

Formation of Excited $\text{CH}(A^2\Delta)$ and $\text{CD}(A^2\Delta)$ Radicals by Collisions of Metastable $\text{Ar}(3^2P_2)$ Atoms with C_2H , C_2D , and C_2H_3 Radicals in an Ar Flowing Afterglow

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Formation of Excited CH(A²Δ) and CD(A²Δ) Radicals by Collisions of Metastable Ar(³P₂) Atoms with C₂H, C₂D, and C₂H₃ Radicals in an Ar Flowing Afterglow

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CH(A²Δ-X²Π_v) and CD(A²Δ-X²Π_v) emission systems have been observed by dissociative excitation of C₂H, C₂D, and C₂H₃ radicals by collisions with metastable Ar(³P₂;11.55 eV) atoms in the Ar flowing afterglow. C₂H, C₂D, and C₂H₃ radicals were generated by the reactions of F atoms with C₂H₂, C₂D₂, and C₂H₄, respectively. The nascent vibrational and rotational distributions of CH(A:ν′=0–2) and CD(A:ν′=0–2) were determined from computer simulation of observed emission spectra. The vibrational distributions of CH(A) and CD(A) rapidly decreased with increasing ν′ in all three reactions. The rotational distributions of CH(A:ν′=0–2) and CD(A:ν′=0–2) states were expressed by single Boltzmann temperatures of 300–1900 K and 600–3800 K, respectively. High rotational excitation of CH(A) and CD(A) in the Ar(³P₂)/C₂H and Ar(³P₂)/C₂D reactions suggested that bending modes of precursor C₂H^{**} and C₂D^{**} Rydberg states are excited. The observed rovibrational distributions of CH(A) and CD(A) in the Ar(³P₂)/C₂H and Ar(³P₂)/C₂D reactions indicated that most of excess energies are deposited into relative translational energies of CH(A) + C and CD(A) + C products. The observed vibrational and rotational distributions were compared with statistical prior ones for characterizing dynamical features of reactions.

Key words: Dissociative excitation, Aliphatic hydrocarbon radicals, Metastable Ar* atoms, Flowing afterglow, Energy transfer, Rovibrational distribution, Statistic dissociation models, Rydberg state

1. Introduction

The chemical vapor deposition of such simple aliphatic hydrocarbons as CH₄ and C₂H₂ in a plasma reactor has been widely used for making carbon films.^{1–3)} In general, hydrocarbons are diluted by a rare gas and H₂ to maintain stable plasma. This caused increased interest in studies on dissociation processes of aliphatic hydrocarbons diluted by rare gases in the plasma reactor. We have made systematic studies on dissociative excitation of simple aliphatic hydrocarbons by collisions with the metastable Kr(³P₂), Ar(³P₂), Ne(³P_{0,2}), and He(2³S) atoms in the flowing afterglow

(FA).^{4–8)} Product state distributions were obtained by analyzing the emission spectra.

As part of the continuing research program to investigate the energy-transfer processes between metastable rare gas atoms and simple aliphatic hydrocarbons, we have previously extended this study to the reactions of Xe(³P₂), Kr(³P₂), and Ar(³P₂) with CH₃ and C₂H₅ radicals, which are the simplest alkyl radicals.^{9,10)} The excited CH(A,B) states were formed as dominant emitting exit channels. The rovibrational distributions were determined by a spectral simulation. These distributions were compared with the results from statistical model calculations for characterizing the dynamical features of the reactions.

In the present study, emission spectra resulting from energy-transfer reactions of Ar(³P₂) atoms with C₂H, C₂D, and C₂H₃ radicals are measured in the FA. The rovibrational distributions of CH(A) and CD(A) are determined by a computer simulation of observed band profiles. The observed

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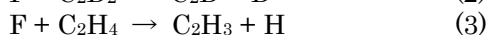
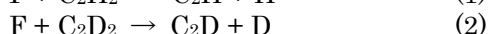
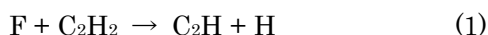
rovibrational distributions are compared with those from statistical two-body and three-body dissociation models to characterize the dynamical features of the reactions. On the basis of these data, energy-transfer mechanisms are discussed.

2. Experimental

Figure 1 shows a schematic diagram of the FA apparatus used in the present study. This flowing system was evacuated continuously with a 10000 l/min mechanical booster pump (ULVAC 006) backed by a 1600 l/min oil rotary pump. The following gases were used in this study: Ar (Nippon Sanso: purity: 99.9999%), C₂H₂ (Eto Sanso: 99.0%), C₂H₄ (Eto Sanso: 99.0%), C₂H₆ (Eto Sanso: 99.0%), and CF₄ (Seitetsu Kagaku: 99.5%). C₂D₂ was synthesized by the reaction of CaC₂ with D₂O as reported in our previous paper.⁷

There are two microwave (MW) discharge sources, which are denoted as MW(A) and MW(B) in Fig. 1. MW(A) was used for the generation of F atoms by MW discharge of Ar/CF₄ mixture. MW(B) was used for the generation of metastable Ar(³P₂: 11.55 eV, ³P₀: 11.72 eV) atoms. Since the [Ar(³P₀)]/[Ar(³P₂)] ratio has been reported to be about 0.01,¹¹ the contribution of the upper Ar(³P₀) spin-orbit component could be negligible in our condition.

The C₂H, C₂D, and C₂H₃ radicals were generated by the following hydrogen abstraction reaction by F atoms:^{12,13}



where fluorine atoms were produced from a

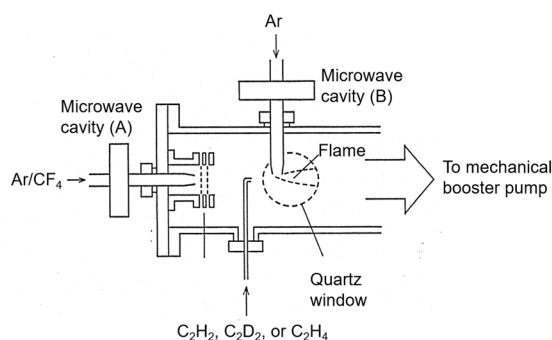


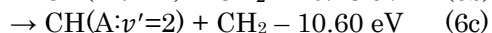
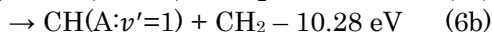
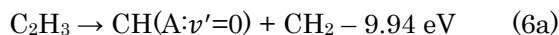
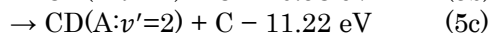
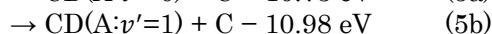
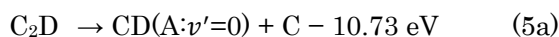
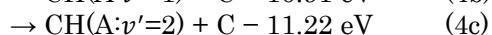
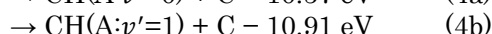
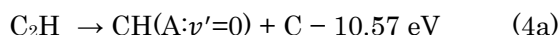
Fig. 1. The flowing afterglow apparatus for studying energy-transfer reactions from metastable Ar(³P₂) atoms to C₂H, C₂D, and C₂H₃ radicals.

MW discharge of dilute (3%) CF₄ in Ar. Typical pressures of Ar and CF₄ gases in the discharge tube were 0.16–0.19 Torr (1 Torr = 133.3 Pa) and 5 mTorr, and those of C₂H₂, C₂D₂, and C₂H₄ were 16, 1, and 16 mTorr, respectively. The total pressure in the reaction zone was 0.19–0.20 Torr, when both MW(A) and MW(B) were operated.

