Magnetic substate transitions in collisions of Sr(5s5p \(^1\)P\(_1\)) with Ar

Ji-ping Zhan, Wei-Qiao Deng, Ke-Li Han, He-Ping Yang, Guo-Zhong He, Nan-Quan Lou

State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China

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Abstract

The collision induced magnetic substate transitions of Sr(5s5p \(^1\)P\(_1\)) from \(M_J = 0\) to \(M_J = \pm 1\) with Ar as collision partner are studied in a beam-gas reaction apparatus. The depolarization rate constant \(k_p = (2.5 \pm 0.5) \times 10^{-9}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\) is obtained, and the magnetic substate transition rate constant \(k_B = (1.25 \pm 0.25) \times 10^{-9}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}\) is deduced from depolarization rate constants.

1. Introduction

The study of atomic and molecular collision processes and interactions is of fundamental importance for a thorough understanding of collision physics as well as chemical reaction dynamics. Even though the subject was first studied very early in this century [1], it is still in many respects in its infancy. The development of modern lasers and modern computers made it possible to study collision processes in detail both experimentally and theoretically. Rettner and Zare studied the effect of orbital alignment on reaction collisions, in which Ca(4s5p \(^1\)P\(_1\)) atoms were aligned by excitation with linearly polarized laser light and reacted with HCl, Cl\(_2\) and CCl\(_4\) [2]. This together with their pioneering works made a strong influence on molecule reaction dynamics. Bahring [3,4], Hale [5] and Bussert [6,7] studied the effect of orbital alignment on electronic energy transfer of electronically excited atoms, which is the study of collisional physics on the substate level. There are many other excellent works being done [8–10]. All these had made the subject a well-established field of investigation.

Even though the physical chemist is usually interested in reactive collisions, which involve atoms and molecules that can undergo a chemical reaction, most studies on the substate-resolved transitions have been carried out on aligned excited P states in collisions with rare gases, or rare-gas-like partners [3–7,11,12]. The simplicity of the rare gas systems with aspect to their symmetry and non-reactive nature makes it easy to treat them theoretically.

In this work, we have studied the magnetic substate transition processes involving the first electronically excited singlet P state of Sr atoms in the presence of Ar as collision partner. A magnetic substate transition rate constant has been obtained.

2. Experimental

The experimental apparatus was essentially similar to that previously reported [13], although the
setup was slightly rearranged for the measurement in this work. A beam of Sr atoms at a constant temperature of 950 K is incident on low-pressure (≤ 2 Pa) argon gas at room temperature. Sr atoms are excited by a linearly polarized laser (YAG laser pumped pulsed tunable dye laser, Quanta-Ray DCR-3 and PDL-1) at 460.7 nm, which matches the Sr atomic resonance transition of 5s5s\textsuperscript{1}S\textsubscript{0}–5s5p\textsuperscript{1}P\textsubscript{1}. The dye laser beam is directed through light baffles horizontally and irradiates the observed zone perpendicularly to the atomic beam. The typical laser energy is as small as 50 μJ per pulse without focusing, so that no two-photon or multi-photon processes occur. The laser is polarized with a Thompson–Taylor prism. The vertical or horizontal polarization direction for the laser beam is parallel or perpendicular to the direction of the atomic beam. The fluorescence of Sr(5p\textsuperscript{1}P\textsubscript{1}) is collected by a group of lenses in a direction orthogonal to both the laser beam and the atomic beam. The fluorescence is also collected at a 45° angle with the laser beam in the same horizontal plane, in order to detect the horizontal component of the fluorescence when the polarization direction of the laser is horizontal. A photomultiplier tube (R943-02), which is connected to a Boxcar time analyzer and a computer, is placed just behind a film polarizer to detect the fluorescence signal. We do not use a monochromator, because only fluorescence of 460.7 nm is strong enough to be detected by the system. In addition, the scattered laser light is so weak that it has no effect on our results.

In our experiment, we record the time evolution of vertical and horizontal components of Sr(5s5p\textsuperscript{1}P\textsubscript{1}–5s5s\textsuperscript{1}S\textsubscript{0}) fluorescence with the pumping laser in both vertical and horizontal polarization directions.

