

# Experimental evaluation of rate coefficients for Rb( $5D_J$ )+H<sub>2</sub> → RbH+H reaction

Qian Wang (王 倩)<sup>1,2</sup>, Yifan Shen (沈异凡)<sup>2\*</sup>, and Kang Dai (戴 康)<sup>2</sup>

<sup>1</sup>School of Science, Xi'an Jiaotong University, Xi'an 710049, China

<sup>2</sup>School of Physics Science and Technology, Xinjiang University, Urumqi 830046, China

\*E-mail: shenyifan01@xju.edu.cn

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The Rb( $5D_J$ )+H<sub>2</sub> → RbH+H photochemical reaction has been studied. Rb vapor mixed with H<sub>2</sub> is irradiated in a glass cell with 778-nm pulses which populate one of the  $5^2D$  states by two-photon absorption. Measurements for the relative intensities of the atomic fluorescence and the absorption of the RbH product near the axis of the cell yield the rate coefficients for the Rb( $5D_{3/2}$ )+H<sub>2</sub> and Rb( $5D_{5/2}$ )+H<sub>2</sub> reactions, which are  $(3.6 \pm 1.3) \times 10^{-11}$  and  $(1.7 \pm 0.6) \times 10^{-11}$  cm<sup>3</sup>/s, respectively. The relative reactivity with H<sub>2</sub> for Rb( $5D_{3/2}$ ) is higher than that for Rb( $5D_{5/2}$ ).

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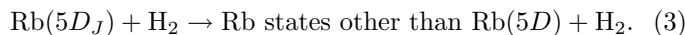
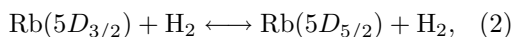
The collisions of excited alkali atoms with molecular hydrogen leading to a nonreactive inelastic scattering and the reactive collision leading to the formation of metal hydride have long been subjects of molecular dynamics<sup>[1–9]</sup>. They represent the simplest three-body problems and have been a very useful testing ground for a nonadiabatic process and other dynamical models. Although the collisions of excited alkali atoms with H<sub>2</sub> have been investigated for decades, there are still a limited number of systems for which one has both extended high-resolution experimental data and reliable theoretical calculations, and the related reaction mechanism is not well understood<sup>[10]</sup>. The reaction of Rb with H<sub>2</sub> has been far less studied than the other alkali-hydrogen reactions since only a few experimental works have been published<sup>[9,11]</sup>.

In this letter, we present experimental results of the reactive collisions between the Rb( $5D_J$ ) state and H<sub>2</sub> molecules. It may be represented as



Since the reaction (1) is exoergic by 0.4 eV, it is easy to occur. We can determine the relative reactivity of the Rb( $5D_{3/2}$ ) and Rb( $5D_{5/2}$ ) atoms with H<sub>2</sub> by the measurements for reaction rate coefficients.

When Rb atoms are selectively excited to one of the  $5^2D$  fine-structure states, its decay to the  $5P_{1/2}$  or  $5P_{3/2}$  state results in the emission of fluorescence. Before decaying, some of the primarily excited atoms may also undergo reactive collisions causing the formation of the ground state RbH molecules. Some others undergo inelastic collisions causing their transfer to the other  $5^2D$  fine-structure state and radiationless transfer to other lower-energy states. Therefore, in the Rb( $5D_J$ )-H<sub>2</sub> system, in addition to the reactive process (1), there exist the following energy transfer processes:



The processes (2) and (3) are nonreactive processes which have influence on the reactive process (1).

A partial energy-level diagram for rubidium, showing the states involved in the experiment as well as the transitions between them, is shown in Fig. 1. In our experiment, the Rb ground-state atom density in the vapor phase was about  $10^{13}$  cm<sup>-3</sup><sup>[12]</sup> while the density of H<sub>2</sub> molecules was about  $10^{17}$  cm<sup>-3</sup>. The collisional energy transfer due to the ground state rubidium may be neglected.