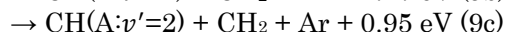
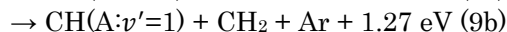
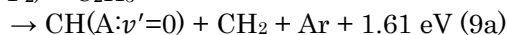
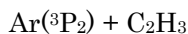
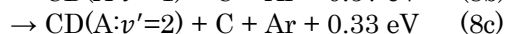
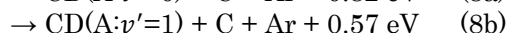
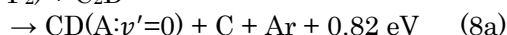
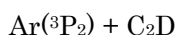
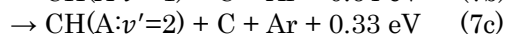
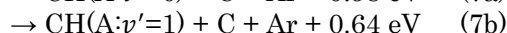
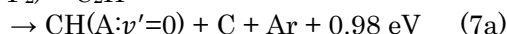
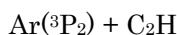
3. Results and Discussion

3.1 Emission spectra and dissociative excitation processes

The minimum energies required for the formation of CH(A:*v*'=0–2) and CD(A:*v*'=0–2) from C₂H, C₂D, and C₂H₃ radicals are as follows.



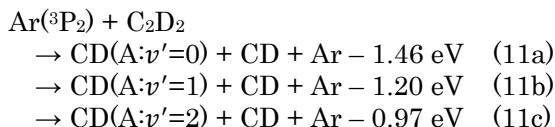
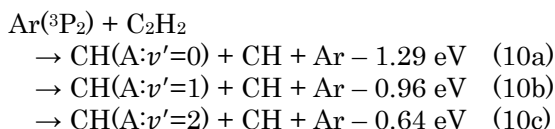
Therefore, the formation of CH(A:*v*'=0–2) and CD(A:*v*'=0–2) from C₂H, C₂D, and C₂H₃ is energetically accessible.



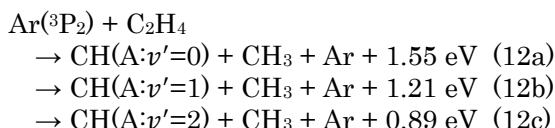
The heats of formation described above were calculated using reported thermochemical and spectroscopic data.^{14,15} Since the heat of formation of C₂D has not been reported, it was estimated to be 559.08 kJ/mol from reported dissociation energy of D–CCD (46754 cm⁻¹)¹⁶ and heats of formation of C₂D₂ and D.¹⁴

The following reactions are endoergic. Therefore, they cannot contribute to the

formation of CH(A: $v'=0-2$) and CD(A: $v'=0-2$) in the Ar afterglow reactions of C₂H₂ and C₂D₂.



On the other hand, the following reactions for C₂H₃ are exoergic, so that they are energetically accessible.



Emission spectra were measured under three different conditions. Figures 2a, 2b, and 2c show emission spectra obtained by switching on both MW(A) and MW(B), only MW(B), and only MW(A), respectively. CH(A²Δ-X²Π₁) emission spectrum with rotational fine structures is observed in Fig. 2a, where strong stray ArI lines are partially overlapped. It is known that not only metastable Ar(³P_{0,2}) atoms but also Ar⁺, Ar²⁺, and Ar⁺*(metastable ions) ions are generated by MW discharge of Ar in an Ar FA.¹⁷⁻¹⁹ Suzuki and Kuchitsu¹⁷ observed CH(A-X) emission system from the Ar afterglow reaction of C₂H₂, where MW was used for the generation of Ar active species. In their study, the CH(A-X) emission reduced its intensity by application of an electrostatic potential on the ion-collector grid placed between the discharge section and reaction zone. Based on this fact and energetics, they concluded that CH(A) is formed by the Ar⁺*/C₂H₂ reaction. We examined the contribution of the Ar⁺*/C₂H₂ reaction to the CH(A-X) emission by switching off MW(A). As shown in Fig. 2b, a weak CH(A-X) emission arising from the Ar⁺*/C₂H₂ reaction is observed. The peak intensity of CH(A-X) in Fig. 2a and 2b is 1:0.33, indicating that the contribution of the Ar⁺*/C₂H₂ reaction is 33% in Fig. 2a. Figure 2c was obtained by switching off MW(B), where weak emissions arising from stray light of MW(A) are observed. We obtained the CH(A-X) emission resulting from the Ar(³P₂)/C₂H

reaction by subtracting the contribution of the Ar⁺*/C₂H₂ reaction and stray light from MW(A), assuming that the CH(A-X) emission resulting from the Ar⁺*/C₂H₂ reaction is unchanged by switching on or off MW(A). The result obtained is shown in Fig. 3a.

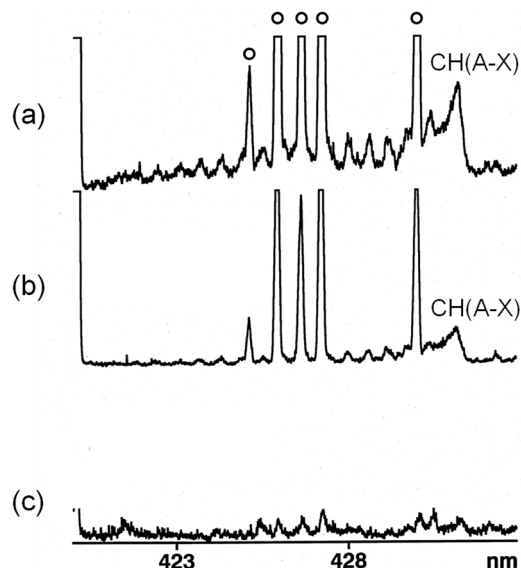


Fig. 2. Emission spectra obtained from (a) Ar(³P₂)/C₂H and Ar⁺*/C₂H₂, (b) Ar⁺*/C₂H₂, and (c) background emission from MW(A) in Fig. 1. Lines marked ○ are stray ArI lines.

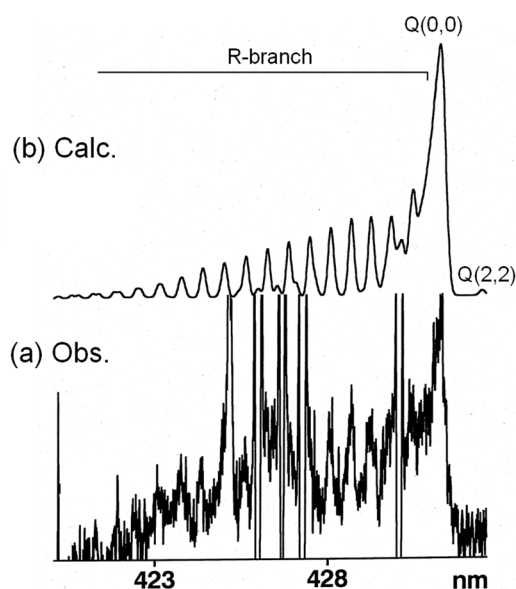


Fig. 3. (a) observed and (b) simulated emission spectra of CH(A²Δ-X²Π₁) band system from the Ar(³P₂)/C₂H reaction. The observed spectrum was obtained from spectra (a) – (b) – (c) in Fig. 2.

Figure 4a shows CD(A-X) emission spectrum obtained from the Ar(³P_{0,2})/C₂D reaction. This spectrum was obtained by subtracting the contribution of the Ar⁺/C₂D₂ reaction and stray light from MW(A), as in the case of the Ar⁺/C₂H reaction.

