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Collision Energy Dependence Measurement of the Total De-excitation and the CF_3^* Chemiluminescence Cross Sections in the $Ar(^3P)$ Reaction with CF_3H

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The collision energy dependences of the total de-excitation and the CF_3^* chemiluminescence cross sections were measured in the reaction of $Ar(^3P)$ with CF_3H using conventional and cross-correlation TOF methods. In the latter method, which is favorable for detecting weak signals, we employed a pseudorandom pulse discharge to generate a metastable argon beam. The collision energy dependence for the CF_3^* chemiluminescence channel gives a positive slope as a function of the collision energy with a threshold of 0.10 eV. The collision energy dependence of the total de-excitation in the entrance channel, on the other hand, shows a steep decrease as a function of collision energy without any threshold. These results provide insight into the detailed dynamics at crossing points of the potential energy surfaces.

Reactions of metastable rare-gas atoms with small molecules have provided a long-standing interest in understanding the branching mechanisms in the entrance as well as exit channels of the reaction. The excitation and dissociation processes of small molecules by metastable atoms have been extensively studied by means of emissions from reaction products in the visible and ultraviolet region. In many cases, because the branching fraction to an emissive product is small, information about such minor exit channels is lacking. Also little is known about its reaction dynamics. To measure the collision-energy dependence of a specific reaction cross section is important to understand the detailed reaction dynamics, which provides details concerning the non-adiabatic transitions on multi-potential energy surfaces.

As for the CF_3^* chemiluminescence channel in the $Ar(^3P) + CF_3H$ reaction, we found a steric effect by using an oriented CF_3H molecular beam, which revealed three reactive sites in the steric opacity function.[1] We temporarily concluded that this stereo-selectivity is due to the efficiency of the electron exchange between the 3p hole of an $Ar(^3P)$ metastable atom and the $6a_1$ molecular orbital of CF_3H. However, it is still an unresolved problem how this chemiluminescence channel competes with the dark channel, which is regarded to be major, while the CF_3^* emission chancel gives only a 0.02 ± 0.01 branching fraction among the total quenching processes of $Ar(^3P)$, which corresponds to a cross section of less than 1 $Å^2$.[2]

In order to clarify whether or not the dark channel is responsible for the branching competition in the exit channels, simultaneous measurement of the collision energy dependence for the entrance as well as in the exit channels are useful. In the present study, a new cross-correlation TOF method was applied to measure the collision energy dependence of the CF_3^* chemiluminescence in addition to a measurement of the collision energy dependence of the total de-excitation cross section by a CF_3H molecule.

Experimental

To determine the collision energy dependence of CF_3^* chemiluminescene in the reaction of $Ar(^3P)$ with CF_3H, we developed a new cross-correlation time-of-flight method (CC-TOF) by generating pseudorandom pulse sequences. In this method, we modulate the grid voltage for metastable atom formation with pseudorandom pulse sequences, which consist of 63 pieces of 35 µs pulses, instead of mechanical chopping.[3] By applying this technique, the collision energy dependence of the CF_3^* channel was studied with a flight length of 90 cm. The chemiluminescence from the cross-beam region was collected by a concave mirror in the reaction chamber, and detected by a photomultiplier (Hamamatsu, R943-02) through a long-path filter ($\lambda_c = 430$ nm). The time profile of the CF_3^* emission was stored in a multichannel scaler. The correlation function of the CF_3^* emission is convoluted by utilizing the standard Hadamard transformation procedure.[3–5]

The collision energy dependent cross section ($\sigma(v_r)$) is determined by following time-of-flight procedure:

$$\sigma(v_r) = \frac{I(v_r)v_{Ar^*}}{v_r I_{Ar^*}(v_r) n_{CF_3H}}, \tag{1}$$

where $I(v_r)$ is the rate of formation of the product, $I_{Ar^*}(v_r)$ is the flux of the $Ar(^3P)$ beam, v_{Ar^*} is the incident velocity of $Ar(^3P)$, v_r is the relative velocity of the two particles, n_{CF_3H} is the number density of the CF_3H beam, which is regarded as being uniform within the beam profile. The velocity distribution of the supersonic CF_3H beam is characterized by a translational temperature of 22 K from time-of-flight measurement. The velocity distribution of the CF_3H beam is very narrow compared with that of the $Ar(^3P)$ beam, and

