Reaktionskanäle, die die Molekülionen liefern, diese stets in angeregten Zuständen erzeugen. Man erhält für Stoßenergien des Ne^+ zwischen 100 und 200 eV etwa 5% N_2^+, 4 bis 6% O_2^+ und 8% CO_2^+. Als Vergleichswerte lassen sich aus den massenspektrometrischen Untersuchungen 3% N_2^+ nach [2] bei 150 eV und 12,5% CO_2^+ nach [4] bei 500 eV anführen. Weitere Messungen sind zur Bestimmung genauer Werte erforderlich.

Herrn Professor Dr. H. RAETHER danke ich für die Überlassung von Institutsmitteln zur Durchführung dieser Untersuchung.

Light Emission in the VUV by Dissociative Excitation of CH_4 with Low-Energy Electrons

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By bombardment of methane with low-energy electrons (0 – 400 eV) the molecule is dissociated in a single collision into excited C and H atoms or into excited H atoms and a free radical. The excited atoms emit a radiation in the vuv (900 Å – 1700 Å). The appearance potentials and excitation functions are measured. Approximate values of the cross sections are given. The excitation cross section for the CII-Lines are extremely small ($\sigma \leqq 10^{-21}$ cm²), whereas those for the H and CI-lines are of the order of $10^{-19} - 10^{-18}$ cm² at 150 eV.

At this time very little is known about the production of excited atoms by low-energy bombardment of methane. In a recent work [1] the production of hydrogen radiation by $e^- - CH_4$ collisions has been reported. But that work is concerned with high energy collisions (some keV). The excitation of the Balmer series and of Ly α has been studied in detail. Only few information was given about the excitation of Ly β.

This work reports on dissociative excitation processes in methane by low-energy electrons (0 – 440 eV). The excitation functions and appearance potentials of Ly α, Ly β, Ly γ, Ly δ and of some carbon multiplets in the vuv have been measured. Furthermore the pressure and current dependencies of the excitation processes have been determined. The absolute cross sections are evaluated approximately.

Apparatus

An electron beam of variable energy (0 – 450 eV) and variable current (0 – 200 μA) passes the collision cell through pressure stages. A magnetic field (100 to 400 gauss) confines the beam. The pressure within the cell ($10^{-5} - 10^{-2}$ Torr) is measured with a capacitance manometer (MKS Baratron). In order to keep the electrodes clean the electron gun is held at a temperature of 200 °C. The light emitted in the collision process is observed with a vacuum monochromator at right angles to the electron beam. In the wavelengths region below 1200 Å a Bendix multiplier (M 306) was used as radiation detector, whereas a sealed multiplier (EMI 9502 S) covered with sodium salicylate was used for longer wavelengths. The latter one is less sensitive than the Bendix multiplier and it registers scattered light from the visible and near uv.

The energy scale of the electron beam is calibrated by measuring the appearance potential of the He-line at 584 Å. In order to determine the absolute values of the cross sections the excitation function of the He-line at 584 Å was measured and corrected for radiation imprisonment. The excitation function of He 584 Å which is sufficiently known [2] is compared with the excitation function whose absolute value is to be determined. Furthermore the variation of the reflectance of the grating and the quantum yield of the multiplier cathode have to be taken into account. In the wavelengths region above 1100 Å our method only gives the order of magnitude of the absolute intensity, but it should be better in the region from 1000 Å to 600 Å. Especially the error of the intensity ratio of neighboured lines is low (20 – 30% for $\Delta\lambda < 200$ Å). A detailed description of the apparatus and the procedure of the measurement is given in [3].

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Measurements

Figure 1 shows the spectrum (900 Å < λ < 1250 Å) obtained by electron bombardment of methane at a pressure of $1.7 \cdot 10^{-3}$ Torr. The energy of the electrons amounted to 180 eV. The hydrogen lines of the Lyman series are excited with high intensity. But there are no CII-lines in the spectrum. Only at about 904 Å there is a weak line which we ascribe to the transition 2p′ $^2P \rightarrow$ 2p ^2P of CII. No radiation components were found below 900 Å.

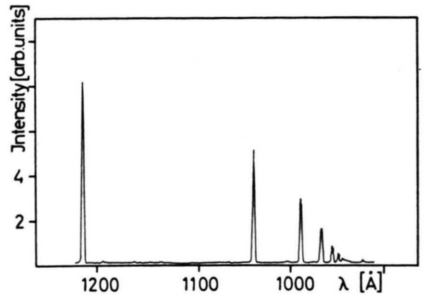

Fig. 1. Spectrum of the wavelength region from 900 Å – 1250 Å.

