Electron Induced Fluorescence Spectra of Methane

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Abstract. Electron induced fluorescence (EIF) emission spectra of methane were measured using a crossed electron molecular beams apparatus in visible and near UV range 180–700 nm at incident electron energies 30, 50 and 70eV. In the EIF spectra atomic emission lines of H Balmers series and C were observed, additionally emission bands of CH^+ and CH fragmends were detected. Relative emission cross sections (emission functions) of some H, CH and C lines were measured and the threshold energies for these processes were determined.
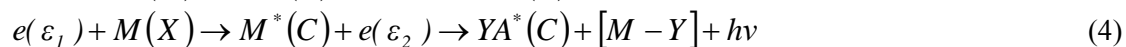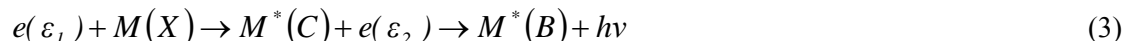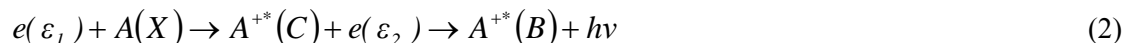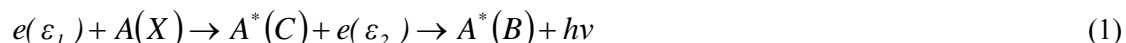
Introduction

Electron induced fluorescence is a tool to study the electronic states of the molecules by observing emission from excited atoms, molecules, or their fragments after impact of monoenergetic electrons. Electrons with well defined energy collide with molecules and excite their electronic, vibrational and rotational states. Unlike photon excitation, the electron impact allows us to study also optically forbidden excited states and their subsequent decay to lower states. Using the crossed-beams apparatus we are able to measure emission spectra at selected electron energy, or the relative emission cross sections for selected spectral line or band. On this way we are able to study the excited states of the molecules, emission from these states and the efficiency of the overall process as a function of the energy of the exciting electrons. Obtained data can be used e.g. to verify and improve theoretical models, or can be applied in chemistry, physics and many applications.

Methane is a very important molecule in extraterrestrial atmospheres like these of Jupiter, Saturn, Uranus and Neptune (emphasis on Saturn's moon Titan) [*e.g., Lutz et al.,* 1976]. The knowledge of the electronic states and their emission is therefore important in order to understand the processes between electrons and molecules in these atmospheres. The electronic structure and their emission spectra is also important for Optical Emission Spectroscopy (OES) diagnostics of low temperature plasma, as well as the edge plasma of tokamaks and stellarators, since the presence of carbon and hydrogen atoms in the outer shell of plasma.

