

# Experimental and theoretical investigation of Fe-catalysis phenomenon in hydrogen thermal desorption from hydrocarbon plasma-discharge films from T-10 tokama<sup>★</sup>

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**Abstract.** Investigations of the effect of Fe impurities on D<sub>2</sub> thermal desorption (TD) from homogeneous CD<sub>x</sub> films ( $x \sim 0.5$ ) formed in the D-plasma discharge of the T-10 tokamak were carried out. The experimental TD spectra of the films showed two groups of peaks at 650–850 K and 900–1000 K for two adsorption states. The main result of the iron catalysis effect consists in the shift of the high-temperature peak by –24 K and in the increase in the fraction of the weakly bonded adsorption states. To describe the effect of iron impurities on TD of hydrogen isotopes, a structural cluster model based on the interaction of the Fe<sup>+</sup> ion with the 1,3-C<sub>6</sub>H<sub>8</sub> molecule was proposed. The potential energy surfaces of chemical reactions with the H<sub>2</sub> elimination were calculated using ab initio methods of quantum chemistry. It was established that the activation barrier of hydrogen TD is reduced by about 1 eV due to the interaction of the Fe<sup>+</sup> ion with the  $\pi$ -subsystem of the 1,3-C<sub>6</sub>H<sub>8</sub> molecule leading to a redistribution of the double bonds along the carbon system.

## 1 Introduction

Fe-based catalysis is well known in solving wide range of energetics problems, from the Fischer-Tropsch synthesis process [1] to the production of materials for hydrogen storage [2]. A comprehensive study of hydrocarbon films obtained in the plasma discharge of large fusion facilities allows, on the one hand, to minimize parasitic capture of the working gas, and, on the other hand, to understand the conditions for the creation of high-performance hydrocarbon matrices for hydrogen energy.

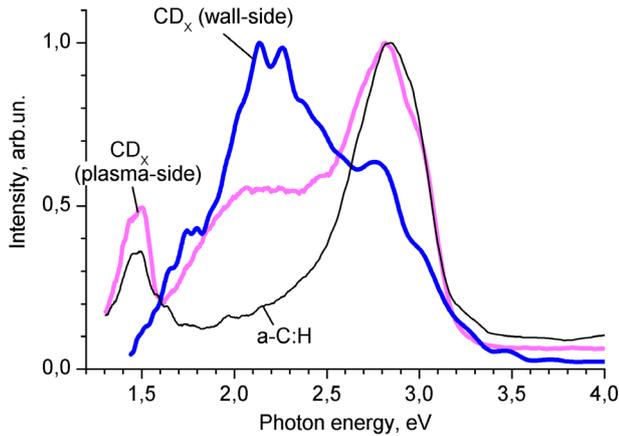
The object of the study is amorphous smooth thick hydrocarbon films with a high deuterium ratio  $D/C$  (0.4–0.8) deposited on the walls of the vacuum chamber at  $T = 300$ – $400$  K out of “direct vision” of central plasma and far from a graphite limiter, contrary to globular films type of “cauliflower” deposited on the limiter at  $T > 2500$  K, with a low ratio  $D/C \sim 10^{-3}$  [3]. They are formed in working discharges of deuterium high-temperature plasma, as well as in cleaning discharges of hydrogen and deuterium low-temperature plasma. After reaching the thicknesses of 10–30  $\mu\text{m}$ , these smooth films – “flakes” – peel off from the chamber walls, fall down, and then are removed when the chamber is opened. These hydrocarbon films are the main accumulator of hydrogen isotopes.

The films differ in color, which reflects different band gap values  $E_g$ , the different concentration of the deuterium working gas and hydrogen, different temperatures of their formation. The film color varies from dark brown for a relative concentration of  $D/C = 0.4 \pm 0.2$  to a golden one with  $D/C = 0.8 \pm 0.2$ . The  $H/C$  ratio about to  $\approx 0.1$ – $0.2$ , is mainly due to the basic vacuum conditions and the duration of storage in the atmosphere that leads to “parasitic” absorption of H, H<sub>2</sub>, OH, etc. It was found [4] that in films there are 12 microimpurities originating from erosion of vacuum chamber stainless-steel walls. This is mainly d-metals Fe, Ni, Mo, Cr, etc., half the concentration of which is iron. At the same time, the iron distribution across the thickness of the film is irregular, the convex (near-wall) side of the film has a larger concentration of iron than the concave one, since it directly border the surface of the stainless steel vacuum chamber. For golden CD<sub>x</sub> films the iron concentration is 0.7 at.%, and for dark brown ones – about 2 at.%. It has been established [5] that in films Fe ions form FeC<sub>6</sub> clusters with a Fe–C distance of 0.211 nm, and iron ions are in a high spin state of  $S = 5/2$ . At that the process of hydrogen (deuterium) thermal desorption (TD) from films is accompanied by the  $sp^3 \rightarrow sp^2$  conversion of the carbon centers.