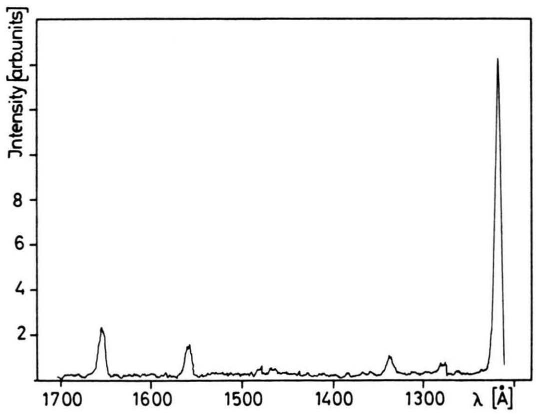

Fig. 2. Spectrum of the wavelength region from 1200 Å – 1700 Å.

Figure 2 shows the spectrum of the wavelengths region from 1200 Å to 1700 Å ($E = 200$ eV; $p = 2.3 \cdot 10^{-3}$ Torr). We could only identify the CI multiplets at 1657 Å (2p3s $^3P \rightarrow 2p^2\,{}^3P$) and 1561 Å ($2s2p^3\,{}^3D \rightarrow 2p^2\,{}^3P$) because of the low sensitivity of the detector.

The excitation functions of the Lyman series are given in Fig. 3. In Table 1 the appearance potentials and the absolute cross sections are listed. The form of the excitation functions depends only slightly on

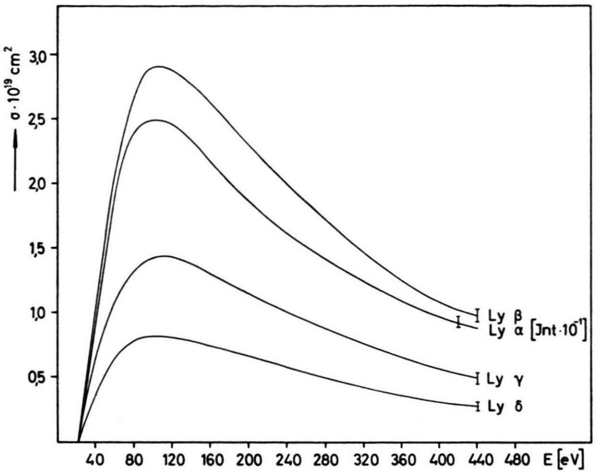

Fig. 3. Excitation functions of the Lyman series. The ordinate has to be multiplied by a factor 10 for Ly α.

the pressure within the collision cell which is demonstrated by Fig. 4. In this figure the quotient of the intensities of Ly α at 110 eV and at 440 eV is represented as a function of the pressure. The cross section given in ref. [1] for the excitation of Ly α is approximately by a factor 4 greater than our value. Better agreement we have found for the absolute values of the intensity of Ly β which amounts to $\sigma(50\,\text{eV}) = 1.5 \cdot 10^{-19}\,\text{cm}^2$ and $\sigma(50\,\text{eV}) = 2.8 \cdot 10^{-19}\,\text{cm}^2$ according to [1]. No corrections concerning the polarisation of the radiation can be given. But according to [1] the degree of polarisation should be small.

Figure 5 shows the excitation functions of the CI multiplets at 1657 Å and 1561 Å. The accuracy of the measurement is lower than in the case of the

Wave-length Å	Transi-tion	Appear. Potent. eV	Cross section at 156 eV $\sigma \cdot 10^{19}$[cm²]	Intensity ratio meas.	accord. to ref. [8]
1657	CI 3s ^{3}p 2p^2 ^{3}p	≈ 26.2	1.8	—	—
1561	CI 2p^3 ^{3}D 2p^2 ^{3}p	≈ 27	2.2	—	—
1215.7	Ly α	20.7	22	29	14.5
1025.8	Ly β	21.2	2.6	3.7	4.6
972.5	Ly γ	21.7	1.3	1.8	2
949.7	Ly δ	21.7	0.7	1	1
904	CII 2p′ ^{2}p 2p ^{2}p	—	—	—	—

Table 1. Summary of the data.

