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Correlation of the intensity ratio of C_2/CH molecular bands with the flux ratio of C_2H_y/CH_4 particles

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Abstract

The chemical erosion of carbon materials in the edge plasma of fusion experiments is commonly quantified by the erosion yield, i.e. the ratio of chemically eroded carbon flux to the incident hydrogen flux. A common diagnostic method for the carbon particle flux is the analysis of radiation from molecular radicals: the correlation of CH radiation with methane particle fluxes. In order to take into consideration the formation of higher hydrocarbons systematic investigations in laboratory plasmas and in the plasma edge of ASDEX Upgrade are carried out. Emphasis is laid on a correlation of C_2 radiation with C_2H_y particle fluxes. It is suggested to use the ratio of the molecular radiation C_2/CH as a monitor tool for C_2H_y/CH_4 particle fluxes. From divertor gas puff relative photon efficiencies are obtained. A simplified formula for the spectroscopic determination of carbon fluxes is presented which considers the formation of higher hydrocarbons.

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1. Introduction

Carbon composites are often used as wall material in present fusion experiments due to their excellent thermal and mechanical properties. However, the plasma wall interaction of hydrogen plasmas with the carbon tiles leads to sputtering and chemical erosion processes, resulting in consumption of material and in carbon and hydrocarbon impurities. Moreover, hydrogen becomes deposited in the surface which is a critical issue for operation with tritium. Therefore, efforts are made to gradually replace carbon composites by other materials, for example, tungsten as it is done in ASDEX Upgrade. Due to the high heat load on divertor tiles, carbon is preferably used in the divertor region and is still planned as divertor material for ITER.

The chemical erosion of carbon is quantified by the erosion yield which is the ratio of the carbon flux to the incident hydrogen flux. The erosion yield depends on a variety of parameters such as ion energy, hydrogen flux, hydrogen isotope, surface temperature and carbon surface itself. For extrapolations to future fusion experiments (ITER) precise measurements of this quantity are needed. Systematic investigations are carried out in laboratory experiments (divertor devices, ion beam experiments, low pressure discharges) and in fusion

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experiments. A common diagnostic method for the carbon particle flux is the analysis of radiation from molecular radicals: the correlation of CH radiation with methane particle fluxes [1]. This means the formation of higher hydrocarbons and their contribution to the erosion yield is neglected in that case. First attempts are started in fusion experiments to obtain a correlation of higher hydrocarbon particle fluxes with radiation of hydrocarbon radicals such as C_2 [2,3].

This paper discusses a correlation of the radiation of C_2 with C_2H_y particles on the basis of detailed measurements in laboratory plasmas supported by a dissociation model with which the main dissociation paths of C_2H_y particles in C_2 radicals are identified. The simple technique of intensity ratios (C_2/CH molecular bands) is suggested to be used as a monitor for particle ratios (C_2H_y/CH_4). Suitable molecular bands are identified and the corresponding excitation rate coefficients are compiled. Scaling factors, which are necessary for the analysis of molecular radiation, are provided. The correlation factors from the photon fluxes to the particle fluxes are determined from experimental campaigns in the divertor of ASDEX Upgrade. An extended formula for the spectroscopic determination of the carbon flux is given, which takes into account the formation of higher hydrocarbons in the chemical erosion process.

2. Molecular radiation and particle fluxes

The basis for a correlation of measured photon fluxes with particle fluxes is the photon efficiency which describes the destruction events of the parent molecule per emitted photon. The method is generally used for the determination of methane particle fluxes Γ_{CH_4} from the radiation of CH molecules Γ_{CH}:$\Gamma_{CH_4} = D/XB \times \Gamma_{CH}$ [1], where D describes the dissociation of methane into CH and XB denote the excitation rate coefficient X from CH ground state into the electronically excited state times the branching ratio B (XB is then the emission rate coefficient). This requires modelling of dissociation and knowledge of excitation mechanisms and implies that CH molecules are produced only from the dissociation chain of methane. In order to verify calculations of photon efficiencies, which depend on plasma parameters, measurements are carried out by using gas (methane) puffs through calibrated valves in the plasma edge of fusion experiments [4–6]. However, data for higher hydrocarbons are scarce and a direct correlation with a suitable radiative transition is missing.

