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Collisional energy pooling for $\mathrm{Sr}(5\,^3P_J) + \mathrm{Sr}(5\,^3P_{J'}) \rightarrow \mathrm{Sr}(6\,^{3,1}S) + \mathrm{Sr}(5\,^1S)$

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Energy pooling (EP) has been observed in Sr vapor following pulsed optical excitation to the $5\,^3P_1$ state. From the time-dependent radiative decay of $6\,^3S_1$ and of $6\,^1S_0$ via the cascade resonance line, the EP rate coefficients have been investigated for the following:

$$\mathrm{Sr}(5\,^3P_J)+\mathrm{Sr}(5\,^3P_{J'})\xrightarrow{k_{JJ'}}\mathrm{Sr}(5\,^1S_0)+\mathrm{Sr}(6\,^3S_1\text{ or }6\,^1S_0).$$

The values of k_{11} have been measured, as well as $k_{JJ'}$ averaged over a thermal distribution of $5\,^3P_J$ populations. The time-dependent $\mathrm{Sr}(5\,^3P_J)$ densities were measured by absorption of lines from a Sr lamp crossing the excitation region. The rate coefficients are surprisingly large; in spite of the small statistical weights of these product states, they are nearly gas-kinetic. The dependence of the rates upon spin, J, and energy defect ΔE has also been examined.

I. INTRODUCTION

The term energy pooling (EP) is used to describe an excitation transfer process in which two excited atoms collide to produce one highly excited atom and one ground-state atom.[1,2] As in all energy transfer, spin change is an important characteristic and the rate is expected to be enhanced when the final-state electronic energy lies close to the initial energy, which is the sum of the two initial excitation energies.

This type of process was first reported by Allegrini *et al.*[3] for collisions between two Na $3P$ atoms. For this sodium case nearly gas-kinetic rate coefficients have been measured[4-6] for energy pooling to the $5S$, $4D$, and $4F$ energy levels, which are 600 to 800 cm^{-1} from the initial electronic energy of two times the $3P$ excitation energy. Energy pooling to the $6S$ and $5D$ states with energy defects $\Delta E \gtrsim 1000\ \mathrm{cm}^{-1}$ was also observed, but with considerably smaller rate coefficients consistent with the fraction of collisions with this ΔE. Nonetheless, all of these energy-transfer rate coefficients are unusually large for thermal atomic collisions involving such large $|\Delta E|$. Strongly coupled, avoided level crossings between many of the relevant molecular states are clearly indicated; this is supported by available (so far incomplete) molecular potentials.[7] As only the Na-Na system has been studied so far, it is not yet apparent if this should be expected as a general property of EP collisions in which the electronic configurations generally undergo major changes and many adiabatic molecular states are involved during the collision. The present Sr-Sr experiment investigates this question by studying a different element, and it also raises a new issue, that of how spin selection rules might affect EP collisions.

In this experiment, we have observed the following processes:

$$\mathrm{Sr}(5\,^3P_J)+\mathrm{Sr}(5\,^3P_{J'})\xrightarrow{k_{JJ'}}\mathrm{Sr}(6\,^3S_1)+\mathrm{Sr}(5\,^1S_0)\ , \qquad (1)$$

$$\mathrm{Sr}(5\,^3P_J)+\mathrm{Sr}(5\,^3P_{J'})\xrightarrow{k_{JJ'}}\mathrm{Sr}(6\,^1S_0)+\mathrm{Sr}(5\,^1S_0)\ . \qquad (2)$$