When the  $5D_{3/2}$  state is optically excited, the population density of the  $5D_{5/2}$  state may be represented by the rate equation

$$\frac{dn'_4(t)}{dt} = k_{34}Nn'_3(t) - (1/\tau_4 + k_4N + k_{43}N + k_{tr4}N)n'_4(t). \quad (4)$$

When the  $5D_{5/2}$  state is optically excited, the population density of the  $5D_{3/2}$  state may be represented by the rate equation

$$\frac{dn''_3(t)}{dt} = k_{43}Nn''_4(t) - (1/\tau_3 + k_3N + k_{34}N + k_{tr3}N)n''_3(t). \quad (5)$$

In Eqs. (4) and (5),  $\tau_s$  and  $n'_s$  (or  $n''_s$ ) are lifetimes and population densities of states with the subscripts  $s = 0 - 4$  corresponding to  $5S_{1/2}$ ,  $5P_{1/2}$ ,  $5P_{3/2}$ ,  $5D_{3/2}$ ,

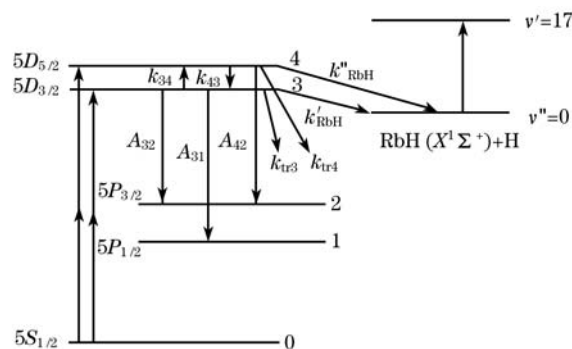


Fig. 1. Energy diagram of the Rb( $5D_J$ )+H<sub>2</sub> reactive and non-reactive energy transfer collisions.

$5D_{5/2}$ , respectively;  $N$  is the density of  $H_2$  molecules;  $k_{34}$  and  $k_{43}$  are the rate coefficients for energy transfers  $5D_{3/2} \rightarrow 5D_{5/2}$  and  $5D_{5/2} \rightarrow 5D_{3/2}$ , respectively, while  $k_{tr3}$  and  $k_{tr4}$  are the rate coefficients for energy transfers to all other Rb states;  $k_s$  ( $s = 3$  and  $4$  for  $5D_{3/2}$  and  $5D_{5/2}$ , respectively) is the rate coefficient for formation of RbH molecules in reaction  $Rb(5D_J) + H_2$ .

Although the population densities of the  $5^2D$  states are time dependent because of pulsed excitation, Eqs. (4) and (5) can be integrated to give<sup>[13]</sup>

$$\frac{N'_3}{N'_4} = \frac{1}{k_{34}\tau_4 N} + \frac{(k_{43} + k_{tr4} + k_4)}{k_{34}}, \quad (6)$$

$$\frac{N''_4}{N''_3} = \frac{1}{k_{43}\tau_3 N} + \frac{(k_{34} + k_{tr3} + k_3)}{k_{43}}, \quad (7)$$

where  $N'_3$  (or  $N''_3$ ) and  $N'_4$  (or  $N''_4$ ) represent the time-integrated density of the  $5D_{3/2}$  and  $5D_{5/2}$  states, respectively.

The intensity of the fluorescence at the photodetector can be written as

$$I(t) = \varepsilon h\nu n(t)AV, \quad (8)$$

where  $\varepsilon$  is the detection system efficiency that depends on the geometry of the detection system and the transmission of the optical elements,  $h\nu$  is the emission photon energy,  $n(t)$  is the population density of the radiating level,  $A$  is the Einstein coefficient for the transition, and  $V$  is the volume of the cell from which fluorescence is detected.