Figures 5a, 5b, and 5c show emission spectra obtained from Ar(³P₂)/C₂H₄ + Ar(³P₂)/C₂H₃ + Ar⁺/C₂H₄, Ar(³P₂)/C₂H₄ + Ar⁺/C₂H₄, and background emission from MW(A), respectively. These emission spectra were observed by switching on both MW(A) and MW(B), only MW(B), and only MW(A), respectively. CH(A-X) emission is observed in Fig 5a, where strong stray ArI lines are partially overlapped. Weaker CH(A-X) emission is also observed in spectrum (b), indicating that Ar(³P₂)/C₂H₄ + Ar⁺/C₂H₄ reactions give CH(A-X) emission. A comparison of peak intensity of CH(A-X) emission between Fig. 1a and Fig. 1b shows that the contribution of the Ar(³P₂)/C₂H₄ + Ar⁺/C₂H₄ reactions to the CH(A-X) emission is 53%. This value was estimated assuming that the intensity of the CH(A-X) emission from the Ar(³P₂)/C₂H₄ + Ar⁺/C₂H₄ reactions was independent of the switching on or off MW(A). The CH(A-X) emission from the Ar(³P₂)/C₂H₃ reaction was obtained by subtracting the contribution of the Ar(³P₂)/C₂H₂ + Ar⁺/C₂H₂ reactions and stray light from MW(A), assuming that the CH(A-X) emission resulting from the Ar(³P₂)/C₂H₄ + Ar⁺/C₂H₄ reactions is

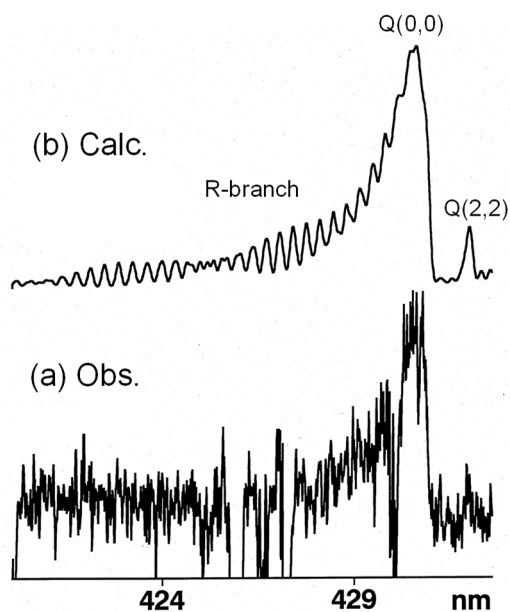


Fig. 4. (a) observed and (b) simulated emission spectra of CD(A²Δ-X²Π_r) band system from the Ar(³P₂)/C₂D reaction.

unchanged by switching on or off MW(A). The result obtained is shown in Fig. 6a.

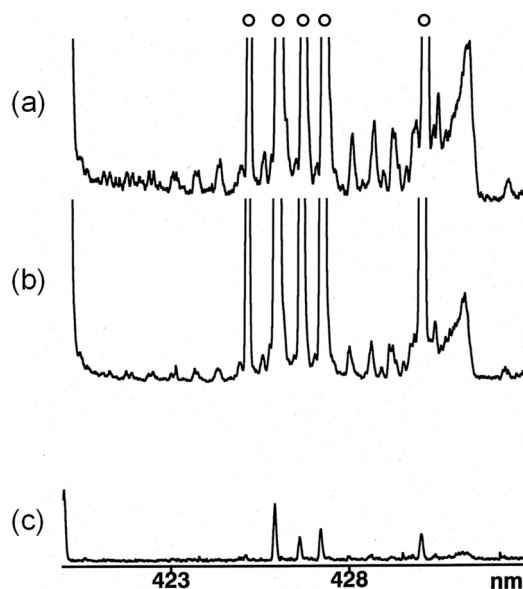


Fig. 5. Emission spectra obtained from (a) Ar(³P₂)/C₂H₄ + Ar(³P₂)/C₂H₃ + Ar⁺/C₂H₄, (b) Ar(³P₂)/C₂H₄ + Ar⁺/C₂H₄, and (c) background emission from MW(A) in Fig. 1. Lines marked ○ are stray ArI lines.

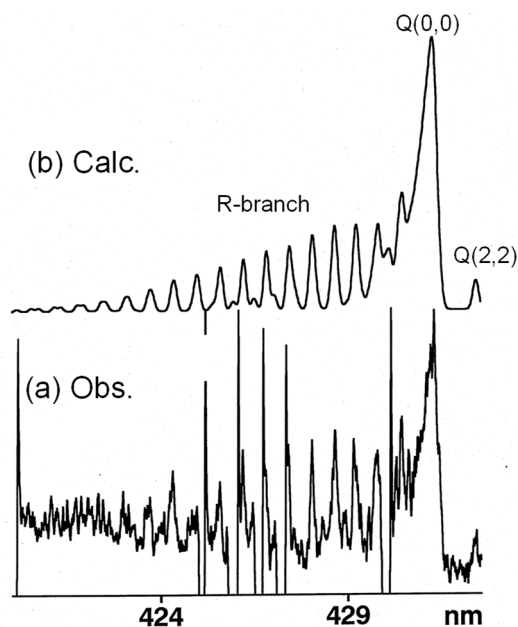


Fig. 6. (a) observed and (b) simulated emission spectra of CH(A²Δ-X²Π_r) band system from the Ar(³P₂)/C₂H₃ reaction. The observed spectrum was obtained from spectra (a) - (b) - (c) in Fig. 5.

Table 1. Observed and prior vibrational distributions (%) of CH(A) and CD(A) produced from the reactions of Ar(3P_2) with C₂H, C₂D, and C₂H₃.

v'	$N_{v'}$	C ₂ H		C ₂ D			C ₂ H ₃		
		$P_{v'}^0$	$P_{v'}^0$	$N_{v'}$	$P_{v'}^0$	$P_{v'}^0$	$N_{v'}$	$P_{v'}^0$	$P_{v'}^0$
		Processes (a)/(b)	Process (c)		Processes (a)/(b)	Process (c)		Process (d)	Process (f)
0	100	100	100	100	100	100	100	100	100
1	25	53	28	25	57	33	25	24	17
2	1	19	4	6	26	7	4	4	2

Table 2. Observed rotational temperatures (K) of CH(A) and CD(A) produced from the reactions of Ar(3P_2) with C₂H, C₂D, and C₂H₃.

	C ₂ H	C ₂ D	C ₂ H ₃
$v'=0$	1900	3800	1900
$v'=1$	1200	2400	1200
$v'=2$	300	600	800

3.3 Rovibrational distributions of CH(A: $v'=0-2$) and CD(A: $v'=0-2$) in the reactions of Ar(3P_2) with C₂H, C₂D, and C₂H₃ radicals

Rovibrational distributions of CH(A: $v'=0-2$) and CD(A: $v'=0-2$) in the Ar(3P_2)/M (M = C₂H, C₂D, and C₂H₃) reactions were determined by a computer simulation of CH(A-X) and CD(A-X) bands. The simulation method used in this study was the same as that reported in our previous studies on CH₄,⁵⁾ C₂H₂,⁶⁾ and C₂D₂.⁷⁾ In Figs. 3b, 4b, and 6b are shown the best fit spectra of the CH(A-X) and CD(A-X) bands from C₂H, C₂D, and C₂H₃, calculated assuming single Boltzmann rotational distributions for each v' level. Vibrational distributions and rotational temperatures thus obtained are given in Tables 1 and 2. From the observed rovibrational distributions of CH(A) and CD(A), we evaluated the average vibrational and rotational energies of CH(A) and CD(A) states, denoted as $\langle E_v \rangle$ and $\langle E_r \rangle$, and average fractions of excess energies deposited into vibrational and rotational energies of CH(A) and CD(A), denoted as $\langle f_v \rangle$ and $\langle f_r \rangle$, respectively. In the Ar(3P_2)/C₂H and Ar(3P_2)/C₂D reactions, the average fractions of excess energies deposited into relative translational energy of neutral fragments, $\langle f_t \rangle$, were estimated from the $\langle f_v \rangle + \langle f_r \rangle$ values. Results obtained are summarized in Table 3. As discussed in our previous paper,⁶⁻⁸⁾ it is expected that the vibrational and rotational

Table 3. Average vibrational and rotational energies (eV) deposited into CH(A) and average fractions of excess energies (%) deposited into vibration and rotation of CH(A) and CD(A) in the reactions of Ar(3P_2) with C₂H, C₂D, and C₂H₃.