The relevant Sr energy levels and radiative transitions are shown in Fig. 1. As in a typical energy-transfer measurement, we measure the ratio of the final to initial-state fluorescent intensities. After any radiative branching corrections, this ratio equals the energy-transfer rate divided by the initial-state spontaneous emission rate. In the present case we detect the 689 nm, initial ($5\,^3P_1$) state fluorescence, the 679- , 688- , and 707-nm fluorescence from $6\,^3S_1$ to $5\,^3P_{2,1,0}$, and 461-nm cascade fluorescence from $6\,^1S_0$ via $5\,^1P_1$. In the more usual energy transfer process $A(i)+B\rightarrow A(j)+B$, the transfer rate measured this way equals the desired rate coefficient k times $[B]$, the perturber density, which is normally easily measured with a manometer. In the EP process $A(i)+A(i)\rightarrow A(0)+A(j)$, the measured rate equals $k[A(i)]$, so that the excited-state density $[A(i)]$ must be obtained. The principal difficulty in these experiments is to measure reliably this excited-state density, and failure to do so has caused some major errors in the literature. In the present experiment we have taken an approach to this problem which is inexpensive, reliable, and can be easily applied to many EP experiments. Specifically, we measure absorption by the $A(i)$ excited atoms in the cell of Sr lines that terminate on $A(i)$. A hollow cathode lamp is used to obtain narrow lines for this purpose. Borisov *et al.*,[8] and more recently our laboratory,[9,10] have also used this absorption method to study collisional mixing within the $5\,^3P_J$ manifold.

Pulsed optical excitation is used to populate the $5\,^3P_1$ state and we detect and analyze all fluorescence and absorption signals as a function of time following this excitation. EP to the $6\,^3S_1$ state by collision of two $5\,^3P_1$ atoms has an energy defect ΔE of only $+30.1\ \mathrm{cm}^{-1}$, while EP to $6\,^1S$ requires $\Delta E \sim +1500\ \mathrm{cm}^{-1}$ (see Fig. 1). A positive ΔE here denotes an endothermic reaction. We have measured the rate coefficients for these two process-

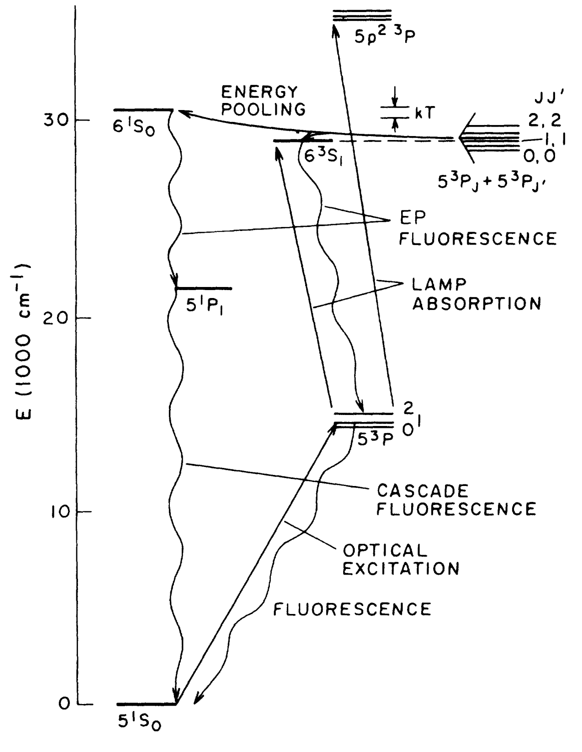

FIG. 1. Sr energy-level scheme, showing the single and pair energies of the $5\,^3P_J + 5\,^3P_{J'}$ states.

es for this $J,J'=1,1$ case, and their dependence on J,J' has also been investigated by measuring EP from a thermal distribution of the $^3P_{2,1,0}$ states (about 0.72:1:0.50, respectively, at $T=673$ K). This was achieved with the addition of a buffer gas which causes $5\,^3P_J$ level mixing at a much faster rate than radiative decay of $5\,^3P_1$.

II. EXPERIMENT

The experimental setup (Fig. 2) has been described in detail in Ref. 9. A Nd-YAG (yttrium aluminum garnet) pumped, pulsed dye-laser beam is directed through a cell, in the form of a cross, containing Sr vapor and an inert gas buffer. The cell was an improved design from that used in Ref. 9 in that sapphire rods were inserted to reduce significantly the optical depth of the vapor through which the fluorescence traveled to reach the detector.[4] Fluorescence is detected at right angles to the laser beam, and is spectrally resolved by a monochromator. Light from a Sr hollow cathode lamp is focused through the excitation region and into the monochromator to isolate individual lines. Each of these lines has $5\,^3P$ as its lower state, and the time-dependent absorption of particular lines provides the $5\,^3P_{2,1,0}$ Sr densities.