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assumed to be equal to a stream velocity of $v_s = 535$ ms^{-1}. For a total de-excitation cross section measurement, a conventional TOF method is used. The time profile of Ar(^{3}P) was measured directly by a secondary electron multiplier mounted on the beam crossing point. The TOF profile for the total de-excitation wasdetermined as the attenuation signal of Ar(^{3}P) beam by CF$_3$H target molecules filled in a 30 cm long gas cell at 10^{-5} Torr.

Results and Discussion

Figure 1 shows the time profiles of the primary Ar(^{3}P) beam, the de-excited Ar(^{3}P) obtained by passing through the CF$_3$H gas cell, and the CF$_3$* emission. As can be clearly seen, these three curves look different from one another. We could obtain the collision energy dependence of the total de-excitation cross section and that of the CF$_3$* emission cross section from the three curves of Fig. 1, which are plotted in Fig. 2.

The collision energy dependence of the total de-excitation cross section shows a monotonous decrease with the collision energy, while the collision energy dependence of the CF$_3$* emission shows a positive slope as a function of the collision energy with a threshold of 0.10 eV. In the photodissociation of CF$_3$H, the threshold energy for CF$_3$* formation is reported to be 10.96 eV (113.1 nm).[6] This threshold energy is much lower than the excitation energy of Ar(^{3}P) (11.55, 11.72 eV). Therefore, the experimental threshold of 0.1 eV is characteristically observed only in the Ar(^{3}P) + CF$_3$H reaction.

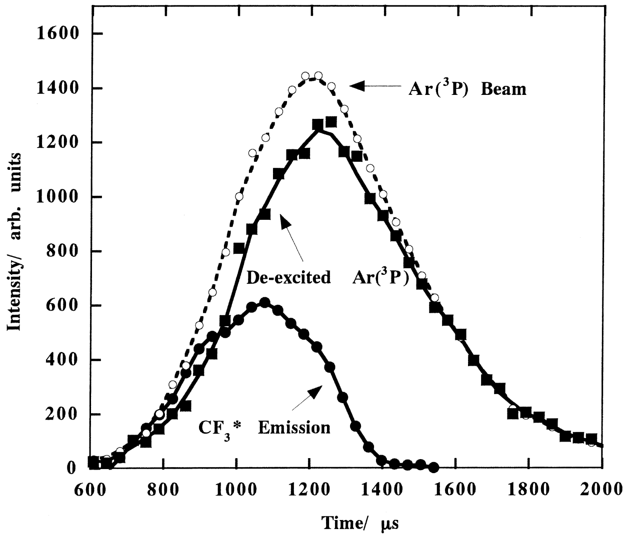

Fig. 1. Time profiles for CF$_3$* emission and for the de-excited Ar(^{3}P) intensity by CF$_3$H with the time profile of Ar(^{3}P) beam.

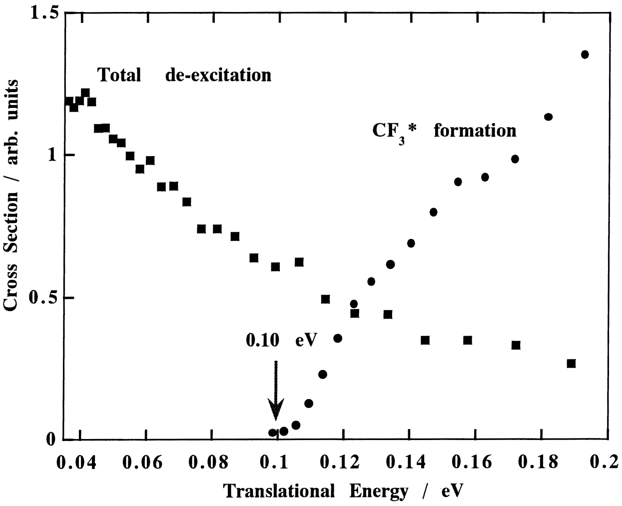

Fig. 2. Collision energy dependence of CF$_3$* formation cross section and that for total de-excitation.