There is a consensus, that any electronically excited state of neutral methane leads to the dissociation of the molecule, which is supported by experiment [*e.g., Aarts et al.,* 1971, *Beenakker et al.,* 1975], where only spectral lines and bands of excited fragments were obtained. Theoretical analysis arrived also to similar conclusion [*e.g., Gil et al.,* 1988]. The methane spectrum in the visible region for electron energies 30 to 80 eV is dominated by Balmer series of Hydrogen ($n \rightarrow 2$), CH ($A^2\Delta \rightarrow X^2\Pi$), CH ($B^2\Sigma^- \rightarrow X^2\Pi$), and CH ($C^2\Sigma^+ \rightarrow X^2\Pi$) transition, and CH^+ transitions [*Hesser et al.,* 1970, *Motohashi et al.,* 1996].
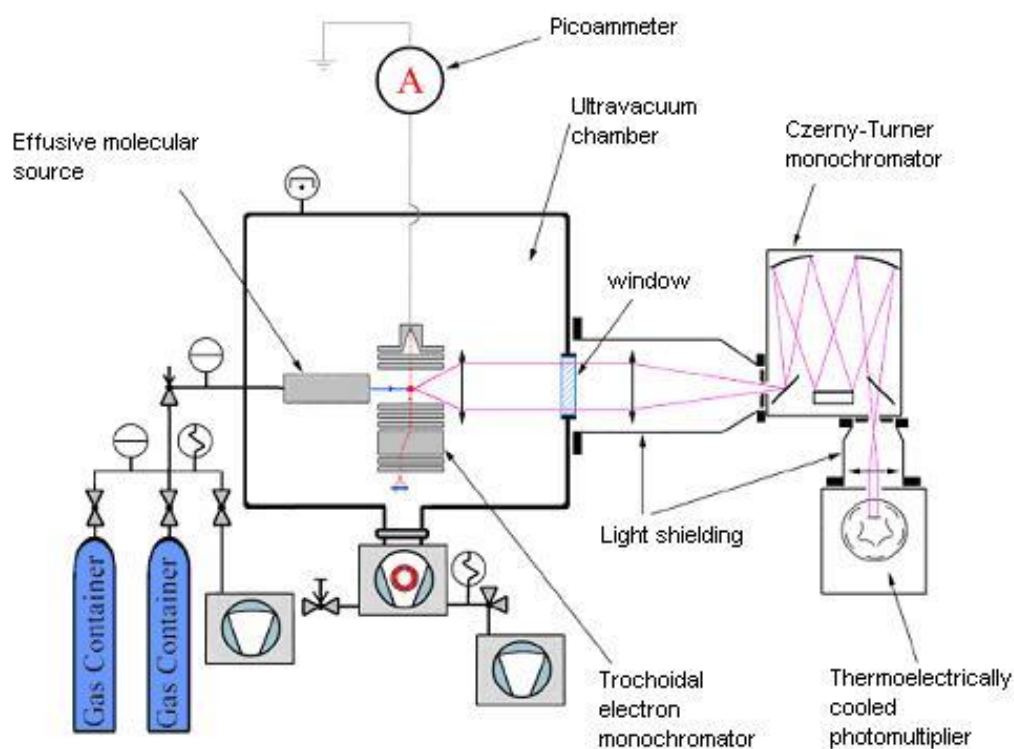
Experimental

We have developed a crossed-beams apparatus to study EIF of the molecules. A beam of electrons with a very narrow energy distribution, and a beam of studied atoms/molecules collide, resulting in excitation of the molecules and subsequent emission of the photons. The most important processes we are able to observe in the apparatus are excitation of atom or molecule (1), (3), ionization excitation of the targets (2), and dissociative excitation of a molecule (4).

$$e(\,\varepsilon_1\,)+A(X)\rightarrow A^*(C)+e(\,\varepsilon_2\,)\rightarrow A^*(B)+h\nu \tag{1}$$

$$e(\,\varepsilon_1\,)+A(X)\rightarrow A^{+*}(C)+e(\,\varepsilon_2\,)\rightarrow A^{+*}(B)+h\nu \tag{2}$$

$$e(\,\varepsilon_1\,)+M(X)\rightarrow M^*(C)+e(\,\varepsilon_2\,)\rightarrow M^*(B)+h\nu \tag{3}$$

$$e(\,\varepsilon_1\,)+M(X)\rightarrow M^*(C)+e(\,\varepsilon_2\,)\rightarrow YA^*(C)+[M-Y]+h\nu \tag{4}$$

where e represents the electron, $A(X)$ or $M(X)$ atom or molecule in their ground state, $A*(C)$ is a particle in any excited state, Y is a molecular fragment, *[M-Y]* molecule stripped of this fragment, and $h\nu$ energy of a photon emitted during deexcitation.

The processes mentioned above can be studied also in discharges. There are two great advantages of the presented method in comparison to discharge experiments. First, we can set electron energy with a very high accuracy and narrow distribution, which is impossible in any type of discharge, and allows us to measure cross sections of the processes. Second, we have optically thin environment with single collision conditions (low pressures), containing only the molecules of interest. This allows us to measure high resolution emission spectra.

