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Orientation Dependence of Transition Matrix Elements for Energy Transfer Reaction $CF_3H+Ar(^3P) \rightarrow CF_3*+Ar+H$

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Transition matrix elements for the energy transfer were explicitly evaluated by *ab initio* SCF calculations in the $CF_3H+Ar(^3P) \rightarrow CF_3*+Ar+H$ reaction. The matrix elements were obtained as functions of mutual orientation and distance between the reactants. The results show that the collision along the symmetry axis of the CF_3H is preferable to produce the excited CF_3H in the B or C state. On the other hand, the E state was found to be preferably generated by the side-on attack of $Ar(^3P)$. The present results agree well with the ones given by the electron density analysis, suggesting that the electron exchange process is dominant for showing the steric anisotropy in the title reaction.

Effects of molecular orientation on the dissociative energy transfer reaction of $CF_3H+Ar(^3P) \rightarrow CF_3*+Ar+H$ have been studied using oriented molecular beams and it was found that steric opacity function showed three reactive sites.[1-5] A recent study of electron density analysis showed that a close correlation exists between the shape of the steric opacity function and the spatial electron density of the relevant molecular orbitals.[4] In this paper we explicitly evaluate the transition matrix elements of the electron exchange process as a function of the mutual orientational angle and the distance between the reactants.

Electron exchange proceeds as follows.[6-8] An electron of the CF_3H molecule is transferred to the vacant 3p inner shell of the metastable Ar atom and simultaneously the electron in the 4s outer shell of the atom moves to a Rydberg orbital of the molecule. The transition matrix element V_{if} ($\equiv H_{if}$) in such a case is given by eq. (1).

$$\begin{aligned} V_{if} &= \langle \varphi_f | H | \varphi_i \rangle \\ &= \langle 3p(1)Ryd(2)\varphi | H | MO(1)4s(2)\varphi \rangle \end{aligned} \quad (1)$$

where 1 and 2 denote the electrons that exchange and φ represents the core molecular orbitals. The initial wavefunction φ_i is represented by the product of the molecular orbital, MO(1) and the Rydberg orbital of the atom, 4s(2). Similarly, the final wavefunction φ_f is represented by the product of the atomic orbital, 3p(1) and the Rydberg orbital of the molecule, Ryd(2). A rule of the matrix element tells that V_{if} ($\equiv H_{if}$) is simply reduced to the following two terms.

$$\begin{aligned} V_{if} &= < 3p(1)Ryd(2)|\ 1/r_{12}|\ MO(1)4s(2) > \\ &= [\ 3p(1)Ryd(2)|\ 1/r_{12}|\ MO(1)4s(2)\ ] \\ &\quad - [\ 3p(2)Ryd(1)|\ 1/r_{12}|\ MO(1)4s(2)\ ] \end{aligned} \qquad (2)$$

The r_{12} is the distance of the two electrons 1 and 2 which exchange. The first term in eq. (2) describes the electron exchange process and the second one is de-excitation of $Ar(^3P)$. Because $Ar(^3P)$ is metastable, the second term is regarded to be negligibly small.[8] It is noteworthy that this expression is valid only if the CI wavefunction of the excited CF_3H can be mainly described by a single configuration. Thus we confirmed the usefulness of this approximation for the present reaction in a previous calculation.[4] The ionization potentials for the $6a_1$(HOMO) and the $1a_2$(HOMO-1) orbital electrons of CF_3H are nearly equal to that of the 3p orbital energy of Ar.[10] Therefore it is likely that the $6a_1$ and $1a_2$ orbital electrons are exchangeable with the 3p electron of the atom.

Although the previous electron density calculation[4] has shown a good agreement between the electron density of $6a_1$ and $1a_2$ orbitals and the three-reactive-sites model, 3p, 4s, and the Rydberg orbitals were assumed to be isotropic in space. In this paper we directly evaluate the transition matrix elements, employing *ab initio* SCF method for the whole reaction system including Ar atom. The matrix element V_{if} expressed as eq. (2) can be expanded by the atomic orbitals,

$$\langle \psi_A(1)\psi_B(1)|1/r_{12}|\psi_C(2)\psi_D(2)\rangle = \sum_{i,j,k,l}^{n} C_{Ai}C_{Bj}C_{Ck}C_{Dl}\langle \phi_i\phi_j/\phi_k\phi_l\rangle \qquad (3)$$

where C_{Ai}, C_{Bj}, C_{Ck}, and C_{Dl} are the LCAO coefficients for the molecular orbitals ψ_A, ψ_B, ψ_C, and ψ_D respectively.For calculating eq. (3), we have developed a simple program routine which is linked to HONDO package.[11] Calculations were carried out in RHF level. Huzinaga's MIDI(C(43/4), F(43/4), Ar(433/43), H(31)) gaussian basis set is used and extended by polarization functions and diffuse type orbitals on carbon(ζ_s = 0.062, ζ_p = 0.013) and Ar(ζ_s = 0.073, ζ_p = 0.018) atoms to describe the Rydberg type orbitals. The computational model constructed here is mainly based on the calculation of Larrieu *et al.*[10] They carried out the multireference SDCI calculation for several electronic excited states of CF_3H and give good correspondence to the experimental energy. They assigned the transition type of the related excited CF_3H, B, C and E states as

follows.

