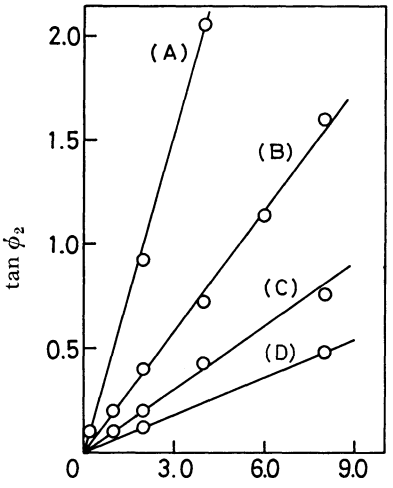

Fig. 2. Plots of tan ϕ_2 against modulation frequencies; p(CO)=0.045 (A),=0.106 (B),=0.20 (C),=0.37 Torr (D), and p(CO)+p(Ar)=10 Torr for all mixtures.

The reciprocal lifetime determined from the data in Fig. 2 is proportional to the CO partial pressure and, thus, gives the rate constant for Hg_0^* deactivation, k_4, which is $(8.89\pm0.27)\times10^{-12}\,cm^3\,s^{-1}$. The spin-orbit relaxation rate, k_2, was determined to be $(1.13\pm0.04)\times10^{-10}\,cm^3\,s^{-1}$ using Eq. 14 and the data listed in Table 2. The rates thus determined may be converted to

TABLE 3. COLLISION CROSS SECTION FOR Hg* IN Å^2

Process	Investigator	Collision partner	
		CO	NO
$Hg_1^* \rightarrow Hg_0^*$, Hg	DPK[a]	21.7	—
	MS[b]	23.2	88.9
$Hg_1^* \rightarrow Hg_0^*$	this work	22.4±0.8	7.0±1.8
	CM[c]	19.5	—
	VTL[d]	16.1	—
$Hg_0^* \rightarrow Hg$	this work	1.80±0.05	37±10(35±2)[f]
	CM[c]	2.06	50.1
	FMCP[e]	7.8	41

a) Deech *et al.*[9] b) Michael and Suess.[10] c) Callear and McGurk.[2] d) Vikis *et al.*[4] e) Freeman *et al.*[11] f) Observed in N_2+NO mixtures.

collision cross sections as summarized in Table 3 together with the results for NO and literature values. The total deactivation cross section of Hg_1^* by a collision with CO (Reactions 2 and 3) has been measured accurately by Deech *et al.*[9] and found to be 21.7 Å^2 at room temperature. This value was determined from a measurement of the 253.7-nm fluorescence decay after pulsed excitation of Hg to Hg_1^*. The value agrees well with the present measurement of 22.4 Å^2 for Reaction 2 within the error limits. This means that the deactivation of Hg_1^* by collisions with CO leads mainly to formation of Hg_0^* and not to ground-state Hg; the latter process may occur with a probability of less than 2% of the Hg_1^* deactivation. Clear evidence for vibrational excitation of CO by the spin-orbit relaxation was not obtained in the present experiment. However, since CO is isoelectronic with N_2 and the resonance is improved ($\Delta E = -373\ \mathrm{cm}^{-1}$ for CO compared with $-563\ \mathrm{cm}^{-1}$ for N_2) in Reaction 2, vibrational excitation is expected to be accompanied by the spin-orbit relaxation.[5]

Formerly, it was difficult to detect Hg_0^* atoms produced in Hg_1^*-NO collisions, and, thus, the rate constant, k_2, could not be determined. However, the present modulation technique makes it possible to detect the a.c. component of $[Hg_0^*]$ which has been so small that rate constants, k_2 and k_4, cannot be determined accurately. A more reliable value for k_4 was obtained from phase-shift measurements of Hg_0^* in a mixture of N_2+NO; the cross section is given in Table 3. Contrary to the case of Hg_1^*-CO collisions, NO deactivates Hg_1^* mainly to the ground state, with only 10% of the Hg_1^* deactivation proceeding *via* spin-orbit relaxation.

The energy transfer mechanism for Hg*-CO collisions can be understood if the non-adiabatic coupling between spin-orbit states is complete in the course of the collisional interaction *via* the simultaneous vibrational excitation of CO, while adiabaticity is preserved between the 6^3P and 6^1S states of Hg. Contrary to this, in Hg*-NO collisions, a large probability for crossing from the 6^3P surface to the 6^1S surface significantly reduces the relative importance of the transition from the 6^3P_1 state to the 6^3P_0 state.

Appendix

For the readers' convenience, the equivalence of the sine or cosine formulation to the vector notation in the complex plane is explained. According to the radiation intensity expressed as

$$I = \bar{I} + I_0 \sin \omega t, \tag{A1}$$

the Hg_1^* and Hg_0^* concentrations are described as

$$x_1 = \bar{x}_1 + \tilde{x}_1 \sin(\omega t - \phi_1) \tag{A2}$$

and

$$x_2 = \bar{x}_2 + \tilde{x}_2 \sin(\omega t - \phi_2). \tag{A3}$$

If these equations are substituted into Eqs. 8 and 9, and the coefficients of $\cos \omega t$ are taken, the following two equations can be derived:

$$\tan \phi_1 = [1/(k_{-1} + k_2\bar{y}_0 + k_3\bar{y}_0)] \times [\omega + k_{-2}\bar{y}_1(\tilde{x}_2 \sin \phi_2/\tilde{x}_1 \cos \phi_1)] \tag{A4}$$

and

$$\tan \phi_2 = [1/(k_{-2}\bar{y}_1 + k_4\bar{y}_0 + k_5)] \times [\omega + k_2\bar{y}_0(\tilde{x}_1 \sin \phi_1/\tilde{x}_2 \cos \phi_2)]. \tag{A5}$$

These equations are equivalent to Eqs. 12 and 13 assuming that

$$\boldsymbol{x}^{\mathrm{r}} = \tilde{x} \cos \phi \text{ and } \boldsymbol{x}^{\mathrm{i}} = \tilde{x} \sin(-\phi).$$

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