Under the assumption that the dissociation chain of C_2H_y particles is the dominant formation mechanism for C_2 particles, the radiation of carbon molecules is correlated with fluxes of C_2H_y particles. The most intense emission of C_2 originates from the diagonal bands of the $d^3\Pi_g$–$a^3\Pi_u$ transition (Swan bands) with a band head at 516.5 nm for the vibrational band $v' = v'' = 0$. Since the ground state of the molecules is in the singlet system of the molecule, excitation from the metastable state $a^3\Pi_u$ of the molecule (optically allowed transition) dominates. This means an interpretation of the band emission correlates with the particles in the metastable state. In order to obtain the particles in the ground state $X^1\Sigma_g^+$ the Mulliken bands ($D^1\Sigma_u^+$–$X^1\Sigma_g^+$ transition, $v' = v'' = 0$–3) in the near UV range are to be analysed. The energy distance between the metastable level and the ground state is only 0.0887 eV which suggests a population ratio according a Boltzmann distribution. A measurement of these populations requires the knowledge of the emission rate coefficients of the Swan and the Mulliken band with electron impact excitation from the metastable and the ground state, respectively (direct excitation). These rate coefficients were calculated with the impact parameter method for atoms (IPProg code [7]) applied to molecules using the oscillator strength of the transition (Swan: $f = 0.024$, Mulliken: $f = 0.055$). The dissociative excitation chain from higher hydrocarbons or methane in electronically excited carbon molecules can be neglected [8]. The commonly used rate coefficient for the emission of the CH molecule ($A^2\Delta$–$X^2\Pi$ transition, $v' = v'' = 0$–2, Gerö band with a band head at 431 nm) is also based on calculations with the IPProg code. In order to check the applicability of the IPProg code a second transition is investigated, namely the $B^2\Sigma$–$X^2\Pi$ transition, $v' = v'' = 0$, around 390 nm. Both transitions are excited from the ground state which means the intensity ratio should reflect directly the ratio of the emission rate coefficients. Fig. 1 shows the emission rate coefficients for these four molecular bands. Since the energy threshold for excitation is around

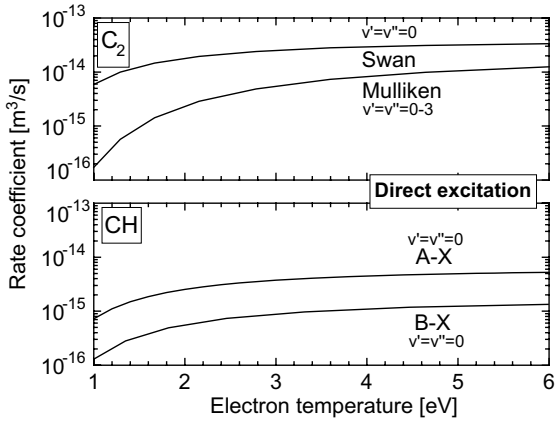

Fig. 1. Emission rate coefficients for the Swan and Mulliken band of C_2 and the A–X and B–X transition of CH (CD) calculated with the IPProg code [7] using the corresponding vibrationally resolved transition probability.