The experimental apparatus is shown on the figure 1. It consists of a trochoidal electron monochromator [*Stamatovic et al.,* 1970] located in an ultrahigh vacuum chamber. The present monochromator supplies typical $\approx$ 100 nA, up to $\approx$ 200 nA electron current with electron energy resolution $\approx$ 300 meV, which is planned to be improved further in the future. Magnetic field of about 5×10^{-3} T is produced by three pairs of coils (x, y, z coordinates) around the vacuum chamber, which allows accurate alignment of the direction of the field with respect to the electron monochromator symmetry axis. The electron current is measured at Farraday cup at the back part of the monochromator by picoammeter. An effusive molecular/atomic beam formed by a capillary crosses the electron beam in the reaction chamber. The ambient chamber pressure is kept around 1.5×10^{-4} mbar. The emitted radiation is collected by a series of lenses and guided onto the slit of the ¼ meter monochromator. We use thermoelectrically cooled Hamamatsu photomultiplier as detector and photon counting technique. The R4220P photomultiplier is sensitive in spectral region 185–710 nm.

Figure 1. The experimental apparatus scheme.

Results and discussion

The aim of our experiment was to measure the emission spectra of methane in UV/VIS range, the emission functions for selected lines and the threshold energies in the excitation cross sections.

The emission spectra of methane were measured using different widths of the entrance and output slits of the optical monochromator. The gas pressure in the main vacuum chamber was about 1.5×10^{-4} mbar during the measurements. The electron energy was set to 30 eV, 50 eV, and 80 eV. The emission spectra measured at these energies were very similar, differences were observed only in relative intensities of the lines and bands present. The low resolution (high sensitivity) spectrum in visible and near UV range 180–700 nm measured at 50 eV electron energy is presented in the Figure 2. The spectrum is dominated by CH and CH^+ bands and by hydrogen Balmer's lines with appearance of one neutral carbon (CI) line. There were no molecular methane lines observed, as expected.

The influence of widths of entrance and output slits of optical monochromator on the resolution of spectral lines is significant and can be seen in comparison between 10 μm slits and 50 μm slits in the Figure 3. Narrow slits result in decrease of the intensity and decrease of the S/N ratio and thus in increase of the time necessary to achieve good quality spectra. The first measurements are carried out with wide slits to get strong signal and high sensitivity. In this way we are able to detect weak lines. In the next step we perform measurements with narrow slits in order to obtain high resolution spectrum of regions of interest.

The present emission spectra show a good agreement with previously presented results [e.g. *Hesser et al.,* 1970, *Aarts et al.,* 1971], however they were measured with better resolution.

Using this apparatus we were able to measure relative emission cross sections (emission functions) σ_{em}. The emission cross section for a given emission line or band is quantity which reflects the overall probability to excite a higher state of the molecule and subsequently to emit the photon:

$$e(\varepsilon_1) + M(X) \xrightarrow{\sigma_{exc}} M^*(C) + e(\varepsilon_2) \xrightarrow{P_{em}} M^*(B) + h\nu$$
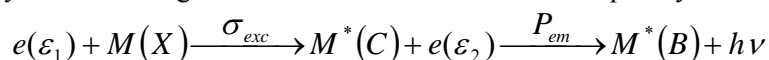
where σ_{exc} is the cross section for excitation of the C excited state of the molecule and the P_{em} is the probability of emission between the C and B states of the molecules. The electron energy has been calibrated using the position of the peak in the relative emission cross section of the (0,0) band in the 2nd Positive System of N_2. For the Balmers series and CH(A-X) transition present results indicate appearance energies lower by 1 to 2 eV to the earlier studies. In the case of CI, CH(B-X), and CH(C-X) transitions, there were no data available for comparison.

We have measured the emission functions of dissociative excitation processes for some Balmer hydrogen lines, CH bands (A-X, B-X and C-X) and the atomic C line. The emission spectra were measured in the electron energy range from approximately 5 eV up to 50 eV and are presented in Figure 4. The values are in arbitrary units, however, the cross sections can be compared with each other.

