Effect of Mutual Configuration between Molecular Orientation and Atomic Orientation in the Oriented Ar ($^3P_2$) + Oriented CF$_3$H Reaction

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The steric effect in the dissociative energy transfer reaction of Ar ($^3P_2$, $M_J = 2$) + CF$_3$H has been observed as a function of the mutual configurations between the molecular orientation and the atomic orientation in the collision frame. The reactivity is significantly changed depending on the mutual configuration between the molecular orientation and the atomic orientation. Especially, the molecular alignment dependence is dramatically changed depending on the configuration of the atomic alignment.

For the reaction between two reactants having anisotropic structure, the mutual configuration between the two reactants should play an important role for the reaction dynamics because the interaction potential is anisotropic depending on the mutual configuration. In this case, the stereoanisotropy of one reactant is not invariant but variable depending on the configuration of another partner reactant. Moreover, it is expected that some combination of the mutual orientation between the two reactants is specifically favorable for the reaction. In other words, some kinds of molecular recognitions are expected even in a gas phase reaction. Here we apply the words "configurational correlation" to such specific stereoselectivity depending on the mutual orientation between the two reactants. However, no direct experimental study has been carried out for such subjects. So far, the studies on steric effects have been performed by using the electrostatic hexapole method [1–3], the optical pumping method [4–6], and the brute force method [7,8]. Despite the fact that steric effects are widely acknowledged as an important factor for the control of reaction dynamics, they are still limited to the study on the stereoanisotropy related to only one of the reactants in a small number of atom-molecular reaction systems.

A more challenging and important subject in reaction dynamics is the study of steric effects in the reaction between two reactants having anisotropic structure under the mutual orientation-controlled condition (i.e., doubly orientation-controlled study).

Here we report on a study of the mutual orientation dependence of the stereoanisotropy in the dissociative energy transfer reaction of Ar ($^3P_2$) + CF$_3$H, performed using both a beam of CF$_3$H molecules oriented by the electric hexapole method and a beam of Ar ($^3P_2$) oriented by the magnetic hexapole. Since the metastable rare-gas atom has the anisotropic electronic structure $np^5(n + 1)s^1$, it is important as a benchmark species to study the configurational correlation for the multiplet systems. The title reaction is one of the well-studied reaction systems to understand the molecular orientation effect on the energy

transfer process [9–11]. It is of great importance to compare the stereoselectivity depending on the mutual configuration of two reactants with the stereoselectivity related to only the molecular orientation previously reported. This energy transfer is known as the formation of two excited states of CF$_3$H that are characterized as the transitions from the $6a_1$ molecular orbital to the different Rydberg orbitals $6e$ and $8e$ for CF$_3$H (B) and $7a_1$ and $8a_1$ for CF$_3$H (C) [12,13]. The main exit channel of the title reaction is estimated to be the H elimination without emission because the CF$_3^*$ formation is competitive with other fast exit channels after the electron transfer has occurred [13].

Figure 1(a) shows a schematic drawing of an experimental apparatus for the doubly orientation-controlled study. The apparatus is composed of two state selectors. One is a 40-cm-long electrostatic hexapole for the oriented molecular beam. Another is a 35-cm-long magnetic hexapole for the oriented atomic beam. We accomplished the double orientation control by using both the oriented molecular and the oriented atomic beams whose configurations in the collision frame are independently controlled.

