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Hydrogenation processes from hydrogen peroxide: An investigation in Ne matrix for an astrochemical purpose

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Abstract

Hydrogenation processes are of paramount importance in the interstellar medium. Many laboratory experiments were carried out from unsaturated species. Herein, the hydrogenation of hydrogen peroxide was experimentally investigated step by step by means of matrix isolation technique. This reaction leads to the formation of water. Moreover, the formation of H_3O_2 and OH radicals as intermediates was characterized. Such a hydrogenation process should take place on the surface of dust grains in the interstellar medium. This reaction is consistent with the very small amount of interstellar hydrogen peroxide. This hydrogenation process also takes place in solid phase.

I. Introduction

Since the first detection of a chemical species in the interstellar medium in 1937, [1, 2] more than 160 compounds were characterized and identified in this dilute medium. In addition with very simple molecules, such as CH_4, NH_3 and H_2O, more complex species are also present in these dilute media, such as fullerenes, anthracene and metallic-containing molecules. It is now well established that complex chemistry can occur in the interstellar medium (ISM), and especially in molecular clouds, on the surface of dust grains.[3,4] As an example, numerous recent studies have shown that hydrogenation reactions efficiently take place in the ISM.[5] Some of these reactions are listed in the Table 1.

Hydrogenation of	Reference
HNCO	Hudson et al. [6]
HCN	Theule et al. [7]
CH_2NH	Theule et al. [7]
CO_2	Bisschop et al. [8]
CO	Fuchs et al. [9], Watanabe et al. [10], Pirim & Krim [11]
O	Oba et al.[12]
O_2	Cuppen et al. [13], Miyauchi et al.[14], Chaabouni et al.[15], Lamberts et al.[16]
O_3	Mokrane et al. [17]
NO	Fedoseev et al. [18]

Table 1: Examples of molecules that undergo hydrogenation processes in the interstellar medium, that were experimentally investigated.

Most of the reactions above mentioned involve unsaturated reagents. May such processes also occur from saturated species? As far as the ISM is concerned, this question seems to be particularly relevant in the case of hydrogen peroxide. Indeed, water is one of the most widespread molecules in the interstellar medium and the amount of water detected is much greater than that predicted by all models. Many laboratory experiments were carried out recently in order to identify and understand the reaction pathways leading to the formation of water in dense and diffuse molecular clouds.[19] Three theoretical models of formation of water in dense clouds have been proposed over the last 30 years: [20]

- a first pathway consists of a successive hydrogenation of oxygen[21,22, 23,24]:

$$O + H \rightarrow OH \qquad (1)$$

$$OH + H \rightarrow H_2O \qquad (2)$$

This two-step mechanism was proposed by Watson & Salpete, [21] and its experimental feasability was demonstrated by Dulieu et al. [25]. No activation energy is required for the reaction (1), whereas the activation energy of the reaction (2) was estimated at 22 kJ/mol. **Error! Bookmark not defined.**

The recombination of hydroxyl radicals may also be a source of water on the surface of ice grains in the ISM.[26, 27, 28]

- a second pathway in 3 steps was proposed by Tielens & Hagen in 1982: [29]

$$O + O_2 \rightarrow O_3 \qquad (3)$$

$$O_3 + H \rightarrow O_2 + OH \qquad (4)$$

$$OH + H_2 \rightarrow H_2O + H \qquad (5)$$

Its experimental feasibility was demonstrated by Mokrane et al. [30]

- a third pathway is also proposed by Tielens & Hagen in 1982 in 3 steps [29]:

$$O_2 + H \rightarrow HO_2 \qquad (6)$$

$$HO_2 + H \rightarrow H_2O_2 \qquad (7)$$

$$H_2O_2 + H \rightarrow H_2O + OH \qquad (8)$$

Reaction (6) is expected to take place without any activation barrier[31], or with a very small activation energy (5.00 kJ.mol^{-1} **Error! Bookmark not defined.** or 2.08 kJ.mol^{-1} [32]). No activation energy is associated to reaction (7). [31]

An activation energy of either 11.64 kJ.mol^{-1} [33], 14.97 kJ.mol^{-1} [34], or 17.15 kJ.mol^{-1} [35] was determined for the reaction (8). Reaction (8) may play an important role in the ISM, even if the amount of hydrogen peroxide present in these media is limited. Indeed, Du and Parise have shown that this reaction may explain the low abundance of H_2O_2 (a few percent in ices), since hydrogen peroxide is constantly transformed into H2O by reacting with the accreted H atoms. **Error! Bookmark not defined.**, [36] Furthermore, hydrogen peroxide is considered to be an intermediate in the formation of water, even in regions in which this molecule is under the detection threshold. [37]

Miyauchi[14], Ioppolo[19] like Oba[12] proved the experimental feasibility of this last reaction pathway. Each one of these ways seems possible in the interstellar environments.

