Influence of Hydrocarbons on Vibrational Excitation of Hydrogen Molecules

Iztok Čadež, Sabina Markelj
Association EURATOM-MHEST, Jožef Stefan Institute (JSI)
Jamova cesta 39, SI-1000 Ljubljana, Slovenia
Iztok.Cadez@ijs.si, Sabina.Markelj@ijs.si

Aleksandar R. Milosavljević
Institute of Physics
Pregrevica 118, 11080 Belgrade, Serbia
vraz@ipb.ac.rs

ABSTRACT

The influence of light hydrocarbons on vibrational excitation of H$_2$ generated in a special source of excited molecules has been studied. Vibrational spectrometer based on analysis of variation of H$^-$ yield produced by dissociative electron attachment in 0-5 eV electron energy range is employed. Molecule dissociation on the hot tungsten filament and atom recombination on cooled walls is used for production of molecular excitation in the source and specific influence of CH$_4$, C$_2$H$_4$ and C$_2$H$_6$ on vibrational distribution of hydrogen molecules from the source is presented here. Vibrational relaxation of H$_2$(v) is observed when mixture of CH$_4$ and H$_2$ is introduced to the source. On the other hand, production of vibrationally excited H$_2$ molecules is observed when C$_2$H$_4$ (ethene) and C$_2$H$_6$ (ethane) are present alone in the source, due to the thermal dissociation of these two molecules on the hot filament. This effect was not found for CH$_4$. Studied processes are relevant for the modelling of edge plasma in tokamaks.

1 INTRODUCTION

The interaction of plasma with surfaces of specific materials and under specific conditions is very active field of research within the program of development of new fusion reactors especially in context with ITER construction. Influence of neutral particles produced by surface recombination on edge plasma in tokamak is recognized as being very important for proper modelling and prediction of power load to the plasma facing components (PFC) and also to plasma performance itself. Reactions with neutrals are even more important for a large tokamak like ITER than for the present day tokamaks [1]. Although the presence of neutral hydrogen atoms and molecules in the edge plasma is well established [2], the details of production and interaction of highly rotationally and vibrationally excited hydrogen with the wall are still not well understood. Data on many atomic and molecular volume collisions and surface reactions are needed for detailed modelling of edge plasma. Vibrationally excited neutral hydrogen molecules and light hydrocarbons [3, 4] are present in the edge plasma of tokamaks with graphite plasma facing components. Presence of hydrocarbons as an impurity will most probably be difficult to avoid even in all metal-wall tokamaks. Small hydrocarbons (e.g. CH$_4$, C$_2$H$_6$) can influence the population of hot hydrogen molecules and therefore chain of reactions.
EXPERIMENTAL METHOD AND SETUP

2.1 Vibrational spectroscopy of hydrogen molecules

Recently developed set-up [5, 6] was used for the vibrational spectroscopy of hydrogen molecules. Diagnostic method is based on the properties of the lowest energy (“4eV process”) dissociative electron attachment (DEA) in hydrogen, \( e + H_2(X^1\Sigma_g^+; v,j) \rightarrow H_2(X^2\Sigma_u^+) \rightarrow H(n=1) + H \). These characteristic properties are: i) production of “zero” energy ions with highest probability at the threshold (3.724 eV for \( v=0 \) of \( H_2 \)), ii) displacement of the threshold to lower energy for excited molecules, and iii) strong increase of DEA cross section with internal excitation. Above characteristics of DEA depend only on electronic states involved in the process, so the same spectroscopic method is applicable to HD, D\(_2\) and other hydrogen isotopologues, as well.

In the present experiment we are using magnetically guided electron beam, special low energy ion extraction optics for ion separation and a channel electron multiplier for ion detection. Electron beam energy is scanned in the range from 0 to 20 eV for standard broad energy range ion yield spectra. Vibrational distribution of hydrogen molecules is determined by appropriate deconvolution procedure of experimentally determined \( H^- \) (or \( D^- \)) yield as a function of electron energy in the range between 0 and 5 eV.

Besides the lowest energy DEA there are two more processes in the low incident electron energy range. The second process, between 5 and 13 eV, proceeds through the repulsive \( 2\Sigma_g^- \) resonant \( H_2^- \) state and leads to higher kinetic energy fragments. Finally, the third process with a threshold at 13.92 eV (“14eV process”) proceeds through another attractive resonant state of the \( 2\Sigma_g^+ \) symmetry that dissociates to low energy \( H^- \) and electronically excited (\( n=2 \)) H atom. For spectroscopic purpose this process is also of interest for lower \( v \)-states especially for heavier isotopes.

