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Observation of three-body collisional transfer between atomic levels

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Collisional J-mixing rates between the $J=0,1,2$ states of the $\mathrm{Sr}(5\,^3P_J)$ multiplet have been measured in the presence of rare-gas perturbers. For Kr and Xe pressures above 100 Torr, the rates are dominated by a component which is quadratic in pressure. We believe this very unusual behavior is brought about by the simultaneous interaction of a Sr atom with two perturbers and not by excimer formation.

Three-body transition rates between the $\mathrm{Sr}(5\,^3P_J)$ fine-structure states due to collisions with rare gases have been measured (see Fig. 1). Such processes have not frequently been investigated. These J-mixing rates have been obtained from the time dependence of the $J=2$, 1, and 0 state populations (n_J) following excitation of the $5\,^3P_1$ state by a pulsed dye laser tuned to the intercombination line at 689 nm. The time-dependent absorption of the Sr $6\,^3S_1$–$5\,^3P_{2,0}$ lines (707, 679 nm) from a hollow-cathode lamp is used to measure the evolution of the metastable ($J=0,2$) state populations following the laser pulse. The $J=1$ state population is obtained from its time-dependent fluorescence at 689 nm. Additional experimental details are given in Ref. 1.

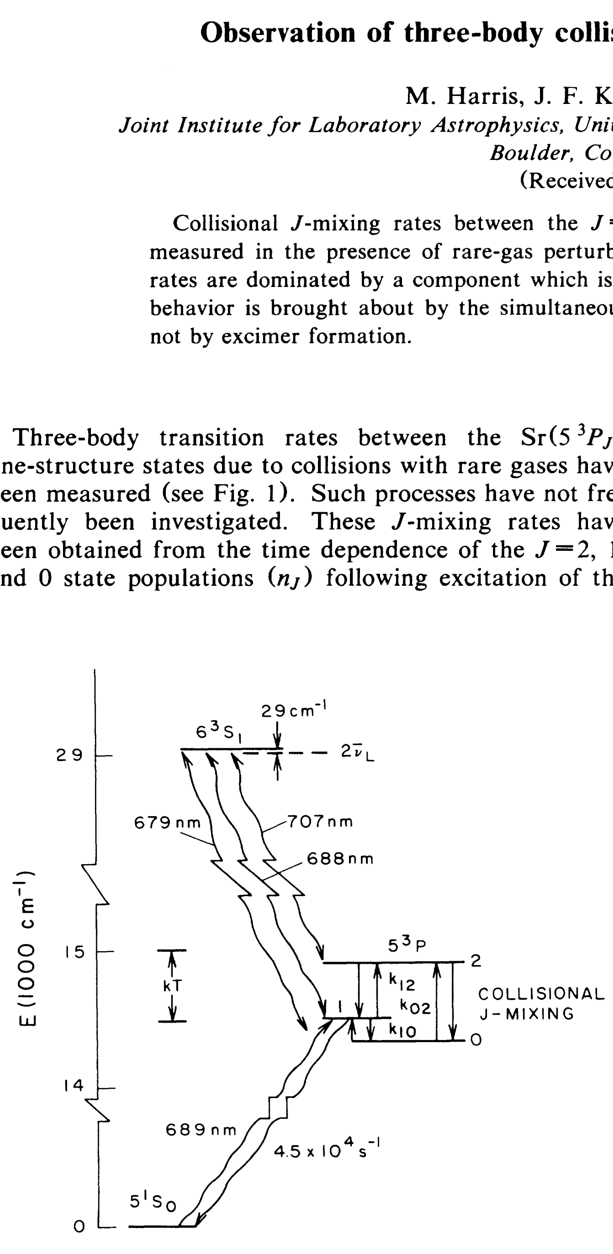

FIG. 1. Sr energy levels relevant to this experiment. The laser at 689 nm excites to the $^3P_1$ state, and the absorption lines at 679 and 707 nm are used to probe the $J=0$ and 2 populations.

Two constraints define a rare-gas pressure range (3×10^{17}–6×10^{18} cm^{-3}) in which useful information has been obtained. The rare-gas density must be sufficient to transfer enough $^3P_1$ population to the $J=0$ and 2 states (before radiative decay) to give an adequate absorption signal. The upper limit arises because the absorption coefficient is reduced as the absorption lines become broadened, and the initial conditions (only $J=1$ populated) are significantly altered by collision-induced $5\,^3P_1$–$6\,^3S_1$ absorption followed by radiative decay to the other $5\,^3P_J$ states.

