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The Dissociative Excitation and Dissociative Ionization of Simple Aliphatic Hydrocarbons by Controlled Electron Impact

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Photoemissions from the following excited species were observed from simple aliphatic hydrocarbons (CH_4, C_2H_2, C_2H_4, 1,3-C_4H_6) under controlled electron-impact excitation (0—400 eV) at wavelengths from 300 to 600 nm: H(Balmer), CH(A–X, B–X, C–X), CH^+(A–X, B–A, b–a), C_2(C–A, d–a; not from CH_4), and $C_4H_2^+$(A–X; not from CH_4). All the excited species except for $C_4H_2^+$ from C_2H_2 and C_2H_4 were confirmed to be primarily produced. The excitation function (0—400 eV) and the appearance potential of H, CH, and CH^+ produced from CH_4 and C_2H_2 were measured, and the corresponding processes of the fragmentation near the threshold were determined. The $CH_4+e \to CH^+(B)+H_2(X)+H(n=1)$ and $C_2H_2+e \to CH^+(B)+CH(X)$ processes were concluded to be responsible for the formation of CH^+(B). The formation of ionic species, H^+ and CH^+, can be considered as the limiting case of the dissociative excitation for producing H and CH. A triplet excitation process may contribute to the formation of CH(A) from C_2H_2. The observed threshold energies indicated that superexcited states were involved in the formation of excited neutral fragment species.

Spectroscopic investigations of the dissociative excitation of simple aliphatic hydrocarbons (CH_4, C_2H_2, C_2H_4, C_2H_6) have been extensively carried out by the irradiation of vacuum ultraviolet photons,[1,2] by the impact of an ion beam,[3,4] and by the impact of an electron beam,[5–11] and photoemissions from the excited atoms (H, CI, CII) and molecular fragments (C_2, CH, CH^+, CH_2) have been observed.

The electron-impact method is a very effective method, partly because the excitation energy is variable over a wider range and partly because a relatively intense photoemission can be obtained even at a low excitation energy near the threshold. Thus, the emission cross section, the excitation function, and the appearance potential of some fragment species of various molecules have been measured under the electron-impact excitation. Sroka[5] and Morgan and Mentall[10] have reported the excited atomic lines, H(Lyman), CI, and CII, from CH_4 in the VUV region. De Heer *et al.*[11] determined the emission cross sections of some excited fragments from simple aliphatic hydrocarbons (CH_4, C_2H_2, C_2H_4, C_2H_6) as a function of the electron-impact energy and clarified the dissociative-excitation processes. Recently, Finn *et al.*,[12] using time-of-flight techniques, investigated the production of hydrogen and carbon atoms in metastable and high-lying Rydberg states by electron impact on CH_4 and CD_4.

The CH^+ ion is an important species in astrophysics, mass spectroscopy, and radiation chemistry; three systems ($A^1\Pi$–$X^1\Sigma^+$, $B^1\Delta$–$A^1\Pi$, $b^3\Sigma^-$–$a^3\Pi$) have been known in the emission spectrum. The latter two systems were first observed and analyzed by Carré[4] under proton bombardment on CH_4 and C_2H_2; they were also identified by Beenakker and de Heer[11] under electron impact on CH_4, C_2H_2, C_2H_4, and C_2H_6. However, no studies have been carried out on the mechanism for the formation of CH^+ in the excited electronic state because of the weakness of the emission intensity. We have previously communicated the emission spectra of CH^+ produced from CH_4 and C_2H_2 by controlled electron impact.[13] The present paper will describe the emission spectra of simple aliphatic hydrocarbons (CH_4, C_2H_2, C_2H_4, 1,3-C_4H_6) and the mechanism for the fragmentation of H(n=4), CH(A), and CH^+(B) from CH_4 and C_2H_2 under the electron-impact excitation.

Experimental

The apparatus and the experimental techniques used in this investigation were similar to those described previously.[14] The electrons emitted from a tungsten filament were accelerated and focused into the collision chamber, where they collided perpendicularly with a molecular jet introduced from a nozzle 0.1 mm in diameter. The electron-beam current in the collision chamber ranged between 0.1 and 3000 μA for electron energies from 0 to 400 eV. The pressure in the collision region was estimated to be of the order of 10^{-3} Torr when the sample gas was introduced.

The emission spectra in the 300—600 nm region were measured by use of a JASCO CT-50 monochromator equipped with an EMI 9558QB photomultiplier, which was connected to a DC amplifier. The spectral bandpass used in this experiment was in the 4—5 Å range.

