# Wave Packet Simulation on the Cage Effect in the Full Scattering : $CF_3H+Ar(^3P) \rightarrow CF_3^*+H+Ar$

Hideaki Takahashi, Toshio Kasai,* and Kizashi Yamaguchi
*Department of Chemistry, Faculty of Science, Osaka University, Machikaneyama, Toyonaka, Osaka 560*

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The orientation-dependent wave packet dynamics was investigated for the dissociative energy transfer reaction : $CF_3H+Ar(^3P) \rightarrow CF_3^*+H+Ar$. Wave packets were propagated numerically by the Chebychev scheme recently developed by Kosloff *et al.* The calculation was done for the two orientations of $CF_3H$, one is the H-end orientation and another is the $CF_3$-end orientation under the collinear geometry. The results showed clear orientation dependence in the dissociation process. The H-end orientation seems to give a quantum effect, while the $CF_3$-end does not.

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Stereo-dynamics is one of the most intriguing problems in chemical reactions. There have been a body of experimental and theoretical studies on the steric effects.[1] As a recent example, using the oriented molecular beam method, the orientation-dependent reactivity was revealed for the dissociative energy transfer reaction: $CF_3H+Ar(^3P) \rightarrow CF_3^*+H+Ar$. In this experiment, the $CF_3$-end orientation is found to be extremely preferable for the reaction as compared with the H-end orientation.[2] Analysis of electronic structure could elucidate the reason for such an effect to some extent.[3] Two analyses were done, one is the electron density calculation for relevant molecular orbitals and the other is computation of electronic coupling between initial and final electronic states within the single and multi-configuration pictures. These theoretical calculations supported the site-specific reactivity experimentally observed.

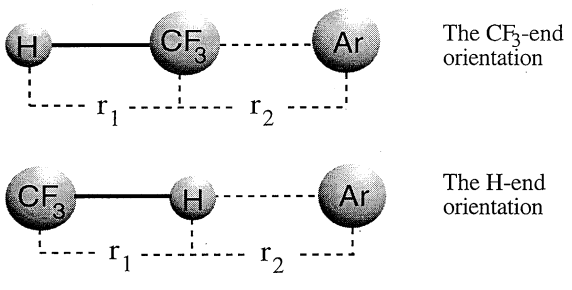

**Figure 1.** Coordinate systems for two collinear orientations.

In this paper, we investigated the orientation-dependent nuclear dynamics of this reaction. Especially, when Ar approaches to H-end, the system forms "heavy-light-heavy" geometry. Such a system is important in the study of clusters and solvation effect. The time propagation of the wave packets is done by solving the coupled time-dependent Schrödinger equation numerically. Calculation was done for the H-end and the $CF_3$-end orientation. Because this reaction proceeds via non-adiabatic process and involves the lightest nuclear, quantum mechanical treatment is essential for the study of nuclear dynamics. We employed the method recently developed by Kosloff *et al*, in which time propagator is expanded into Chebyshev polynomials.[4] To obtain intermediate results, propagation is split into smaller intervals. The interval is defined as 20 a.u. For a system with two electronic states involved, time-dependent Schrodinger equation is expressed in 2×2 matrix,

$$i\frac{\partial}{\partial t}\begin{pmatrix}\phi_a\\ \phi_b\end{pmatrix}=\begin{pmatrix}H_{aa} & H_{ab}\\ H_{ba} & H_{bb}\end{pmatrix}\begin{pmatrix}\phi_a\\ \phi_b\end{pmatrix} \qquad (1)$$

where $\phi_a$ and $\phi_b$ are the nuclear wavefunctions on the two electronic states($\hbar=1$ throughout this article, unless otherwise specified). Representation of Hamiltonian is done by finite difference scheme. In this calculation $CF_3$ group is approximated as a rigid ball and three particles are restricted in the collinear geometry. Consequently, two degrees of freedom are considered throughout this calculation. Coordinates for two degrees of freedom for two orientations are shown in Figure 1 for an easy reference. This coordinates define a kinetically coupled Hamiltonian,

$$H=-\frac{1}{2\mu_{12}}\frac{\partial^2}{\partial r_1^2}+\frac{1}{2\mu_{13}}\frac{\partial^2}{\partial r_1\partial r_2}-\frac{1}{2\mu_{23}}\frac{\partial^2}{\partial r_2^2}+V_{a,b}(r_1,r_2) \qquad (2)$$

where $\mu_{12}$,$\mu_{13}$ and $\mu_{23}$ are the reduced masses for each coordinate system and $V_{a,b}(r_1,r_2)$ are the orientation-dependent potential energies for ground and excited electronic state. The electronic excited state participated in this calculation is the C state of $CF_3H$, which was suggested to be most relevant for the reaction in Ref. 3. The electronic couplings $H_{ab}$ in Eq. (1) and orientation-dependent potential energies $V_{a,b}$ in Eq. (2) are calculated by CASSI and CASSCF method and the computational details are described in previous papers.[3] The potential parameters suggested by Wagner *et al.* are adopted for Ar-H repulsive potential.[5] The momentum of the initial wavepacket is adjusted to the experimental collision energy 0.12eV for both orientations.