The corresponding time-integrated fluorescence intensities are

$$\Omega'_{31} = \int_0^\infty I_{31}(t)dt = h\nu_{31}\varepsilon_{31}N'_3A_{31}V, \quad (9)$$

$$\Omega'_{42} = \int_0^\infty I_{42}(t)dt = h\nu_{42}\varepsilon_{42}N'_4A_{42}V. \quad (10)$$

The time-integrated density ratios in Eqs. (6) and (7) can be determined from the corresponding measured time-integrated fluorescence intensities. The density ratios versus  $N^{-1}$  can be fitted by straight lines,  $k_{34}$ ,  $k_{43}$ ,  $k_{tr4} + k_4$ , and  $k_{tr3} + k_3$  can be determined from the gradients and intercepts.

Since RbH is created instantaneously<sup>[14]</sup>, the RbH density  $N_{RbH}(t)$  is related to the  $Rb(5D_J)$  concentration by

$$\frac{dN_{RbH}(t)}{dt} = N \sum_s k_s n_s. \quad (11)$$

This relation is only valid in the early part of RbH evolution when diffusion losses are still negligible. Because of the short lifetime of  $Rb(5D_J)$ , the maximum RbH density is

$$\begin{aligned} N_{RbH} &= \int_0^{t_m} \frac{dN_{RbH}(t)}{dt} dt = N \sum_s k_s \int_0^{t_m} n_s(t) dt \\ &\approx N \sum_s k_s \int_0^\infty n_s(t) dt = N \sum_s k_s N_s, \end{aligned} \quad (12)$$

where  $t_m$  is the time corresponding to the maximum RbH density.

A single-mode diode laser was used for the absorption measurement of the ground state RbH product of  $Rb(5D_J) + H_2$  reaction<sup>[15]</sup>. We directly measured the absorption of RbH molecules near the axis of the cell. The absorption intensity  $\Delta I$  can be expressed as

$$\Delta I(t) = \varepsilon N_{RbH}(t)h\nu w_{fi}L, \quad (13)$$

where  $\nu$  is the frequency of absorption line,  $w_{fi}$  is the transition rate, and  $L$  is the length of the cell.

The corresponding time-integrated absorption intensity is

$$\begin{aligned} \Delta\Omega &= \int_0^\infty \Delta I(t)dt \approx \varepsilon h\nu w_{fi}L \int_0^{t_m} N_{RbH}(t)dt \\ &= \varepsilon h\nu w_{fi}N_{RbH}\Delta t^*, \end{aligned} \quad (14)$$

where  $\Delta t^*$  represents the equivalent time span.

We can obtain from Eqs. (12) and (14) that

$$\frac{\Delta\Omega'}{\Delta\Omega''} = \frac{k_3 \frac{N'_3}{N'_4} + k_4}{k_3 \frac{N''_3}{N'_4} + k_4 \frac{N''_4}{N'_4}}, \quad (15)$$

where  $\Delta\Omega'$  and  $\Delta\Omega''$  are the time-integrated absorption intensities for optical excitation of the  $5D_{3/2}$  and  $5D_{5/2}$  states, respectively.

Equation (15) can be rearranged to obtain

$$\frac{\Delta\Omega'}{\Delta\Omega''} \cdot \frac{N''_3}{N'_4} = \frac{\frac{k_3}{k_4} \cdot \frac{N'_3}{N'_4} + 1}{\frac{k_3}{k_4} + \frac{N''_4}{N'_4}}. \quad (16)$$

The measured quantity  $\frac{\Delta\Omega'}{\Delta\Omega''} \cdot \frac{N''_3}{N'_4}$  versus  $N^{-1}$  can be fitted by least square method and the value of  $k_3/k_4$  can be obtained.