In the present work, the catalytic effect of iron impurities on the physico-chemical properties of CD<sub>x</sub> films is investigated. TD spectra revealed a decrease in the desorption temperature of D<sub>2</sub> in the strongly bound state, as well as a decrease in their relative fraction for a sample with a higher Fe content. To describe the effect of iron impurity on TD, a model of the interaction of iron ions with the C–H(D) systems

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**Fig. 1.** Laser photoluminescence spectra ( $E_{exc.} = 3.68$  eV) for the plasma and near-wall sides of the golden  $CD_x$  and a-C:H/Si(100) films.

in the form of a  $[Fe(C_6H_8)]^+$  cluster is proposed. On its basis, with the help of ab initio methods of quantum chemistry, the potential energy surfaces of chemical reactions with the  $H_2$  ( $D_2$ ) elimination were calculated, and the decreasing of the activation barrier of the hydrogen isotopes desorption in the presence of  $Fe^+$  ions was determined.

## 2 Experimental setup

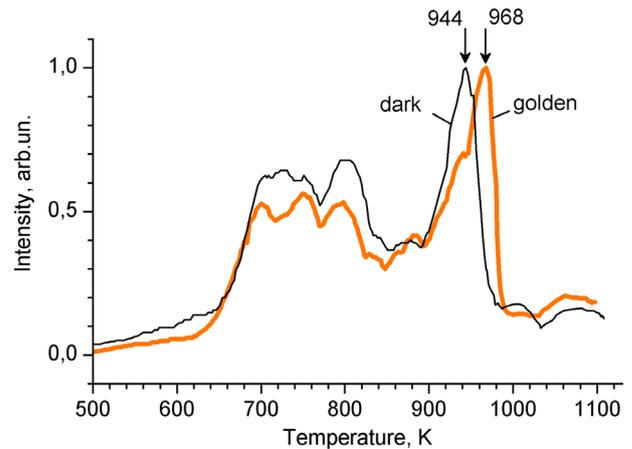
Photoluminescence spectra for two sides of golden  $CD_x$  films were obtained at room temperature in an ultrahigh vacuum setup with excitation by a pulsed nitrogen laser ILGI-503 (excitation energy 3.68 eV) and spectra recording with the aid of an MDR-2 monochromator and a FEU-100 photomultiplier.

TD spectra of deuterium were obtained using the Knudsen mass spectroscopy method at a setup of the National Research Centre “Kurchatov Institute” on the basis of an ultrahigh vacuum facility USU-4 with a base vacuum of  $\sim 10^{-9}$  mbar. TD spectra were measured with a quadrupole mass spectrometer APDM-1 ( $m/z = 1-100$ ) in a temperature range of 300–1100 K at a constant heating rate of 10 K/min.

## 3 Results

### 3.1 Experimental results on photoluminescence and TD

Obviously, the presence of impurities in the investigated films, and, first of all, iron, significantly affects their properties. Figure 1 shows the photoluminescence spectra of both sides of the golden  $CD_x$  film and its model analogue – a polymeric (soft) a-C:H film on Si(100) substrate without Fe. As evident, all spectra occupy a wide energy interval 1.3–3.3 eV, forming three main bands: 1.3–1.6 eV, 1.6–2.5 eV and 2.5–3.3 eV. The two extreme bands of the spectrum refer to an intrinsic luminescence of the exciton type [6]. In the central part of the spectrum, there are significant differences, depending on the concentration of iron impurity. Thus, for both sides of the  $CD_x$  film the high-energy band 2.5–3.3 eV is partially quenched, and the 1.3–2.5 eV band flares up in