A supersonic CF$_3$H beam generated from a pulsed valve with a stagnation pressure of 400 torr was state selected by the electrostatic hexapole. The velocity distribution was determined to be the stream velocity of $v_s = 535 \pm 60$ ms^{-1} and the translational temperature of $T_{\text{trans}} = 22$ K by using a conventional time-of-flight measurement [14]. In order to estimate the orientational distribution, the trajectory simulation for state selection was carried out [15]. Figure 2(a) shows the focusing curve that is defined as the chemiluminescence intensity from the product CF$_3^*$ as a function of the hexapole voltage (V). The calculated focusing curve with the rotational temperature of $T_{\text{rot}} = 25 \pm 5$ K is in good agreement with the experimental one, which is shown in Fig. 2(a) as a solid line. According to the trajectory simulation, the orientational distribution of the molecular axis was calculated for the observed experimental condition at the hexapole voltage of 7 kV [16,17]. The calculated orientational distribution is shown in the inner panel in Fig. 2(a). The nth Legendre moments $\langle P_n \rangle$ for the
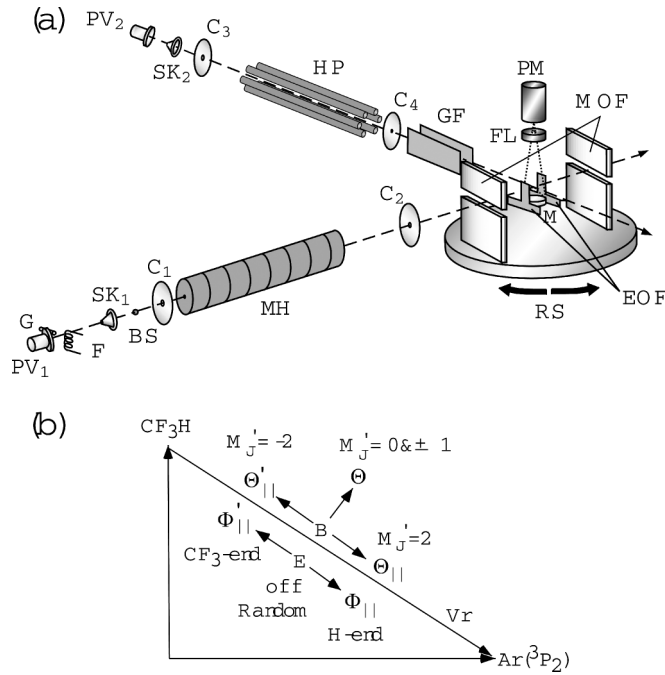
FIG. 1.   (a) A schematic drawing of the experimental apparatus for the doubly orientation-controlled study. PV_1: pulsed valve for the Ar (^3P) beam; G: grid; F: filament; SK_1, SK_2: skimmer; BS: beam stop; C_1, C_2, C_3, C_4: collimators; MH: magnetic hexapole; HP: electrostatic hexapole; RS: rotatable stage; PV_2: pulsed valve for the supersonic CF_3H beam; M: concave mirror; MOF: magnetic orientation field; GF: guiding field; EOF: electric orientation field; FL: filter; PM: photomultiplier. (b) Relationship between the nine mutual configurations of magnetic orientation field $\boldsymbol{B}$ and electric orientation filed $\boldsymbol{E}$ to the relative velocity v_r.

orientational distribution are summarized to be $\langle P_1 \rangle = 0.37$, $\langle P_2 \rangle = -0.082$, $\langle P_3 \rangle = -0.064$, $\langle P_4 \rangle = 0.032$, and $\langle P_5 \rangle = 0.013$. The error of the Legendre moments is estimated to be less than 10%. The molecular orientation in the collision frame was controlled to be CF_3-end, H-end, and random orientation by changing the direction of a uniform electric field at the beam crossing point. The electric orientation field of 200 V cm^{-1} was prepared by a pair of aluminum electrode plates tilted at a 37.5° angle against the direction of the Ar $(^3P_2)$ beam axis that corresponds to the direction of relative velocity v_R.

A metastable Ar $(^3P_2)$ beam was generated by a pulsed grow discharge with a pulse width of 100 μs and state selected by the magnetic hexapole. The M_J state distribution of the state-selected Ar $(^3P_2)$ beam was directly determined by separating each M_J state using a Stern-Gerlach–type inhomogeneous magnetic state selector (SGIM). As shown in Fig. 2(b), the state-selected metastable Ar $(^3P_2)$ beam within the time region (I) ($1.28 \leq t_0 \leq 1.54$ ms) is composed of almost pure Ar $(^3P_2, M_J = 2)$ (more than 93%). The chemiluminescence signal within this time region (I) is used for further study. The velocity of the Ar $(^3P_2, M_J = 2)$ beam within this time region corre-
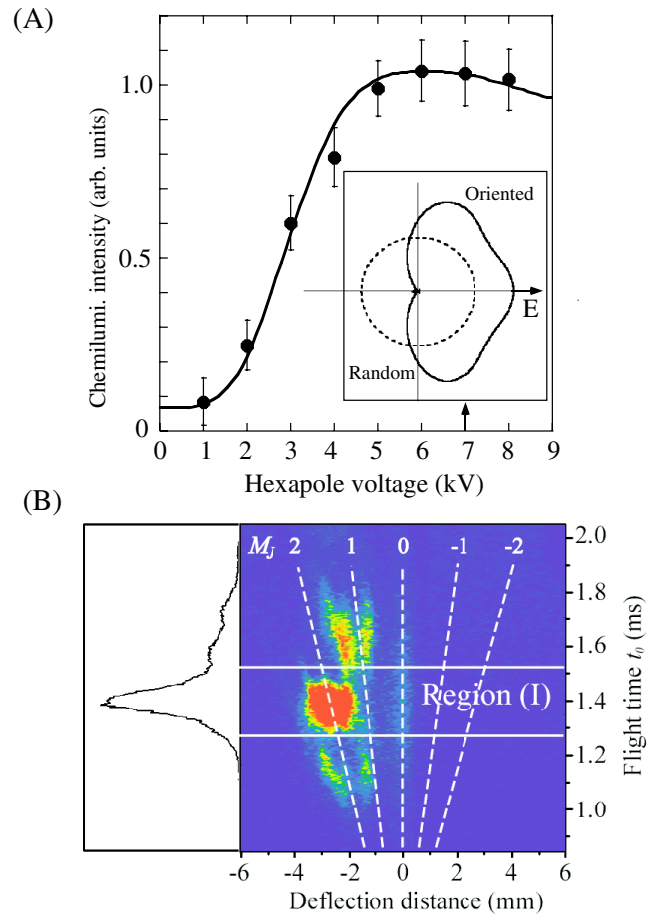