3 eV the dependence of the rate coefficients on electron temperature is very weak. The molecular bands are readily observed in hydrocarbon plasmas of low pressure discharges. The RF and MW discharges which are used are equipped with absolutely calibrated spectrometers for the visible and the UV range. In methane plasmas CH emission ratios of $A - X/B - X = 4.2 \pm 0.8$ are measured in pressure and power scans. These values are well in agreement with the expected ratio of 4 (see Fig. 1). Gas puff experiments in ASDEX Upgrade yield almost the same value independent on the isotope (CH_4 and CD_4 particle puff). From this it is concluded that the IPProg code is applicable to these transitions. The analysis of the Swan and Mulliken bands of the C_2 molecule yields particle densities of the metastable state and ground state [8]. The plasma parameters of the discharges are known from other diagnostic methods. In the MW discharge a density ratio of metastable/ground = 0.5 ± 0.1 is measured whereas the RF discharge shows ratios of 1.4 ± 0.1. Since the statistical weights are 6 (metastable) and 1 (ground) the measured ratios correspond to a Boltzmann population according a temperature of 420 ± 40 K (MW discharge) and 700 ± 40 K (RF discharge), which are in agreement with the measured neutral particle temperature in these two discharges. In fusion experiments often only the Swan emission is accessible. Results from the low pressure discharges can now be used to obtain the C_2 particles from the emission of the Swan band by applying the Boltzmann population at the temperature of the molecules or, the other way round, to predict the Swan radiation from dissociation modelling.

In fusion devices molecular emission of the CH (CD) and C_2 radicals (Gerö band and Swan emission) is often disturbed by carbon lines (CII). It is a common method to use the integral of the first 1.5 nm from the band head of the CH (CD) emission as a reference for the emission of the full band. A scaling factor of two is typically used for the full band emission. However, this conversion factor depends on the rotational (and also vibrational) population. Simulation of spectra are used to obtain these values from the best fit of simulations to spectra with the rotational temperature (and relative vibrational populations) as fit parameter. As shown in Fig. 2, the scaling factor for CH and CD depends slightly on the rotational temperature, a vibrational population of $v' = 0{:}1{:}2 = 1{:}0.4{:}0.06$ is applied (best fit to a variety of measured spectra). For C_2 it is suggested to use an integral of 1.2 nm from the $v' = v' = 0$ band head of the Swan system. The corresponding scaling factors (Fig. 2) depend considerable on the rotational temperature. As indicated in the figure, typical rotational temperatures obtained in the divertor of ASDEX Upgrade are around 3000 K, which means the scaling factor for CH and C_2 differs by a factor of 1.5. In the following discussion the intensity ratios refer always to the full band emission.

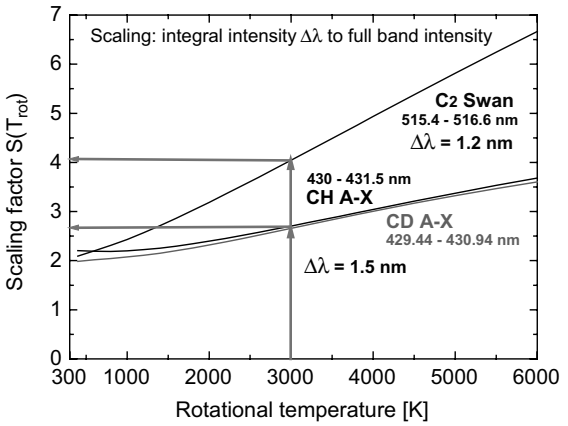

Fig. 2. Scaling factors from the intensity integral of a certain wavelength range ($\Delta\lambda$) to the full band intensity for the A–X transition ($v' = v'' = 0$–2) of CH and CD and the Swan band ($v' = v'' = 0$) of C_2.

3. Results

The considerations above offer a simple diagnostic tool for the C_2H_y/CH_4 particle ratio. The Swan band of C_2 and the Gerö band of CH are correlated with the C_2 and CH particles which are mainly formed by dissociation of C_2H_y and CH_4, respectively. As a consequence the intensity ratio C_2 (Swan, $v' = v'' = 0$–0)/CH(A–X, $v' = v'' = 0$–2) (abbr. C_2/CH) represents the particle ratio C_2H_y/CH_4. Systematic investigations are carried out in laboratory plasmas with well-known plasma parameters as well as in gas (hydrocarbons) puff experiments in the divertor of ASDEX Upgrade.