The experimental setup is shown in Fig. 2. A cylindrical cell which was made of Pyrex glass, was 10 cm long and 2.5 cm in diameter. The cell was connected to a vacuum and gas-filling system through a greaseless stopcock mounted inside the oven, which allowed the cell to be evacuated and filled with variable gas pressures. The oven was heated electrically. A few tens milligrams of Rb metal was redistilled under vacuum and distilled into the cell which had a vacuum of about  $10^{-7}$  torr. Temperatures were measured by several thermocouples attached to the cell. The cell was typically operated at a temperature of 393 K, at which the Rb vapor pressure was about 2 m torr.  $H_2$  gas was filled in the cell for use both as a buffer gas and as a reaction partner, and its pressure was measured with a capacitance manometer. The  $H_2$  gas pressure was varied over the range of 0 – 2 torr.

The radiation source was an optical parametric oscillator (OPO, Rainbow/NIR-D/S, which was called “pump laser”) pumped by a frequency-doubled  $Q$ -switched Nd:YAG laser (Brilliant B) with a pulse duration of 4 – 8 ns. The laser power was monitored simultaneously by an energy meter and adjusted in the range of 0.1 – 1 mJ.

The Rb( $5D_{3/2}$ ) and Rb( $5D_{5/2}$ ) states were populated by two-photon absorption, which was carefully confirmed by the quadratic laser-power dependence of their respective atomic fluorescence intensities. For the Rb( $5D_{3/2}$ ) excitation experiment, the pump laser was tuned to the Rb  $5S_{1/2} \rightarrow 5D_{3/2}$  two-photon atomic transition at 778.19 nm. For the Rb( $5D_{5/2}$ ) excitation experiment, the pump laser was tuned to the Rb  $5S_{1/2} \rightarrow 5D_{5/2}$  transition at 778.08 nm. The pump laser beam was directed along the axis of the cell. Fluorescence intensities from  $5D_{5/2} \rightarrow 5P_{3/2}$  (775.8 nm) and  $5D_{3/2} \rightarrow 5P_{1/2}$  (761.8 nm) transitions were measured as a function of H<sub>2</sub> gas pressure. The fluorescence was collected by a pair of lenses and an optical fiber at right angles to the laser beam's propagation direction. Fluorescence intensities from  $5D_{5/2} \rightarrow 5P_{3/2}$  and  $5D_{3/2} \rightarrow 5P_{1/2}$  transitions were analyzed by an optical multichannel analyzer (OMA, INS-300-122B, the integrated-time was set to 1 ms), while the stray light and dark count were deducted as background. The wavelength-dependent relative detection system efficiency  $\varepsilon$  was measured using a calibrated tungsten-halogen lamp.

A single-mode diode laser (DL100) was used for the absorption measurement of the ground state RbH product<sup>[16]</sup>. The power of the diode laser was cut down in the tens of nanowatts range with neutral density filters (NDFs). The diode laser beam was oppositely directed in a very small crossing angle to the pump laser beam and was chopped at an angular frequency  $\omega$ . The transmitted intensity of the diode laser beam was detected by a photomultiplier tube (PMT). The PMT signal was fed into a lock-in amplifier (SR830, the reference frequency was  $\omega$  and the integrated-time was set to 30 ms) and its output was then processed by a personal computer. The absorption spectrum of RbH was measured by monitoring the transmitted intensity of the diode laser beam while the diode laser was scanned across the spectral range from 852 to 863 nm covering the R branch of rovibrational level ( $\nu'' = 0 \rightarrow \nu' = 17$ ) of the ground state RbH molecules.

We centered at the location of stronger absorption spectral peak (861.1 nm) and calculated the time-integrated absorption intensity  $\Delta\Omega$  by integrating intensity over the R(2) spectral full width.

Figure 3 shows plots of Eqs. (6) and (7) against  $N^{-1}$  for selectively pumping the  $5D_{3/2}$  state or the  $5D_{5/2}$  state. It is shown that the experimental points can be fitted by straight lines very well. The

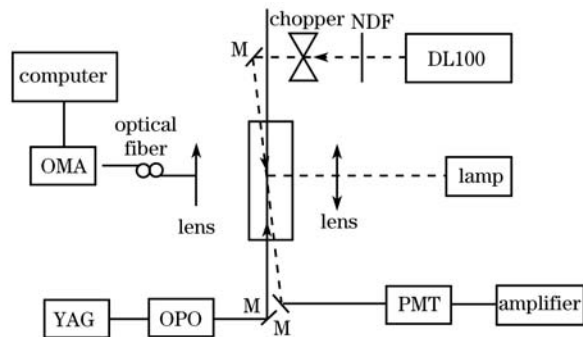


Fig. 2. Experimental setup. M: mirror; FM: frequency modulation; FSG: function signal generator.

