

Electron Induced Emission of Methane

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Electron induced fluorescence (EIF) emission spectra of CH₄ were measured using a crossed electron molecular beams apparatus in visible and near UV range 240-700 nm at incident electron energy of 50eV. In the EIF spectra atomic emission lines of H Balmer series and C were observed as well as emission bands corresponding to CH⁺ and CH fragments.

Electron induced fluorescence is a tool to study the electronic states of the molecules by observing emission from the 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 emission cross sections for selected spectral line or band. In 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 knowledge can be used e.g. to verify and improve theoretical models, or can be applied in chemistry, physics and many applications.

We have developed a crossed-beams apparatus to study EIF to the molecules. A beam of electrons with a very narrow energy distribution and beam of studied molecules collide resulting in excitation of the molecules and subsequent emission of the photons. The electron beam is produced by trochoidal electron monochromator and the molecular beam by an effusive capillary. The emitted photons are collected by series of lenses and guided into the 1/4m monochromator. The Hamamatsu photomultiplier used as a detector is sensitive in the range 185-710nm.

In the figure 1 part of the measured spectrum can be seen.

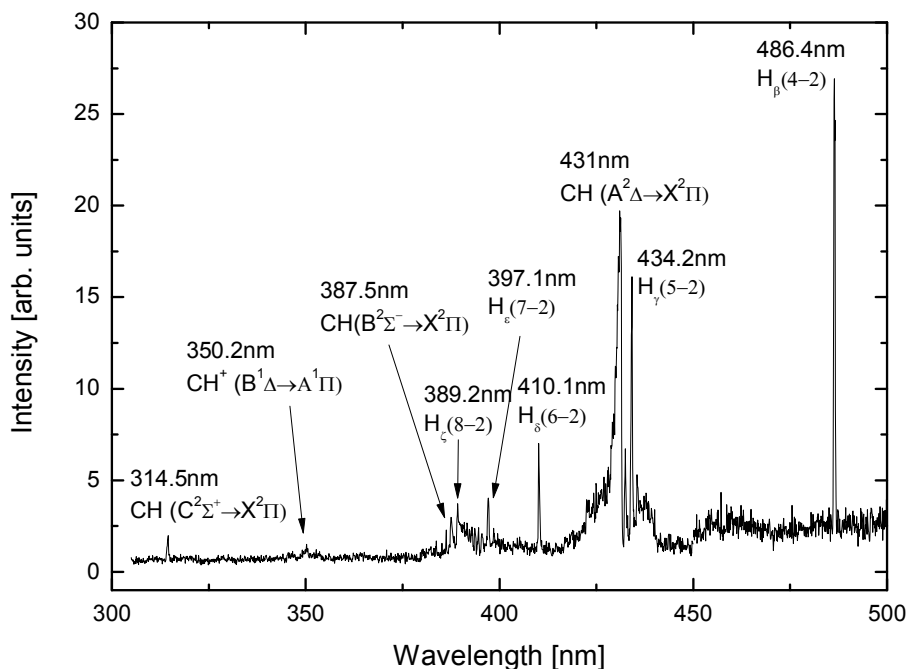


Fig. 1: Part of the emission spectrum with identified lines corresponding to H, CH and CH⁺ transitions.

The spectrum is dominated by CH, CH⁺ and H bands and lines. Apart from them the CI (3s¹p⁰→2p²1S) as well as H_α lines were detected (figure not shown). No molecular methane line was detected.

The gas pressure in the main vacuum chamber was kept during the measurements in the order of 10⁻⁴ mbar. The electron energy was set to 50 eV. The spectrum in the figure 1 was corrected according to the spectral sensitivity of the detection system. The P, Q and R branches of the CH (A-X) transition are clearly visible. The H_β is within the R branch.

We have measured the emission cross sections of dissociative excitation processes for some Balmer hydrogen lines, CH bands (A-X, B-X and C-X) and the atomic C line. The threshold energies for particular dissociative excitation reactions were evaluated from the relative cross sections and are presented in the Table 1. The threshold energies for particular dissociative excitation reactions were evaluated from the relative cross sections and are presented in the Table 1. 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. The thresholds for first three lines 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(A²Δ→X²Π) transition. The thresholds for CH(B²Σ⁻→X²Π) and CH(C²Σ⁺→X²Π) were determined for the first time. In the case of CH(B²Σ⁻→X²Π) there was mixing with H_ξ (8-2) and thus the obtained emission cross section may correspond to the superposition of the cross sections for both lines.

Tab. 1: Comparison of the threshold energies.

Fragment	Transition	Wavelength (nm)	Threshold energy (eV)			
			Present	Motohashi [1]	Aarts [2]	Donohue [3]
H	H _α (3-2)	656.9	20.1	20.2	21.9±0.5	
H	H _β (4-2)	486.4	19.6	20.5	21.8±0.5	22
H	H _γ (5-2)	434.2	21.03	20.7	22.3±0.5	22.6
H	H _δ (6-2)	410.1	20.5	21, 27		
H	H _ε (7-2)	397.1	20.66			
H	H _ξ (8-2)	389.2	20.7			
H	H _η (9-2)	383.7	24.3			
CI	3s ¹ P ⁰ →2p ² 1S	248.2	24.1			
CH	A ² Δ → X ² Π	430.9	12.96	14.2	14.6	13.4
CH	B ² Σ ⁻ →X ² Π	387.5	14.05			
CH	C ² Σ ⁺ →X ² Π	314.5	17.35			13.9
CH ⁺	B ¹ Δ → A ¹ Π	350.2	31.35			31.6

Acknowledgment

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References

- [1] K. Motohashi, H. Soshi et al, *Chemical Physics* **213** (1996) 369-384.
- [2] J.F.M. Aarts, C.I.M. Beenaker, F.J. De Heer, *Physica* **53** (1971) 32-44.
- [3] D.E. Donohue, J.A. Schiavone, R.S. Freund, *J. Chem. Phys* **67** (1977) 769-780.