Neutral and Ionic Chemistry in Low Pressure DC Plasmas of Hydrogen and Deuterium Mixtures

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1. Introduction

Isotope scrambling plays a determinant role in the chemistry of plasmas with H₂ and D₂, which are of interest in a variety of environments, including nuclear fusion reactors, planetary atmospheres and star forming regions. [1-3]. Understanding of hydrogenic ion chemistry in cold plasmas in contact with the surface of experimental fusion reactors, as well as fuel recycling in the walls, are presently major subjects of interest for the design and operation of next reactors like ITER [4]. On the other hand, in spite of intensive work by many groups, prompted largely by the unexpected enrichment in deuterated molecules found in interstellar clouds [3,5], many questions concerning the chemistry of the isotopic redistribution in hydrogenic plasmas in these regions remain open.

In a former work [6], we studied the kinetics of plasmas of H₂ generated at low pressures in a hollow cathode discharge reactor similar to that employed in the present case. The most noticeable effects observed were: 1. The highly efficient dissociation of H₂, which gave rise to high concentrations of H atoms, partially compensated by recombination of H atoms in the surface to produce H₂, even with small wall reaction coefficients.

2. The conversion of primary H₂⁺ ions, generated by electron impact ionization, in H⁺ ions, through the very effective protonation process

\[ \text{H}_2^+ + \text{H} \rightarrow \text{H}_3^+ + \text{H} \] (1)

with rate constant \( k_1 \approx 2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \). This conversion became predominant just from pressures \( \sim 1-2 \text{ Pa} \), where the mean free path of H₂⁺ for this process is similar to the radius of the reactor. Effective protonation processes have been observed too in plasmas of different mixed precursors containing H₂ [7-9].

In order to investigate H/D isotopic scrambling in H₂/D₂ plasmas under controlled conditions, we have performed a systematic study of low pressure H₂/D₂ hollow cathode discharges, combining various experimental techniques. The pressures studied have been low enough to neglect three body reactions in the gas phase, which enhances the effect of recombination of neutral atoms in the surfaces; but high enough to allow two-body homogeneous reactions between ions and neutrals to become relevant and start giving rise to a rich and complex ion chemistry.

2. Experimental set-up

Experiments have been carried out in a stainless steel grounded hollow cathode DC reactor (10 cm diameter, 34 cm length) with a central anode, described elsewhere [5,6].

A quadrupole mass spectrometer (Balzers, Prisma QMS 200) installed in a differentially pumped vacuum chamber samples neutral species from the plasma through a \( \sim 150 \mu \text{m} \) diaphragm. A plasma process monitor (Balzers PPM421) with a quadrupole mass filter and an ion energy analyzer is used for mass and energy resolved detection of ions [8,9], which are extracted directly from the plasma through a 100 \( \mu \text{m} \) diameter sampling orifice in the cathode. During operation, pressures in the two detection chambers are kept in the \( 10^{-5} \text{ Pa} \) range by means of their respective turbomolecular and dry pump systems. Electron temperatures and charge densities are measured with double Langmuir probes.

H₂/D₂ mixtures of varying proportions, with total pressures 1, 2 and 8 Pa, checked with a capacitance manometer, have been employed for plasma generation. The desired pressure and gas mixture composition are selected by balancing input and output gas flows for each gas, by means of a needle valve in the respective gas inlet and a butterfly valve placed at the gas exit between the reactor and its vacuum system. Residence times for H₂ and D₂ calibrated according to [6,10], are 0.2 s for 1-2 Pa and 0.4 s for 8 Pa. The H₂/D₂ ratios before turning on the discharges are checked by measuring the peak intensities at 2 and 4 a.m.u. with the Prism mass spectrometer, previously calibrated for the pure gases, subtracting background signals. Steady-state plasma currents \( \sim 150 \text{ mA} \) and voltages \( \sim 300 - 450 \text{ V} \) (depending on gas composition and pressure) are maintained during the experiments. An electron gun is employed for plasma ignition.