The threshold energies for particular dissociative excitation reactions were evaluated from the relative cross sections and are presented in the Table 1. They represent the superposition of minimal energy required to break the fragment off the methane molecule, and excite it subsequently into the particular state. We compared the present results with earlier published results. In the case of dissociative excitation to excited states of atomic hydrogen, we have measured so far transitions to H_β, H_γ, H_δ, and H_ε. For the first three lines present values are lower than those in the literature. We believe that present values are correct, because they have been measured using high resolution electron beam. The earlier data were measured in experiments without an electron monochromator. Similar situation appears also in the case of $CH(A^2\Delta \rightarrow X^2\Pi)$ transition. The thresholds for $CH(B^2\Sigma^- \rightarrow X^2\Pi)$ and $CH(C^2\Sigma^+ \rightarrow X^2\Pi)$ were determined for the first time. In the case of $CH(B^2\Sigma^- \rightarrow X^2\Pi)$ there was mixing with H_ξ (8-2) and thus the obtained relative emission cross section may correspond to the superposition of the cross sections for both lines.

Conclusion

It is important to understand processes associated with electron impact to methane molecule since it plays an important role in atmospheres of many planets, e.g. gas giants of the solar system and some of their moons, and also in low and high temperature plasma diagnostics. We have measured emission
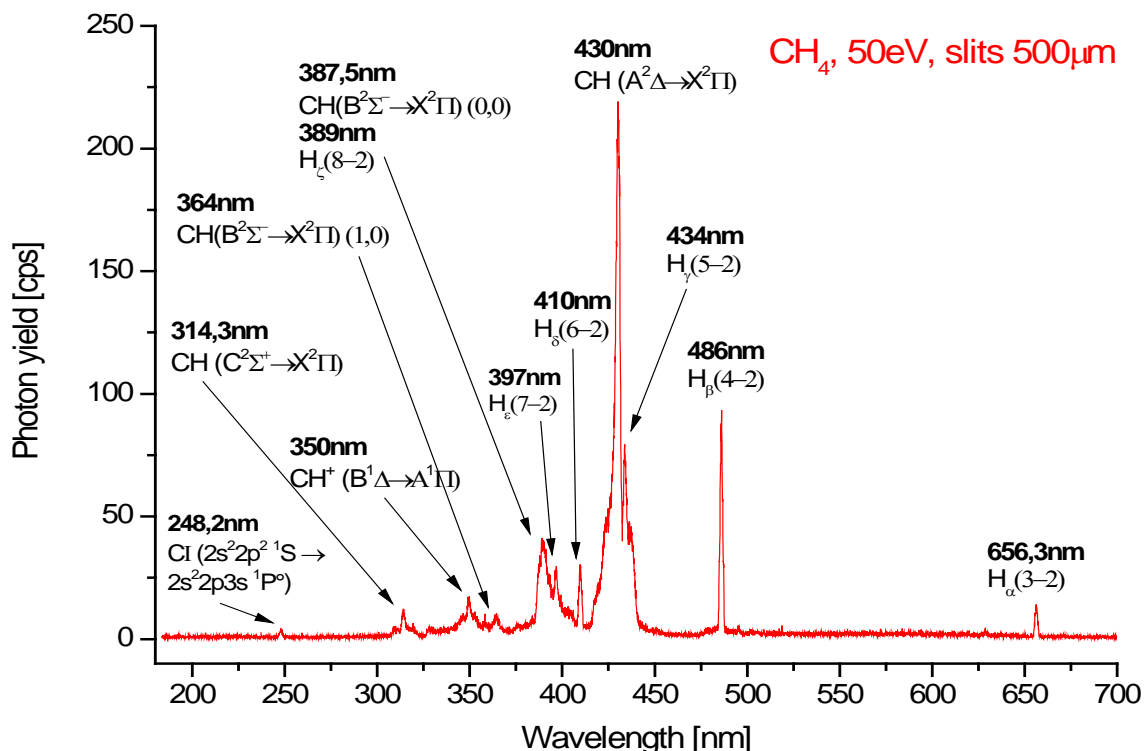
Figure 2. Emission spectrum of methane at 50 eV colliding electron energy, slits 500 μm. Bands and lines of fragments are identified. No methane lines were observed.
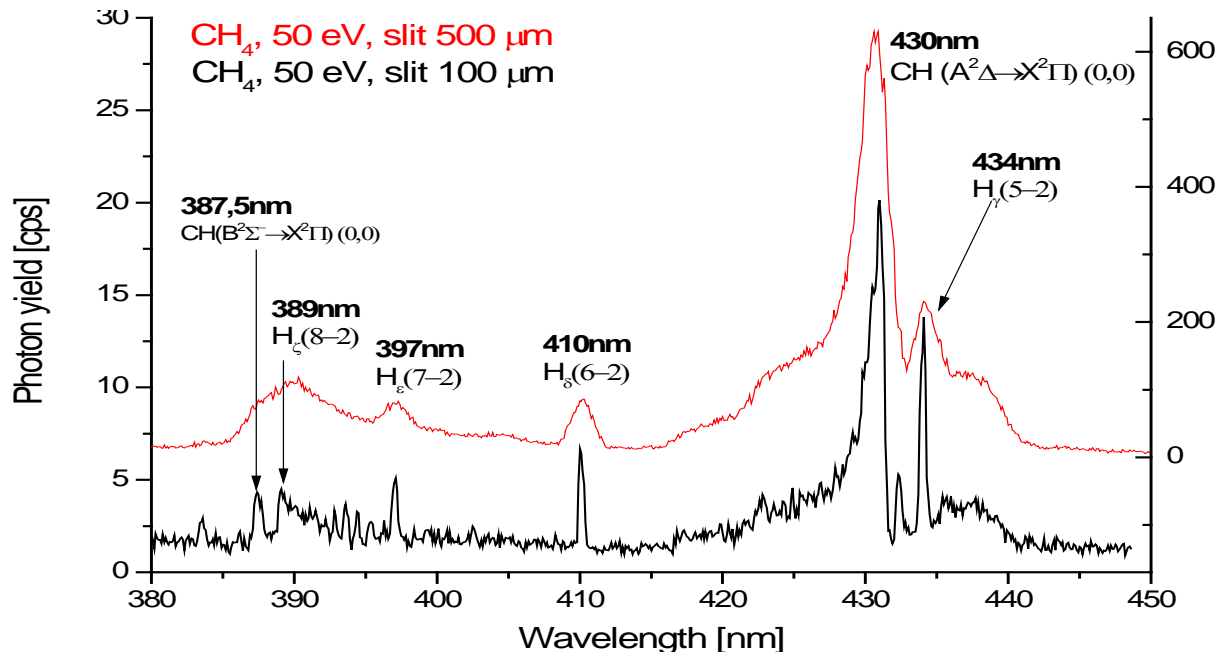


Figure 3. Emission spectrum of the methane molecule obtained in the wavelength range 380–450 nm. Comparison of measurements with slits 500 μm and 100 μm.

spectra of methane in range 180–700 nm initiated by impact of electrons with 30, 50 and 80 eV energies. Using different slit widths of the optical monochromator we obtained high sensitivity spectra and high resolution spectra. We measured relative emission cross sections for different dissociative excitation processes including hydrogen lines of Balmer series, CH(A-X, B-X and C-X) transitions and C line. Their threshold energies were identified and compared with previously released data. The results obtained show good functionality of our new apparatus, and since it is still under development, the results are planned to be enhanced in the future.

Table 1. Threshold energies obtained from the measured relative emission cross sections compared with results of other researchers.

