Quenching Cross-Sections of the Metastable Mercury Atom (6^3P_0)

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Recently, Callear and McGurk[1] reported that the cross-sections for the deactivation of $Hg(6^3P_0)$ atoms were larger by an order of magnitude than their former data[2] which showed a considerablly less reactivity of $Hg(6^3P_0)$ atoms compared to that of $Hg(6^3P_1)$ atoms. Cambell *et al.*[3] measured the absorption of $Hg(6^3P_0)$ in the gaseous mixture of N_2, quencher and mercury which was excited by the 2537 Å radiation. Their data support the larger cross-sections for quenching $Hg(6^3P_0)$ atoms. We proposed a method[4] to determine the cross-section for each process, $6^3P_1 \rightarrow 6^3P_0$, $6^3P_1 \rightarrow 6^1S_0$, and $6^3P_0 \rightarrow 6^1S_0$, and found that the cross-sections for $6^3P_0 \rightarrow 6^1S_0$ were not so small as Callear and William's results.[2] Recently, we measured the time-history of the 4047 Å absorption of $Hg(6^3P_0)$ after the flash irradiation of the 2537 Å radiation, and observed the cross-section of a reactive molecule for quenching $Hg(6^3P_0)$ atoms. The results are shown in Table 1.

The cross-sections for quenching the 6^3P_0 state are in agreement with the new data of Callear and McGurk[5] within a factor of 5. It is seen from Table 1 that the ratio of the quenching corss-section for the process $6^3P_1 \rightarrow 6^1S_0$ to that for $6^3P_0 \rightarrow 6^1S_0$ is close to 3 except for the case of quenching by N_2, CH_4, or CO_2, which has a larger ratio. Recent results of Vikis and Moser[6] by a chemical method show that the reactivity of $Hg(6^3P_0)$ is much less than that of $Hg(6^3P_1)$, but this is not consistent with the present experiment. Kang Yang[7] proposed that from the conservation of angular momentum, the cross-section of H_2 for quenching $Hg(6^3P_0)$ may be smaller than that of alkane. However, our results differ as has been pointed out by Vikis and Moser.[6] The present results suggest the conclusion that if a molecule has a large cross-section ($\gtrsim 1$ Å^2) for the process $6^3P_1 \rightarrow 6^1S_0$, the corresponding 6^3P_0 cross-section is of the same order of magnitude, and that a molecule with a very small cross-section ($\lesssim 0.1$ Å^2) for quenching the 6^3P_1 state has a much smaller cross-section to deactivate the 6^3P_0 state. If the former case corresponds to the strong coupling between the excited Hg atom and a quenching molecule. the quenching rate of $Hg(6^3P_1)$ would be the same order of magnitude as that of $Hg(6^3P_0)$, because the degeneracy of $^3P_1$ state is removed by a collisional perturbation of a quenching molecule (Q),[8] and the mixing of two states $Hg(6^3P_1)+Q$ and $Hg(6^3P_0)+Q$ occurs in the course of non-adiabatic transition to $Hg(6^1S_0)+Q$. This seems to explain qualitatively the present results for CO, NO, H_2, and D_2.

TABLE 1. QUENCHING CROSS-SECTION (σ^2, Å^2) OF EXCITED MERCURY ATOMS

Quencher	$^3P_1 \rightarrow {}^1S_0$	$^3P_1 \rightarrow {}^3P_0$	$^3P_0 \rightarrow {}^1S_0$		$\sigma^2(^3P_1 \rightarrow {}^1S_0)/\sigma^2(^3P_0 \rightarrow {}^1S_0)$	
	this work	this work	this work	C & M[5]	this work	V & M[6]
N_2	≤ 0.03	0.36	$< 8\times10^{-6}$	—	—	—
CO	0.60	2.1	0.21	0.66	2.9	—
NO	20	5	8.0	1.62	2.5	—
H_2	8.3	≤ 0.1	2.1	0.96	3.9	47
D_2	10.0	≤ 0.1	2.9	—	3.4	49
CH_4	0.04	0.03	1.4×10^{-4}	2.86×10^{-4}	290	1400
CO_2	2.48	≈ 0.002	0.035	0.033	71	—

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