FIG. 2 (color online).   (a) Focusing curve defined as the signal intensity of the product CF_3^* as a function of the hexapole voltage V; experiment ($\bigcirc$) and calculated one via a trajectory simulation (solid line). (Inner panel) Polar coordination representation of the orientational distribution of the state-selected CF_3H beam at $V = 7$ kV (solid line) and random orientation (dashed line). (b) 3D image of the state-selected Ar $(^3P_2)$ beam by the magnetic hexapole after the deflection by the SGIM.

sponds to $v_s = 700 \pm 30$ ms^{-1}. The atomic orientation in the collision frame was controlled by rotating the direction of the magnetic orientation field $\boldsymbol{B}$ that was prepared by four pieces of ferrite magnet mounted on a motor-driven rotatable stage.

Under the doubly orientation-controlled conditions, the state-selected Ar $(^3P_2, M_J = 2)$ beam was collided with the oriented CF_3H beam at the beam crossing point. The chemiluminescence signal in the visible region from the product CF_3^* was detected by a cooled and magnetic-shielded photomultiplier through a band-pass filter (FL: $\lambda = 500 \sim 700$ nm) [18]. Only the signal enhanced by the electric hexapole field was extracted as the substantial chemiluminescence signal from the oriented CF_3H + oriented Ar $(^3P_2, M_J = 2)$ reaction. The net signal was obtained by subtracting the background signal measured at the electrostatic hexapole voltage of 0 kV. The chemiluminescence intensity from the product CF_3^*, $I(\Theta, \Phi)$, was

measured at several mutual configurations between the atomic orientation Θ and the molecular orientation F. For the atomic orientation of Ar ($^3P_2$), three configurations were representatively selected against the direction of the relative velocity: i.e., parallel ($\Theta_{\parallel}$), perpendicular ($\Theta_{\perp}$), and antiparallel ($\Theta'_{\parallel}$) configuration. The contribution of each M'_J state at three configurations can be simply expressed by $|d^2_{M'_J 2}(\Theta - \Theta_{\parallel})|^2$ using the Wigner d function [17]. Here M'_J is the magnetic quantum number in the collision frame. These three configurations for the atomic orientation correspond to $M'_J = 2, 0$ and ± 1, and -2 states for Ar ($^3P_2$), respectively. Similarly, three representative configurations were selected for the molecular orientation: i.e., CF$_3$-end ($\Phi'_{\parallel}$), H-end ($\Phi_{\parallel}$), and random orientation (orientation field off). These configurations are illustrated in Fig. 1(b).

The electric orientation field direction Φ was changed every 100 pulses in turn at three configurations of the atomic orientation Θ. The configurations of the atomic orientation were changed every 3000 pulses in turn. To obtain an acceptable signal to noise ratio, the data were accumulated up to 1.4×10^5 beam pulses at each mutual configuration condition.

