

Kinetic Study on the Relaxation of Vibrationally Excited $S_2(a^1\Delta_g)$ by Collisions with SF_6

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Vibrational energy transfer between nonpolar molecules is generally slow because of small interactions. There, however, are a few cases such as $O_2(X^3\Sigma_g^-, \nu)$ and CF_4 showing extraordinarily high efficiency.¹ In the present study, the rate coefficients for vibrational relaxation of $S_2(a^1\Delta_g, \nu)$ by SF_6 have been determined to find a propensity rule governing the energy transfer of nonpolar molecules.

A gaseous mixture of $OCS(40 \text{ mTorr})/He$ (10 Torr) in a flow cell at 298 K was irradiated with laser light at 248 nm. Resultant $S(^1D)$ reacts with OCS , generating vibrationally excited $S_2(a^1\Delta_g, \nu)$.² The dispersed laser-induced fluorescence (LIF) of a single vibrational level ($\nu = 2-5$) was excited via the $f^1\Delta_u-a^1\Delta_g$ transition.

The profiles of the LIF intensities of the vibrational levels were recorded as a function of the delay time between the photolysis and probe laser. The time profiles at varying pressures of SF_6 (Fig. 1) were analyzed by the integrated profiles method,³ and the $[SF_6]$ -dependent pseudo first-order decay rate coefficients k_ν were determined. The slopes of the straight line fit from regression analysis of the plots of k_ν vs. $[SF_6]$ (Fig. 2) have given the rate coefficients for vibrational relaxation of $S_2(a^1\Delta_g, \nu = 2-4)$ by SF_6 .

It has been found that the V-V energy transfer of a homonuclear diatomic molecule A by a nonpolar polyatomic molecule B with energy defect ΔE , $A(\nu_A) + B(\nu_B = 0) \rightarrow A(\nu'_A) + B(\nu'_B = 1) + \Delta E$, is governed not only by the magnitude of the defect but also by the infrared photoabsorption cross section of $B(\nu_B = 1 \leftarrow 0)$.

References

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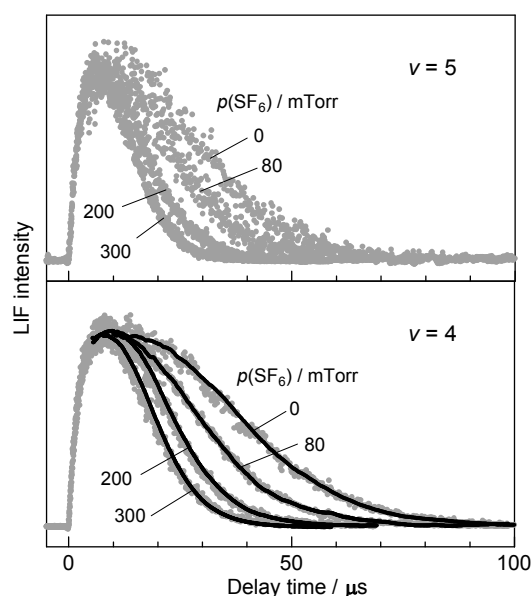


Fig. 1. Time-resolved LIF intensities of $S_2(a^1\Delta_g, \nu = 4$ and $5)$ recorded at varying pressures of SF_6 . The gray and black dots denote observed data and the results of simulation, respectively.

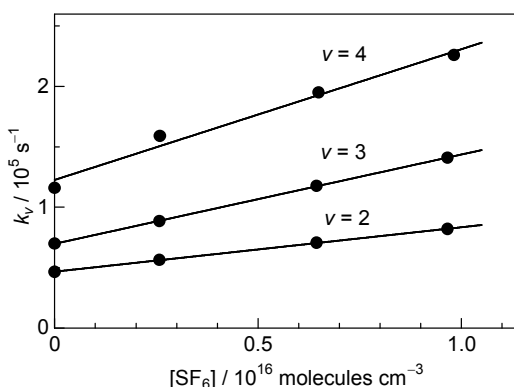


Fig. 2. Plot of the pseudo first-order decay rates of $S_2(a^1\Delta_g, \nu = 2-4)$ versus $[SF_6]$.