3. Results and discussion

3.1. The depolarization rate constants

It is known, according to the quantum theory, that polarized laser radiation tuned to an atomic resonance transition, excites atoms into an excited state with a well-defined alignment of their magnetic substates. In our experiment, for example, linearly polarized laser light can excite Sr atoms from the 5s5s\textsuperscript{1}S\textsubscript{1} ground state to the 5s5p\textsuperscript{1}P\textsubscript{1} excited state only with magnetic quantum number \( M_I = 0 \). As a consequence, fluorescence from the 5s5p\textsuperscript{1}P\textsubscript{1} → 5s5s\textsuperscript{1}S\textsubscript{1} should be highly polarized; the polarization direction of the fluorescence will be in accordance with that of the laser light, which we call the parallel polarization component. But if a fraction of the excited atoms transit into adjacent magnetic sublevels (\( M_I = \pm 1 \)), the perpendicular polarization component of the fluorescence will be observed. This process is generally called depolarization. In fact, it is a magnetic substate transition process of the atom. In some works, a depolarization rate constant was obtained for the process, but in this work, from the depolarization process, we deduce another important rate constant, that is the collisional magnetic substate transition rate constant.

The degree of polarization, \( P \), is calculated from the expression \[ P = (I_\parallel - I_\perp)/(I_\parallel + I_\perp), \] (1)
where \( I_\parallel \) and \( I_\perp \) are the intensities of the fluorescence polarized parallel and perpendicular, respectively, to the electric vector of the laser beam.

A pair of typical polarization fluorescence signals versus time is given in Fig. 1. The degree of polarization of the Sr(5p\textsuperscript{1}P\textsubscript{1}–5s\textsuperscript{1}S\textsubscript{0}) emission following laser excitation is obtained by measuring \( I_\parallel \) and \( I_\perp \) and then calculating \( P \) from Eq. (1) as a function of time over the pressure range 0.4–1.8 Pa. The initial value of \( P \) at a time just following the laser excitation is 1.0. This is different from the result obtained

![Fig. 1. Time variation of the degree of polarization fluorescence signals. The pressure of argon \( P_{Ar} = 0.8 \) Pa. The solid line and the dashed line are \( I_\parallel \) and \( I_\perp \), the parallel and perpendicular polarized components of the fluorescence signals respectively.](image-url)
in other works on inert gas, for example, Ku and Setser’s work [15], in which the initial $P$ value for the excited Xe atom is 0.60 rather than 1.0. Since our Sr alkali metal atom has no nuclear spin and is prepared in a singlet state, we can in principle prepare the electronic orbital in a 100% aligned state. The value of $P$ is found to slowly decay from the initial time as shown in Fig. 2 for different Ar pressures. The time evolution of $P$ then is fitted to a single exponential decay function. We take the signal after the initial short time period about 10 ns, which is greater than the laser pulse width (7–9 ns) and the lifetime of Sr($5^p\,^1P_1$) (6 ns), to avoid the complicated treatment with the laser excitation process. The decay rate constant versus Ar pressure is plotted in Fig. 3. The slope of the plot in Fig. 3 leads to a depolarization rate constant $k_p$ of $(2.5 \pm 0.5) \times 10^{-9}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

In order to examine the effect of the relative velocity vector on the depolarization, the polarization direction of the incident laser is set either parallel or perpendicular to the direction of the atom beam. The fluorescence signal is detected at a 45° angle with the laser beam. Both $I_\parallel$ and $I_\perp$ are detected in each case for calculating the degree of polarization using Eq. (1). No apparent difference is found between the two cases within the experimental uncertainty. However, in our experiments with other systems, we do observe different deactivation rate constants and depolarization rate constants for different configurations. These results will be submitted soon.

3.2. From the depolarization rate constant to the magnetic substate transition rate constant

The main processes in the Sr($5^p\,^1P_1$)–Ar system, including collision induced magnetic substate transitions, spontaneous emission and collisional deactivation, are listed below:

Sr($5^p\,^1P_1$, $M_I = 0$) + Ar

$$\rightarrow k_e \text{Sr}(5^p\,^1P_1, M_I = \pm 1) + \text{Ar},$$

(2)

Sr($5^p\,^1P_1$, $M_I = \pm 1$) + Ar

$$\rightarrow k'_e \text{Sr}(5^p\,^1P_1, M_I = 0) + \text{Ar},$$

(3)

Sr($5^p\,^1P_1$, $M_I = 0$) $\rightarrow 1/\tau, \text{Sr}(\text{ground}),$

(4)

Sr($5^p\,^1P_1$, $M_I = \pm 1$) $\rightarrow 1/\tau', \text{Sr}(\text{ground}),$

(5)

Sr($5^p\,^1P_1$, $M_I = 0$) + Ar $\rightarrow k_d \text{Sr}(\text{ground}) + \text{Ar},$

(6)

