1F4b Rate Coefficients for Vibrational Relaxation of O_2 Determined by the Integrated-Profiles Analysis

○Shinji Watanabe, Shin-ya Usuda, Hiroshi Kohguchi, Katsuyoshi Yamasaki

Grad. Sc. Sci., Hiroshima Univ.

We have developed a simple kinetic analysis, called integrated-profiles method (IPM)[1], to determine the rate coefficients for multistep reactions. A linear analysis can be made for obtaining the rate coefficients of level-to-level relaxation in vibrational cascade.

In the present study, we have measured the rate coefficients for vibrational energy transfer from $O_2(X\,^3\Sigma_g^-, v = 6 - 13)$ to O_2. Vibrationally excited $O_2(X\,^3\Sigma_g^-, v = 6 - 14)$ was generated in the UV laser flash photolysis of O_3 and single vibrational level was detected via laser-induced fluorescence (LIF) in the $B\,^3\Sigma_u^- - X\,^3\Sigma_g^-$ system. To record the time-profiles of the LIF intensities of vibrational levels, the wavelength of the probe laser was tuned to a rotational line, and time delays between the photolysis and probe laser were automatically scanned with a pulse delay controller.

Fig. 1 shows the recorded time-profiles of the LIF intensities of the levels $v = 10$ and 11 in the presence of O_2. The profiles have been analyzed using IPM as shown in Fig. 2. The parameters $x(t)$ and $y(t)$ are derived from the integrals of the signal intensities. The slope of the linear regression analysis (the gray line of Fig. 2) gives the pseudo-first-order decay rate coefficient of the level $v = 10$. The bimolecular vibrational relaxation rate coefficient has been obtained from $[O_2]$-dependence of the pseudo-first-order decay rates. The rate coefficient of relaxation of $O_2(v = 10)$ by O_2 is $[9.4 \pm 0.8(2\sigma)] \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. We also have determined the relaxation rate coefficients of other levels ($6 \le v \le 13$) and found that the relaxation is mainly governed by single-quantum change ($\Delta v = 1$).

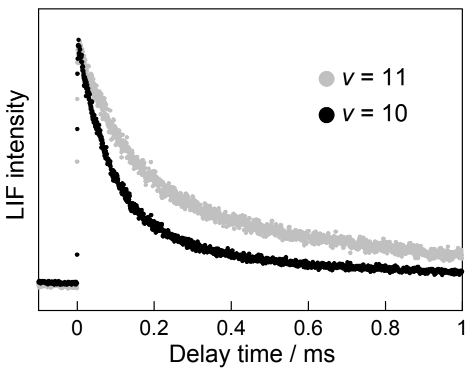

Fig. 1 Time-profiles of LIF.
P_{total}(Ar) = 50 Torr, $P(O_2)$ = 5 Torr

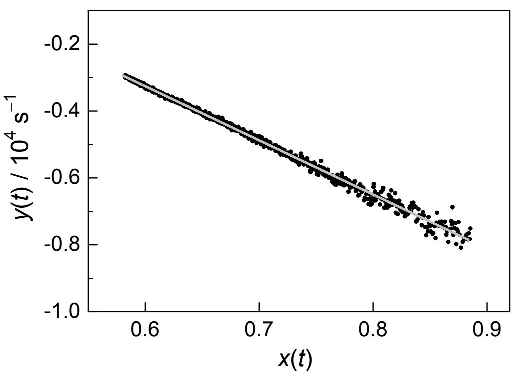

Fig. 2 Plot of the IPM.

1. K. Yamasaki and A. Watanabe, *Bull. Chem. Soc. Jpn.*, **70**, 89–95 (1997).