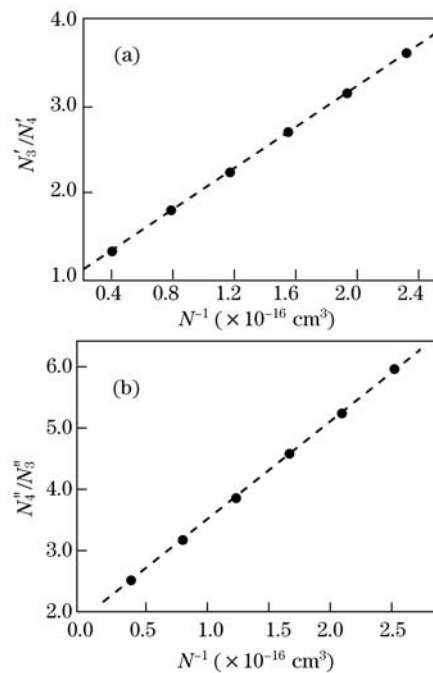


Fig. 3. Population ratios determined from observed fluorescence intensities against  $N^{-1}$ . (a) For pumping the  $5D_{3/2}$  state, (b) for pumping the  $5D_{5/2}$  state.

Einstein coefficients for three transitions  $5D_{3/2} \rightarrow 5P_{1/2}$ ,  $5D_{3/2} \rightarrow 5P_{3/2}$ , and  $5D_{5/2} \rightarrow 5P_{3/2}$  are derived from the known oscillator strengths<sup>[17]</sup>:  $A_{31} = 2.44 \times 10^6 \text{ s}^{-1}$ ,  $A_{32} = 0.64 \times 10^6 \text{ s}^{-1}$ ,  $A_{42} = 2.70 \times 10^6 \text{ s}^{-1}$ , and  $\frac{1}{\tau_3} = A_{31} + A_{32}$ ,  $\frac{1}{\tau_4} = A_{42}$ . The gradients and intercepts of the lines give the following rate coefficients:

$$\begin{aligned} k_{34} &= (2.4 \pm 0.5) \times 10^{-10} \text{ cm}^3/\text{s}, \\ k_{\text{tr}4} + k_4 &= (4.9 \pm 1.2) \times 10^{-11} \text{ cm}^3/\text{s}, \\ k_{43} &= (1.7 \pm 0.3) \times 10^{-10} \text{ cm}^3/\text{s}, \\ k_{\text{tr}3} + k_3 &= (6.8 \pm 1.7) \times 10^{-11} \text{ cm}^3/\text{s}, \end{aligned}$$

The uncertainties are due to errors in Einstein coefficients (10%), fluorescence ratio measurements (15%), pressure measurements (5%), least square analysis (5%). The uncertainty in  $k_{34}$  and  $k_{43}$  is estimated as 20% and the uncertainty in  $k_{\text{tr}3} + k_3$  and  $k_{\text{tr}4} + k_4$  is estimated as 25%, which is due to the uncertainties in both  $k_{34}$  and  $k_{43}$  (20%) and the extrapolation of the straight lines in Fig. 3 to zero  $N^{-1}$ .

Two observed absorption spectra of the RbH product, resulting separately from the reaction of Rb( $5D_{3/2}$ ) with H<sub>2</sub> and the reaction of Rb( $5D_{5/2}$ ) with H<sub>2</sub>, are shown in Fig. 4, in which pertinent spectral assignments are identified by using the given Dunham-type coefficients<sup>[18]</sup> for the ground state RbH. It is confirmed that the Rb( $5D_J$ ) atoms react with H<sub>2</sub> to produce the ground state RbH.