In the present work, we focused on the dissociation dynamics for two collinear orientations. Density currents of the dissociating wavepacket were calculated at each time step and plotted as a function of time. To calculate the density current of the dissociating wavepacket, the probability was integrated along the $r_2$ coordinate with $r_1$ fixed at 3.7au for the $CF_3$-end orientations and similarly wavefunction is integrated along the $r_1$ coordinate with $r_2$ fixed at 9.5 au for the H-end orientation. Therefore, the density current thus defined is identical to probability flux. The results for the two orientations are shown in Figure 2. One can recognize differentiating feature in time-profiles of density current between two orientations. For the $CF_3$-end orientation, at the beginning density current increases uniformly and at the end decreases, which corresponds

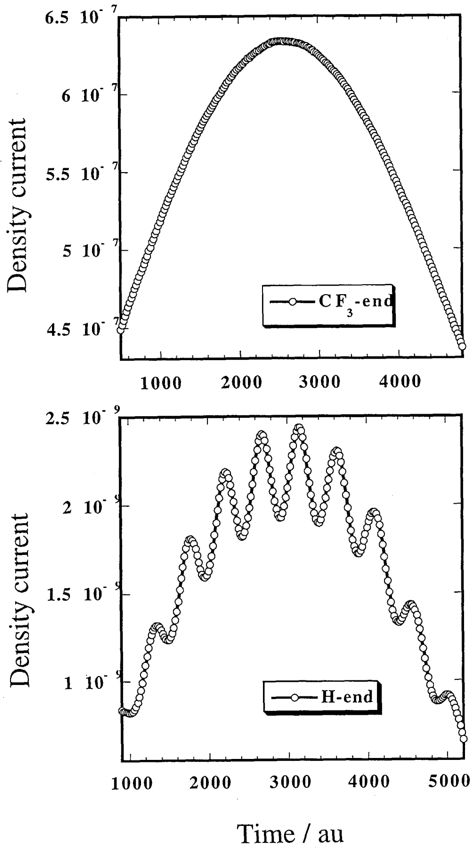

**Figure 2.** Time profiles of density current for the $CF_3$-end and the H-end orientations of $CF_3H$.

to approach and separation of the Ar atom, respectively. So the smooth curve represents the dynamics of argon atom near the turning point. For the H-end orientation, on the other hand one can find significant oscillations on the smooth curve, which could be attributed to interference effects of H atom. Recently, photodissociation of HCl in Ar-HCl van der Waals cluster has been investigated by Gerber *et al.*[6] and they found significant interferences in angular and kinetic energy distributions of H photofragment. Such a phenomenon is called "cage effect". The cage effect refers to the influence of the surrounding medium on the dynamics of the reaction intermediates or products as analogue to solvation effects in liquid-phase.[7] Cage molecules or atoms could prevent the mutual separation of the products and cause recombination or delay of dissociation. In the case that $CF_3H$ is H-end oriented, hydrogen is caged by heavy particles, Ar and $CF_3$. Therefore, we may be able to regard the present results as a cage effect in a *full scattering* process. In a more realistic image of the collision of atom with an oriented molecule, Ar-$HCF_3$ may be slightly bent in its most probable geometry, though impact parameter is assumed to be zero. However collinear collision is a over-simplified model, same effect will be expected in a realistic collision since substantial amount of hydrogen wavepacket could reach the interaction region of Ar potential. As was shown by Schröder *et al.* in ref. 6, more than 50 percent of the wavepacket is deflected by the repulsive potential of Ar atom in the photodissociation of Ar-HCl in the bent geometry. In this wave packet simulation, another interest is the magnitude of the product which can be compared to experimental results. Since this simulation includes not only the orientation-dependent couplings but also the anisotropic potential energy, quantitative comparisons can be made for the two orientations. In Figure 2 one can estimate that the intensity of the density current of the $CF_3$-end orientation at the turning point of Ar atom is about 250 times larger than that of the H-end orientation. This means that the $CF_3$-end orientation is more than $10^4$ times preferable than the H-end orientation for the total reaction probability. We conclude that dissociating products are not uniformly produced when $CF_3H$ is H-end oriented. This effect will vanish when Ar approaches to $CF_3$-end.

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