The duration of the laser pulse ($\sim$6 ns) is much less than the time scale of the radiative decay of $^3P_1$ ($\tau \sim 22$ μs),[9] and also of the energy pooling rate at our Sr* density. An approximation of instantaneous excitation is therefore used. Also, the buffer pressure is always sufficient to randomize the polarization of the $5\,^3P_1$ atoms within a very short time (<100 ns).

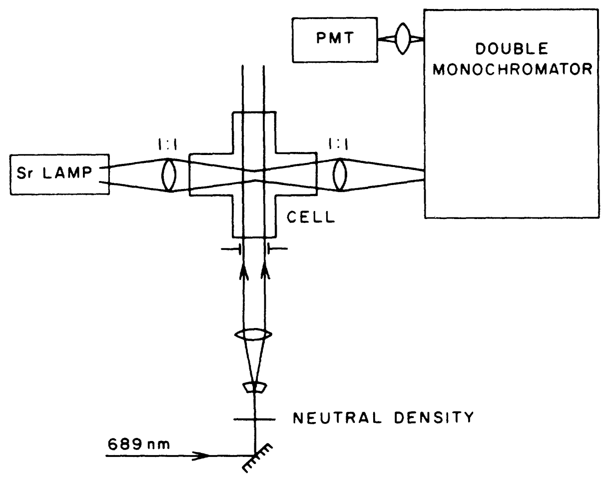

FIG. 2. Experimental setup.

The Sr* density is always kept sufficiently low ($\sim 10^{11}$ cm^{-3} immediately after the laser pulse) that EP to $6\,^3S_1$, and radiation back to $5\,^3P$, only causes a minor ($<1\%$) perturbation to the populations of the $5\,^3P_J$ multiplet. For low (<10 Torr of Ar) buffer-gas pressures, intramultiplet collisional transfer to $J=0$ and 2 is negligible and the EP results from collisions of two $5\,^3P_1$ atoms. Since $6\,^1S_0$ and $6\,^3S_1$ radiatively decay in <100 ns and the experiment time scale is ~ 10 μS, these states can be considered to decay instantaneously. Thus, when only $5\,^3P_1$ is populated, the EP fluorescence signal decays at twice the rate of the $5\,^3P_1$ population:

$$I_{\mathrm{EP}} \propto [^3P_1][^3P_1] \propto e^{-2\Gamma t} ,$$

where Γ is the $5\,^3P_1$ radiative decay rate.

Fully J-mixed conditions are achieved with the addition of $\sim$20 Torr of He, which has a very large J mixing rate coefficient.[9] This creates a thermal distribution among the $5\,^3P_J$ states in about 0.3 μs, without causing any significant change in the absorption coefficient by pressure broadening the line. All three members of the coupled $5\,^3P_J$ manifold then decay at a slower rate, given by

$$\Gamma_{\mathrm{mixed}} = \frac{[^3P_1]\Gamma}{\sum_J [^3P_J]} \sim 0.45\Gamma \quad \text{at } T=673 \text{ K} .$$

The EP signal, caused by collisions between all combinations of J,J' then decays with a rate constant $\Gamma_{\mathrm{mixed}} \times 2$. Observation of these time dependences for the $6\,^3S$ and $5\,^1P$ ($6\,^1S_0$ cascade) fluorescence signals is used to verify that $5\,^3P + 5\,^3P$ EP collisions are responsible for populating these levels.

In the experiment, three sets of time-dependent signals were averaged over $\sim 10^3 - 10^4$ laser pulses, recorded by a transient digitizer and stored for computer analysis. These were (i) the EP signals due to populating $6\,^1S_0$

(detected at 461 nm) and $6\,^3S_1$ (679, 688, 707 nm); (ii) the fluorescence signal from the $5\,^3P_1$ decay; and (iii) the time-dependent absorption of light from the Sr lamp as it crossed the excitation region, measured successively for four different lines which connect to the $5\,^3P$ multiplet.

