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Overall rate coefficient and branching ratio for quenching of $S(3p^3 4p\ ^3P_J)$ by collisions with He

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The detectability of the laser-induced fluorescence (LIF) technique greatly depends on the efficiency of quenching of the electronically excited states. In this study, we have measured the rate coefficients for quenching of $S(3p^3 4p\ ^3P_J)$ by collisions with He.

Fig. 1 shows the scheme of the optical transitions relevant to the present study. $S(3p^4\ ^3P_2)$ is excited to the $3p^3 4p\ ^3P_2$ state with two photons at $\lambda_1 = 308\,\mathrm{nm}$. The $3p^3 4p\ ^3P_J$ state transfers to the $3p^3 4s\ ^3S$ state via infrared transition or collisions with ambient gases. The $3p^3 4s\ ^3S$ state emits vacuum ultraviolet fluorescence ($\lambda_2 = 180\,\mathrm{nm}$) via the transition to the $3p^4\ ^3P_J$ state.

A gaseous mixture of OCS (30 mTorr) and He (8–80 Torr) in a flow cell at 298 K was irradiated with laser light at 248 nm. $S(3p^4\ ^3P)$ was generated from the photoproduct $S(3p^4\ ^1D)$ by collisions with OCS.

Fig. 2 shows the time-resolved fluorescence from $S(3p^3 4s\ ^3S)$ following excitation to the $3p^3 4p\ ^3P_2$ state at varying pressures of He. The profiles of the fluorescence decay of the $3p^3 4s\ ^3S$ state are nearly identical to those of the $3p^3 4p\ ^3P_J$ state since the radiative lifetime of $S(3p^3 4s\ ^3S)$ (≈1.5 ns) is much shorter than the decay of $S(3p^3 4p\ ^3P_J)$ under the present experimental conditions. A single-exponential analysis cannot be made because the duration of excitation laser is not sufficiently short compared to the decay period of the fluorescence. Deconvolution based on the integrated profiles method has been made to derive pseudo first-order decay rates k_{1st}. Fig. 3 shows the plot of k_{1st} vs [He]. The slope of straight line fit from regression analysis has given the rate coefficient for quenching of $S(3p^3 4p\ ^3P_J)$ by collisions with He. He pressure dependence of the intensity of the VUV fluorescence was measured as shown in Fig. 4. The branching ratio of state-specific quenching $3p^3 4p\ ^3P_J \rightarrow 3p^3 4s\ ^3S$ to the overall quenching also has been determined.

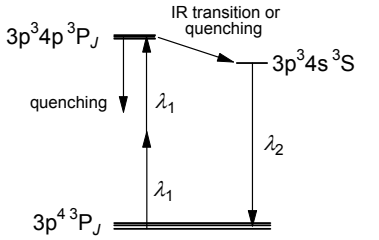

Fig. 1. Scheme of the optical transitions.

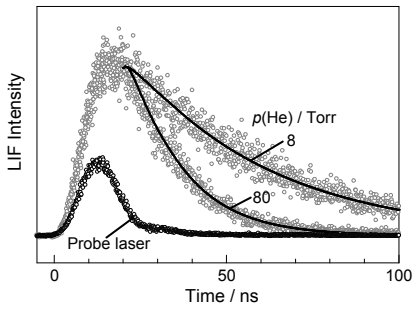

Fig. 2. Time-resolved fluorescence from $S(3p^3 4s\ ^3S)$ at varying pressures of He. The black curves denote the results of simulation.

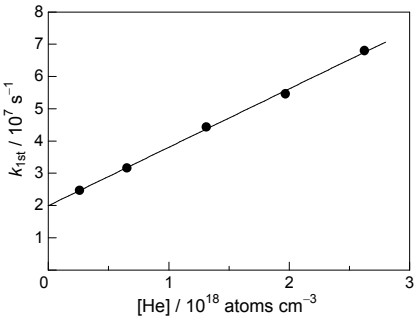

Fig. 3. [He]-dependence of the 1st-order decay rates of the VUV fluorescence.

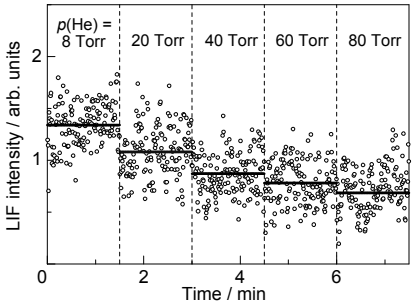

Fig. 4. The LIF intensity of $S(3p^3 4s\ ^3S)$ at varying pressures of He.