**Fig. 2.** Normalized spectra of  $D_2$  TD for golden and dark brown  $CD_x$  films.

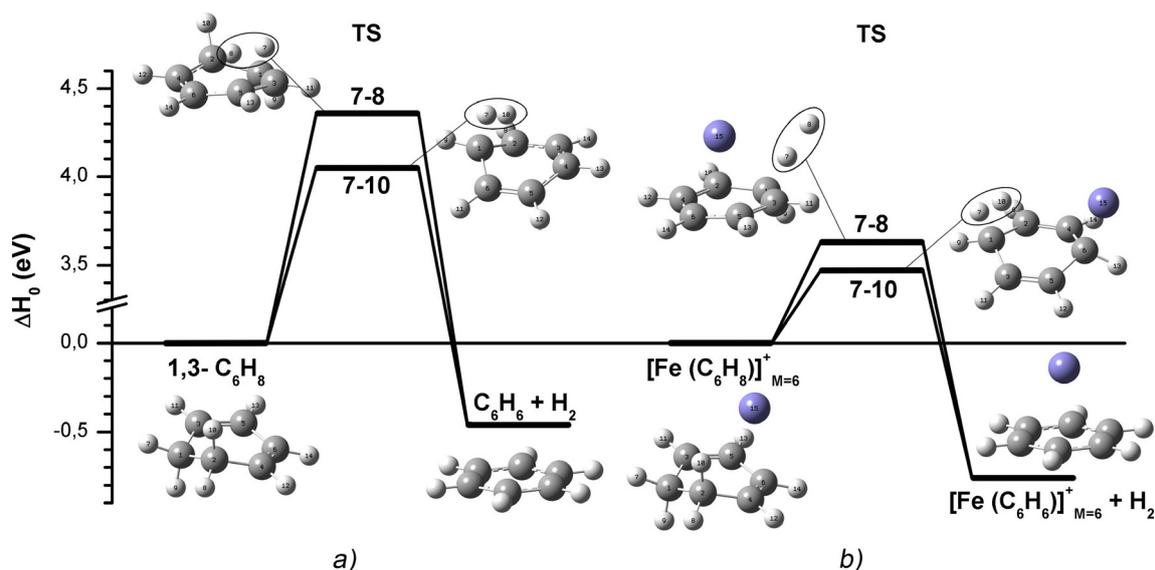
proportion to the concentration of iron. This luminescence can be attributed to the impurity photoluminescence of  $3d FeC_6$  clusters found in  $CD_x$  films [5].

Figure 2 shows spectra of  $D_2$  TD for golden and dark brown  $CD_x$  films normalized to the maximum intensity. The spectra consist of two main groups of peaks in the region of  $\sim 650-850$  K and  $900-1000$  K. A wide group of peaks with a center at about 750 K has a symmetrical form, which is characteristic of the second-order desorption. Peaks at  $\sim 970$  K have a narrow, asymmetric appearance, characteristic of the first-order desorption. Eventually, as a result of the experimental data analysis, it was established that the desorption process can be explained with the help of two adsorption states of deuterium and different desorption mechanisms [7]. Desorption of deuterium atoms in the region of low-temperature peaks occurs by hopping diffusion from a weakly bound state with an activation energy of desorption  $\sim 0.65$  eV/D, followed by rapid pair recombination on a common structural element, and then desorption of deuterium molecules. For high-temperature peaks, it is associated with a process of resonance type with simultaneous rupture of stronger carbon-deuterium bonds ( $\sim 1.25$  eV/D) and recombination followed by desorption.

Based on the above, and by comparing the spectra of  $D_2$  TD shown in Figure 2, one can draw the following conclusions. First, the position of the first group of peaks is not changed by temperature, i.e. the structure of weakly bound states does not depend on the iron concentration, while their fraction increases for dark brown films with a higher Fe concentration. The absence of desorption barrier reduction is connected with the lack of Fe influence on the D hopping diffusion which is crucial stage of second-order desorption. Second, the position of the narrow resonance peak shifts from 968 K for golden films to 944 K for dark films, i.e. a shift of  $-24$  K indicates a reduction of desorption barrier for higher Fe concentration.

### 3.2 Structural cluster model

At present there is no complete clarity on the effect of Fe-impurity on the decrease of the activation energy of hydrogen desorption from hydrocarbon films. As men-



**Fig. 3.** Potential energy diagram ( $\Delta H_0$  ( $T=0\text{K}$ ), eV) at the MP2/6-311++G\*\* level of theory for the reaction of  $\text{H}_2$  elimination without (a) and with (b) the  $\text{Fe}^+$  ion participation in the ground electronic spin state  $S=5/2$  (multiplicity  $M=6$ ).