Figure 5 shows a plot of Eq. (16) against  $N^{-1}$ . It can be fitted by least square method, yielding the value  $k_3/k_4 = 2.10$ . If we assume  $k_{\text{tr}3} = k_{\text{tr}4}$ , we can obtain

$$\begin{aligned} k_3 &= (3.6 \pm 1.3) \times 10^{-11} \text{ cm}^3/\text{s}, \\ k_4 &= (1.7 \pm 0.6) \times 10^{-11} \text{ cm}^3/\text{s}, \text{ and} \end{aligned}$$

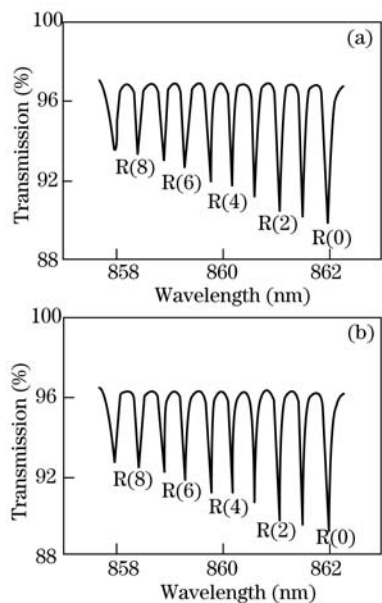


Fig. 4. Absorption spectra of the RbH ( $\nu=0$ ) products for (a) Rb( $5D_{3/2}$ )+H<sub>2</sub> and (b) Rb( $5D_{5/2}$ )+H<sub>2</sub>. The H<sub>2</sub> pressure is 1.5 torr.

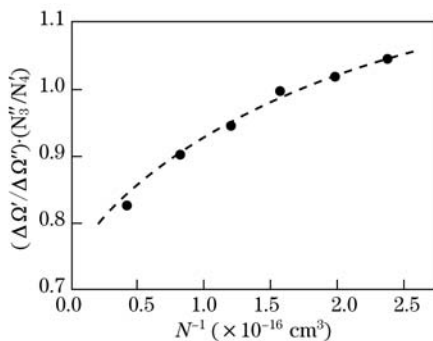


Fig. 5. Plot of the left-hand side of Eq. (16) against  $N^{-1}$ .

$$k_{tr3} = k_{tr4} = (3.2 \pm 1.1) \times 10^{-11} \text{ cm}^3/\text{s}.$$

The uncertainty in  $k_3$  and  $k_4$  is estimated as 35% due to errors in fluorescence ratio measurements (15%), absorption measurements (15%), pressure measurements (5%), least square analysis (5%), and the uncertainty in  $k_{tr3} + k_3$  and  $k_{tr4} + k_4$  (25%). The relative reactivity with H<sub>2</sub> for the two studied atoms is in an order of Rb( $5D_{3/2}$ ) > Rb( $5D_{5/2}$ ).

In conclusion, two reactions of Rb( $5D_{3/2}$ )+H<sub>2</sub> and Rb( $5D_{5/2}$ )+H<sub>2</sub> have been studied by measurements for

the atomic fluorescence intensity and the absorption of the RbH product. The reaction rate coefficients for Rb( $5D_{3/2}$ )+H<sub>2</sub> and Rb( $5D_{5/2}$ )+H<sub>2</sub> reactions are studied considering the influence of fine-structure mixing and quenching on the reactive process. The rate coefficients for the two reactions are obtained, and the relative reactivity with H<sub>2</sub> for Rb( $5D_{3/2}$ ) is higher than that for Rb( $5D_{5/2}$ ). Our derived relative reactivity is consistent with the previous conclusion made by Luh *et al.*<sup>[9]</sup>. We will continue a further comprehensive study for reactions in Rb\*-H<sub>2</sub> systems.

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