For the measurements of the excitation function and the appearance potential, a cell whose inside wall was made of brass was employed to reduce the space-charge effect on the wall. In this case, photons modulated by a mechanical chopper were detected by the same monochromator equipped with a HTV R585 photomultiplier, which was connected to an NF PC545A photon counter. The excitation functions and the appearance potentials of N_2 (3371 Å; the (0, 0) band of the second positive system) and N_2^+ (3914 Å; the (0, 0) band of the first negative system) produced from N_2 were measured in order to check the efficiency of this apparatus and to calibrate the electron energy. The satisfactory agreement with the results by Stanton and John[15] indicated that our apparatus could be used for the measurements of the excitation function and the appearance potential.

The gas samples were of a Research Grade obtained from the Takachiho Trading Co.; their purities were specified as 99.95% for CH_4, 99.6% for C_2H_2, 99.8% for C_2H_4, and 99.5% for 1,3-C_4H_6. They were subjected to several freeze-pump-thaw cycles before use.

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Results and Discussion

The Spectra of Methane and Acetylene. Photoemissions from excited fragments and a dimeric ion were found in the 300—600 nm region, as is shown in Figs. 1 and 2. In the longer wavelength region (above 390 nm) of both spectra, the Balmer series of the hydrogen atom ($H_{\beta,\gamma,\delta,\varepsilon,\zeta}$), and the 4300 Å system ($A^2\Delta$–$X^2\Pi$) and the 3900 Å system ($B^2\Sigma^-$–$X^2\Pi$) of CH are identified. In addition, the line at 423 nm, which is superimposed upon the intense band of CH(A–X), is assigned to the (0, 0) band of $CH^+(A^1\Pi$–$X^1\Sigma^+)$.[16] In the spectrum of C_2H_2, the $\Delta v=1$, 0, and -1 sequences of the Swan system of $C_2(d^3\Pi_g$–$a^3\Pi_u)$, and the (0, 0) sequence of the Schüler's T spectrum of $C_4H_2^+(A^2\Pi_g$–$X^2\Pi_u)$, designated as A,[16] are also identified.

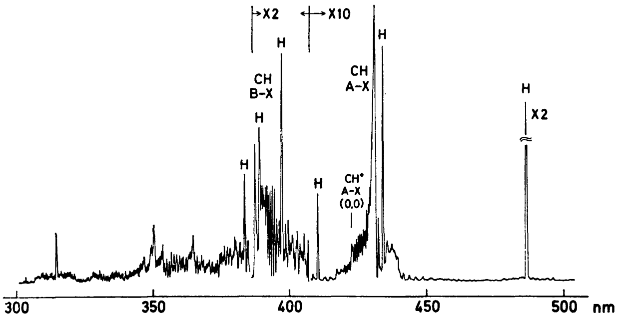

Fig. 1. Emission spectrum of CH_4 by controlled electron impact. Electron energy 200 eV, electron-beam current 800 μA.

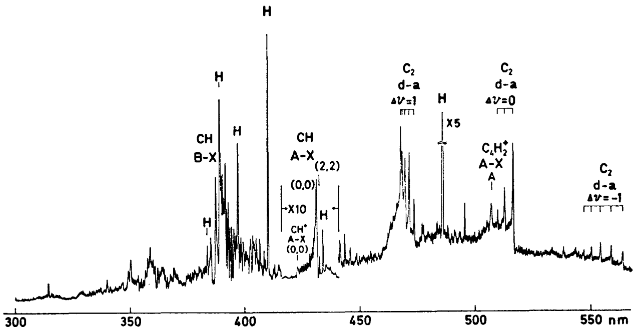

Fig. 2. Emission spectrum of C_2H_2 by controlled electron impact. Electron energy 200 eV, electron-beam current 500 μA.

In the shorter-wavelength region of both spectra, some weak features come out, as is shown in detail in Fig. 3. The $H_{\gamma,\theta}$ lines of the Balmer series of the hydrogen atom, the (1, 0) band of the CH(B–X), and the 3100 Å system ($C^2\Sigma^+$–$X^2\Pi$) of CH are identified in both spectra. In addition, the features at 347—362 nm, which are more clearly observed in the spectrum of CH_4, are assigned to the $B^1\Delta$–$A^1\Pi$ and $b^3\Sigma^-$–$a^3\Pi$ transitions of CH^+ by reference to Carré's results on CH_4 and C_2H_2 by proton bombardment.[4] The (0, 0) and (1, 1) bands of the B–A transition are observed at 350 and 347 nm. The (0, 0) band of the b—a transition is observed at 349—362 nm, superimposed upon the (0, 0) band of the B–A transition; the band head is located at 349 nm, and its rotational structure extends towards the longer wavelengths (up to 362 nm). Some weak features at 327—347 nm are probably related to these two systems, as was observed by Carré.