Sr($5^p\,^1P_1$, $M_I = \pm 1$) + Ar $\rightarrow k'_d \text{Sr}(\text{ground}) + \text{Ar}.$

(7)

The rate equations for the system can be written as:

$$d[\left|0\right\rangle]/dt = -k_e[\text{Ar}][\left|0\right\rangle] + k'_e[\text{Ar}][\left|\pm 1\right\rangle]$$

$$-k_d[\text{Ar}][\left|0\right\rangle] - [\left|0\right\rangle]/\tau,$$

(8)

$$d[\left|\pm 1\right\rangle]/dt = k_e[\text{Ar}][\left|0\right\rangle] - k'_e[\text{Ar}][\left|\pm 1\right\rangle]$$

$$-k_d[\text{Ar}][\left|\pm 1\right\rangle] - [\left|\pm 1\right\rangle]/\tau',$$

(9)
where $[\text{Ar}]$, $[|0\rangle]$ and $[|\pm 1\rangle]$ denote the number densities of argon, $\text{Sr}(5p^1\text{P}_1, M_f = 0)$ and $\text{Sr}(5p^1\text{P}_1, M_f = \pm 1)$ respectively.

Assuming the magnetic substate transition processes in both directions have the same rate constants, and that the three magnetic substates of excited Sr atom have the same spontaneous emission and collisional deactivation processes, then, we have $k_E = k_E', \tau_i = \tau_i'$, $k_d = k_d'$, and the rate equations (8) and (9) can be written as:

$$d[|0\rangle]/dt = -k_E[\text{Ar}][|0\rangle - [|\pm 1\rangle]]$$
$$- k_d[\text{Ar}][|0\rangle - [|0\rangle]/\tau_i, \quad (10)$$
$$d[|\pm 1\rangle]/dt = k_E[\text{Ar}][|0\rangle - [|\pm 1\rangle]]$$
$$- k_d[\text{Ar}][|\pm 1\rangle - [|\pm 1\rangle]/\tau_i. \quad (11)$$

Assuming that the number density of argon stays constant during the process, it is very easy to get the solutions of Eqs. (10) and (11) in terms of the combined number densities of $[0\rangle$ and $[\pm 1\rangle$ as:

$$[|0\rangle + [|\pm 1\rangle] = [[|0\rangle + [|\pm 1\rangle]]_{t=t_0} \times \exp(-k_d[\text{Ar}]t - t/\tau_i), \quad (12)$$

$$[|0\rangle - [|\pm 1\rangle] = [[|0\rangle - [|\pm 1\rangle]]_{t=t_0} \times \exp(-k_d[\text{Ar}]t - t/\tau_i) \times \exp(-2k_E[\text{Ar}]t). \quad (13)$$

Since the intensities of the parallel and perpendicular components of $\text{Sr}(5p^1\text{P}_1)$ fluorescence are in direct proportion to the number densities of $\text{Sr}(5p^1\text{P}_1)$ in the relevant magnetic substates $|0\rangle$ and $|\pm 1\rangle$, the degree of polarization $P$ from formula (1) can be simply expressed as:

$$P = \frac{[[|0\rangle - [|\pm 1\rangle]]_{t=t_0} \times \exp(-2k_E[\text{Ar}]t)}{[[|0\rangle + [|\pm 1\rangle]]_{t=t_0}}. \quad (14)$$

From Eq. (14), we conclude $k_p = 2k_E$. Thus from the experimental result mentioned above, we can get the collision-induced magnetic substate transition rate constant $k_E = (1.25 \pm 0.25) \times 10^{-9}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

The discussion in Ref. [10] had mentioned the dealignment rate constant which was related to the polarization index. By using the deduced results of expressions (13) and (12), the polarization index, $R = (I_g - I_l)/(I_g + 2I_l)$, then can be written as:

$$R = 2 \exp(-2k_E[\text{Ar}]t)/(3 - \exp(-2k_E[\text{Ar}]t)), \quad (15)$$

in which we have assumed $[|\pm 1\rangle]_{t=t_0} = 0$ and $[|0\rangle]_{t=t_0} = [|0\rangle]$ to simplify the expression. The right-hand side in (15) can be expanded to $1 - 3k_E[\text{Ar}]t + \cdots$ which is just equivalent to the expansion of $\exp(-3k_E[\text{Ar}]t)$, thus the dealignment rate constant $k_d = 3k_E$. It just equals 1.5 times the depolarization rate constant $k_p$ which agrees with Setser’s discussion [15]. Our analysis shows that the dealignment rate constant $k_d$ is equal to $(3.5 \pm 0.7) \times 10^{-9}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

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References