Figure 3 shows schematic potential energy curves that are relevant to the de-excitation processes in the Ar(^{3}P) + CF$_3$H reaction. The excited states of CF$_3$H have been well studied.[7] The entrance surface is designated as U, and the exit channels would be on the U$_A$ and U$_{B,C}$ surfaces. All three surfaces encounter the ionic surface (U$_{Ion}$). Therefore, there are two possible pathways for energy transfer at the curve crossings. One is charge transfer at intermediate distances, designated as (i) and (iii). The other one is electron exchange at a short distance, designated as (ii). So far, ArF* excimer formation and Penning ionization of CF$_3$H have not been reported, and the CF$_3$* chemiluminescence channel is known to be a minor channel;[2] the main channel should be the dissociative CF$_3$ + H channel (dark channel). In fact, the large hydrogen atom yield (0.75) was measured.[8] This non-emissive main channel must be attributed to the excitation to U$_A$ through crossings (i) and (iii), because no CF$_3$* formation in the A state has been reported for the photodissociation of CF$_3$H.[6] The transition probability at crossing point (iii) is expected to have little dependence on the collision energy, because the velocity at crossing point (iii) is determined mostly by acceleration on the ionic surface. Since the Rydberg orbital is essentially nonbonding in nature,[9] it is expected that the CF$_3$H excited in the A state will efficiently dissociate into CF$_3$ + H. Therefore, any non-adiabatic transition from the surface U$_A$ to the ionic surface U$_{Ion}$ is expected to be negligible at crossing point (iii). Consequently, the main channel would be controlled by the non-adiabatic transition from the initial surface (U(CF$_3$H + Ar(^{3}P))) to the ionic surface(U$_{Ion}$) at crossing (i), the so-called "harpooning type mechanism". This total de-excitation cross section is known to be 64 Å^2.[10] Therefore, the harpooning distance can be calculated by using the simple relation $r_c = e^2/(\mathrm{IP}-\mathrm{EA})$,[11] where IP is the ionization potential of Ar(^{3}P) and EA is the electron affinity of CF$_3$H. The electron affinity of CF$_3$H can be derived as 1.0 eV from the experimental cross section and the ionization potential (4.2 eV). Since the estimated electron affinity of CF$_3$H seems to be reasonable compared with that for analogous molecules, CF$_3$Br (0.91 eV) and CF$_3$I (1.4 eV),[12] the transition probability for the excitation to U$_A$ at crossing points (i) and (iii) is expected to be very efficient:

$$P_d = 1 - P_a = 1 - e^{-\kappa/v_r} = 1 - e^{-\kappa'/E^{1/2}}. \tag{2}$$

Equation 2 represents the adiabatic P_a and the diabatic P_d transition probabilities at crossing point (i), where κ and v_r are the non-adiabatic coupling and the relative velocity between the Ar(^{3}P) atom and the CF$_3$H molecule in the Landau–Zener approximation, respectively.[13] E is the collision energy at the relative velocity of v_r. Since the absolute value of the experimental de-excitation cross section ($\sigma(E)$) is difficult to determine,

