CH spectroscopy for carbon chemical erosion analysis in high density low temperature hydrogen plasma

Citation for published version (APA):

DOI:
10.1063/1.3238295

Document status and date:
Published: 01/01/2009

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 08. Mar. 2021
CH spectroscopy for carbon chemical erosion analysis in high density low temperature hydrogen plasma

J. Westerhout,1 N. J. Lopes Cardozo,1,2 J. Rapp,1,3 and G. J. van Rooij1,a)
1FOM Institute for Plasma Physics Rijnhuizen, Association EURATOM-FOM, Trilateral Euregio Cluster;
P. O. Box 1207, 3430 BE Nieuwegein, The Netherlands
2Eindhoven University of Technology, P. O. Box 513, 5600 MB Eindhoven, The Netherlands
3Institut für Energieforschung—Plasmaphysik, Forschungszentrum Jülich, Association EURATOM-FZJ,
Trilateral Euregio Cluster, D-52425 Jülich, Germany

(Received 3 August 2009; accepted 8 September 2009; published online 12 October 2009)

The CH A–X molecular band is measured upon seeding the hydrogen plasma in the linear plasma generator Pilot-PSI [electron temperature $T_e=0.1–2.5$ eV and electron density $n_e=(0.5–5) \times 10^{20}$ m$^{-3}$] with methane. Calculated inverse photon efficiencies for these conditions range from 3 up to $>10^6$ due to a steeply decreasing electron excitation cross section. The experiments contradict the calculations and show a constant effective inverse photon efficiency of $\sim 100$ for $T_e<1$ eV. The discrepancy is explained as the CH A level is populated through dissociative recombination of the molecular ions formed by charge exchange. Collisional de-excitation is observed for $n_e>5 \times 10^{20}$ m$^{-3}$ and 0.1 eV $<T_e<1$ eV. These results form a framework for in situ carbon erosion measurements in future fusion reactors such as ITER. © 2009 American Institute of Physics. [doi:10.1063/1.3238295]

Interaction between the plasma and the material wall is a key issue for the success of the future fusion reactor ITER.1 Carbon can withstand extreme heat loads and is therefore considered for ITER as wall material in the areas of strongest particle and power loads. A serious problem of carbon is that chemical processes induce erosion of the wall even at low incident particle energies. The immediate consequence is the compromise of the life time of the plasma facing component.2 A second order effect is that the eroded material will be deposited elsewhere as hydrogen rich amorphous layers and as such form a fuel retention problem.3 Finally, disintegration of these layers, for example by the impact of so-called ELMs (quasiperiodic burst of power and particles reaching the material wall),4 contributes to dust formation and as such to an explosion risk.5

Spectroscopy on the molecular CH A–X Gerö band makes it possible to quantify in situ the chemical erosion of carbon wall elements in contact with hydrogen plasma. CH is the only hydrocarbon that is accessible by emission spectroscopy in the visible. CH spectroscopy relies on the correlation between CH radiation and methane particle fluxes;6 the main reaction product formed upon chemical erosion of carbon.7 The method is widely applied in fusion experiments and provides insight that is presently used to make predictions for ITER plasma wall issues. Also for ITER it would be an obvious diagnostic. This requires, however, that it has to be applied in the extreme and unexplored plasma regime of densities $>10^{20}$ m$^{-3}$ and temperatures 1–10 eV. Due to steep gradients in the rate coefficients that govern the relation between the CH radiation and the chemical erosion, it is generally regarded as impossible to apply the existing methodology to plasma temperatures below $\sim 3$ eV.

In this letter, we demonstrate that the interpretation of the spectroscopic data has to be revised for these high density low temperature plasmas on the basis of experiments in the linear plasma generator Pilot-PSI. We start with a brief analysis of $D/XB$ values (where $D$ stands for the dissociation rate of the molecule and $XB$ for the excitation rate weighted with the branching ratio, i.e., the inverse photon efficiency that relates photon fluxes to particle fluxes) calculated for the above mentioned plasma conditions, which indeed exhibit a steep gradient. Subsequently, experiments on methane seeding into the hydrogen plasma of Pilot-PSI are presented, which show still a significant amount of CH A–X light at temperatures of $\sim 1$ eV. Finally, the difference between the calculated $D/XB$ and measured inverse effective photon efficiency is explained on basis of the chemistry underlying the formation of the CH radical.