tioned above, the process of hydrogen TD is accompanied by the  $\text{sp}^3 \rightarrow \text{sp}^2$  conversion of the carbon centers, while Fe ions form  $\text{FeC}_6$  clusters with a Fe–C distance of 0.211 nm, and iron ions are in a high spin state of  $S=5/2$ . We constructed a structural cluster model that takes into account these features of Fe-catalysis. The basis of the model is a molecule of 1,3-cyclohexadiene  $\text{C}_6\text{H}_8$  (Fig. 3a), whose carbon atoms are sixfold coordinated to the  $\text{Fe}^+$  ion in the ground electronic spin state  $S=5/2$  (Fig. 3b). In the framework of this model, with the GAUSSIAN 03 program [8], using an abinitio quantum chemical approach, second order Møller-Plesset perturbation theory (MP2), in combination with the set of basis functions 6-311++G\*\* [8], there were calculated reactants, transition structures (TS) and  $\text{H}_2$  desorption reaction products both without the  $\text{Fe}^+$  ion (Fig. 3a), and in its presence (Fig. 3b). All calculations by the MP2/6-311++G\*\* method include a full geometry optimization of the structures shown in Figure 3 with the subsequent taking into account of zero-point energy corrections in the reaction enthalpies and their barriers.

In comparison with the methods of the density functional theory (DFT) popular in quantum chemistry, the MP2/6-311++G\*\* method improves the accuracy of describing the relative positions of the three lower terms of the Fe atom from 0.5 to 0.3 eV. Unlike the DFT methods, the MP2 method correctly determines the ground sextet electronic state of the  $\text{Fe}^+$  ion. The excited quartet state of the  $\text{Fe}^+$  ion is 0.16 eV in energy above the ground state (the corresponding experimental value equals 0.25 eV [9]). The region of the transition state in chemical reactions with the  $\text{H}_2$  elimination is also described by the MP2 method with an accuracy of 0.3 eV. The experimental value of the binding energy 4.5 eV [10] in the  $\text{H}_2$  molecule is reproduced with the same accuracy. As a result, the preliminary performed comparative analysis made it

possible to recommend the procedure developed by us on the basis of the MP2 method for studying Fe-catalyzed desorption of hydrogen from hydrocarbon films.

As follows from Figure 3a, according to our calculations, the  $\text{H}_2$  elimination reaction:  $1,3\text{-C}_6\text{H}_8 \rightarrow \text{C}_6\text{H}_6 + \text{H}_2$ , is an exothermic process with a thermal effect of  $-0.46\text{ eV}$  (vs.  $-0.31\text{ eV}$  from experimental data [11]). Whereas in the presence of iron, the exothermicity of the reaction:  $[\text{Fe}(\text{C}_6\text{H}_8)]^+ \rightarrow [\text{Fe}(\text{C}_6\text{H}_6)]^+ + \text{H}_2$  becomes larger by 0.30 eV. According to the well-known Polanyi-Semenov rule, the activation energy decreases with increasing exothermicity of the reactions. This fact was confirmed as a result of direct calculations of the activation energies of these reactions by two mechanisms of  $\text{H}_2$  desorption: for H7 and H10 atoms lying on one side of the carbon cycle and for atoms H7 and H8 lying on different sides of it. The transition state for the reaction in Figure 3a is not found with the H9–H10 desorption mechanism, therefore this mechanism is excluded from further consideration. Due to the interaction of the  $\text{Fe}^+$  ion with the  $\pi$ -subsystem of the 1,3- $\text{C}_6\text{H}_8$  molecule, double bonds are redistributed along the carbon cycle: the double bond moves from the C6–C4 position to the C4–C2 position with the C2–H10 bond breaking (7–10 mechanism in Fig. 3b), or moves from position C6–C4 to position C4–C2 with C2–H8 bond breaking (7–8 mechanism in Fig. 3b). As a result of the catalytic effect of the  $\text{Fe}^+$  ion, the  $\text{H}_2$  activation desorption barrier decreases by 0.6 eV via the 7–10 mechanism, and by 0.7 eV via the 7–8 one. Note that substitution of the H atoms by D atoms does not change the conclusion on reduction of the activation barrier for hydrogen desorption under the influence of a  $\text{Fe}^+$  ion. According to our estimates, the isotopic replacement of H by D will increase the activation barrier for both mechanisms by only 0.1 eV, i.e. within the calculation error of the MP2/6-311++G\*\* method. Note that an isotopic substitution of deuterium by tritium will lead to an even smaller change in the barrier height.

## 4 Conclusions

The catalytic effect of iron impurities on hydrogen (deuterium) TD from studied  $CD_x$  system was experimentally observed and theoretically confirmed. Presence of Fe ions does not influence on weakly bounded H (D) states, while the activation barrier of hydrogen desorption from strong bonded is reduced by about 1 eV.

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