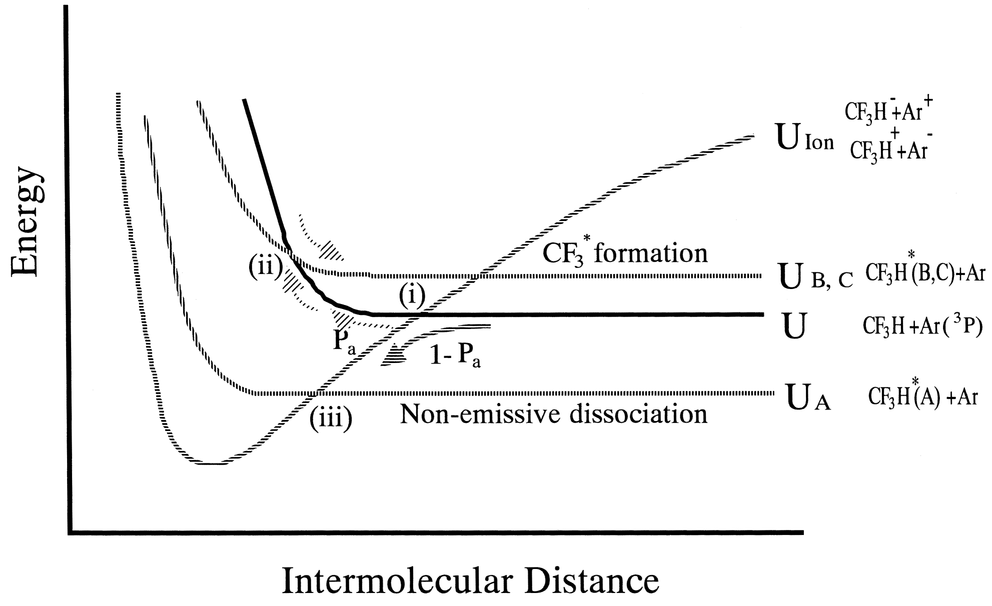

Fig. 3. Schematic potential energy curves for $CF_3H + Ar(^3P)$ reaction.

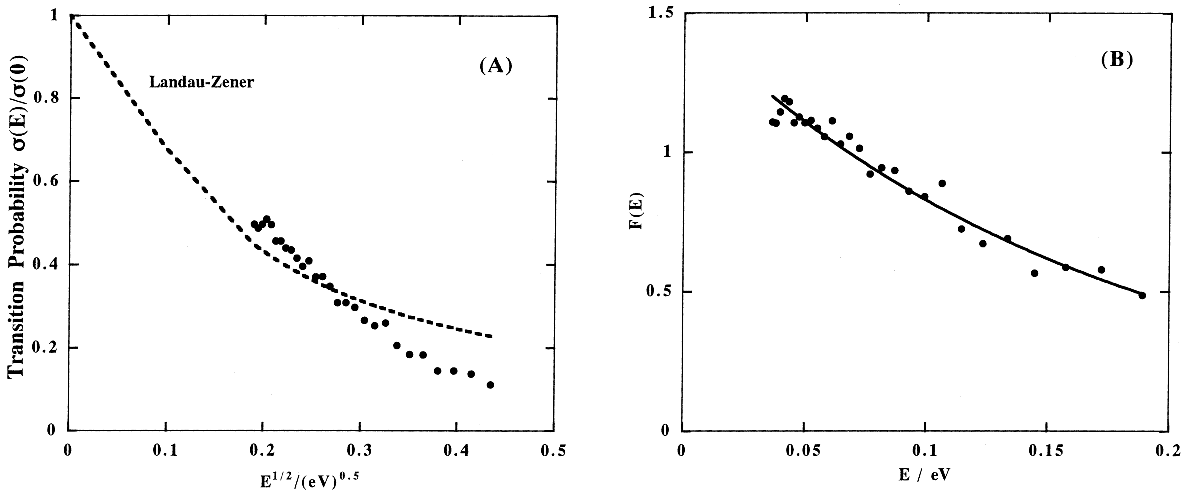

Fig. 4. (A) Comparison of the collision energy dependence of the total de-excitation cross section (solid circles) with the non-adiabatic transition probability by Landau–Zener relation (dashed line) under the assumption of $\sigma(0.04) = 0.5 \times \sigma(0)$. (B) Collision energy dependence of $F(E)$ under the assumption of $\sigma(0.04) = 0.5 \times \sigma(0)$.

the experimental data can not be directly compared with the Eq. 2. In order to compare the experimental data with Eq. 2, it is necessary to assume the absolute value of the experimental data. In this case, the experimental cross section ($\sigma(E)$) can be expressed as

$$\sigma(E) = F(E)P_d = F(E)\,(1-e^{-\kappa'/E^{1/2}}). \tag{3}$$

If the de-excitation is only determined by the diabatic transition probability (P_d) at crossing point (i), $F(E)$ must be constant. As an example, a comparison of the experimental data with the Landau–Zener approximation is carried out for the case that the cross section at $E = 0.04$ eV, $\sigma(0.04)$ is equal to $0.5 \times \sigma(0)$. The value of κ' is the fitting parameter.