The absorption lines used were 688 nm ($5\,^3P_1$-$6\,^3S_1$), 707 nm ($5\,^3P_2$-$6\,^3S_1$), 472 nm ($5\,^3P_1-5p^2\,^3P_2$), and 481 nm ($5\,^3P_2-5p^2\,^3P_2$). The light from the Sr lamp passed through a well-defined slab of excited atoms of 0.4 cm thickness, within which the density of excited Sr had spatial variations of $\lesssim 10\%$. Absorption of the four lines was typically 20–40% corresponding to $5\,^3P_J$ densities of $\sim 10^{11}$ cm^{-3}; the lamp was run at a sufficiently low temperature and pressure that its lines had a 300-K Doppler profile. The lamp profile was investigated with a piezo-electrically scanned Fabry-Perot etalon, and also by measuring the absorption of its spectral lines by the Sr vapor as a function of lamp current. The absorption profiles were also Doppler at the cell temperature, since buffer pressures were always sufficiently low that pressure broadening was much smaller than Doppler broadening. Thus, standard two-Doppler absorption tables could be used to interpret the data.

For the signal due to EP to the $6\,^3S_1$ state, a spectral calibration was not necessary for the calculation of absolute EP rate coefficients since the line $6\,^3S_1$-$5\,^3P_1$ (688 nm) is very close in wavelength to the $5\,^3P_1$-$5\,^1S_0$ line (689 nm). However, for EP to $6\,^1S_0$, a calibration is required, as the resonance line cascade is detected at 461 nm. The relative sensitivity of the double-monochromator plus photomultiplier detection system for 461-nm photons, compared to 689 nm photons, was measured with a standard tungsten-iodide filament lamp of known spectral output. Also, radiative trapping of the resonance line was significant; the effective lifetime of the $5\,^1P_0$ state at the Sr densities used was measured to be 20–60 ns whereas $\tau_{\text{natural}} \sim 5$ ns.[11] However, this had only a minor effect on the measured signal, as the cell geometry ensured that almost all 461-nm photons ultimately exit through the sapphire rods. This was verified by measuring the ratio of 688 to 461 nm EP fluorescence signals over a range of Sr densities spanning a factor of 3. This ratio remained constant to $\sim 20\%$.

III. ANALYSIS AND RESULTS

Typical time-dependent data from the transient digitizer is displayed in Fig. 3 for the case of only the $5\,^3P_1$ state populated. Least-squares fits were performed on all the data. For the fluorescence data the signals were analyzed in terms of a single exponential: $I = I_0 e^{-t/\tau}$; I_0 and τ for $6\,^3S_1$ and $5\,^1P_1$ fluorescence typically has $\sim$2–5 % uncertainty while the uncertainty was $\sim 1\%$ for the much stronger $5\,^3P_1$ fluorescence. For $5\,^3P$ absorption data, the fractional absorptions were first converted to absorption coefficient, and then analyzed in the same way as the fluorescence data, with $\sim$2–5 % uncertainty.

Care must be taken to define correctly the EP rate coefficient. For a general EP (or energy transfer) collision between two atoms in different states 1 and 2, the rate coefficient k_{12}^{EP} is defined by

$$R = k_{12}^{\text{EP}} n_1 n_2 ,$$

where R is the EP collision rate per unit volume and n_1, n_2 are the densities of atoms in states 1 and 2. For collisions between atoms in the same state 1, a distinction must be made between thermal collisions in a cell and collisions in double atomic beam experiments. In this latter case

$$R = k_{11}^{\text{EP}} n_a n_b ,$$

where n_a, n_b are the densities in beams a and b. However, for collisions in a cell, each colliding pair will be counted twice unless a factor of $\frac{1}{2}$ is included in the definition of the rate coefficient:

$$R = \tfrac{1}{2} k_{11}^{\text{EP}} n_1^2 .$$

While this factor of $\frac{1}{2}$ has been correctly included in Ref. 12 and 13, it has been omitted in most previous cell EP measurements.[1–6] The values of k^{EP} (or cross section σ^{EP}) in these references must therefore be doubled.

