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

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Interaction between the plasma and the material wall is a key issue for the success of the future fusion reactor ITER.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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),\textsuperscript{4} contributes to dust formation and as such to an explosion risk.\textsuperscript{5}

Spectroscopy on the molecular CH\textsubscript{2} in the visible. CH\textsubscript{2} spectroscopy relies on the correlation between CH radiation and methane particle fluxes,\textsuperscript{6} the main reaction product formed upon chemical erosion of carbon.\textsuperscript{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 \(>10^{20} \text{ m}^{-3}\) 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 ~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 ~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,\textsuperscript{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.\textsuperscript{9} The results are plotted in Fig. 1 as a function of \(T_x\) for \(n_e=1.0 \times 10^{20} \text{ m}^{-3}\) and \(0.1 \text{ eV} < T_x < 1 \text{ eV}\). The measured inverse effective photon efficiencies are constant within the error bars in the same temperature range.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{\(D/XB\) 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 < \(T_x\) < 1 eV. The measured inverse effective photon efficiencies are constant within the error bars in the same temperature range.}
\end{figure}
$10^{20} \text{ m}^{-3}$. It shows that indeed the $D/XB$ 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 with 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 $D/XB$ 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. Reversion of carbon deposits on particularly the target also contributes to the CH $A-X$ emission. This contribution of up to 25% of the total emission is characterized before and after each methane seeding experiment and is corrected for. Figure 3 shows the resulting two-dimensional photon flux profile for the perpendicular view. The peak intensity is located at the injection location and decays exponentially. The axial $e$-folding length, illustrated by the upper inset in the plot, is 2 mm. The radial decay length is similar as seen in the left side inset, with a half $1/e$ width of 1 mm. We note that these numbers indicate a limited spatial resolution of the spectrally.

Comparison of this perpendicularly measured photon flux profile with one measured in the tangential view (data not shown) learns 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$_4$ 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 $D/XB$ values in Fig. 1. The experiments show within the error bars a constant inverse effective photon efficiency of $\sim 100$ over the range 0.1–1 eV, which is in contrast to the steeply increasing calculated $D/XB$ 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:

$$H^+ + CH_4 \rightarrow H + CH_4^+,$$

$$H^+ + CH_4 \rightarrow H_2 + CH_3^+.$$
reaction to lead directly to the formation of excited CH $^1A$ on basis of the excess of energy,

$$
25\% \quad e + CH_4 \rightarrow CH + H_2 + H + 3.42 \text{ eV},
$$

$$
14\% \quad e + CH_3 \rightarrow CH + H_2 + 5.1 \text{ eV}.
$$

The excess energy in these reactions is sufficient to excite the 431 nm radiation of 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 Gerô 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 $\sim 30\%$.

The length scales of the emission plume are also in agreement with the above explanation. The charge exchange rate for $H^+ + CH_4$ is according to the online HYDKIN solver equal to $8 \times 10^{-15}$ m$^3$/s at $T_e = 1$ eV. For $n_e = 1 \times 10^{20}$ m$^{-3}$ and a velocity of $10^5$ m/s for the hydrocarbon, this gives a mean free path of 1.3 mm, close to the 2 mm $\alpha$-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 Gerô band is expected to be dominant at $T_e = 2.5$ 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 $1.1 \times 10^{-15}$ m$^3$/s at $T_e = 2.5$ eV (Ref. 8)] and dissociative excitation of CH into neutrals [total rate is $1.6 \times 10^{-15}$ m$^3$/s at $T_e = 2.5$ eV (Ref. 8)]. The sum of these rates gives at the plasma density of the particular experiment ($3 \times 10^{20}$ m$^{-3}$) a collisional lifetime of 1.2 $\mu$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 $n_e \geq 5 \times 10^{20}$ m$^{-3}$ in the temperature range $T_e \geq 1$ eV, i.e., a threshold at higher density compared to the $T_e = 2.5$ eV case. The effective photon efficiency data in Fig. 1 for $T_e \leq 1$ 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 $\sim 100$ for $0.1$ eV $< T_e < 1$ eV, independent of $n_e$. Second, collisional de-excitation increases the value of the inverse effective photon efficiency for densities of $n_e > 5 \times 10^{20}$ m$^{-3}$. One example at $T_e = 2.5$ eV indicates that this boundary shifts to lower densities for $T_e > 1$ eV.

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