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EMISSION SPECTRA OF CH^+ PRODUCED FROM CH_4 AND C_2H_2 BY CONTROLLED ELECTRON IMPACT

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Under the controlled electron-impact excitation (0 - 450 eV) of CH_4 and C_2H_2 at low pressures, photoemission was observed from such excited fragments as H, CH, CH^+, C_2 and $C_4H_2^+$. The excitation function and the appearance potential of the CH^+ emission were measured, and the dissociation process was discussed.

UV and visible photoemissions of the excited fragments resulting from the dissociative excitation of simple aliphatic hydrocarbons(CH_4, C_2H_2) have been investigated at low pressures by VUV photolysis, ion bombardment and electron impact. In the studies by electron-impact excitation[1-7] photoemissions of atomic and diatomic species(H, C, CH, CH^+ and C_2) have been observed and the mechanism of the dissociative excitation of H, C, CH and C_2 has been discussed in terms of the excitation function and the appearance potential. This communication describes the emission spectra of CH_4 and C_2H_2 under the impact of electron beam(0 - 450 eV) and the mechanism of the excited CH^+ formation. The apparatus used in the present study is the same as that described previously,[8] although some improvements[9] have been carried out.

The emission spectra of CH_4 and C_2H_2 in the 300 - 600 nm region under electron-impact excitation are found to consist of the bands of several fragments. One example of the resulting spectra of CH_4 and C_2H_2 in the 310 - 385 nm region is shown in Fig. 1. The $H_{\eta,\theta}$ lines of the Balmer series, the (0,0) and (1,1) bands of CH(C-X) and the (1,0) band of CH(B-X) are identified in both spectra. The features at 347 - 362 nm are assigned to two systems of $CH^+(B^1\Delta - A^1\Pi,\ b^3\Sigma^- - a^3\Pi)$, as observed by proton bombardment

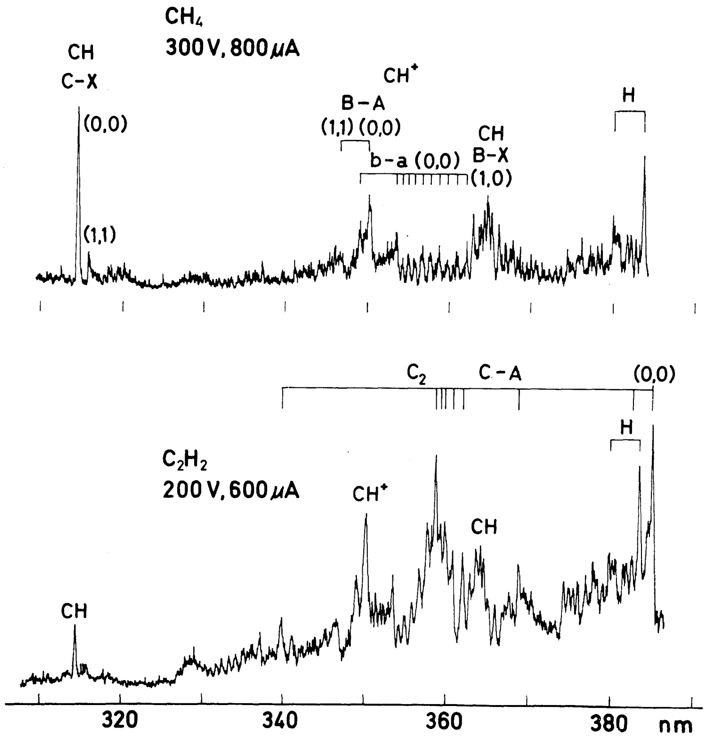

Fig. 1. Part of the emission spectra of CH_4 and C_2H_2 by electron impact.

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on CH_4 and C_2H_2.[10] The bands at 350 nm and 347 nm are identified as the (0,0) and (1,1) bands of the B-A system. The (0,0) band of the b-a system is identified in the 349 - 362 nm region, although it is partially superimposed upon the (0,0) band of the B-A system; the band head is observed at 349 nm and the rotational structure extends towards the red. Some of the additional features at 327 - 347 nm may be related to CH^+ B-A and b-a systems. These two systems were obtained by Beenakker and de Heer,[6] although none of the spectra were described. Other numerous bands, which appear only in the spectrum of C_2H_2, are assigned to the Delandres-d'Azambuja system(C-A) of C_2. In the 385 - 600 nm region, the Balmer lines of $H_{\beta,\gamma,\delta,\varepsilon,\zeta}$, and the CH(A-X, B-X), CH^+(A-X), C_2(d-a, only from C_2H_2) and $C_4H_2^+$(A-X, only from C_2H_2) bands are observed.

The emission intensities of the H, CH, CH^+ and C_2 bands are found to be linear with respect to both the electron-beam current and the gas pressure. However, the intensity of the $C_4H_2^+$ band produced from C_2H_2 is the exception.[9]

The excitation function and the threshold of the CH^+(B-A) emission at 350 nm have been measured and analyzed on the assumption that the contribution of the b-a system to the B-A band at 350 nm is negligible. Figure 2 shows the excitation function of the CH^+(B-A) emission from C_2H_2. A similar excitation function is obtained for CH_4. Possible dissociative ionization mechanism and their minimum threshold energies are given in the following table.

	Dissociation Processes	Threshold Energies (eV) (calc.)	(obs.)
$CH_4^* \longrightarrow$	(1) $CH^+(B) + H_2(X) + H(n=1) + e$	26.8	30.2±1.0
	(2) $CH^+(B) + 3H(n=1) + e$	31.3	
$C_2H_2^* \longrightarrow$	(3) $CH^+(B) + CH(X) + e$	27.5	
	(4) $CH^+(B) + CH(A) + e$	30.4	29.3±1.0
	(5) $CH^+(B) + C(^3P) + H(n=1) + e$	30.9	

By comparing the observed values with the calculated ones, it is concluded that the formation of CH^+(B) proceeds through processes (1) and (3) near the observed threshold. The difference of the energy between the observed threshold and the calculated energy is imparted to the fragments as the vibrational, rotational and kinetic energies.

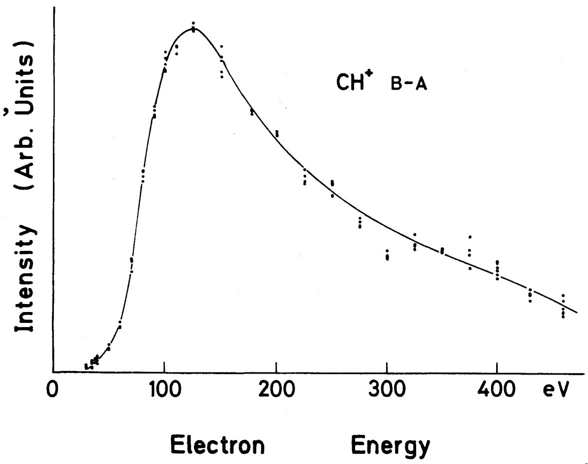

Fig. 2. Excitation function for CH^+ emission by electron impact on C_2H_2.

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