The mixing rates $R_{J\rightarrow J'}$ are obtained by least-squares fitting solutions of the coupled linear equations for the three $n_J(t)$ (detailed in Ref. 1). Here the six mixing rates in Fig. 1 are reduced to three independent rates by applying detailed balancing to forward and backward rates. The three independent mixing rates and the $^3P_1$ radiative lifetime are determined by the fitting. This fit is relatively insensitive to the R_{02} (and the related R_{20}) rate due to the initial condition of starting in the $J=1$ state, and also the fact (from the computed fits) that the R_{02} rate is much less than R_{10} or R_{12}. The latter two rates are very well determined, within typically ∼5% statistical uncertainty at each pressure, and the $5\,^3P_1$ radiative lifetime value (22.0 μs) obtained at all pressures agrees within ∼5%, except at the highest temperatures and Sr densities when

$5\,^3P_1$–$5\,^1S_0$ radiation trapping becomes observable. The Sr density range was 10^{11}–10^{13} cm^{-3}.

Care has been taken to reduce to acceptable levels other causes of transfer between the J states. These are (i) energy pooling (Sr*+Sr* collisions) and (ii) collisional-induced absorption, both to $6\,^3S_1$, followed by rapid radiative decay back to $5\,^3P_{2,1,0}$, and (iii) collisions with impurities or Sr. Also, loss mechanisms from the $5\,^3P_J$ multiplet other than by radiation at 689 nm (i.e., diffusion, quenching, energy pooling) have been considered. These are normally negligible, but occasionally a small diffusion correction is required at low rare-gas pressures.

The binary collisional transfer rates [for the process $\mathrm{Sr}(5\,^3P_J)+X\rightarrow \mathrm{Sr}(5\,^3P_{J'})+X$) (where X denotes a rare-gas atom)] have been measured for each of the rare gases, and these will be presented in a later paper (Ref. 1) together with a more detailed account of the experiment. Here it is only relevant that these rate coefficients are orders of magnitude below gas kinetic (typically 10^{-11}–10^{-12} cm^{3}s^{-1}), as is characteristic of slow thermal collisions between noncrossing levels (the Sr fine-structure splittings are 187 and 394 cm^{-1}).

In the case of krypton and xenon perturbers the transfer rates are no longer proportional to pressure; at pressures above ~100 Torr a term quadratic in pressure begins to dominate. This is indicative of three-body collisions of the type

$$\mathrm{Sr}(5\,^3P_J)+2X\xrightarrow{k^Q_{JJ'}}\mathrm{Sr}(5\,^3P_{J'})+2X\ .$$

This very unusual behavior is observable in this situation because of the long-lived nature of these metastable states, and the very small, competing binary collisional transfer rate.

Figure 2 shows the dependence of the transfer rates R_{10} and R_{12} upon perturber density for Kr and Xe. Some evidence of three-body collisions is also found with Ne and Ar perturbers, but not shown here. In Fig. 2, the best fit contributions from the linear (two-body) and quadratic (three-body) terms to the transfer rate are plotted for one temperature, together with their sum, to show the fit to the data. The fit also includes a small pressure-independent contribution to the rates. This constant term is due to collisions of the type Sr-Sr*, and/or Sr*–molecular impurity, and its presence was confirmed by observation of transfer rates at very low (~2 Torr) perturber pressures. The measured three-body rate coefficients are presented in Table I.

TABLE I. Three-body collisional transfer rate coefficients for $5\,^3P_J\rightarrow 5\,^3P_{J'}$ in units of 10^{-33} cm^{6}s^{-1}.

J,J'	Ne (688 K)	Ar (688 K)	Kr (800 K)	Xe (800 K)
1,0	0.7 ± 0.2	1.8 ± 0.8	3.6 ± 0.3	9.0 ± 0.5
1,2	$\lesssim0.3$	$\lesssim0.3$	1.1 ± 0.1	4.2 ± 0.3

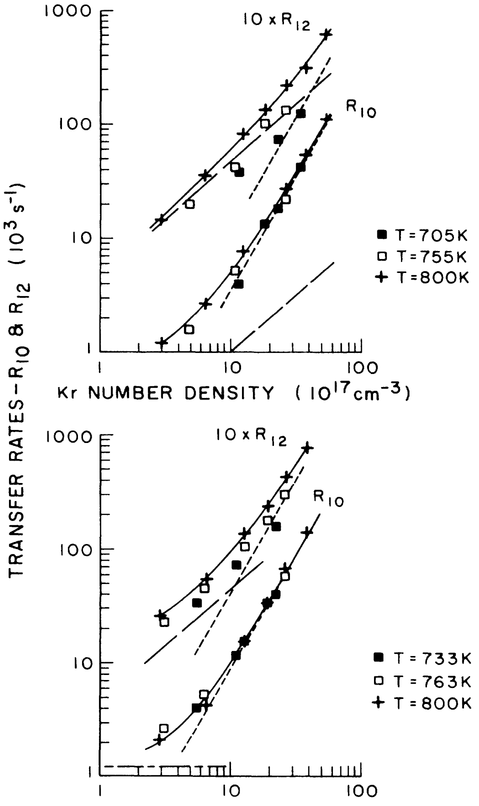

FIG. 2. Collisional transfer rates R_{10} and R_{12} for Kr and Xe perturbers. The linear and quadratic components which contribute to the rates are plotted separately: solid curve, best fit to 800 K data; short-dashed curve, quadratic term; long-dashed curve, linear term; long- and short-dashed curve, constant term.