Figure 3 shows the chemiluminescence intensity $I(\Theta, \Phi)$ under the nine different combinations of the configuration between the molecular orientation ($\Phi'_{\parallel}$, $\Phi_{\parallel}$, and random) and the atomic orientation ($\Theta_{\parallel}$, $\Theta_{\perp}$, and $\Theta'_{\parallel}$). It is easily found that the Θ dependence (atomic orientation) significantly depends on the molecular orientation. For the CF$_3$-end orientation, the reactivity at $M'_J = 0$ and ± 1 states is found to be higher than that at $|M'_J| = 2$ states.
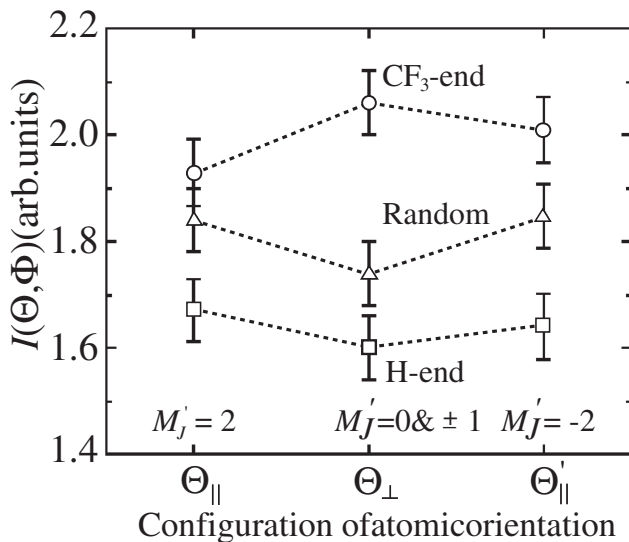
On the other hand, the reactivity at $M'_J = 0$ and ± 1 states is lower than that at $|M'_J| = 2$ states for both the H-end and random orientations. A clear configurational correlation between the atomic orientation and the molecular orientation was observed for the first time.

In order to extract the qualitative information on the configurational correlation, the orientation and the alignment terms for the steric effect on molecule are defined as follows:

$$\text{Orientation: } O(\Theta) \equiv 1/2 \times [I^O_{CF_3}(\Theta) - I^O_H(\Theta)],$$
$$\text{Alignment: } A(\Theta) \equiv 1/2 \times [I^O_{CF_3}(\Theta) + I^O_H(\Theta)] - 1. \quad (1)$$

Here $I^O_{CF_3}(\Theta)$ and $I^O_H(\Theta)$ are the steric effect at CF$_3$-end and H-end orientation, respectively, defined as the relative cross section to that at the random orientation:

$$I^O_{CF_3}(\Theta) \equiv I_{CF_3}(\Theta)/I_{Random}(\Theta),$$
$$I^O_H(\Theta) \equiv I_H(\Theta)/I_{Random}(\Theta). \quad (2)$$

The orientation and the alignment terms are shown in Fig. 4 as a function of the configuration of the atomic orientation.

Because the orientation terms $O(\Theta)$ are positive for every Θ configuration, the CF$_3$-end orientation is found to be the most reactive for every configuration of the atomic orientation according to the positive orientation term $\langle P_1 \rangle = 0.37$ for the orientational distribution of the CF$_3$H beam. The collision of Ar ($^3P_2$) with the configuration of $M'_J = 0$ and ± 1 states is most anisotropic with respect to the molecular orientation because of the largest $O(\Theta)$.
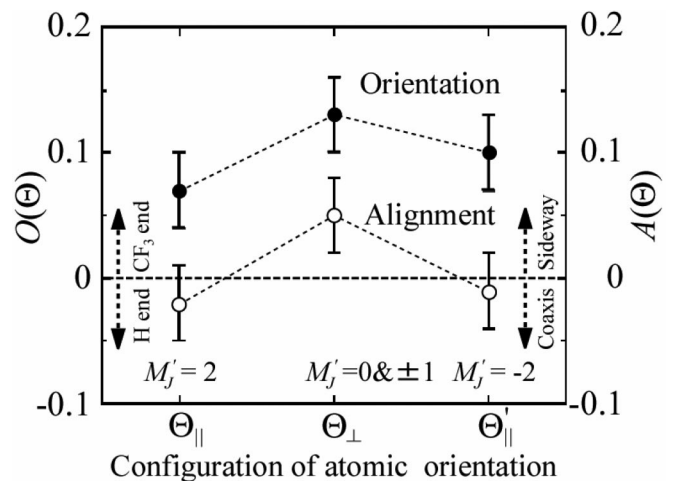

FIG. 3. M'_J dependence for the chemiluminescence intensity of CF$_3^*$ in the reaction of Ar ($^3P_2$, $M_J = 2$) + CF$_3$H under the three orientation conditions: CF$_3$-end collision (●), H-end collision (■), and random orientation (▲). The error bar shows the confidence interval for 95% confidence coefficient.