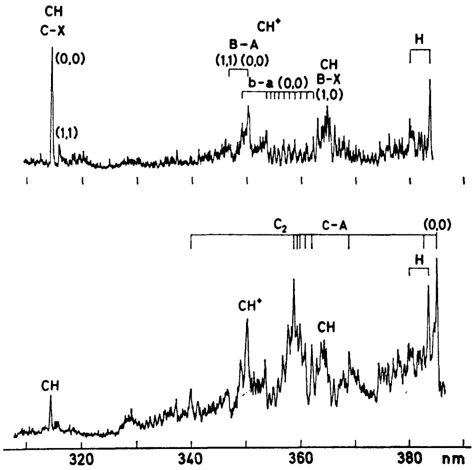

Fig. 3. Emission spectra of CH_4 and C_2H_2 in the 310—385 nm region by controlled electron impact (expanded for the detailed analysis). Top; CH_4, electron energy 300 eV, electron-beam current 800 μA. Bottom; C_2H_2, electron energy 200 eV, electron-beam current 600 μA.

Other numerous bands, which complicate the spectrum of C_2H_2, are ascribed to the Delandres-D'Azambuja system of $C_2(C^1\Pi_g$–$A^1\Pi_u)$; the (0, 0) band is found at 385 nm. Principal bands of this system, described in the Pearse and Gaydon table,[16] are indicated by the straight lines; most of the other features observed in C_2H_2 may be assigned to this system.

Mass-spectrometric studies have shown that the CH^+ ion is an important primary ion produced by electron impact on CH_4 and C_2H_2 and that it constitutes 2—3% of the total ions at a 50—500 eV electron impact on CH_4[17] and 2—4% of the total ions at a 50—500 eV electron impact on C_2H_2.[18] The calculated potential energy curves of the CH^+ ion show that the repulsive $c^3\Sigma^+$ state crosses with the $B^1\Delta$ and $b^3\Sigma^-$ states.[19] The weakness of the emission intensity of CH^+ compared with that of H and CH may be partly due to the competition of the predissociation with photoemission.

Current and Pressure Dependence of the Emission Intensity. The number of the electron and the molecule which participate in the formation of excited species can be determined by the dependence of the photoemission intensity on the electron-beam current and the gas pressure. The intensity of the CH^+ emission was measured on the band at 350 nm under the assumption that the band overlapping with the b–a transition is negligible. This assumption is supported by the finding that the triplet system did not affect the lifetime measurement of the (0, 0) band of the B–A system.[6]

Figures 4 and 5 show that the band intensities of H, CH, C_2, and CH^+ from C_2H_2 are proportional both to the electron-beam current and to the gas pressure at the constant electron energy. Similar linear relationships have been obtained for other fragment species (H, CH, CH^+) from CH_4, as was reported for H and CH by one of the present authors.[7] These results suggest

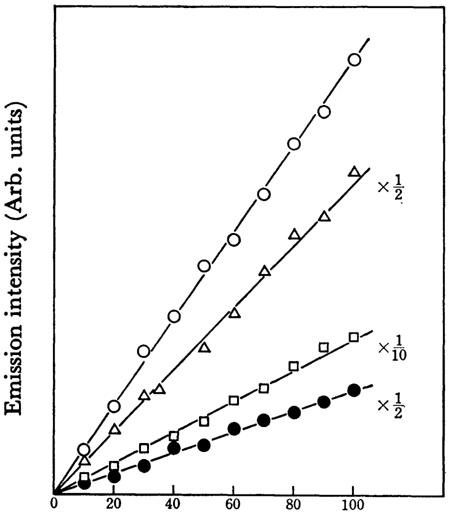

Fig. 4. Dependence of photoemission intensities of C_2H_2 on the electron-beam current. Electron energy 200 eV. ○: CH(431 nm), △: H_γ, □: CH^+ (350 nm), ●: C_2 (468 nm).