C ₂ H	$\langle E_v \rangle$	0.073
	$\langle E_r \rangle$	0.15
	$\langle f_v \rangle$	7.4
	$\langle f_r \rangle$	15.4
	$\langle f_v \rangle + \langle f_r \rangle$	22.8
	$\langle f_t \rangle$	77.2
C ₂ D	$\langle E_v \rangle$	0.072
	$\langle E_r \rangle$	0.29
	$\langle f_v \rangle$	8.8
	$\langle f_r \rangle$	35.5
	$\langle f_v \rangle + \langle f_r \rangle$	44.3
	$\langle f_t \rangle$	55.7
C ₂ H ₃	$\langle E_v \rangle$	0.086
	$\langle E_r \rangle$	0.15
	$\langle f_v \rangle$	5.4
	$\langle f_r \rangle$	9.3
	$\langle f_v \rangle + \langle f_r \rangle$	14.7

relaxation of CH(A) by collisions with the buffer rare gas is insignificant within their radiative lifetimes of about 500 ns for CH(A),^{20,21)} so that observed rovibrational distributions in the Ar FA reflect nascent distributions.

The following tendencies are found for the observed rovibrational distributions of CH(A) and CD(A).

- (1) The vibrational population of CH(A: $v'=0-2$) and CD(A: $v'=0-2$) rapidly decrease with increasing v' . The N_1/N_0 ratio for the three reactions were the same (0.25), whereas the N_2/N_0 ratio decreases from

0.06 to 0.01 in the order of C₂D, C₂H₃, and C₂H.

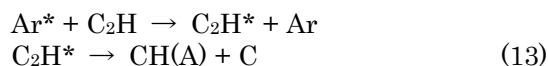
- (2) The rotational temperatures of CH(A: $v'=0-2$) and CD(A: $v'=0-2$) decrease with increasing v' . The rotational temperatures of CD(A: $v'=0-2$) from C₂D are higher than those of CH(A: $v'=0-2$) from C₂H by a factor of 2. The rotational temperatures of CH(A: $v'=0-2$) from C₂H₃ are similar to those from C₂H.
- (3) There is no significant difference in the $\langle f_i \rangle$ value between C₂H and C₂D, whereas the $\langle f_i \rangle$ value of C₂D is larger than that of C₂H by a factor of 2.3. The $\langle f_i \rangle$ and $\langle f_i \rangle$ values of C₂H₃ are smaller than those of C₂H and C₂D.
- (4) The $\langle f_i \rangle$ values of C₂H and C₂D are large ($\geq 56\%$), indicating that most of excess energies are partitioned into relative translational energies of neutral CH(A) + C and CD(A) + C fragments. It is therefore reasonable to assume that CH(A) and CD(A) are formed through highly repulsive potentials.

3.4 The formation mechanisms of CH(A) and CD(A) from the reactions of Ar(³P₂) with C₂H, C₂D, and C₂H₃ radicals

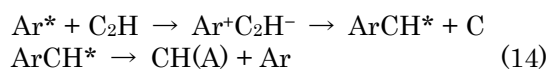
3.4.1 Statistical models

The formation dynamics of CH(A) and CD(A) from the Ar(³P₂)/C₂H and Ar(³P₂)/C₂D reactions is discussed assuming two-body and three-body dissociation mechanisms, which have been used in the formation of CH(A²Δ) from Ar(³P₂)/CH₃ and Ar(³P₂)/C₂H₅,^{9,10} OH(A²Σ⁺) from Ar(³P_{0,2})/H₂O,²² and NH(A³Π_i) from Ar(³P_{0,2})/NH₃.²³ Possible processes for CH(A) are as follows. Similar processes can be applied to the formation of CD(A) from the Ar(³P₂)/C₂D reaction.

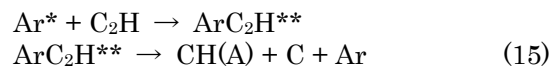
- (a) Two-body dissociation process through resonant excitation transfer



- (b) Two-body dissociation process through ion-pair formation



- (c) Three-body dissociation process through collision complex



In process (a), energy is resonantly transferred from Ar* to C₂H, and then C₂H** dissociates into CH(A) + C. In processes (b) and (c), CH(A) is produced through collision complexes, ArCH* and ArC₂H*, respectively. ArCH* originates from an ion-pair potential V(Ar⁺-C₂H⁻). In order to produce ArCH*, the ion-pair potential must be sufficiently low to couple with the entrance V(Ar*⁻-C₂H) potential. Since the electron affinity of C₂H is relatively high (2.97 eV),²⁴ V(Ar⁺-C₂H⁻) potential is located just 1.24 eV above the entrance V(Ar*⁻-C₂H) potential at dissociation limits. Therefore, the ion-pair potential is expected to be sufficiently low to interact strongly with the entrance potential. Thus, the second process cannot be excluded from the formation mechanism of CH(A).

Statistical vibrational and rotational distributions were calculated for the above three processes. According to a simple statistical theory,²⁵⁻²⁷ the probability of forming a CH(A: v', N') rovibrational level and a CH(A: v') vibrational level through processes (a) and (b) is expressed by the same equation

$$P_{vN'}^o \propto (2N' + 1)(E_{\text{tot}} - E_{v_{\text{CH}^*}} - E_{r_{\text{CH}^*}})^{1/2} \quad (16a)$$

$$P_{v'}^o \propto (E_{\text{tot}} - E_{v_{\text{CH}^*}})^{3/2}. \quad (16b)$$

On the other hand, that through process (c) is given by

$$P_{vN'}^o \propto (2N' + 1)(E_{\text{tot}} - E_{v_{\text{CH}^*}} - E_{r_{\text{CH}^*}})^2 \quad (17a)$$

$$P_{v'}^o \propto (E_{\text{tot}} - E_{v_{\text{CH}^*}})^3. \quad (17b)$$

The prior vibrational and rotational distributions of CH(A: $v'=0-2$) calculated for processes (a)/(b) and (c) are compared with the observed ones in Table 1 and Figs. 7a-7c. The prior vibrational distribution of CH(A: $v'=0-2$) and rotational distributions of CH(A: $v'=0-2$) predict higher vibrational and rotational excitation than the observed ones for both two-body models (a)/(b) and three-body dissociation model (c).

The deviation from prior vibrational and rotational distributions can often be expressed in the form of surprisal,²⁷

$$I_v = -\ln[P(v)/P^o(v)], = \lambda_0 + \lambda_v f_v \quad (18a)$$

$$I_R = -\ln[P(v, N)/P^o(v, N)] = \theta_0 + \theta_R g_N \quad (18b)$$

where $f_v = E_v/E_{tot}$, $g_N = E_N/(E_{tot}-E_v)$, $P(v) = N_{v'}$ and $P(v, N) = N_{v'N}$.