Ion fluxes are calculated by integrating the ion energy distributions recorded with the plasma monitor. Relative ion concentrations in the plasma are obtained by multiplying the ion fluxes by the corresponding square roots of their masses [8]. The relative sensitivity of the plasma monitor (including electrical filters and electron multiplier) to H₂⁺ and D₂⁺ has been checked by filling the chamber of the PPM421 with small pressures of H₂ and D₂ (\( \sim 10^{-3} \text{ Pa} \)) and comparing in each case the PPM signal, weighted by the respective ionization cross section at the chosen electron energy (70 eV), with the chamber pressure, as determined from the reading of a Bayard-Alpert gauge with the appropriate correction factor [7]. As shown by Pecher [11] this calibration procedure is also...
adequate for ions extracted from the plasma. The calibration has led to similar sensitivities for \( \text{H}_2^+ \) and \( \text{D}_2^+ \).

Charge densities and electron temperatures measured for pure \( \text{H}_2 \) and \( \text{D}_2 \) plasmas with the Langmuir probe, assuming Maxwellian distributions and weighting for the relative ion composition in each case, were \( n_e=(1.2\pm0.3)\times10^{10} \text{ cm}^{-3} \), \( T_e=4\pm1 \text{ eV} \) for (1-2) Pa, and \( n_e=(2.7\pm0.3)\times10^{10} \text{ cm}^{-3} \), \( T_e=2.5\pm0.6 \text{ eV} \) for 8 Pa.

3. Results

The mass spectra of neutrals in the discharge are dominated by the peaks of the precursor species, but an appreciable amount of HD is also formed. The relative concentrations of the three neutrals (\( \text{H}_2 \), \( \text{D}_2 \) and HD) derived from the measured mass spectra are displayed in Figure 1 for the five mixture proportions investigated, varying from 100% \( \text{D}_2 \) to 100% \( \text{H}_2 \), and for the two extreme pressures, 1 and 8 Pa (the results for 2 Pa are very similar to those for 1 Pa and are not shown for brevity). The symmetry of the Figure reflects the regular variation in the initial precursor concentrations.

\[
\text{H}_2 + \text{e} \rightarrow 2\text{H} + \text{e} \quad (2)
\]

has a rate constant \( k_2\approx1.755\times10^{-7}\times T_e^{-1.24}\times\exp\left(12.6/T_e\right) \), where \( T_e \) is the electronic temperature in eV [6]. Therefore, for the typical electron densities and temperatures of our discharges, the characteristic dissociation times \( (1/k_2n_e) \) are of the order of 0.1 s, comparable to the residence times. Previous estimations of high atomic hydrogen concentrations (up to 17%) in pure \( \text{H}_2 \) discharges, obtained from emission spectroscopic data, support also these conclusions.

Fig. 1 Measured relative concentrations of molecules in the reactor before discharge on (circles), and when the plasma has been ignited (dots), for 1 and 8 Pa and different \( \text{H}_2/(\text{H}_2+\text{D}_2) \) ratios. Lines are only to guide the eye.

Under the low pressure conditions of our experiment, characterized by a practical absence of three body collisions in the gas phase, HD must be formed essentially through wall recombination of H and D atoms. Therefore, this fact evinces the efficient dissociation of the precursors and recombination in the wall, pointed out in the introduction for the case of pure \( \text{H}_2 \) [6]. The relative amount of HD hardly varies when the pressure is increased from 1 to 2 Pa, but grows significantly when the pressure is raised to 8 Pa. In fact, for this pressure, equivalent amounts of \( \text{H}_2 \), \( \text{D}_2 \) and HD are obtained in the equimolecular mixture. The reason for this growth of HD concentration is the change in the residence time of the molecules in the discharge vessel commented on above. For the 8 Pa discharge, the residence time (0.4 s) is twice as large as that for the lower pressures; consequently, the precursor \( \text{H}_2 \) and \( \text{D}_2 \) molecules have a higher probability of dissociation and the subsequent wall recombination increases isotopic scrambling. For the mixtures with a higher proportion of one of the precursors, HD formation is limited by the concentration of the less abundant precursor, and the effect of recombination is not so obvious in the mass spectra but, by analogy with the equimolecular mixtures, one can conclude that, in any case, a significant amount of the remaining \( \text{H}_2 \) and \( \text{D}_2 \) molecules are dissociated by electron impact and formed again through \( \text{H} \) and \( \text{D} \) recombination at the walls. An analysis of typical dissociation times supports this conclusion. The reaction of electron impact dissociation:

Typical mass spectra of the ions are shown in Figure 2, for 2 Pa discharges of pure \( \text{H}_2 \), pure \( \text{D}_2 \) and an equimolecular mixture of \( \text{H}_2 \) and \( \text{D}_2 \). In the case of the pure mixtures, the tri-atomic species \( \text{H}_3^+ \) and \( \text{D}_3^+ \), appearing at 3...
and 6 a.m.u respectively, are seen to dominate the ionic distributions. These ions are produced in the transformation of the H₂⁺ and D₂⁺ primary ions through reaction (1) and:

\[ \text{D}_2^+ + \text{D}_2 \rightarrow \text{D}_3^+ + \text{D} \]  

(3)

with rate constant \( k_3 = 1.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \) [12]. In the mass spectrum of the equimolecular mixture, all masses in the 1 to 6 range are represented in appreciable amounts. In that case, the primary precursor of the HD⁺ ion, HD, is present in noticeable concentrations, as formerly shown. Besides, reactions like (1) and (3) between diatomic ions and neutrals with different isotopic composition and large rate constants [12] are relevant.

To quantify the concentration of each ion species, the signals at masses 1, 5 and 6 a.m.u can be attributed unambiguously to the ions H⁺, D₂⁺ and D₃⁺ respectively, but more than one ion can contribute to masses 2 (D⁺ and H₂⁺), 3 (HD⁺ and H₃⁺) and 4 (D₂⁺ and H₂D⁺). The ambiguity can be partly removed in some cases by inspection of the ion energy distributions [8,9].

Figure 3 shows the energy distributions of the ions corresponding to the spectra of Figure 2. The distributions are essentially concentrated in large and sharp maxima at energies very close to those of the discharge potential, but have peculiar features for the distinct species: Atomic ions have a characteristic high energy peak corresponding to fast ions generated in the direct electron impact dissociative ionization of the diatomic molecules [9]. Although collisions in the sheath are rare for the low pressures of the discharges studied, they cause a low intensity tail extending to lower energies in the energy distribution. Among the low intensity tails, those of diatomic ions, most likely due to symmetric charge exchange, are highest.

Figure 4 shows the ion concentrations for the three discharge pressures and for all the mixture proportions investigated. In the middle part of each panel, the appearance of isotopically mixed diatomic and, especially triatomic ions, leads to a partition of the total positive charge among all possible masses. At the left and right extremes of each panel, corresponding to discharges of pure H₂ or pure D₂, only three ions remain, but their proportion varies markedly with pressure.

Fig. 3 Ion energy distributions corresponding to the spectra of Figure 2.

Fig. 4 Ion concentrations for the three discharge pressures investigated at the different mixture proportions. Symbols: experimental data. Lines are only to guide the eye.
The most significant effects of pressure on the ion distributions are illustrated in Figure 5, where the results of Figure 4 are displayed as a function of total pressure for the pure precursors and for the equimolecular mixture. For the case of pure D₂ and pure H₂ plasmas, primary diatomic ions (D₂⁺, H₂⁺), formed directly by electron impact of the neutral molecules, are the most abundant ions at the lowest pressure (1 Pa). With increasing collision frequency, triatomic ions become dominant through reactions (1) and (3). For our conditions, the transition between the two regimes takes place at pressures between 1 and 2 Pa, similar to that found in pure H₂ discharges [6].

In the 50% equimolecular mixture, the situation is more complex, due to the appearance of H/D mixed ions, but the similitude of the ion production mechanisms and an analysis of the shapes of the ion energy distributions suggest that the proportions of total diatomic to triatomic ions is similar to that found in the discharges of pure gases. For the 8 Pa discharges, where the collision frequency is highest, virtually all diatomic ions are transformed to triatomic ions. In the case of the 50% equimolecular mixture, a high number of reactions between molecules and diatomic ions with different isotopic compositions take place [12]. In the steady state, H₃D⁺ and D₃H⁺ (masses 4 and 5) are found to be roughly twice as abundant as ions H₃⁺ and D₃⁺.

Conclusions
In the present work, isotope scrambling has been observed to be produced very effectively in H₂⁺D₂ plasmas, concerning both, neutrals and ions. The HD molecule is generated mainly by reactions of H and D atoms in the surfaces of the hollow cathode reactor. Reactions between the molecules H₂, D₂ and HD, and the corresponding primary ions, lead to high concentrations of triatomic ions when plasma pressure reaches values where the corresponding mean free paths of the ions are comparable to the radius of the reactor. A more detailed study is presently underway to work out the details of the neutral and ion chemistry in the different pressure regimes.

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References