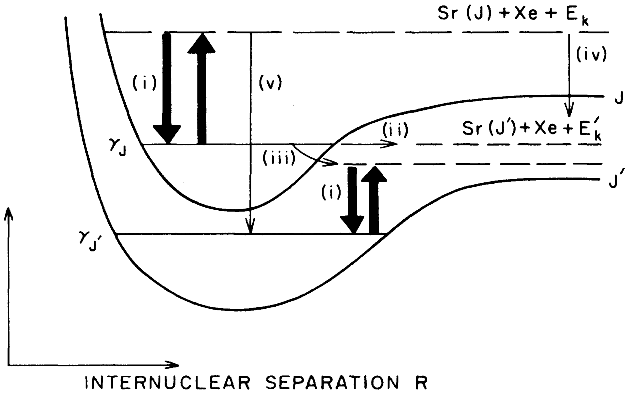

FIG. 3. Schematic Sr-Xe potential curves and collision processes. The following transfer processes are depicted (E_k is the kinetic energy): (i) Three-body association and its inverse without J change, $\mathrm{Sr}(J)+2\mathrm{Xe}\rightleftarrows \mathrm{XeSr}(\gamma_J)+\mathrm{Xe}$. These are shown as heavy lines to indicate larger rates than the other, J-changing processes. (ii) Vibrational predissociation from bound excimer to free-atom state with J change, $\mathrm{XeSr}(\gamma_J)\rightarrow \mathrm{Xe}+\mathrm{Sr}(J')$. (iii) Collisional dissociation of a bound excimer with J change. (iv) J-changing collision of a free Sr atom with two free perturbers, $\mathrm{Sr}(J)+2\mathrm{Xe}\rightarrow \mathrm{Sr}(J')+2\mathrm{Xe}$. (v) J-changing three-body association, $\mathrm{Sr}(J)+2\mathrm{Xe}\rightarrow \mathrm{XeSr}(\gamma_{J'})+\mathrm{Xe}$.

For the microsecond time scale and $\sim 10^{18}$ cm^{-3} rare-gas densities of the present data, the densities $[\mathrm{XeSr}^*(\gamma_J)]$ (and $[\mathrm{KrSr}^*]$) of bound excimers in each adiabatic state γ_J should be in equilibrium with [Xe] $[\mathrm{Sr}^*(J)]$, where γ_J is a diatomic electronic state adiabatically connected to atomic level J (see Fig. 3). This follows, for the expected shallow (< 10 kT, $T \sim 700$ K) binding of these diatomic states,[2] from the fact that collisional dissociation occurs on a much faster time scale than J mixing or radiation, so that the equilibrium distribution of bound excimers is maintained.[3] Also, for this relatively shallow binding and [Xe] range the equilibrium balance highly favors the atomic form, and the (equilibrium) bound excimer density is proportional to [Xe]. Thus, the reported $[\mathrm{Xe}]^2$-dependent J transfer is not due to the $[\mathrm{Xe}]^2$ dependence of a three-body association reaction to γ_J [process (i) in Fig. 3] followed by vibrational (bound-to-free) predissociation of $\mathrm{XeSr}^*(\gamma_J)$ excimers to $\mathrm{Xe}+\mathrm{Sr}(J')$ [(ii) in Fig. 3], as this would be proportional to $[\mathrm{XeSr}^*(\gamma_J)]$ and thus to [Xe]. The J change must occur when two Xe atoms are near the Sr*, and there is then little difference between the collision of a free Xe with a bound $\mathrm{XeSr}^*(\gamma_J)$ [(iii) in Fig. 3] or the collision of two free Xe with $\mathrm{Sr}^*(J)$ [(iv) and (b) in Fig. 3]. (The only difference is in the distribution of relative velocities and distances.) In essence, a simultaneous perturbation by two Xe atoms produces the observed fine-structure transitions.

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[1] J. F. Kelly, M. Harris, and A. Gallagher (unpublished).

[2] We assume that the $5\,^3P$ binding is comparable to the $5\,^1P_1$ binding reported by P. S. Julienne, in *Spectral Line Shapes*, edited by K. Burnett (de Gruyter, Berlin, 1983), Vol. 2.

[3] R. Scheps and A. Gallagher, J. Chem. Phys. **65**, 859 (1976).