Figure A1 in Appendix shows vibrational and rotational surprisal plots of CH(A: $v'=0-2$). When the two-body and three-body dissociation models for processes (a)/(b) and (c) are used for $P_{v'N'}$ and $P_{v'}$, good linear relationships are found in the surprisal plots of CH(A: $v'=0-2$) in the f_v and g_N range given in Table A1 in Appendix. These results imply that an exponential gap behavior is present between the experimental and statistical distributions in most cases. From slopes of each surprisal plot, positive vibrational and rotational surprisal parameters are obtained in all cases for the cases of C₂H (Table A1 in Appendix) because the observed vibrational and rotational distributions are lower than prior ones. The

rotational surprisal parameter of CH(A: $v'=0-2$) increases with increasing v' , in both processes (a)/(b) and (c), suggesting that the deviation from prior distribution increases with increasing v' .

The prior vibrational and rotational distributions of CD(A: $v'=0-2$) calculated for processes (a)/(b) and (c) are compared with the observed ones in Table 1 and Figs. 8a–8c. The prior vibrational distribution of CD(A: $v'=0-2$) for processes (a)/(b) is much higher than the observed one, whereas that for process (c) is slightly higher than the observed one (Table 1). The prior rotational distributions of CD(A: $v'=0-2$) for process (a)/(b) are much higher than observed ones. On the other hand, a reasonable agreement is found between prior rotational distributions of CD(A: $v'=0,1$) for process (c) for low N' levels below $N' \approx 15$,

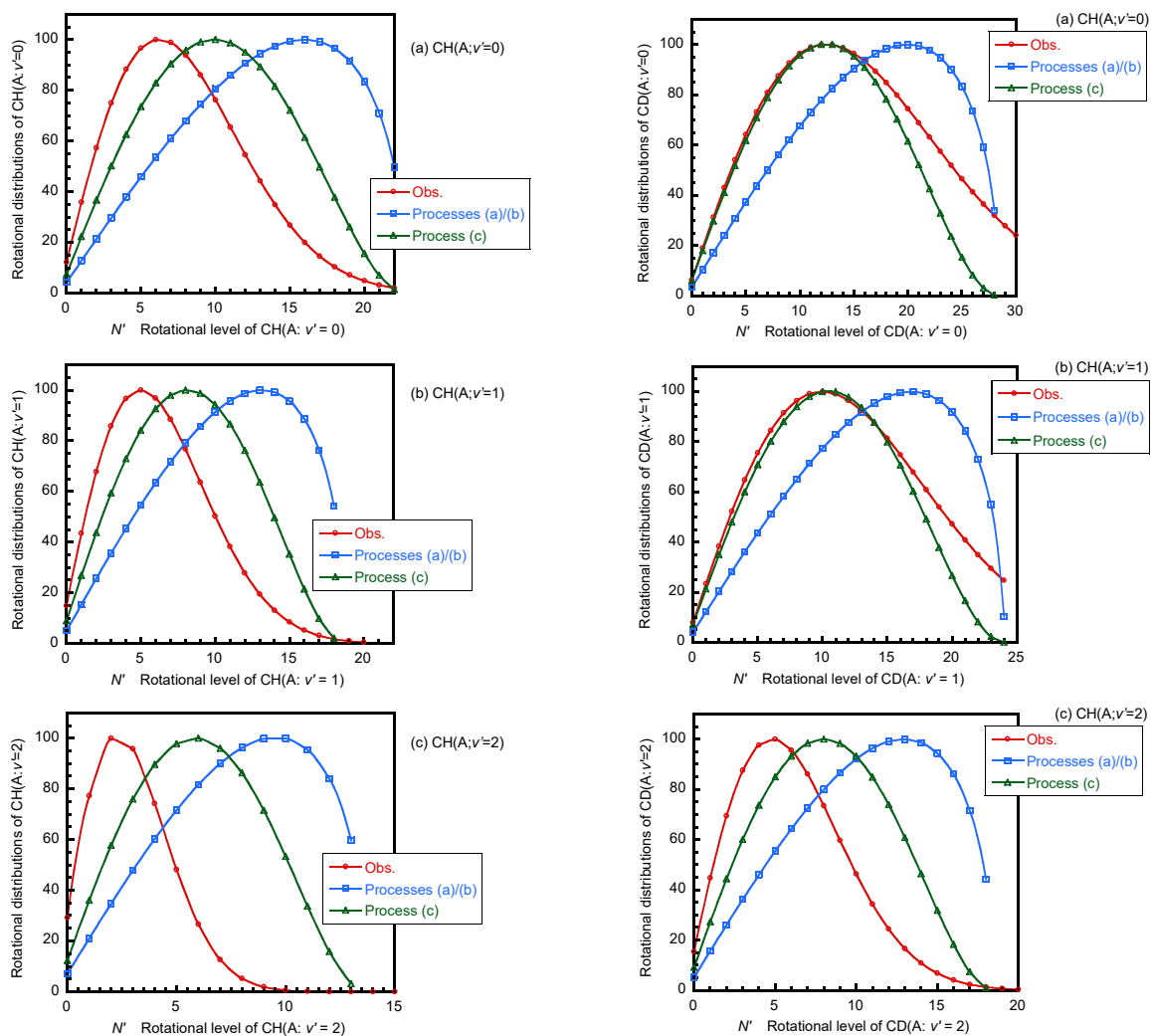


Fig. 7. Observed and two-body and three-body prior rotational distributions of CH(A: $v'=0-2$) in the Ar(³P₂)/C₂H reaction.

Fig. 8. Observed and two-body and three-body prior rotational distributions of CD(A: $v'=0-2$) in the Ar(³P₂)/C₂D reaction.

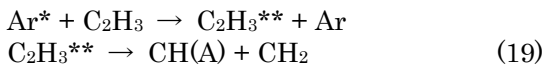
whereas the prior rotational distribution of CD(A: $v'=2$) for process (c) is higher than the observed one.

Figure A2 in Appendix shows vibrational and rotational surprisal plots of CD(A: $v'=0-2$). When the two-body and three-body dissociation models for processes (a)/(b) and (c) are used for $P_{v'N'}^o$ and $P_{v'}^o$, good linear relationships are found in the surprisal plots of CD(A: $v'=0-2$) in the f_v and g_N range given in Table A1 in Appendix. The vibrational surprisal parameter of CD(A: $v'=0-2$) for processes (a)/(b) gave a positive value (2.5) because the observed vibrational distribution is lower than that expected from prior one. On the other hand, the vibrational surprisal parameter for process (c) (0.18) is small, suggesting that there is no significant difference between the observed and prior distributions. The rotational surprisal parameters for CD(A: $v'=0-2$) for processes (a)/(b) are positive because the observed rotational distributions are lower than those expected from prior ones. The rotational surprisal parameters for CD(A: $v'=0,1$) for process (c) are small negative values (-0.50 and -0.38), suggesting that the observed rotational distributions are slightly higher than those expected from prior ones. The rotational surprisal parameter of CD(A: $v'=2$) is positive (3.3), indicating that the observed distribution is lower than the prior one. The rotational surprisal parameter of CD(A: $v'=0-2$) increases with increasing v' , in both processes (a)/(b) and (c), suggesting that the deviation from prior distribution increases with increasing v' .

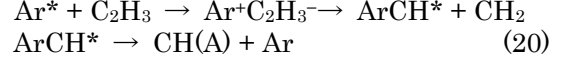
It should be noted that deviations of observed vibrational and rotational distributions of C₂H and C₂D from prior ones for three-body process (c) are smaller than those for two-body processes (a) and (b). Therefore, three-body processes are more favorable if energy-transfer processes are governed by statistical models. Vibrational and rotational surprisal parameters obtained for C₂D are smaller than those for C₂H, indicating that deviations from prior distributions are small for the case of C₂D.

The following three processes may be responsible for the production of CH(A) from the Ar(³P₂)/C₂H₃ reaction.