The online HYDKIN solver,8 a reaction kinetic solver for the catabolism of hydrocarbons in hydrogen plasma, is used to calculate $D/XB$ values for methane in the plasma conditions in Pilot-PSI using the Janev–Reiter database.9 The results are plotted in Fig. 1 as a function of $T_e$ for $n_e=1.0$

---

*Electronic mail: rooij@rijnhuizen.nl.*

![FIG. 1. D/XB values calculated with HYDKIN and the inverse of the effective photon efficiencies measured in Pilot-PSI by relating the CH A−X emission to the methane flux injected into hydrogen plasma. The D/XB shows a steep decrease over orders of magnitude over the range 0.1 eV $<T_e<1$ eV. The measured inverse effective photon efficiencies are constant within the error bars in the same temperature range.](image-url)
It shows that indeed the $D/\lambda B$ value varies strongly with temperature, in accordance with the general view that CH $A-X$ spectroscopy becomes difficult to quantify at low $T_e$. Evaluation of the underlying reaction rates gives insight in which processes are important for the observed behavior. At low $T_e$, in particular <2 eV, the chemistry simplifies greatly as all electron-neutral processes become negligible compared to the charge exchange reactions followed by dissociative recombination. The rate determining step is the charge exchange reaction, which varies much less than an order of magnitude over the temperature range 0.1 eV < $T_e$ < 2 eV. The reason that the $D/\lambda B$ does increase steeply toward lower $T_e$ lies solely in the electron excitation rate of CH, which decreases orders of magnitude.

The behavior of the CH $A-X$ emission as a function of the low temperature high density plasma conditions is experimentally investigated by seeding the hydrogen plasma of the linear plasma generator Pilot-PSI with methane and relating the absolute CH $A-X$ emission to the methane flux. A description of the experimental details of Pilot-PSI can be found elsewhere. The aspects relevant for the measurements presented here are given in Fig. 2 and caption. The CH photon flux is determined by integrating the CH $A-X$ band from 430.0 to 431.5 nm, multiplied by a factor of 2.8 to obtain the photon flux of the full CH $A-X$ band. These measurements present an example that up to 5% of the emission is emitted inside the seeding hole. All following analysis has been corrected for this effect. Furthermore, similar measurements in a scan of the CH$_2$ seeding flow rate scan from 0.3 to 1.2 SCCM (SCCM denotes standard cubic centimeter per minute) show a perfect linear response of the total emission. This proves that the seeding is small compared to the plasma flux densities and has no effect on the local plasma conditions that are relevant for the formation of CH $A-X$ light.

The CH $A-X$ photon flux profiles have been measured in a scan of $T_e$ from 0.1 to 2.5 eV. Integration over the entire profiles and dividing by the injected methane particle flux gives the effective photon efficiency. The inverse of this quantity is compared with the calculated $D/\lambda B$ values in Fig. 1. The experiments show within the error bars a constant inverse effective photon efficiency of ~100 over the range 0.1–1 eV, which is in contrast to the steeply increasing calculated $D/\lambda B$ toward lower temperatures. This is explained by taking the chemistry underlying the formation of the CH radical into account. As all electron-neutral processes become negligible compared to the charge exchange processes, the main reactions of interest for the production of CH are as follows:

$$\text{H}^+ + \text{CH}_4 \rightarrow \text{H} + \text{CH}_4^+.$$ 

$$\text{H}^+ + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3^+.$$ 

Both processes are equally important around 0.1 eV, whereas the formation of CH$_3^+$ is dominant (>85%) at 1 eV. These molecular ions undergo dissociative recombination, which occurs an order of magnitude faster than the charge exchange step. The products from the dissociative recombination process are most probably excited due to the nature of the process, i.e., electron capture to a doubly excited repulsive state of the CH$_3$ molecule. Two of the many possible pathways have sufficient excess energy from the exothermic copy measurements. A volume with a diameter of 7.2 mm has to be integrate in order to cover 67% of the total emission. This means that the $T_e$ dependencies discussed below concern in fact an average over the $T_e$ profiles, which have a FWHM of typically 12 mm.
reaction to lead directly to the formation of excited CHA on basis of the excess of energy,

\[ e + \text{CH}_2 \rightarrow \text{CH} + \text{H}_2 + \text{H} + 3.42 \text{ eV}, \]

\[ e + \text{CH}_3 \rightarrow \text{CH} + \text{H}_2 + 5.1 \text{ eV}. \]