The EP rate coefficient is calculated (for the $J=1$, $J'=1$ case) as follows:

$$k_{11}^{\text{EP}} = \frac{2\Gamma I^{\text{EP}}}{[\text{Sr}^*] I^{\text{FL}}} = \frac{2\Gamma I_0^{\text{EP}}}{N_0 I_0^{\text{FL}}} , \tag{3}$$

where Γ is the radiative decay rate of $5\,^3P_1$; I^{EP} is the photon flux of the EP signal (summed over all possible decay modes from $6\,^3S_1$ or $6\,^1S_0$) and $I^{\text{EP}} = I_0^{\text{EP}} e^{-2\Gamma t}$; I^{FL} is the photon flux of the 689 nm fluorescence from $5\,^3P_1$ and $I^{\text{FL}} = I_0^{\text{FL}} e^{-\Gamma t}$; and the $5\,^3P_1$ density $[\text{Sr}^*] = N_0 e^{-\Gamma t}$.

Transition probabilities for the $5\,^3P$ absorption lines are needed to convert the measured absorption to the number density N_0. For this we have used measurements[14] of the upper-state lifetimes, as shown in Table I.

The dominance of $5\,^3P + 5\,^3P$ collisions as the mechanism for populating the $6\,^3S_1$ and $6\,^1S_0$ states is verified by the observation of the correct time dependences (Fig. 3). Specifically, the energy pooling signals decay at twice the rate of the 689-nm fluorescence. In the unmixed case, this is determined by the lifetime ($\tau = 22$ μs), and in the mixed case the effective lifetime is slower by a factor of 2.2 ($\tau_{\text{eff}} = 48$ μs).

The unmixed experiment gives a direct measurement of the EP rate coefficient, $k_{J=1,J'=1}$. The mixed data provide an averaged rate coefficient over the thermal distribution for $J=0,1,2$:

$$\overline{k_{JJ'}} = \frac{\sum_{JJ'} k_{JJ'} [^3P_J][^3P_{J'}]}{\left(\sum_J [^3P_J]\right)^2} . \tag{4}$$

Table II gives the measured rate coefficients. The major source of the 25% uncertainty for the $6\,^3S_1$ value lies in the determination of the Sr($5\,^3P$) number density, caused primarily by an uncertainty of $\sim 20\%$ in the lifetime measurements of Ref. 12 and thus in the absorption oscillator strengths used. The values of $[^3P_J]$ measured from the absorption of the 472 and 481-nm lines were typically 30% greater than those from the 688 and 707-

TABLE I. Absorption lines used to measure [Sr*].

λ (mn)	Transition	Upper-state lifetime[a] (10^{-8} s)	Inferred A (10^7 s^{-1})
687.8	$5\,^3P_1$-$6\,^3S_1$	0.88	3.0
707.0	$5\,^3P_2$-$6\,^3S_1$	0.78	5.0
472.2	$5\,^3P_1$-$5p^2\,^3P_2$	0.88	2.8
481.2	$5\,^3P_2$-$5p^2\,^3P_2$	0.78	8.5

[a] Reference 12.

nm lines. Smaller errors ($\sim$5%) arise from inhomogeneities in the Sr* density and uncertainty in the lamp linewidth. In particular, diffraction of the laser beam at the slit (Fig. 2) could create significant Sr* density outside the expected excitation region since the laser power produced considerable saturation of the ^1S-$^3P_1$ transition. This may result in an underestimate of the values of k^{EP}, although a check on the laser power dependence of the absorption signals demonstrated that the resulting error was $<10\%$. $5\,^3P$-state diffusion is expected to have a negligible effect, and this is supported by the observation of the correct time constants for both EP and $5\,^3P_1$ fluorescence.

The $6\,^1S$ EP measurement has some additional sources of uncertainty. The attenuation due to 461-nm trapping was considered, and also the uncertainty in the detection sensitivity at 461 nm versus 688 nm. We assess the overall uncertainty in the energy pooling rate coefficient to $6\,^1S_0$ to be $\sim$40%.