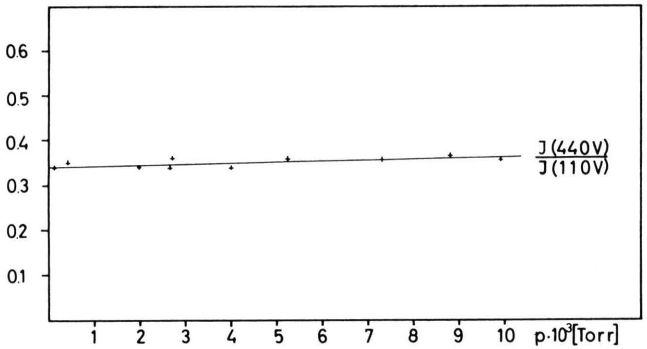

Fig. 4. Quotient of the intensities of Ly α at 110 eV and 440 eV.

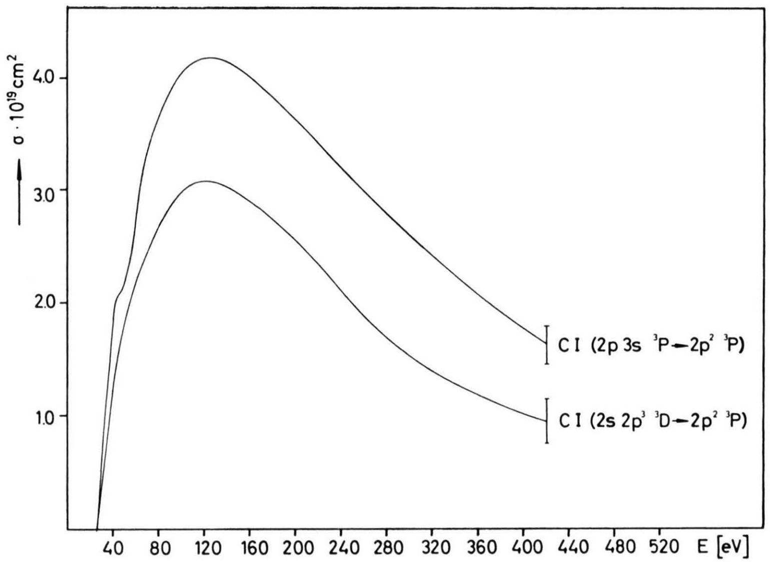

Fig. 5. Excitation functions of the CI multiplets.

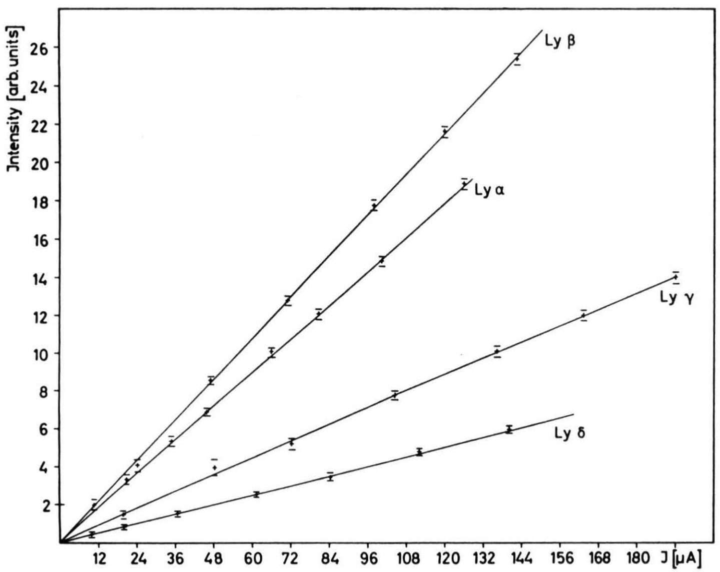

Fig. 6. Intensity of the hydrogen lines versus beam current.