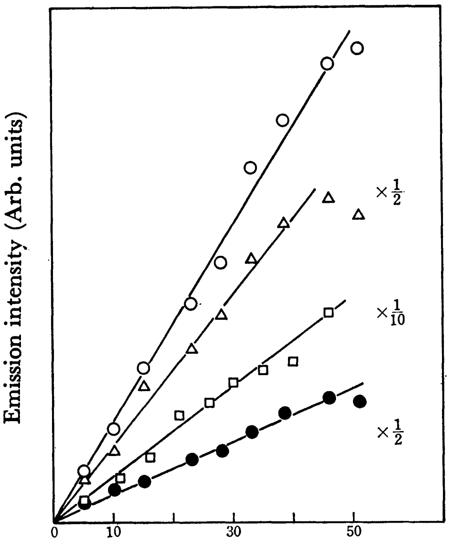

Fig. 5. Dependence of photoemission intensities of C_2H_2 on the pressure in the gas reservoir. Electron energy 200 eV, electron-beam current 50 μA. ○: CH(431 nm), △: H_γ, □: CH^+ (350 nm), ●: C_2 (468 nm).

that emitting excited species are produced through a primary collision of an incident electron with a molecule and that they are not collisionally deactivated within their radiative lifetimes. However, the behavior of the intensity of $C_4H_2^+$ from C_2H_2 to the electron-beam current is exceptional; it is probably produced in a dimerization-excitation process.[20)]

Dissociation Processes from Methane. The dependence of the photoemission intensities of H_γ, CH(A–X), and CH^+(B–A) from CH_4 on the electron-impact energy up to 400 eV is shown in Figs. 6 and 7. The energy dependence of H_β was similar to that of H_γ. No discrete structure can be observed on these excitation functions,

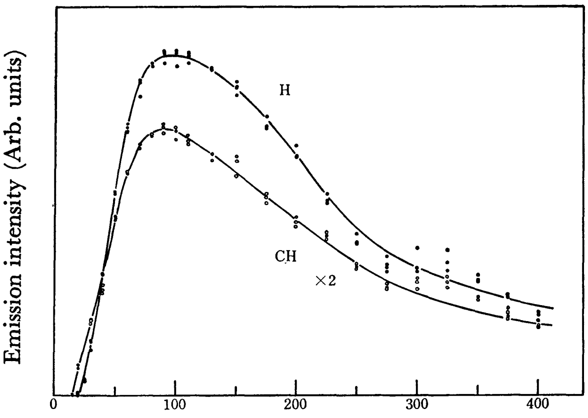

Fig. 6. Excitation functions of H and CH produced by electron impact on CH_4. ●: H_γ electron-beam current 3 μA, ○: CH(431 nm) electron-beam current 3 μA.

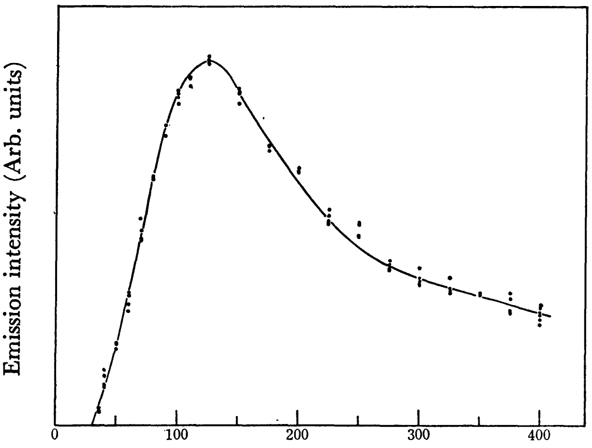

Fig. 7. Excitation function of CH^+ (350 nm) produced by electron impact on CH_4. Electron-beam current 15 μA.

and the maximum emission cross section is located at about 100 eV for H_γ, at about 90 eV for CH(A–X), and at about 130 eV for CH^+(B–A). The maximum positions of H_β and H_γ in the present study nearly agree with those of the previous investigations of the Balmer and Lyman series[5,8,10,11)] and of the metastable and high Rydberg hydrogen fragments.[12)] On the other hand, the maximum position of CH(A–X) is higher than the values reported by Aarts *et al.*[11)] (about 60 eV) and by Fujita[8)] (about 80 eV), while that of CH^+(B–A) is also higher than the maximum ionization cross section of CH^+ as measured by means of a mass spectrometer[17)] (about 80 eV).