2.2 Source of vibrationally excited hydrogen

Vibrationally excited hydrogen molecules (in present experiment only \( H_2(v) \)) are created in a special source (ISPEC) [7], which is schematically shown in figure 1. Hydrogen gas is introduced into the source and partially dissociated by thermal dissociation on a hot tungsten filament mounted in the first part of the source (dissociation chamber). \( H_2(v) \) are produced by recombination of hydrogen atoms on the water-cooled walls (evaporated with tantalum or with inserted W liner) of the second, recombination chamber. Gas containing vibrationally hot molecules and also some non-recombined neutral atoms flows out from the source in the high vacuum to the detection region of vibrational spectrometer where it is intercepted by electron beam of variable energy from 0 to 20 eV.

The body of ISPEC is made of OFHC copper and dissociation filament is about 10 cm long 0.25mm diameter tungsten wire. The filament temperature as a function of heating current was determined separately by means of an optical pyrometer.
Figure 1: The source of excited molecules used in the present study.

By standard vacuum conductivity consideration and some calibration measurements by means of absolute capacitance pressure gauge it is possible to get realistic estimate of the pressure distribution in the source. This is shown for a typical flow rate of hydrogen in figure 2. Most of experiments were performed with 6 mm diameter exit aperture of the source but some measurements with methane were performed also with smaller one (2mm dia.), as well, in order to increase pressure in the source.

Figure 2: Pressure variation along axis (Z-coordinate) of ISPEC for H\textsubscript{2} for two sizes of exit aperture (EA) and for the case when EA is not mounted.

In the present experiment, pure hydrogen or hydrogen mixtures with methane, ethene or ethane was used. In order to check for the effect of the filament temperature, tests measurements were performed with pure hydrocarbons as well. No measurements were performed with D\textsubscript{2} at the present stage of the study but these are planned in the near future.
3 RESULTS AND DISCUSSION

3.1 Methane

Preliminary results obtained with methane have been recently reported elsewhere [8] and only short conclusion is given here. Only a single maximum at about 10 eV appears in the yield of H⁻ ions when pure methane is introduced in ISPEC. This is in agreement with a study of DEA in methane [9]. For this case no variation of shape or structure of ion yield is observed when tungsten dissociation filament was heated. Noticeable vibrational relaxation of H₂(v) distribution is observed when mixture of H₂ and CH₄ was introduced to the source instead of pure hydrogen under otherwise same conditions. This was checked for two different exit aperture sizes and also compared to the case when H₂ and Ne mixture was introduced. Vibrational relaxation was observed for the case of methane but not for the case of neon so that vibrational relaxation is most probably do to V-V collisions of H₂(v) and CH₄.

3.2 Ethene and ethane

The H⁻ yield spectra recorded without dissociation in the source (filament heating off) for electron energy range 0-20 eV are given in figure 3a (left panel). The top spectrum shows ion yield for the background pressure when no gas is introduced through ISPEC. This background signal is always present and it is due to H⁻ from water in background vacuum (in agreement with [9]). The next lower spectrum is obtained when H₂ is flown through ISPEC. This is typical spectrum for cold hydrogen and shows two characteristic peaks at about 3.7 eV and 14 eV, for DEA channels leading to H (n=1 and n=2) respectively. Ions from middle energy DEA in hydrogen (5-13 eV) having higher kinetic energy do not contribute to the signal as detection system is tuned to high efficiency for only low energy ions. Yield of H⁻ for pure C₂H₄ and C₂H₆ is shown in the lowest two graphs in figure 3a. In the case of ethene one observes appearance of two peaks at 9 and 11 eV while for the case of ethane only single peak is observed at 9.5 eV. It is worth noting here that DEA in polyatomic molecules has rich branching ratio of resonance decay, therefore heavier negative fragment ions are produced, as well. However our vibrational spectrometer is tuned to low energy H⁻ ions, so that only production of these ions represents the signature of particular species.