3.1. Laboratory plasmas (ECR discharges) and C_2H_y dissociation

Plasmas with 10% admixture of hydrocarbons (CH_4, C_2H_2, C_2H_4 and C_2H_6) in helium and argon are generated in an ECR discharge ($f = 2.45$ GHz, $P = 100$ W) at a pressure of 10 Pa ($n_e = 10^{17}\,m^{-3}$, $T_e = 1.5$–3 eV, depending on gas mixture). The left part of Fig. 3 shows measured intensity ratios. CH radiation dominates in methane since the CH_4 density is much higher than the density of C_2H_y particles (roughly a factor of 10 [8]). The C_2H_y particles are produced by heavy particle collisions of methane radicals. In C_2H_y plasmas the intensity ratio rises by a factor of 10 caused by an increase of C_2 radiation which correlates obviously with C_2H_y density. Methane and methane radicals are produced in this case only from the C_2H_y dissociation. A weak dependence of the ratio on the species itself is observed: C_2H_2 plasmas show a slightly higher ratio than C_2H_6 plasmas. This indicates that C_2H_2 particles are a dominant species in

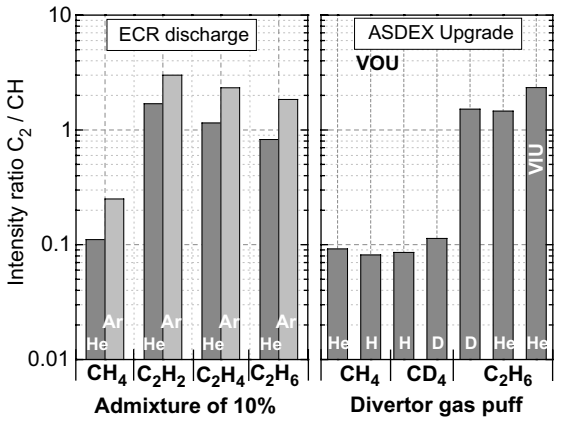

Fig. 3. Intensity ratios of the C_2 Swan band ($v' = v'' = 0$) to the CH (CD) Gerö band measured in ECR rare gas discharges (He, Ar) with admixtures of hydrocarbons (left) and in divertor gas puff experiments in ASDEX Upgrade where hydrocarbons are puffed in H, D and He discharges.

the dissociation chain of C_2H_y particles into C_2. In plasmas with argon as background gas, intensity ratios are generally a factor of two higher than in the case of helium.

In order to get an insight into the dominant formation channels from C_2 particles from C_2H_y particles, a 0-dim. particle balance is applied. C_2H_2 is chosen as the parent molecules since the dissociation paths of C_2H_6 and C_2H_4 go through C_2H_2 particles. Electron impact and heavy particle collisions are taken into account in the calculation with focus on the reaction channels with the highest probability which results in 15 reactions in total [8,9]. A parameter study showed clearly that the C_2H radical plays the key role in the C_2 formation based on the following path (among the other reactions): $C_2H_2 + e \rightarrow C_2H + H + e$ with $C_2H + C_2H \rightarrow C_2 + C_2H_2$. Argon increases the dissociation via an energy transfer from the metastable argon particles Ar*: $C_2H_2 + Ar^* \rightarrow C_2H + H + Ar$ and $C_2H + Ar^* \rightarrow C_2 + H + Ar$, which explains the enhanced intensity ratios measured in argon with respect to helium although T_e is lower (roughly 0.5 eV) in argon plasmas than in helium plasmas.