Fragment	Transition	Wavelength [nm]	Measured threshold energy [eV]	Previously determined values [eV]
CI	$2s^22p^2\ ^1S \rightarrow 2s^22p3s\ ^1P°$	248,6	26,5	—
CH	$C^2\Sigma^+ \rightarrow X^2\Pi$	314,6	18,9	—
CH	$B^2\Sigma^- \rightarrow X^2\Pi$	389,2	13,5	—
CH	$A^2\Delta \rightarrow X^2\Pi$	430,6	13,0	14,2 [Motohashi et al, 1996] 14,6 [Aarts et al, 1971]
H	$H_\varepsilon(7\text{-}2)$	397	19,0	—
H	$H_\delta(6\text{-}2)$	409,85	18,7	21,0 [Motohashi et al, 1996]
H	$H_\gamma(5\text{-}2)$	434,4 nm	19,6	20,7 [Motohashi et al, 1996] 22,3 [Aarts et al, 1971]
H	$H_\beta(4\text{-}2)$	486,4 nm	19,7	20,5 [Motohashi et al, 1996] 21,8 [Aarts et al, 1971]
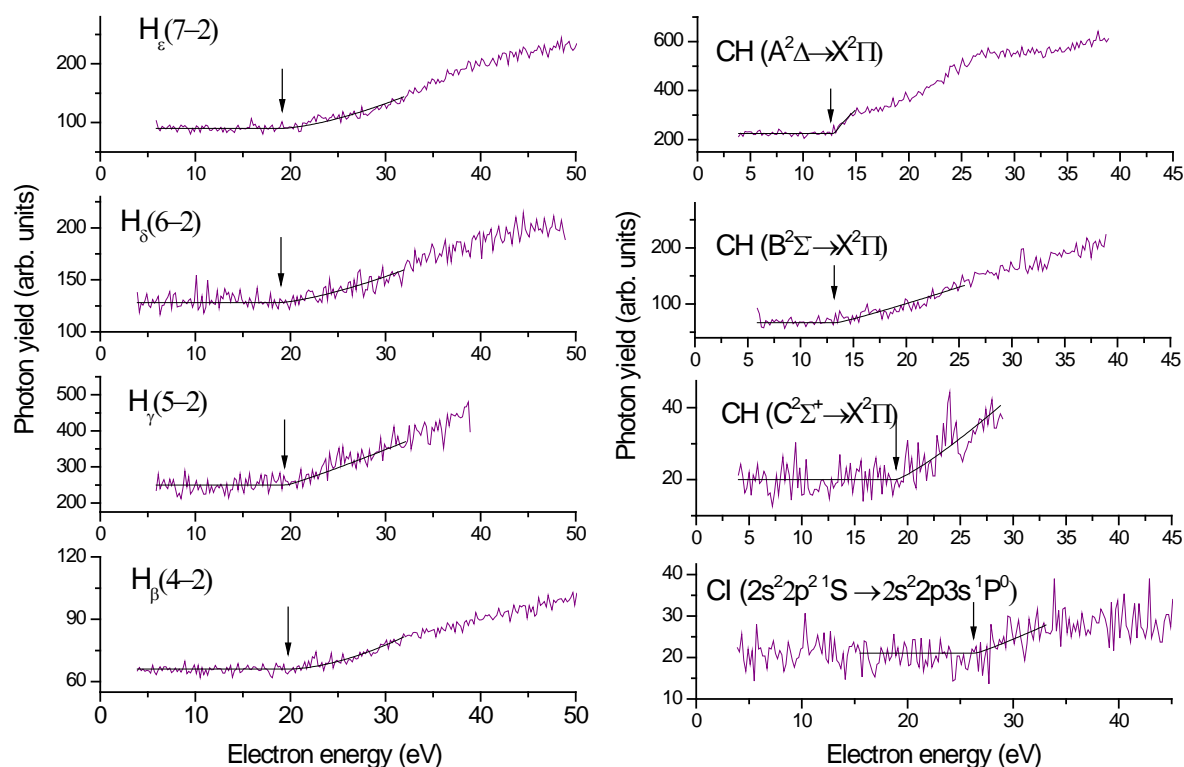
Figure 4. Relative emission cross sections (emission functions) of the peaks of methane fragments.

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