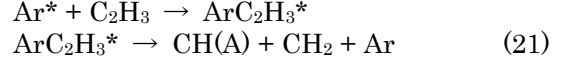
- (d) Two-body dissociation process through resonant excitation transfer



- (e) Two-body dissociation process through ion-pair formation



- (f) Three-body dissociation process through collision complex



The electron affinity of C₂H₃ is small (0.667 eV),¹⁴ V(Ar⁺-C₂H₃⁻) potential is located 3.54 eV above the entrance V(Ar^{*}-C₂H₃) potential at dissociation limits. Therefore, the ion-pair potential is too high to interact strongly with the entrance potential at a long distance between Ar^{*} and C₂H₃. Thus, it is reasonable to assume that the ion-pair process (e) is not important compared with the case of C₂H. Thus, process (e) was excluded from possible processes in this study.

The probability of forming a CH(A: v', N') rovibrational level and a CH(A: v') vibrational level through process (d) is expressed by the equation

$$P_{v'N'}^o \propto (2N' + 1)(E_{\text{tot}} - E_{v_{\text{CH}^*}} - E_{r_{\text{CH}^*}})^5 \quad (22a)$$

$$P_{v'}^o \propto (E_{\text{tot}} - E_{v_{\text{CH}^*}})^6. \quad (22b)$$

On the other hand, that through process (f) is given by

$$P_{v'N'}^o \propto (2N' + 1)(E_{\text{tot}} - E_{v_{\text{CH}^*}} - E_{r_{\text{CH}^*}})^{6.5} \quad (23a)$$

$$P_{v'}^o \propto (E_{\text{tot}} - E_{v_{\text{CH}^*}})^{7.5}. \quad (23b)$$

The prior vibrational distribution of CH(A: $v'=0-2$) and rotational distributions of CH(A: $v'=0-2$) calculated for processes (d) and (f) are compared with the observed ones in Table 1 and Figs. 9a-9c. Surprisal plots and surprisal parameters obtained for CH(A) from C₂H₃ are given in Figure A3 and Table A1 in Appendix. Although a good agreement is observed between the prior vibrational distribution and observed one for process (d), the prior vibrational distribution of CH(A: $v'=0-2$) for process (f) is lower than the observed one. The prior rotational distribution of CH(A: $v'=0-2$) for processes (d) and (f) predict higher vibrational and rotational excitation than the observed ones for both two-body model (d) and three-body dissociation

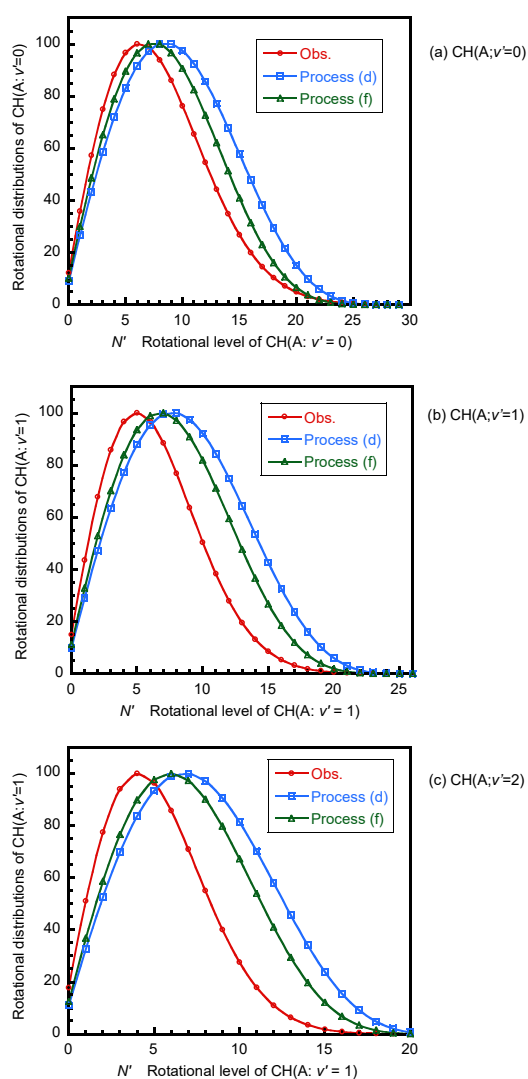


Fig. 9. Observed and two-body and three-body prior rotational distributions of CH(A: $v'=0-2$) in the Ar(3P_2)/C₂H₃ reaction.

model (f). The rotational surprisal parameter of CH(A: $v'=0-2$) increases with increasing v' , in both processes (d) and (f), suggesting that the deviation from prior distributions increases with increasing v' , as in the cases of C₂H and C₂D. The deviation of observed vibrational distribution of CH(A) from prior one for two-body process (d) is smaller than that for three-body process (f). On the other hand, deviations of observed rotational distributions of CH(A: $v'=0-2$) from prior ones for two-body process (d) are larger than those for three-body process (f).

3.4.2 Dissociative excitation process

In general, energy transfer from metastable rare gas atoms to molecules proceeds through near-resonant processes, where spin-

conservation rule holds between reactants and products.^{11,28-31} Therefore, it is likely that C₂H, C₂D, and C₂H₃ radicals are initially excited into near-resonant doublet and/or quartet states at the energy of Ar(3P_2 :11.55 eV) because the ground states of these radicals and CH(A) are both doublets and the ground state of carbon atom is 3P . The ionization potentials (IPs) of C₂H, C₂D, and C₂H₃ were measured as 11.61, 11.58, and 8.25 eV, respectively.^{14,32} Here, IP of C₂D was estimated from reported appearance potential of C₂D⁺ under electron-impact ionization and dissociation energy of D(D-CCD).^{14,32} The IPs of C₂H and C₂D are slightly higher than the energy of Ar(3P_2 :11.55 eV), whereas that of C₂H₃ is lower than the energy of Ar(3P_2). It is therefore reasonable to assume that precursor states for C₂H and C₂D are not superexcited states above their first IPs, whereas that for C₂H₃ is superexcited state located above first IP of C₂H₃. In the Ar(3P_2)/C₂H reactions, most probable precursor states are doublet and/or quartet Rydberg states converging to the ground ionic states of C₂H. According to *ab initio* calculations by Koures and Harding,³³ many doublet and quartet Rydberg states exist below first IP for C₂H. Some of them will be precursor states. Higher energy deposition into rotation than into vibration even though the ground state of C₂H is linear³⁴ suggests that bending modes of precursor C₂H^{**} Rydberg states are excited after energy transfer.

Analogous Rydberg states will exist for C₂D below its IP. It is therefore expected that the formation of CD(A) from the Ar(3P_2)/C₂D reaction proceeds through similar Rydberg states converging to the ground state of C₂D⁺. A higher rotational excitation of CD(A) than CH(A) is explained by larger torque in CD(A) after dissociation of C₂D^{**} due to larger moment of inertia. The high position of excess energies into translational energies of CH(A) + C and CD(A) + C indicates that CH(A) and CD(A) are formed through curve crossing between precursor Rydberg states and highly repulsive CH(A) + C and CD(A) + C potentials.

The formation of CH(A) from C₂H₃ probably proceeds through superexcited states above the first IP of C₂H₃. Unknown Rydberg states of C₂H₃^{**} converging to excited ionic states of C₂H₃⁺ are possible precursor states leading to CH(A) + CH₂. Although excess energies in the Ar(3P_2)/C₂H₃ reaction are larger than those in the Ar(3P_2)/C₂H reaction, no significant enhancement of deposition of excess energy

into vibration and rotation of CH(A) was observed. Since the degree of freedom of CH₂ fragment is much larger than C from the Ar(³P₂)/C₂H reaction, CH₂ can accept more excess energy after reaction. This will be one reason for the low energy deposition of excess energy into vibration and rotation of CH(A) in the Ar(³P₂)/C₂H₃ reaction.