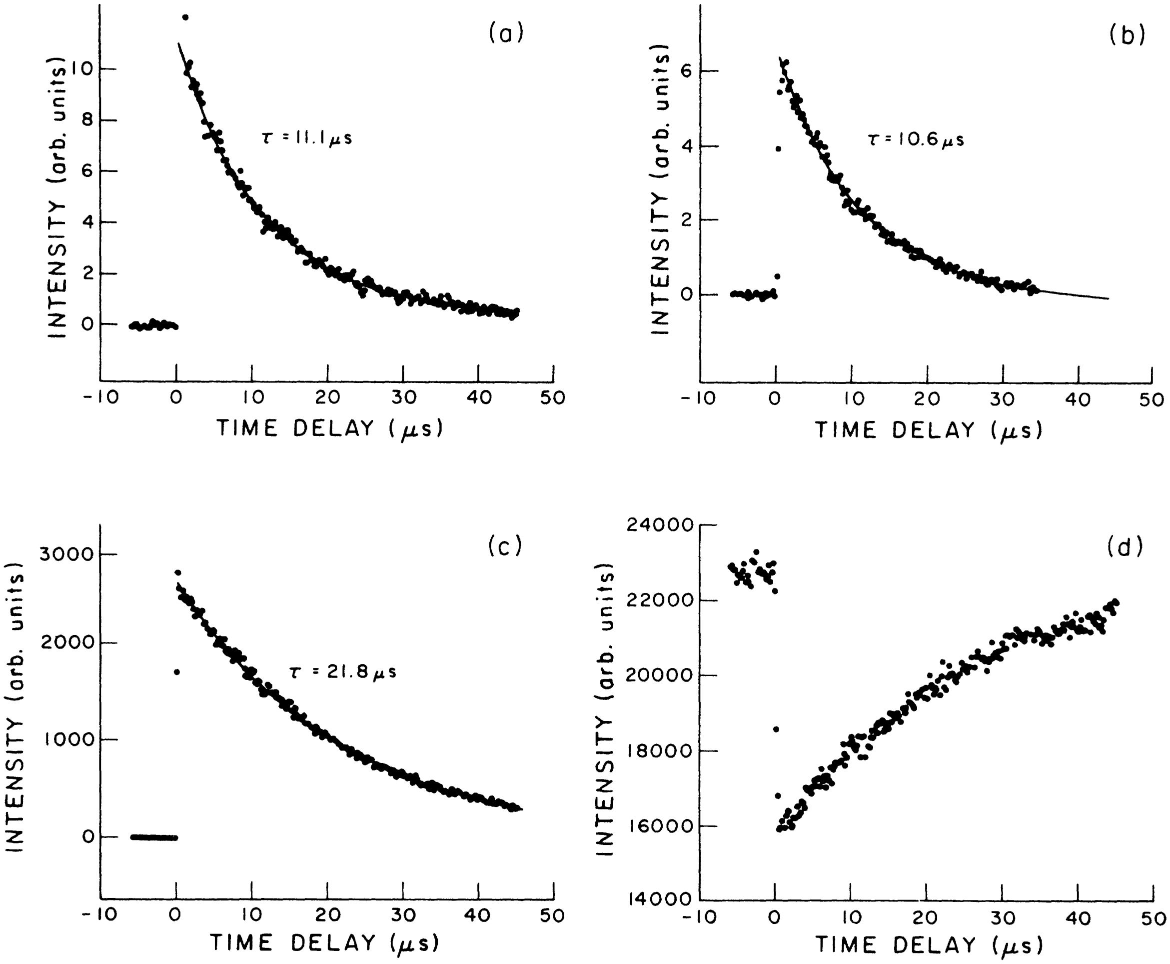

FIG. 3. Time dependent signals, for the case of only $5\,^3P_1$ populated. (a) 688-nm fluorescence (due to EP to $6\,^3S$), (b) 461-nm fluorescence (due to EP to $6\,^1S$), (c) 689-nm fluorescence (from $6\,^3P_1$), and (d) 688-nm lamp radiation, after traversing the cell. Solid curves represent the computed best-fit exponential through the points. In the mixed (thermal distribution) case not shown, signals are similar except the decay rates are all slower by a factor of 2.2.

TABLE II. Energy pooling rate coefficients (10^{-10} cm^3 s^{-1} at $T=673$ K).

