1B2b

Acceleration of the Reaction $OH + CO \rightarrow H + CO_2$ by Vibrational Excitation of OH

○Nanase KOHNO[1], Hiroshi KOHGUCHI[1], and Katsuyoshi YAMASAKI[1]
[1] Grad. Sc. Sci., Hiroshima Univ.

A chemical reaction, $OH + CO \rightarrow H + CO_2$, is a pivotal process to remove OH in the troposphere. There have been few reports on the effect of vibrational excitation of OH on the reaction. In the present study, we have employed the laser-based photolysis and probe techniques to measure the branching ratios between the chemical reaction, $OH(v) + CO \rightarrow H + CO_2$, and vibrational relaxation, $OH(v) + CO \rightarrow OH(v{-}1) + CO$ for $v = 1 - 4$.

The gaseous mixture $O_3/H_2/CO/He$ in a flowing cell was irradiated with the fourth harmonic wave (266 nm) from a Nd^{3+}:YAG laser. $OH(X^2\Pi,\ v = 0 - 4)$ was generated by the reaction $O(^1D) + H_2 \rightarrow OH + H$ and detected via laser-induced fluorescence (LIF) of the $A^2\Sigma^+–X^2\Pi$ transition. To record the time profiles of the LIF of $OH(v)$, the delay times between the photolysis and probe laser were automatically scanned.

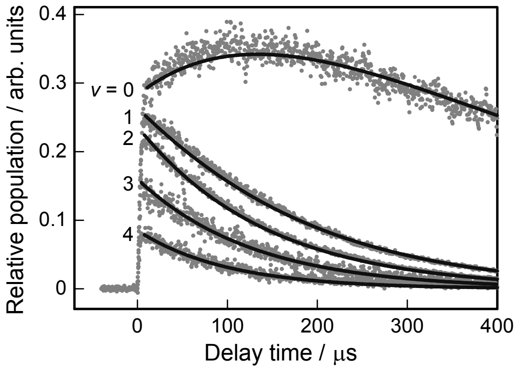

Fig. 1. Time-resolved LIF intensities of $OH(v \le 4)$. $p(O_3) = 0.5$ mTorr, $p(H_2) = 150$ mTorr, $p(CO) = 200$ mTorr, and $p_{tot}(He) = 10$ Torr.

Fig. 1 shows the time profiles of the relative populations of $OH(v = 0 - 4)$ in the presence of 200 mTorr of CO. The rate coefficients for reaction and relaxation have been determined by numerical integration of the rate equations, and all the profiles are well-reproduced (black lines in Fig. 1). The vibrational level dependences of the rate coefficients for the two processes are shown in Fig. 2. Reaction is accelerated and relaxation is decelerated by vibrational excitation of OH. Reactive processes are dramatically enhanced by vibrational excitation of OH and completely dominant over vibrational relaxation at $v \ge 3$.

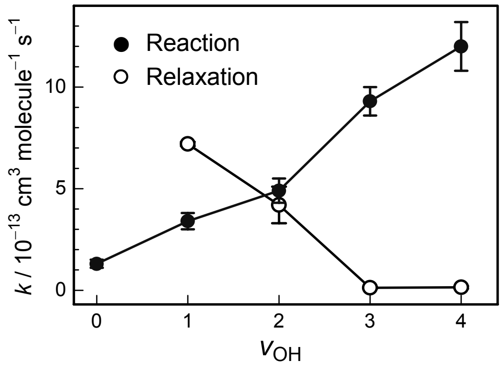

Fig. 2. Vibrational level dependences of the rate coefficients for chemical reaction and vibrational relaxation.

Table 1. Rate Coefficients for Chemical Reaction and Vibrational Relaxation $OH(v \le 4)$ in Collisions with CO

v	0	1	2	3	4
Chemical reaction	$1.3 \pm 0.2^*$	3.4 ± 0.4	4.9 ± 0.6	9.3 ± 0.7	12 ± 1.2
Vibrational relaxation		7.2 ± 0.1	4.2 ± 0.9	0.12 ± 0.04	0.14 ± 0.07

* Rate coefficients are in units of 10^{-13} cm^3 molecule^{-1} s^{-1} and the stated confidence limits are $\pm 2\sigma$.