The appearance potentials of H_β, CH(A–X), and CH^+(B–A) were measured through the careful determination of the excitation function at a low energy; the results obtained are given in Table 1. Table 1 also enumerates the possible dissociative-excitation and dissociative-ionization processes for the formation of H(n=4), H(high Rydberg states), H^+, CH(A), CH^+(X), and CH^+(B); their minimum excitation energies were calculated by making use of the following dissociation

Table 1. Threshold energies for dissociative excitation and dissociative ionization of CH_4 by electron impact

Dissociation processes	Threshold energies (eV)				
	(calcd)	(obsd)			
		Present results	Electron impact	Photo-excitation	Mass spectral data
$CH_4+e\longrightarrow CH_3(\tilde{X})+H(n=4)$	(1) 17.2				
$CH(X)+H(n=4)+H_2(X)$	(2) 22.0	21.0 ± 1.0	$21.8\pm0.5(H_\beta)$[a]	19.8—20.3(H_β)[d]	
$CH_2(\tilde{X})+H(n=4)+H(n=1)$	(3) 22.1		$21.7\pm0.8(Ly_\gamma)$[b]		
$CH_3(\tilde{B})+H(n=4)$	(4) 22.9				
$CH_3(\tilde{X})+H(n=R)$	(5) 18.0		$22.0\pm0.5(R)$[c]		
$\longrightarrow CH_3(\tilde{X})+H^+$	(6) 18.0				
$CH(X)+H^++H_2(X)$	(7) 22.9				22.7 ± 0.5[e]
$CH_2(\tilde{X})+H^++H(n=1)$	(8) 22.9				24.0 ± 0.5[f]
$CH_3(\tilde{B})+H^+$	(9) 23.7				
$\longrightarrow CH(A)+H_2(X)+H(n=1)$	(10) 12.2				
$CH(A)+3H(n=1)$	(11) 16.6	14.5 ± 0.5	14.6 ± 0.5[a]	12.0[d]	
$CH(A)+H_2(X)+H(n=2)$	(12) 22.4				
$\longrightarrow CH^+(X)+H_2(X)+H(n=1)$	(13) 20.4				
$CH^+(X)+3H(n=1)$	(14) 24.9				22.4 ± 0.1[g]
$CH^+(X)+H_2(X)+H(n=2)$	(15) 30.6				23.3 ± 0.6[e]
$\longrightarrow CH^+(B)+H_2(X)+H(n=1)$	(16) 26.9				
$CH^+(B)+3H(n=1)$	(17) 31.3	30.2 ± 1.0			
$CH^+(B)+H_2(X)+H(n=2)$	(18) 37.1				

a) Ref. 11. b) Ref. 5. c) Ref. 12. d) Ref. 1. e) Ref. 23. f) Ref. 24. g) Ref. 25.

(D) and ionization (I) energies: D(H–H) = 4.48 eV,[21] D(CH_3–H) = 4.41 eV,[22] D(CH_2–H) = 4.90 eV,[22] D(CH–H) = 4.46 eV,[11] and I(CH) = 11.1 eV.[21] In the right column of Table 1, the threshold energies of $H_\beta(n=4-2)$ and CH(A–X) obtained by Aarts *et al.*,[11] of $Ly_\gamma(n=4-1)$ obtained by Sroka,[5] and of high Rydberg hydrogen fragments obtained by Finn *et al.*[12] under electron-impact excitation, and those of H_β and CH(A–X) obtained by Welch and Judge[1] under photo-excitation, are given, in addition to the appearance potentials of H^+[23,24] and CH^+.[23,25]

The observed threshold energy of H_β is slightly lower than those of H_β and Ly_γ reported by the other investigators, while it is higher by approximately 1 eV than that of H_β obtained by photo-excitation. By comparing the experimental value with the calculated energies, the most significant process for the formation of H(n=4) near the threshold is concluded to be the process (1). The excess energy of 3.8±1.0 eV, which is close to the translational energy of high Rydberg hydrogen fragments (4.0±0.5 eV),[12] is imparted to the fragments as the rotational, vibrational, and translational energies. The coincidence of the excess energy may indicate that H(n=4) and H(R) are produced by a similar process.

By photo-excitation Welch and Judge[1] observed the threshold energy of CH(A–X) near 12.0 eV. The present result, which agrees well with the finding of Aarts *et al.*, is higher by 2.5 eV than that obtained under photo-excitation. From the energy consideration, near the threshold it is believed that the process (10) is responsible for the formation of CH(A) and that about 2.3 eV is released as internal and kinetic energies.