FIG. 4. Molecular orientation $O(\Theta)$ and alignment $A(\Theta)$ effects in the Ar ($^3P_2$, $M_J = 2$) + CF$_3$H reaction under the three configurations for the atomic orientation: parallel ($\Theta_{\parallel}$), perpendicular ($\Theta_{\perp}$), and antiparallel ($\Theta'_{\parallel}$); $A(\Theta)$ (○), $O(\Theta)$ (●). The error bar shows the confidence interval for 95% confidence coefficient.
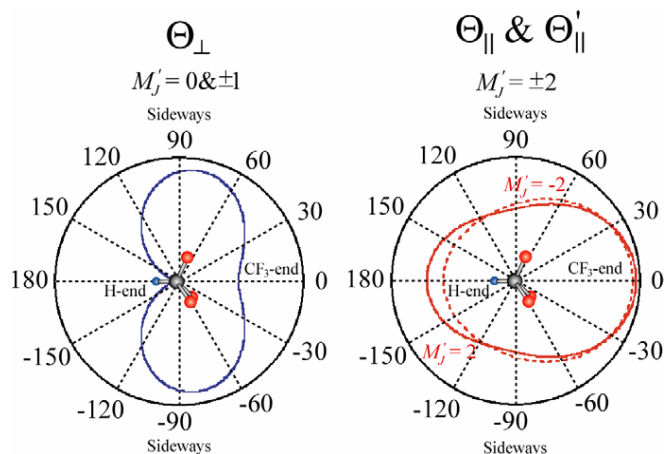
FIG. 5 (color online).　Molecular steric opacity functions calculated by using $O(\Theta)$ and $A(\Theta)$ for three atomic orientations $M'_J = 0$ and ± 1 and $M'_J = \pm 2$ under the approximation that the Legendre expansion of the orientational distribution can be truncated up to $n = 2$.

It is found that the alignment terms $A(\Theta)$ have small negative values for $|M'_J| = 2$ states, while the $A(\Theta)$ for $M'_J = 0$ and ± 1 states have a positive value. This result indicates that the favorable molecular alignment is changed depending on the configuration of the atomic alignment. Under the approximation that the Legendre expansion of the orientational distribution can be truncated up to $n = 2$, the molecular steric opacity functions with Legendre fitting were calculated by using $O(\Theta)$ and $A(\Theta)$. They are summarized in Fig. 5. According to the negative alignment term of $\langle P_2 \rangle = -0.082$ for the orientational distribution of the CF$_3$H beam, the collision of Ar ($^3P_2$) with the configuration of $M'_J = 0$ and ± 1 states is found to be favorable for the approach from the sideways direction. On the other hand, the collision of Ar ($^3P_2$) with the configuration of $|M'_J| = 2$ states is favorable for the coaxial approach. The existence of three reactive sites at both the coaxial and the sideways directions is in good agreement with the steric opacity function on molecular orientation previously reported [9] and the molecular orientation dependence for the emission spectra of product CF$_3^*$ [10].

We have calculated the transition matrix element for the electron exchange processes by the CASSI (CASSCF state interaction) method [11]. The theoretical calculation of the electron exchange matrix indicated that the most favorable mutual configuration is the $L_z = 0$ atomic orbital configuration for the coaxial approach at the CF$_3$ end, and the $|L_z| = 1$ configuration is extremely less reactive as compared with the $L_z = 0$ configuration. Therefore, it is apparent that the observed configurational correlation conflicts with the calculated mutual orientation dependence of the electron exchange probability. In other words,

the energy transfer cross section does not simply reflect the mutual orientation dependence of the transition matrix. Although it is difficult to correctly understand the nature of the configurational correlation at this stage, it is expected that the spin interaction and/or the dynamical effect give a significant effect for the energy transfer probability. On the basis of the molecular orientation dependence of the emission spectra previously reported [10], the observed configurational correlation strongly suggests that the mutual orientation between two reactants plays an important role for the selectivity of the final Rydberg states of CF$_3$H having different symmetry, e symmetry for CF$_3$H (B) and a_1 symmetry for CF$_3$H (C) [12].

In conclusion, we performed the study of the steric effect for the energy transfer process under the doubly orientation-controlled condition. A clear stereoselectivity depending on the mutual orientation between two reactants (configurational correlation) was recognized.

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