Figure 4A shows the least-squares fitting of the experimental data using Eq. 2. $F(E)$ can be determined as the relative intensity of the experimental data to the fitting curve. It is plotted in Fig. 4B. $F(E)$ is found to have a negative dependence on the collision energy. This tendency is extensively recognized for all assumptions of the absolute value of the experimental data. As a result, it is concluded that the decreasing slope for the collision energy dependence of the de-excitation cross section is steeper than the calculated Landau–Zener curve. One of the reasons is an enhancement of the non-adiabatic transition probability at low collision-energy regions, because the effective potential decelerates the velocity at the crossing region. Another one is the dynamical effect from the attractive force for collecting the trajectories to the crossing region.

In the photodissociation of CF_3H, CF_3^* formation has been attributed to the dissociation from the B and/or C excited states.[6,7] For the $Ar(^3P) + CF_3H$ reaction, it is also plausible that the CF_3^* radical is produced via the direct dissociation of

CF_3H from the B and/or C states. If this is the case, CF_3^* is formed via electron exchange at crossing point (ii), and hop to the $U_{B,C}$ surface; then, the CF_3H^* molecule in the B/C state dissociates to form the emissive CF_3^*. The experimental threshold of 0.1 eV for the CF_3^* emission implies that crossing (ii) takes place at the repulsive wall on surface U. This crossing seems to be reasonable. The potential U(CF_3H + Ar(^{3}P)) should have a repulsive wall at a longer intermolecular distance as compared with other surfaces, because the 4s orbital of Ar(^{3}P) is a widely spread orbital. A large fluorescence quantum yield (0.3) was reported for the photodissociation of CF_3H in the B/C states,[6] while the branching fraction of the CF_3^* chemiluminescence channel is only 0.02 to the total de-excitation of Ar(^{3}P).[2] Therefore, the branching fraction for excitation to the B/C states is estimated to be 0.06. One must take into account two rate-determining steps: namely, the adiabatic transition probability at crossing point (i) and the electron exchange probability at crossing point (ii). The experimental result shown in Fig. 2 clearly states that the collision energy dependence of the chemiluminescence and the total de-excitation cross section are quite opposite. Thus, the collision energy dependence of the CF_3^* emission is not determined by the dynamical effect at the entrance before crossing (i). Suppose the diabatic transition probability (P_d) at crossing point (i) is crucial, and the collision energy dependence of the CF_3^* emission behaves is a similar way to that of the adiabatic transition probability (P_a) at crossing point (i). On the other hand, if the cross section of the CF_3^* chemiluminescence is governed by an electron-exchange mechanism at point (ii), the collision-energy dependence would be different from P_a. The collision-energy dependence of CF_3^* formation seems to be different from that for P_a, although it is difficult to estimate the absolute value of P_a. Thus, we may conclude that CF_3^* formation should be mostly controlled by the electron exchange probability at crossing point (ii). The experimental threshold of 0.1 eV for CF_3^* emission implies that 0.1 eV is required to reach crossing point (ii). In this context, we may say that the steric effect observed in CF_3^* chemiluminescence could directly reflect stereo-anisotropy of the electron exchange at crossing point (ii). Collisions with small impact parameters would lead to CF_3^* emission, because electron exchange occurs at a short intermolecular distance. In this case, the electron-exchange probability is apparently enhanced as the collision energy increases, because the closer is the turning point, the more efficient is the overlap electron density for the electron exchange. In addition, collisions with small impact parameters would be little affected by the dynamical effect from the attractive force for collecting the trajectories to the crossing region. The collision energy dependence of a specified reaction channel provides valuable insight into the detailed dynamics of reaction branching.

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