The appearance potential of the CH^+(B–A) emission was observed at 30.2±1.0 eV. As to the dissociative-ionization process for CH^+(B), the three following mechanisms through highly excited states of methane designated as CH_4^{**} and/or through the highly excited methane ion are possible:

$$CH_4 + e \longrightarrow (CH_4^{**},\ CH_4^{+*}) \longrightarrow \begin{cases} CH^+(B^1\Delta) + H_2(X^1\Sigma_g^+) + H\,(n=1) \\ CH^+(B^1\Delta) + 3H\,(n=1) \\ CH^+(B^1\Delta) + H_2(X^1\Sigma_g^+) + H\,(n=2). \end{cases}$$

The most likely mechanism is the process (16), and the excess energy of about 3.3 eV is released to the fragments as internal and kinetic energies at the threshold.

The appearance potential of the ion upon mass spectroscopy gives information on the formation of ionic species in the ground state. Smith[23] and McDowell and Warren[25] found the appearance potential of CH^+ from CH_4 at 23.3±0.6 eV and 22.4±0.1 eV respectively. From Table 1, the energetically possible process at the threshold is the process (13) and the excess energy of 2—3 eV is imparted to the fragments. The most likely process for the formation of CH^+(B) in the present study is similar to that of CH^+(X).

Since the production of ionic species can be considered as a limiting case of the formation of the corresponding neutral excited species, a similar mechanism can be expected to be involved in the dissociative-excitation and related dissociative-ionization processes. The facts that the process for the formation of CH(A) is similar to that of CH^+(X) and that the excess energy of the former (2.3±0.5 eV) is close to that of the latter (2.0±0.1 eV,[25] 2.9±0.6 eV[23]) support the above expectation.

Four reactions can account for the formation of H^+ near the threshold, as is shown in Table 1. Smith[23] found the appearance potential of H^+ at 22.7±0.5 eV, and recently Appell and Kubach[24] observed H^+ ions with kinetic energies between 1.4 and 3.4 eV at an appearance potential of 24.0±0.5 eV. Both values indicate that the energetically possible process is the process (6), which is similar to the process (1).

Platzman pointed out that neutral primary products are formed in a radiation-induced reaction through a highly excited neutral state just above the first ionization potential (IP_1) of the molecule named the superexcited state, where dissociation and preionization are competitive.[26] The isotope effect of the Balmer emission from CH_4 under electron-impact excitation has been interpreted as support that excited hydrogen atoms originate from such a superexcited state.[8,11] Since the observed threshold energies of H_β and CH(A–X) are larger than the IP_1 of CH_4 (12.99 eV[22]) and the ionic fragment is not involved in the resulting species, it is concluded that they are produced through the superexcited states.

The superexcited state of CH_4 has been investigated on the basis of the difference between the absorption (energy loss) and ionization spectrum,[26–28] and recently Backx *et al.*[28] have found two regions of superexcited states by means of electron-electron and electron-ion coincidence measurements at keV electron impact. The first state ranged between the IP_1 and 17 eV, which was attributed to high vibrationally-excited Rydberg states converging to the ground state of CH_4^+, $(1t_2)^{-1}$, with reference to the interpretation of Nishikawa and Watanabe.[29] The second state occurred in the region of 22—24 eV, which was connected with the second ionic state, $(2a_1)^{-1}$. The observed threshold energy of CH(A–X) emission indicates that the formation of CH(A) near the threshold proceeds through the first superexcited states. The threshold energy of H_β in the present study and that of the Balmer and Lyman series,[1,5,10–12] and high Rydberg hydrogen fragments[12] are all in the range between 20 and 22 eV. Therefore, superexcited states can be expected to exist in this energy region, although the possibility of excitation to these superexcited states may be small because excited hydrogen atoms are formed by optically forbidden processes.[11] However, Backx *et al.*[28] found no superexcited states in the region of 17—22 eV, which is consistent with the works of Platzman[26] and Nishikawa and Watanabe.[29] Meanwhile, the results by Metzger and Cook,[30] and Rebbert and Ausloos (the ionization efficiency η_i=0.96 at 21.2 eV)[31] under photo-excitation, and by Ehrhards and Linder[27] under 70 eV electron-impact excitation, support the existence of superexcited states in the same energy range.