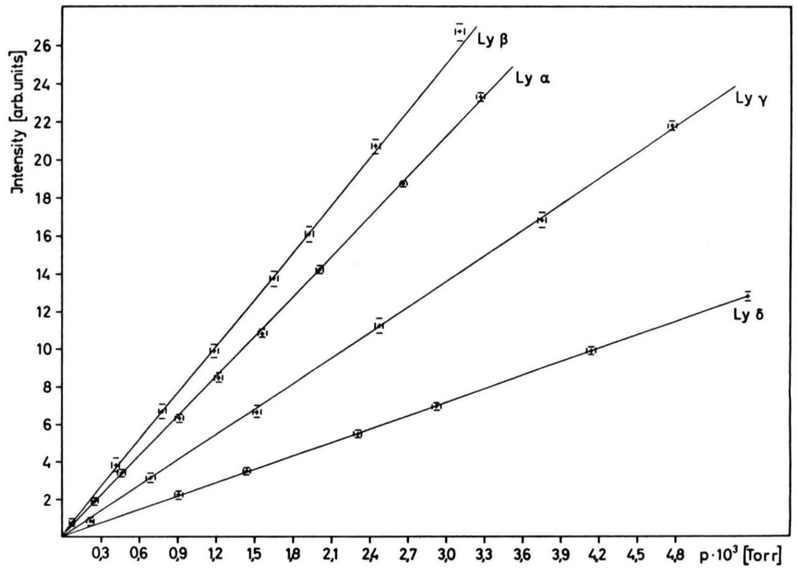

Fig. 7. Intensity of the hydrogen lines versus pressure within the collision cell.

hydrogen lines. Especially the values of the cross section (see Table 1) only give the order of magnitude.

The intensities of the hydrogen lines are represented in Fig. 6 as a function of the beam current at constant electron energy and at constant pressure. The diagram demonstrates that the intensity is a linear function of the beam current. Similarly the intensity depends linearly on the pressure within the collision chamber which is shown in Fig. 7; these measurements were performed at constant beam current and at constant electron energy.

Discussion

It follows from the spectra that vuv-radiation of carbon and hydrogen atoms can be excited by bombarding CH_4 with low-energy electrons. The radiation is excited in a one-step process. This follows from the linear dependency of the intensity on pressure and current.

The probability for the formation of excited carbon ions is extremely small e. g. $\sigma(180\ \text{eV}) \approx 10^{-21}$ cm^2 for the transition CII ($2p'\,^2P \rightarrow 2p\,^2P$) at 904 Å. In opposition to the observations in CH_4 this multiplet is excited with high intensity by electron bombardment of CO or CO_2 [4]. On the other hand the probability for exciting the states $2p3s\,^3P$ and $2s2p^3\,^3D$ of CI is about a factor 100 greater than those for exciting CII ($2p'\,^2P$). Assuming a dissociation energy of CH_4 to free atoms of 17.1 eV the energy required for the process $CH_4 + e^- \rightarrow C + 4\,H$ is $E = 24.6$ eV for $2p3s\,^3P$ and $E = 25$ eV for $2s2p^3\,^3D$. The measured appearance potentials amount to $E \approx 26.2$ eV and $E \approx 27$ eV. Therefore the dissociation products carry of a kinetic energy of $1-2$ eV. But it is possible that primarily a higher level is excited, which in turn populates the level from which the radiation was observed.

Excited H atoms can be produced by several processes:

	Process	Calcul. min. energy in eV for excitat. of Ly α	Ly δ
a)	$CH_4 + e^- \rightarrow CH_3 + H + e^-$	14.7	17.6
b)	$CH_4 + e^- \rightarrow CH_2 + H + H + e^-$	19.6	22.5
c)	$CH_4 + e^- \rightarrow CH + 2\,H + H + e^-$	23.8	26.7
d)	$CH_4 + e^- \rightarrow CH + H_2 + H + e^-$	19.3	22.2
e)	$CH_4 + e^- \rightarrow C + 3\,H + H + e^-$	27.3	30.2
f)	$CH_4 + e^- \rightarrow C + H_2 + H + H + e^-$	22.8	25.7

The minimum energies required for the excitation of Ly α and Ly β are calculated by using the following dissociation energies: $D(CH_3-H) = 4.5$ eV, $D(CH_2-H) = 4.9$ eV, $D(CH-H) = 4.2$ eV and $D(C-H) = 3.5$ eV. Unfortunately only the dissociation energies $D(CH_3-H)$ [5] and $D(C-H)$ [6] are known with certainty whereas those for the other processes are approximate values [7]. The measured appearance potentials are listed in Table 1. Immediately above threshold a production of excited H atoms is energetically possible by the processes a), b) and d). Assuming process a) the dissociation products must carry off an energy excess of some eV.

There are some interesting features concerning the excitation of the Lyman series by electron bombardment of methane. Within the limits of error the excitation functions can be represented by nearly the same curve if they are normalized to equal values at maximum. The appearance potentials are equal to eachother within the accuracy of the measurement ($\Delta E = 0.8$ eV; see Table 1). Furthermore the intensity ratios are nearly the same as those calculated under the assumption that every level is populated by the same number of electrons [8]. Only the intensity of Ly α seems to be too great. This is understandable because the work function of the multiplier cathode (tungsten) may be lowered by small contaminations. It may be possible that the excited H atoms are produced via an intermediate state of the CH_4 molecule. But this can only be elucidated by further investigations.

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