We found that the observed vibrational and rotational distributions are lower than statistical two-body and three-body dissociation models in most cases. One reason may be the fact that lifetimes of intermediate states are too short to randomize excess energies into all degrees of freedom. Another reason may be the fact that electronic structures and molecular structures of precursor Rydberg states and repulsive potential curves leading to CH(A) and CD(A) play more important role in their decomposition processes.

4. Summary and Conclusion

Dissociative excitation of C₂H, C₂D, and C₂H₃ radicals by collisions with metastable Ar(³P₂) atoms has been studied by observing CH(A-X) and CD(A-X) emissions in the Ar FA. The nascent vibrational and rotational distributions of CH(A: *v*'=0–2) and CD(A: *v*'=0–2) were determined from spectral simulation. The vibrational distributions of CH(A) and CD(A) rapidly decreased with increasing *v*' in all reactions. The rotational distributions of CH(A: *v*'=0–2) and CD(A: *v*'=0–2) states were expressed by single Boltzmann temperatures of 300–1900 K and 600–3800 K, respectively. In most cases, the observed vibrational and rotational distributions are lower than statistical prior ones obtained by assuming two-body and three-body dissociation models. In the Ar(³P₂)/C₂H and Ar(³P₂)/C₂D reactions, more excess energies are deposited into rotational modes than into vibrational ones of CH(A) and CD(A). Taking account of the linear C₂H and C₂D molecules in the ground states, we concluded that rotational excitation of CH(A) and CD(A) arises from excitation of bending modes of precursor C₂H** and C₂D** Rydberg states. It was found that most of excess energy (≥56%) is deposited into relative translational energies of CH(A) + C and CD(A) + C products. Therefore, we concluded that CH(A) and CD(A) are formed through highly repulsive potentials.

Acknowledgments

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References

- 1) N. Mutsukura and K. Miyatani, *Diamond Relat. Mater.*, 4, 342 (1995).
- 2) P. Yang, S. C. H. Kwok, R. K. Y. Fu, Y. X. Leng, J. Wang, G. J. Wan, N. Huang, Y. Leng, and P. K. Chu, *Surf. Coat. Tech.*, 177/178, 747 (2004).
- 3) S. Avtaeva and V. Gorokhovskiy, *Plasma Chem. Plasma Process.*, 41, 815 (2021).
- 4) M. Tsuji, K. Koburai, H. Obase, H. Kouno, and Y. Nishimura, *J. Chem. Phys.*, 94, 277 (1991).
- 5) M. Tsuji, T. Komatsu, M. Tanaka, M. Nakamura, Y. Nishimura, and H. Obase, *Chem. Lett.*, 26, 359 (1997).
- 6) M. Tsuji, T. Komatsu, K. Uto, J.-I. Hayashi, and T. Tsuji, *Eng. Sci. Rep., Kyushu Univ.*, 43, 8 (2021).
- 7) M. Tsuji, T. Komatsu, K. Uto, J.-I. Hayashi, and T. Tsuji, *Eng. Sci. Rep., Kyushu Univ.*, 43, 23 (2021).
- 8) M. Tsuji, T. Komatsu, K. Uto, J.-I. Hayashi, and T. Tsuji, *Eng. Sci. Rep., Kyushu Univ.*, 43, 1 (2022).
- 9) M. Tsuji, H. Kouno, Y. Nishimura, H. Obase, and K. Kasatani, *J. Chem. Phys.*, 95, 7317 (1991).
- 10) M. Tsuji, H. Kouno, H. Ujita, and Y. Nishimura, *J. Chem. Phys.*, 96, 6746 (1992).
- 11) J. M. Tsuji, K. Koburai, and Y. Nishimura, *J. Chem. Phys.*, 93, 3133 (1990).
- 12) *NIST Chemical Kinetics Database*, Standard Reference Database 17, Version 7.0 (Web Version), Release 1.6.8., Data Version 2015.09, and references therein.
- 13) J. Berkowitz, C. A. Mayhew, and B. Rušćić, *J. Chem. Phys.*, 88, 7396 (1988).
- 14) *NIST Chemistry WebBook*, NIST Standard Reference Database, Number 69 (2018): <http://webbook.nist.gov/chemistry>.
- 15) K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules*, Van Nostrand Reinhold, New York (1979).
- 16) S. H. S. Wilson, C. L. Reed, D. H. Mordaunt, M. N. R. Ashfold, and M. Kawasaki, *Bull. Chem. Soc. Jpn.*, 69, 71 (1996).
- 17) K. Suzuki and K. Kuchitsu, *J. Photochem.*, 10, 401 (1979).
- 18) H. Obase, M. Tsuji, and Y. Nishimura, *Chem. Phys.*, 87, 93 (1984).
- 19) M. Endoh, M. Tsuji, and Y. Nishimura, *Chem. Phys. Lett.*, 109, 35 (1984).
- 20) J. Carozza and R. Anderson, *J. Opt. Soc. Amer.*, 67, 118 (1977).
- 21) M. Ortiz and J. Campos, *Physica B+C*, 114, 135 (1982).
- 22) H. L. Snyder, B. T. Smith, T. P. Parr, and R. M. Martin, *Chem. Phys.*, 65, 397 (1982).
- 23) H. Sekiya, N. Nishiyama, M. Tsuji, and Y. Nishimura, *J. Chem. Phys.*, 86, 163 (1987).
- 24) T. R. Taylor, C. Xu, and D. M. Neumark, *J. Chem. Phys.*, 108, 10018 (1998).
- 25) R. D. Levine and J. L. Kinsey, *Atom-Molecule Collision Theory*, ed. by R. B. Bernstein, Plenum, New York (1979), p. 693.
- 26) R. B. Bernstein, *Chemical Dynamics via Molecular Beam and Laser Techniques*, Oxford University Press (1982).

- 27) R. D. Levine, *Bull. Chem. Soc. Jpn.*, 61, 29 (1988).
- 28) M. Tsuji, K. Kobara, S. Yamaguchi, H. Obase, K. Yamaguchi, and Y. Nishimura, *Chem. Phys. Lett.*, 155, 481 (1989).
- 29) M. Tsuji, K. Kobara, S. Yamaguchi, and Y. Nishimura, *Chem. Phys. Lett.*, 158, 470 (1989).
- 30) M. Tsuji, K. Kobara, S. Yamaguchi, H. Obase, and Y. Nishimura, *Chem. Phys. Lett.*, 166, 485 (1990).
- 31) M. Tsuji, K. Kobara, H. Kouno, H. Obase, and Y. Nishimura, *Jpn. J. Appl. Phys.*, 30, 862 (1991).
- 32) M. Davister and R. Loch, *Chem. Phys.*, 189, 805 (1994).
- 33) A. G. Koures and L. B. Harding, *J. Phys. Chem.*, 95, 1035 (1991).
- 34) R. Tarroni and S. Carter, *J. Chem. Phys.* 119, 12878 (2003).