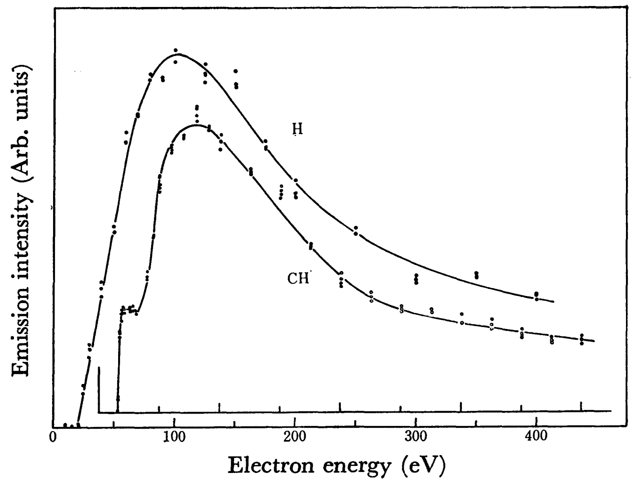

Fig. 8. Excitation functions of H and CH produced by electron impact on C_2H_2. ●: H_β electron-beam current 1.5 μA, ○: CH(431 nm) electron-beam current 1 μA.

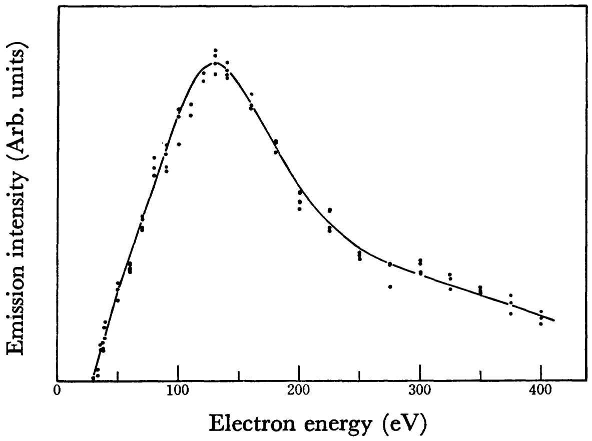

Fig. 9. Excitation function of CH^+ (350 nm) produced by electron impact on C_2H_2. Electron-beam current 5 μA.

Dissociation Processes from Acetylene. The excitation functions of H_β, CH(A–X), and CH^+(B–A) from C_2H_2 are shown in Figs. 8 and 9. The excitation function of H_γ was nearly identical with that of H_β when it was normalized at the maximum. The excitation functions of H_β and CH^+(B–A) have no structure; the former has a maximum at about 100 eV, and the latter, at about 130 eV. The excitation function of CH(A–X) rapidly increases near the threshold; the second threshold can be observed at about 30 eV, as was found by Beenakker and de Heer[11] at 28±2 eV. The maximum position of the emission cross section of H_β agrees with the Beenakker and de Heer's result, while that of CH(A–X) is higher than theirs (about 60 eV). The maximum position of CH^+(B–A) is also higher than that of the ionization cross section of CH^+ as measured by a mass spectrometer (about 90 eV).[18] At present no explanation can be given for the discrepancy in the maximum positions of CH and CH^+ from CH_4 and C_2H_2 between the present work and the others; the excitation functions were measured with as low an electron-beam current as possible to avoid the space-charge effect, although higher currents are required for CH^+(B–A) because of the weakness of the intensity.

The appearance potentials and the predominant dissociation channels for the formation of H(n=4), CH(A), and CH^+(B) are enumerated in Table 2. Table 2 also shows the possible dissociative-ionization processes for H^+ and CH^+, and their appearance potentials as obtained in mass-spectrometric studies.[18,32] The threshold energies were calculated using data

Table 2. Threshold energies for dissociative excitation and dissociative ionization of C_2H_2 by electron impact

Dissociation processes	Threshold energies (eV) (calcd)	(obsd) Present results	Beenakker *et al.*[a]	Mass spectral data
$C_2H_2+e \longrightarrow C_2H(\tilde{X})+H(n=4)$	(1)18.1	20.6±1.0	20.6±1.0	
$C_2(X)+H(n=4)+H(n=1)$	(2)23.4			
$C_2H^+(\tilde{X})+H(n=4)$	(3)30.1			
$\longrightarrow C_2H(\tilde{X})+H^+$	(4)19.0			21.7±1.0[b]
$C_2(X)+H^++H(n=1)$	(5)24.2			
$C_2H^+(\tilde{X})+H^+$	(6)30.9			
$\longrightarrow CH(A)+CH(X)$	(7)12.8	13.5±1.0	13.0±1.5	
$CH(A)+CH(A)$	(8)15.6			
$CH(A)+C(^3P)+H(n=1)$	(9)16.2			
$CH(A)+CH^+(X)$	(10)23.9			
$CH(A)+C^+(^2P)+H(n=1)$	(11)27.5			
$CH(A)+C(^3P)+H^+$	(12)29.8			
$\longrightarrow CH^+(X)+CH(X)$	(13)21.0			21.9[c]
$CH^+(X)+CH(A)$	(10)23.9			
$CH^+(X)+C(^3P)+H(n=1)$	(14)24.5			
$CH^+(X)+CH^+(X)$	(15)32.1			
$\longrightarrow CH^+(B)+CH(X)$	(16)27.5	29.3±1.0		
$CH^+(B)+CH(A)$	(17)30.3			
$CH^+(B)+C(^3P)+H(n=1)$	(18)30.9			
$CH^+(B)+CH^+(X)$	(19)38.6			

a) Ref. 11. b) Ref. 18. c) Ref. 32.