B: $6a_1 \rightarrow$ 6e, 8e (Ryd 3p)

C: $6a_1 \rightarrow 7a_1$, $8a_1$ (Ryd 3p)

E: $1a_2 \rightarrow$ 6e, 8e (Ryd 3p)

Based on this assignment, we determine the simplified configurations for the B, C and E states as $6a_1 \rightarrow$ 6e, $6a_1 \rightarrow 7a_1$ and $1a_2 \rightarrow 6e$, respectively. The configuration of the initial state which describes the Arexcitation(^3P) is ($3p_x$, $3p_y$ $3p_z$) $\rightarrow$ 4s. Thus $|V_{if}|^2$ are calculated for the region from 0 to 1 angstrom with an interval 0.2 angstrom for each orientational angle γ. The calculated points were fitted by an analytic function $f(r) = ar\exp(-br)$. We integrate $f(r)$ from R_t to ∞, and make it a measure for the transition probability.

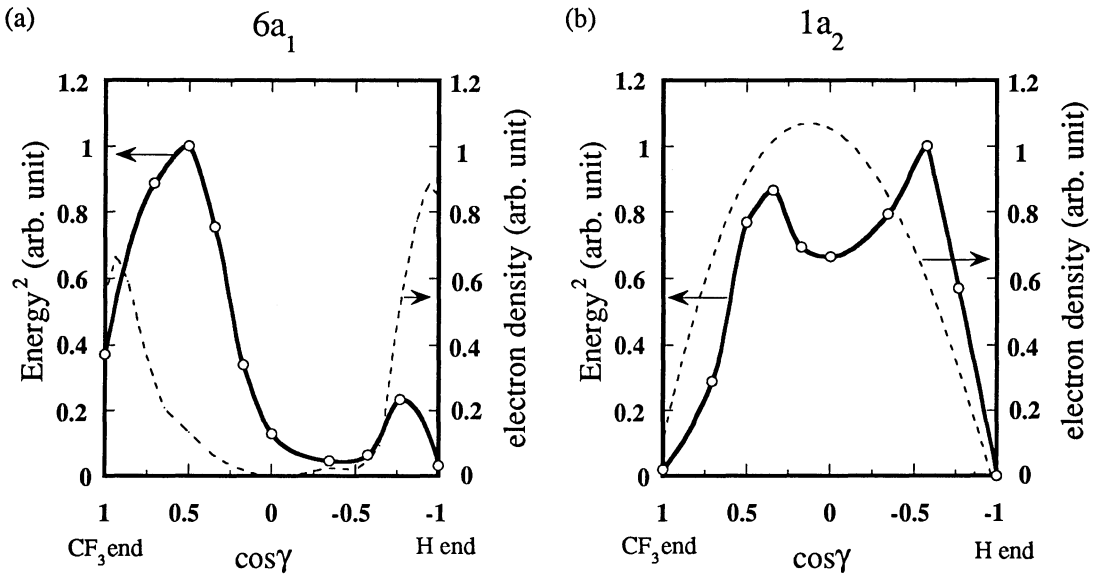

Fig. 1. Orientational dependence of the integrated square of transition matrix elements(open circles with solid lines) for the B or C state; (a), and for the E state; (b). The broken line shows the electron density on the van der Waals surface for $6a_1$; (a) and $1a_2$; (b) sited from Ref. 4. The maximum values of (a) and (b) are normalized to 1.

The open circles of the solid line in Fig. 1(a), (b) show the result of the integration for each orientational angle. Figure 1(a) exhibits two sites of high transition probability to the B or C state near the CF_3-end and the H-end. The CF_3- end attack of Ar(^3P) is found to be more preferable than the H-end attack in this calculation. The broken line also shows two peaks.[4] The two lines have a similar tendency, but the relative height of the two peaks of the solid line in Fig. 1(a) was found to agree better with the steric opacity function. It is noticeable that the two peaks shift to off axis at the two ends. Figure 1(b) shows a reactive site peaked at the side-on, however, there is a depression near $\cos\gamma = 0$. Transition to the E state exhibits alignment behavior in either the present or the previous calculation(broken line).[4] This peak can be assigned to the reactive site

peaked at $\gamma = 70°$ in the steric opacity function. As a whole, the calculation of transition matrix elements has given common characteristic with the electron density analysis. Significant improvements as mentioned above can be achieved by including the interaction of the Ar atom. How the contributions from the 3p and 4s orbital of Ar differ may be an open question.

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