Appendix

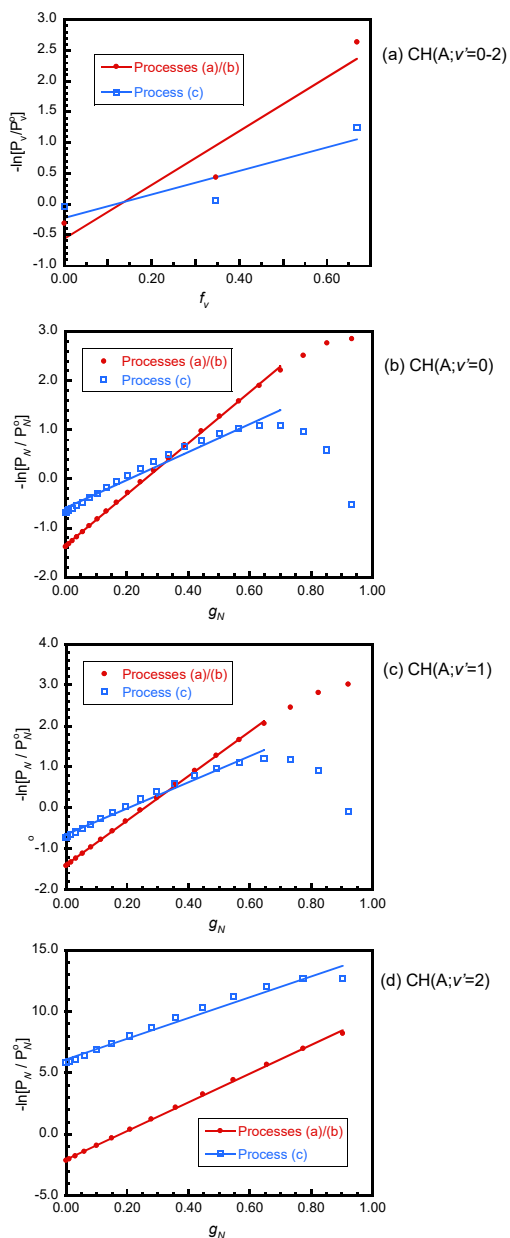


Fig. A1. Vibrational and rotational surprisal plots of CH(A: $v'=0-2$) in the Ar(3P_2)/C₂H reaction.

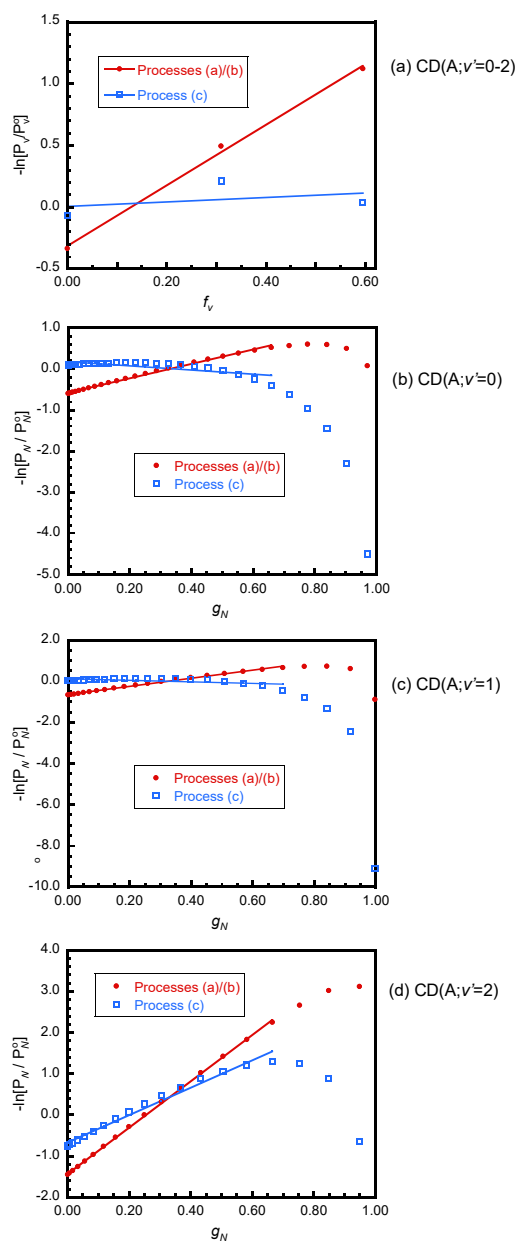


Fig. A2. Vibrational and rotational surprisal plots of CD(A: $v'=0-2$) in the Ar(3P_2)/C₂D reaction.

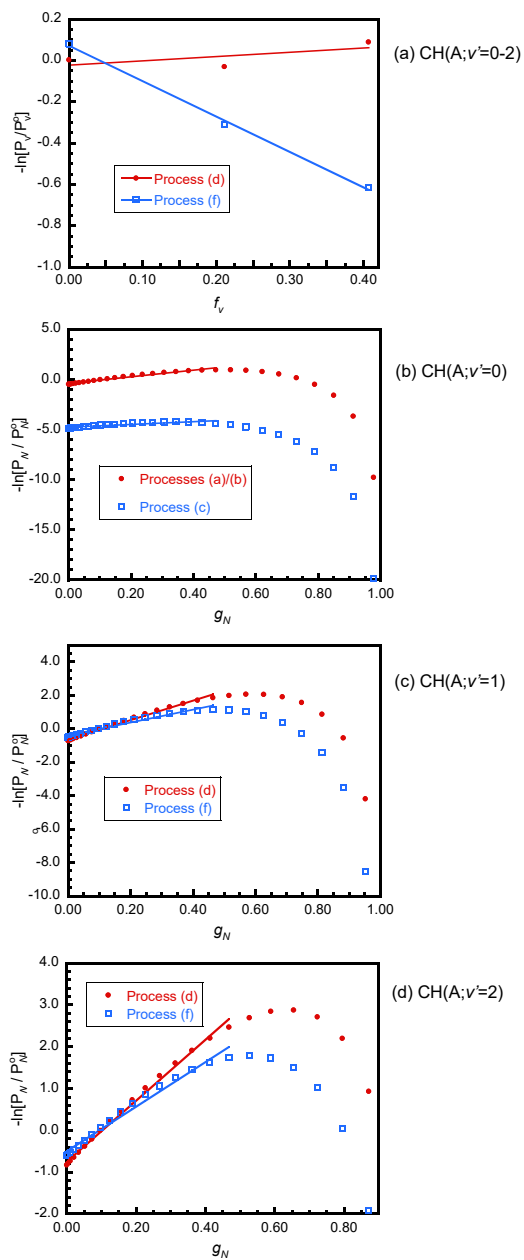


Fig. A3. Vibrational and rotational surprisal plots of CH(A: $v'=0-2$) in the Ar(3P_2)/C₂H₃ reaction.

Table A1. Vibrational and rotational surprisal parameters for CH(A) and CD(A) produced from the reactions of Ar(3P_2) with C₂H, C₂D, and C₂H₃.

		Vibrational surprisal parameter		Rotational surprisal parameter		f_v or g_N range
		Two-body processes (a)/(b)	Three-body process (c)	Two-body processes (a)/(b)	Three-body process (c)	
C ₂ H	CH(A: $v'=0-2$)	4.4	1.9			$f_v \leq 0.67$
	CH(A: $v'=0$)			5.2	2.8	$g_N \leq 0.7$
	CH(A: $v'=1$)			5.4	3.2	$g_N \leq 0.65$
	CH(A: $v'=2$)			8.5	11.7	$g_N \leq 0.90$
C ₂ D	CD(A: $v'=0-2$)	2.5	0.18			$f_v \leq 0.60$
	CD(A: $v'=0$)			1.8	-0.50	$g_N \leq 0.66$
	CD(A: $v'=1$)			2.0	-0.38	$g_N \leq 0.7$
	CD(A: $v'=2$)			5.6	3.3	$g_N \leq 0.67$
		Two-body process (d)	Three-body process (f)	Two-body process (d)	Three-body process (f)	
C ₂ H ₃	CH(A: $v'=0-2$)	0.21	-1.7			$f_v \leq 0.41$
	CH(A: $v'=0$)			3.3	1.4	$g_N \leq 0.47$
	CH(A: $v'=1$)			5.8	3.9	$g_N \leq 0.46$
	CH(A: $v'=2$)			7.3	5.3	$g_N \leq 0.47$