EP to $6\,^3S_1$	EP to $6\,^1S_0$
Unmixed case 5.2×(±25%) $k_{J=1,J'=1}$ $(E_f-E_i=+30\ \text{cm}^{-1})$	1.1×(±40%) $(E_f-E_i=+1583\ \text{cm}^{-1})$
Fully mixed 2.6×(±25%) $\overline{k_{JJ'}}$	1.1×(±40%)

IV. CONCLUSIONS

The EP rate coefficients measured here are all nearly gas-kinetic. Since the energy defects are +30 and +1500 cm^{-1}, this is a surprising lack of dependence on ΔE. Very similar rate coefficients are also observed[4–6] for Na $3P+3P\rightarrow 3S+5S$, $4D$, or $4F$, where the energy defect ΔE is typically $\sim\pm500$ cm^{-1}. Since the electron wave functions of the doubly excited states are spatially very different from those of the ground plus single, highly excited state, the potentials should also be very differently shaped. Thus, many avoided crossings are expected, and perhaps gas-kinetic rates occur more readily than in the more usual energy transfer process $A(i)+B\rightarrow A(j)+B$. However, two Sr atoms in the $5\,^3P$ state have a product-state statistical weight of 81, and connect to dozens of molecular adiabatic states as the atoms approach. In contrast, the final states of the EP process measured here are $6\,^3S_1+5\,^1S_0$ and $6\,^1S_0+5\,^1S_0$ which have a statistical weight of only 3 and 1, respectively, and each connects to only one molecular adiabatic state. Thus on a statistical basis the probability that two atoms approach as $5\,^3P_J+5\,^3P_{J'}$ and exit as $6\,^3S_1+5\,^1S_0$ or $6\,^1S_0+5\,^1S_0$ (as opposed to $5\,^3P+5\,^3P$), would be only $\sim\frac{3}{81}$ or $\frac{1}{81}$, respectively. In addition, the $6\,^1S_0+5\,^1S_0$ state is ~ 3 kT above $5\,^3P_1+5\,^3P_1$, so that only 11% of these 700-K collisions have sufficient KE (kinetic energy) to exit as these products. The fact that the EP rate to $6\,^3S_1$ and 5 times the $6\,^1S_0$ rate are essentially gas-kinetic is thus quite surprising. We have no explanation for this.

The averaged fully-mixed EP rate to $6\,^3S_1$ is a factor of 2 smaller than the unmixed EP rate. This indicates that, as expected, the nearly resonant process for $J,J'=1$ ($\Delta E=30$ cm^{-1}) is significantly enhanced in comparison to the other possible J,J' combinations. (The energy defects for these other JJ' pairs are 100–400 cm^{-1}.) From Eq. (4) and the measured k_{11} and $\overline{k_{JJ'}}$ one calculates that the k_{11} term is responsible for approximately 40% of $\overline{k_{JJ'}}$ so that $k_{JJ'}$ averaged over the remaining JJ' pairs is about half of k_{11}.

For EP to the $6\,^1S_0$ state, the data do not show evidence of strong J dependence. However, J dependence is to be expected by activation energy considerations (Fig. 1); the rates from higher J states should be considerably enhanced. We suggest that the apparent lack of J dependence may be fortuitous; enhancement of the $J,J'=2,2;2,1;2,0$ rates being balanced by a corresponding reduction for the $J,J'=0,0;0,1$ rates.

Detection of 461-nm fluorescence does not rule out two processes other than direct EP to $6\,^1S_0$. Firstly, $6\,^3S_1$ atoms created by EP may be collisionally transferred to $6\,^1S_0$. However, no variation in the rates was found over an order of magnitude range of low buffer pressures ("low" here means that J mixing within the $5\,^3P_J$ multiplet was insignificant) and so $6\,^3S_1$-$6\,^1S_0$ collisional transfer was not responsible for the observed 461-nm fluorescence. Collisional transfer from a pure triplet (such as $6\,^3S_1$) to a pure singlet ($6\,^1S_0$) state is in any case expected to be highly forbidden on theoretical grounds, as has been confirmed recently.[15] A second possibility is that of EP directly to the $5\,^1P$ state. The measured EP rate is, in fact, the sum of the rates to $6\,^1S$ and $5\,^1P$. Although EP to $5\,^1P$ could not be ruled out experimentally, the energy surplus of ~ 7300 cm^{-1} make it a much more unlikely possibility than EP to $6\,^1S_0$ (with energy defect $\sim+1500$ cm^{-1}).

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