3.2. Divertor gas puff experiments in ASDEX Upgrade

Hydrocarbon particles (CH_4, CD_4 and C_2H_6) were puffed through calibrated valves into the outer divertor of ASDEX Upgrade in L-mode discharges in H, D and He. A particle flux of $\Gamma_{\text{particle}} = 3 \times 10^{18}\,\text{s}^{-1}$ was chosen for more than 1 s in order to steady state. Details on gas puff experiments, divertor geometry and spectroscopic lines of sight are described in [6]. The parameters of the divertor plasma in these L-mode discharges are typically: $T_e = 5$–$15\,\text{eV}$, $n_e = 10^{18}$–$10^{19}\,\text{m}^{-3}$ and $\Gamma_{H^+} = 10^{21}$–$10^{22}\,\text{m}^{-2}\,\text{s}^{-1}$, obtained from Langmuir probe measurements. The intensities of the Swan and Gerö band (and the B–X transition) are recorded simultaneously with an absolutely calibrated high resolution survey spectrometer (ESA3000) in the time interval of saturation during the gas puff. The right part of Fig. 3 shows the intensity ratios measured in the different scenarios. Almost the same intensity ratio is observed for CH_4 puffs in He and H as well as for CD_4 in H and D. Thus, the intensity ratio shows only a weak dependence on the background plasma and the isotope. Differences in absolute photon fluxes of Swan and Gerö bands are less than a factor 1.5 without systematic deviations. Therefore, an isotope effect in the dissociation and excitation path is not observed. When changing from methane to C_2H_6 puffs intensity ratios rise roughly a factor of 10, again showing almost no dependence on the background plasma. Even in the inner divertor (labelled with VIU in Fig. 3) the intensity ratio shows very similar values as in the outer divertor, a small enhancement can be noticed due to the difference in plasma parameters of outer and inner divertor. Photon fluxes of the Gerö band are comparable to the one measured in methane puffs. However, the C_2 radiation is increased by the factor of 10.

Intensity ratios measured in the ASDEX Upgrade experiments are in quite good agreement with intensity ratios obtained in the laboratory experiment (ECR discharges): methane dissociation yields intensity ratios of typically $C_2/CH = 0.1$ and dissociation of C_2H_y particles yields typically $C_2/CH = 1$. The dependence on plasma parameters is weak and the dominant species, C_2H_y or CH_4, determines the intensity ratio.

Analysis of the absolutely measured photon fluxes with known particle fluxes allows a determination of the corresponding D/XB ratios. Absolute values for CH and methane, are presented in [6]. Here, emphasis is laid on the relations between photon efficiencies for the correlation of the following photon fluxes with particle fluxes:

$$\Gamma_{CH_4} = \frac{D}{XB}\Big|_{CH}^{CH_4} \Gamma_{CH}^{CH_4}, \quad \Gamma_{CH_4} = \frac{D}{XB}\Big|_{C_2}^{CH_4} \Gamma_{C_2}^{CH_4},$$
$$\Gamma_{C_2H_6} = \frac{D}{XB}\Big|_{C_2}^{C_2H_6} \Gamma_{C_2}^{C_2H_4}, \quad \Gamma_{C_2H_6} = \frac{D}{XB}\Big|_{CH}^{C_2H_6} \Gamma_{CH}^{C_2H_6}. \qquad (1)$$

The first two photon efficiencies are obtained from methane puffs, whereas the last two are obtained from C_2H_6 puffs. Since identical particle fluxes are used for the species the analysis is straightforward. The CH radiation was almost independent on the species of the gas puff and intensity ratios of $C_2/CH = 1$ in C_2H_6 puffs result in equal photon efficiencies for CH from CH_4, CH from C_2H_6 and C_2 from C_2H_6. Together with the inten-

sity ratio $C_2/CH = 0.1$ in CH_4 puffs the following relations are obtained:

$$\left.\frac{D}{XB}\right|_{CH}^{CH_4} \cong \left.\frac{D}{XB}\right|_{C_2}^{C_2H_6} \cong \left.\frac{D}{XB}\right|_{CH}^{C_2H_6} \cong \frac{1}{10}\left.\frac{D}{XB}\right|_{C_2}^{CH_4}. \quad (2)$$

Within the uncertainty of the absolute calibration of the spectroscopic system a D/XB value for the CH full band emission from CH_4 of 55 ± 5 is deduced, being in satisfactory agreement with [6] which focuses on absolute values. It should be kept in mind that this relationship is obtained in L-mode discharges in ASDEX Upgrade which means the data are proven in the limited parameter range mentioned above.