Spectra obtained with heated tungsten filament for pure H₂, C₂H₄ and C₂H₆ are shown in figure 3b (right panel). Heating current for these spectra was 6 A corresponding approximately to T∮ = 2150K. This was determined by optical pyrometer performed on the filament of same length mounted separately in the high vacuum. Filament temperature in the real conditions in ISPEC is presumably somewhat lower due to the gas cooling and different environment. Distinct feature of ethene and ethane is appearance of the change of ion spectrum structure for these two cases, while no variation in spectrum was observed for methane. Observed change in spectra is due to the appearance of signal from DEA in hydrogen thus indicating strong dissociation of ethene and ethane on hot tungsten. Furthermore, form of the spectra in the region of 4 eV peak clearly indicates vibrational excitation of H₂ molecules formed from ethene and ethane dissociation. These H₂(v) might be produced directly from thermal dissociation of molecules, (e.g. C₂H₆ + W(T∮) → C₂H₄ + H₂(v) + W(T∮)) on the filament or indirectly by H-atoms created on the filament and then recombined on the cold wall of ISPEC, in the same way as for hydrogen. In order to elucidate which of the mechanisms is responsible for H₂(v) production more experiments are needed.
Figure 3: H\(^-\) yield spectra for H\(_2\), C\(_2\)H\(_4\) and C\(_2\)H\(_6\) for cold filament (a)-left panel, and for W-filament heated (b)-right panel. Background signal due to H\(^-\) from H\(_2\)O is shown on the top of spectra for cold filament.

Ion yield spectra in the “4 eV DEA” range, i.e. from 0 to 5 eV, for H\(_2\) and C\(_2\)H\(_6\) together with cold (dissociation filament turned off) H\(_2\) spectrum are shown in figure 4. To illustrate instrument performance electron beam current is also shown. Two curves are normalised to the same value of the signal at 14 eV peak so that mutual relation manifests higher relative excitation of hydrogen from C\(_2\)H\(_6\).

Figure 4: H\(^-\) yield spectra indicating strong vibrational excitation produced as a consequence of ethane dissociation on the tungsten filament.
Dependence of molecular hydrogen yield on dissociation filament temperature is shown in figure 5 for the case of \( \text{C}_2\text{H}_6 \). One observes that surface dissociation starts at about 2 A of heating current, which corresponds to 900°C and increases steadily until 6 A (1900°C). This dissociation threshold is lower than for occurrence of hydrogen vibrational excitation characteristic for \( \text{H}_2 \) atomization on the filament thus indicating much lower dissociation energy than 4.48 eV. However, the shown characteristic is exhibiting hysteresis so that dissociation disappears at higher temperature when filament is cooled down. This indicates also surface modification of tungsten filament presumably by reaction with carbon.

![Figure 5: \( \text{H}^+ \) at characteristic energy of \( \text{H}_2 \) resonance as a function of filament heating current (i.e. filament temperature – also shown) for pure \( \text{C}_2\text{H}_6 \) flown through ISPEC.]

Working with methane and ethane did not influence characteristics of vibrational spectrometer but ethene did have noticeable influence on the cathode of electron gun. Electron emission under constant cathode current was steadily increasing what is indicative of probable thinning of the cathode.

3.3 Conclusions

Main results from the present work are the following:
- Vibrational population of \( \text{H}_2 \) is decreased when \( \text{CH}_4 \) is present indicating vibrational relaxation of hydrogen excitation by V-V energy transfer. Under similar conditions no vibrational relaxation is observed when methane is replaced by neon.
- Both, \( \text{C}_2\text{H}_4 \) and \( \text{C}_2\text{H}_6 \) thermally dissociate on hot tungsten producing vibrationally excited \( \text{H}_2 \). It can not yet be explained whether these molecules are formed from atoms created by dissociation on the filament and their subsequent recombination in ISPEC or they are direct product of dissociation on the filament. At the present time the first case seems to be more probable due to strong dependence of signal on ISPEC temperature (cooling).
- Strong vibrational excitation is observed mainly of lower vibrational states up to \( v=3 \) what is different with respect to the hydrogen recombination on clean tungsten indicating possible formation of C:H layer on the wall of ISPEC.
ACKNOWLEDGMENTS

Studies of processes with vibrationally excited hydrogen molecules which are relevant to fusion edge plasma performed at JSI are supported by the project “1.4.1 Hydrogen-deuterium molecule wall interaction” of Association EURATOM-MHEST. Present work is also partially supported by the project of bilateral scientific collaboration between Serbia and Slovenia 2008-2009 (“Electron induced fragmentation of organic molecules and small hydrocarbons”).

REFERENCES