The excess energy in these reactions is sufficient to excite the CH A-X transition. Considering the pathways given above, it requires 5% of the dissociative recombination events to lead to CH A-X radiation in the Gerö band to explain the measured inverse effective photon efficiency of 100. It is noted that also second (and further) order charge exchange reactions followed by dissociative recombination have been taken into account for this estimate and contribute up to 30%. The length scales of the emission plume are also in agreement with the above explanation. The charge exchange rate for \( \text{H}^+ + \text{CH}_2 \) is according to the online HYDKIN solver equal to \( 8 \times 10^{-15} \text{ m}^2/\text{s} \) at \( T_e = 1 \text{ eV} \). For \( n_e = 1 \times 10^{20} \text{ m}^{-3} \) and a velocity of \( 10^3 \text{ m/s} \) for the hydrocarbon, this gives a mean free path of 1.3 mm, close to the 2 mm e-folding length of the plume in axial direction in Fig. 3.

The graph of Fig. 1 shows also an experiment performed at a plasma temperature of 2.5 eV. Electron excitation of the Gerö band is expected to be dominant at \( T_e = 2.5 \text{ eV} \), so that the measured inverse effective photon efficiency should compare to the calculated \( D/XB \) value. However, it is seen in Fig. 1 that the inverse effective photon efficiency has become even higher, more than \( 10^3 \), instead of dropping to the \( D/XB \) value of \( \sim 10^0 \). This is due to collisional de-excitation of the CH A level. A quick estimate confirms the effectiveness of collisional de-excitation. The main processes are charge or particle exchange of CH [total rate is \( 1.1 \times 10^{-15} \text{ m}^2/\text{s} \) at \( T_e = 2.5 \text{ eV} \) (Ref. 8)] and dissociative excitation of CH into neutrals [total rate is \( 1.6 \times 10^{-15} \text{ m}^2/\text{s} \) at \( T_e = 2.5 \text{ eV} \) (Ref. 8)]. The sum of these rates gives at the plasma density of the particular experiment (3 \( \times 10^{19} \text{ m}^{-3} \)) a collisional lifetime of 1.2 \( \mu \text{s} \), which is close to the radiative lifetime of the CH A level. It is noted that these estimates do not take the excitation energy of the CH A level into account. Most likely, the dissociative excitation rate has therefore been underestimated and also direct ionization should have been taken into account. Both would have decreased the collisional lifetime even further, which emphasizes the importance of collisional quenching. Thermal decomposition of the methane is not expected to be important at the estimated injection channel temperatures of below 500 °C. Otherwise, methane could have decomposed into atomic carbon inside the channel, which would also have increased the measured inverse photon efficiency.

Measurements of the effective inverse photon efficiency in scans of \( n_e \) show that collisional de-excitation becomes important at \( n_e \geqslant 5 \times 10^{20} \text{ m}^{-3} \) in the temperature range \( T_e \approx 1 \text{ eV} \), i.e., a threshold at higher density compared to the \( T_e = 2.5 \text{ eV} \) case. The effective photon efficiency data in Fig. 1 for \( T_e \leqslant 1 \text{ eV} \) do not contain this effect.

In conclusion, the experiments at Pilot-PSI demonstrate that the interpretation of CH spectroscopy has to be revised for low temperature, high density plasma conditions as will appear in ITER. First, the inverse effective photon efficiency is measured to be \( \sim 100 \text{ for } 0.1 \text{ eV} < T_e < 1 \text{ eV} \), independent of \( n_e \), for \( n_e < 5 \times 10^{20} \text{ m}^{-3} \). The constancy of the effective inverse photon efficiency is explained by population of the CH A level via charge exchange of higher hydrocarbons promptly followed by dissociative recombination. Second, collisional de-excitation increases the value of the inverse effective photon efficiency for densities of \( n_e > 5 \times 10^{20} \text{ m}^{-3} \). One example at \( T_e = 2.5 \text{ eV} \) indicates that this boundary shifts to lower densities for \( T_e > 1 \text{ eV} \).

The authors acknowledge the assistance of R.S. Al and B. de Groot, H.J. van der Meiden, M.J. van de Pol, A.E. Shumack, W.A.J. Vijvers, and G.M. Wright with the experiments and the useful discussions with S. Brezinsek, D. Borodin, A. Kirschner, V. Philipps, and D.C. Schram. This work was supported by the European Communities under the contract of Association between EURATOM/FOM and carried out within the framework of the European Fusion Programme with financial support from NWO and the NWO Grant No. RFBR 047.018.002. The views and opinions expressed herein do not necessarily reflect those of the European Commission.