3.3. Consequences on measurements of carbon fluxes

The common measurement of the chemically eroded carbon flux can now be extended by the formation of higher hydrocarbons, namely the C_2H_y group ($\Gamma_C = \Gamma_{CH_4} + 2 \times \Gamma_{C_2H_y}$) using the C_2 radiation (Swan emission) as an indicator for the formation of higher hydrocarbons:

$$\Gamma_C = \left.\frac{D}{XB}\right|_{CH}^{CH_4} \Gamma_{CH}^{CH_4} + 2 \times \left.\frac{D}{XB}\right|_{C_2}^{C_2H_6} \Gamma_{C_2}^{C_2H_6}. \quad (3)$$

However, measured CH and C_2 radiation originate also from the dissociation of C_2H_y and CH_4, respectively, i.e. $\Gamma_{CH} = \Gamma_{CH}^{CH_4} + \Gamma_{CH}^{C_2H_6}$ and $\Gamma_{C_2} = \Gamma_{C_2}^{CH_4} + \Gamma_{C_2}^{C_2H_6}$. These additional channels are to be taken into account. Together with the relations for the photon efficiencies (Eq. (2)) Eq. (3) is then transferred to

$$\Gamma_C \cong \left.\frac{D}{XB}\right|_{CH}^{CH_4} \Gamma_{CH}\left(1 + \frac{\Gamma_{C_2}}{\Gamma_{CH}}\right). \quad (4)$$

Again, it should be mentioned that this simplified formula is valid only for the limited parameter range where the relations of Eq. (2) are proven. In hydrogen L-mode discharges in ASDEX Upgrade without divertor gas puffs an intrinsic intensity ratio C_2/CH of typically 0.3 is measured which means the carbon particle flux and therefore the erosion yield increases by a factor of 1.3 when the formation of higher hydrocarbons C_2H_y is taken into consideration. For laboratory plasmas similar relations can be deduced and it was shown that erosion yields increases by a factor of 1.2–2 [10]. In addition, the spectroscopic determination of the erosion yield in these laboratory plasmas agrees only with weight loss measurements in a wide parameter range of ion energy and substrate temperature and isotope (H or D) when this extension is considered in the analysis.

4. Conclusions

The molecular radiation of hydrocarbons provides a diagnostic tool for chemically eroded carbon by hydrogen. The well-known correlation of CH radiation (Gerö band) with methane particles was completed by a correlation of C_2 radiation (Swan band) with C_2H_y particles. Experimental investigations in laboratory plasmas showed the sensitivity of the intensity ratio C_2/CH on the particle density ratio C_2H_y/CH_4. Emission rate coefficients for the direct excitation channels were calculated and partly verified by measurements. Dominant dissociation paths of C_2H_y particles were identified where C_2H plays a key role for formation of C_2. Scaling factors for the evaluation of molecular spectra in fusion experiments which are usually disturbed by carbon line emission are provided. The relevance of the rotational population of molecules is emphasised. Hydrocarbon gas puffs through calibrated divertor valves of ASDEX Upgrade were used to determine the relations between the molecular radiation (CH, CD, C_2) and particle fluxes (CH_4, CD_4, C_2H_6). With these photon efficiencies the formula for the spectroscopic determination of chemically eroded carbon (methane) fluxes from the radiation of CH molecules was extended by the intensity ratio of the Swan band to the CH Gerö band. Thus, the formation of higher hydrocarbons (C_2H_y) can now be taken into account for the determination of carbon fluxes by the simple technique of relative measurements.

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