identical with those employed by Beenakker and de Heer.[11] The observed appearance potentials of H_β and CH(A–X), which agree well with the work of Beenakker and de Heer,[11] indicate that the significant dissociative-excitation processes for H(n=4) and CH(A) near the threshold are both the lowest-energy processes, (1) and (7). The excess energies of about 2.5 eV for H(n=4) and about 0.7 eV for CH(A) are imparted to the resulting fragment species as the internal and kinetic energies. Meanwhile, mass-spectrometric studies show that the dissociative-ionization processes (4) and (13), which are similar to the dissociative-excitation processes for H(n=4) and CH(A), contribute to the formation of H^+ and CH^+. It should be noticed that the excess energies of H^+ (2.7±1.0 eV) and CH^+ (0.9 eV) are in good agreement with those of H(n=4) and CH(A) described above. Thus, the formation of H^+ and CH^+ from C_2H_2 can be considered as the limiting case of the excitation of H and CH.

The excitation function of CH(A–X) differs from that of the other fragments in the inclination near the threshold; it increases steeply and has the second threshold. The excitation function for a spin-forbidden transition is known to exhibit a sharp maximum at a slightly higher energy than the threshold and to drop rapidly at a still greater electron energy; meanwhile, the maximum cross section for an optically allowed transition is located at a fairly higher energy than the threshold, and the peak is not very sharp.[11] These features in the excitation functions for the excitation and the ionization of the parent molecule are also manifest in those for the dissociative excitation. The dissociative-excitation process (7) can proceed both through the singlet and the triplet states of the excited parent molecule, according to the spin-conservation rule. Thus, the steep increase and the first threshold of the excitation function of CH(A) from C_2H_2 can probably be interpreted as the contribution of the spin-forbidden process, and the further increase up to 80 eV, as that of one or a few optically allowed processes. The second threshold may be due to the superposition of the two excitation processes. The shape of the excitation function of CH(A) from CH_4 indicates that the contribution of the triplet excitation process is unimportant in the dissociative excitation of CH_4 into CH(A).

The threshold energy of the CH^+(B–A) emission was found at 29.3±1.0 eV. Above this threshold, CH^+(B) is probably formed in the process (16), which is the lowest-energy process, as in the case of CH^+(X), and the fragment species carry off an excess energy of about 1.8 eV.

Since the threshold energies of H_β and CH(A–X) emissions exceed the IP_1 of C_2H_2 (11.41 eV[22]) and no ions are produced in the reactions, they are produced through superexcited states of C_2H_2. It is noteworthy that all the dissociation processes of CH_4 in Table 1 need more excess energy than that required in the corresponding dissociation processes of C_2H_2 in Table 2, assuming that the calculated threshold energies are accurate. This can be interpreted by means of the fact that energy between the cross point of a repulsive potential with the primarily prepared highly-excited states and the dissociation limit is larger in all cases of CH_4, where the energy of the cross point determines the observed appearance potential.

Ethylene and 1,3-Butadiene. The emission spectra of C_2H_4 and C_4H_6 in the 300—600 nm region were measured. The resulting spectra consist of H(Balmer), CH(A–X, B–X, C–X), CH^+(A–X, B–A, b–a), C_2(C–A, d–a), and $C_4H_2^+$(A–X), which are qualitatively identical with the spectrum of C_2H_2. However, the intensity of the CH^+ emission relative to the H and CH emissions is much weaker than that in the cases of CH_4 and C_2H_2. This is consistent with the lower fraction of the CH^+ ions relative to the total ions observed in the mass-spectrometric studies.[33]

The formation of excited H, CH, CH^+, and $C_4H_2^+$ except for $C_4H_2^+$ from C_2H_4[20] are confirmed to be primarily produced by the linear dependence of the intensities on both the electron-beam current and the gas pressure. A more sensitive device will make it possible to measure the excitation function and the threshold energy of the CH^+ emission.

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