Alternatively, Oba et al. [38] investigated the possibility to form water from a tunnelling effect in the reaction between OH radicals and molecular hydrogen.[39]

More precisely, the main laboratory's experiments on reactions that may lead to the formation of water in the interstellar medium are presented in Figure 1.

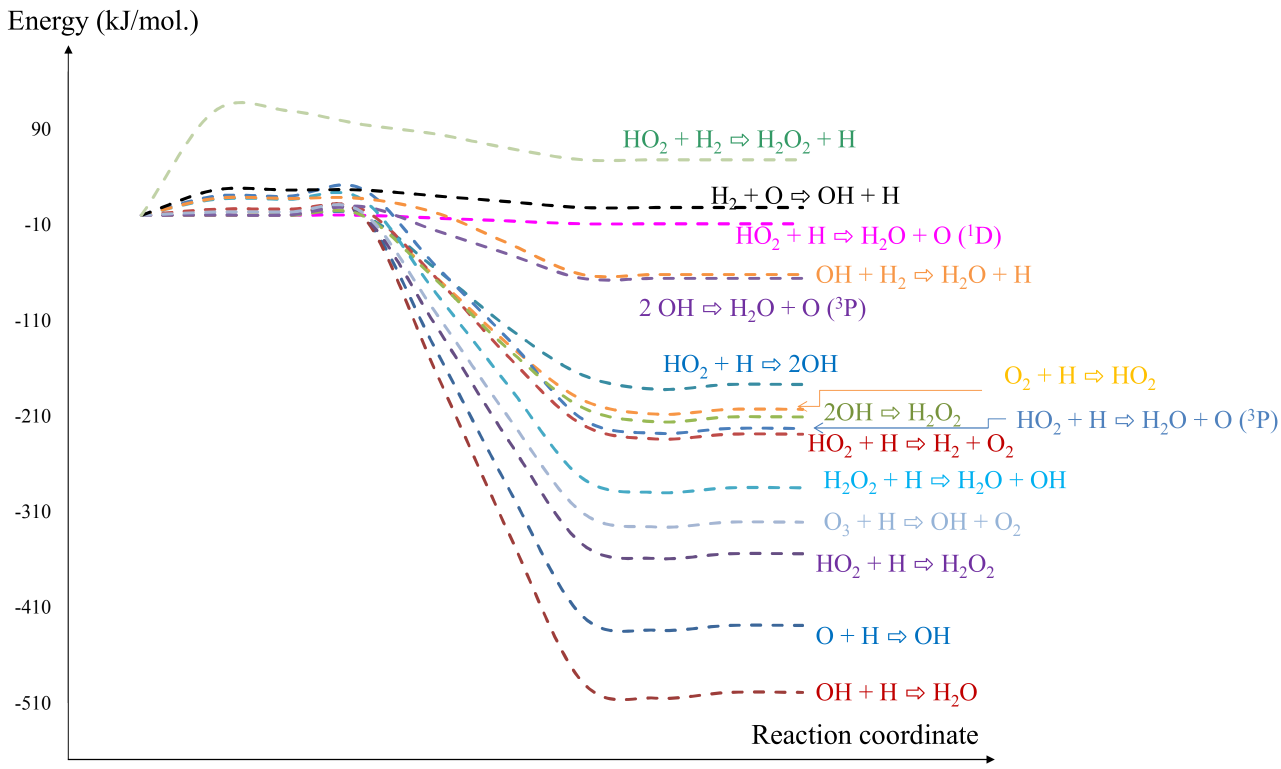

Figure 1: Main reactions that may lead to the formation of water in the interstellar medium. For a sake of comparison of the activation energies and the enthalpies change for the gas-phase reactions, all the initial states were put at zero. All these values were taken from Surface Processes on Interstellar Amorphous Solid Water: Adsorption, Diffusion, Tunnelling Reactions, and Nuclear-Spin Conversion, Tetsuya Hama and Naoki Watanabe, Chem. Rev. 2013, 113, 8783. [40]

From this figure, we can conclude that peroxide hydrogen can be formed without any activation energy, from HO_2 or OH radicals, and these two reactions are exothermic (-354 and -211 kJ/mol, respectively). Furthermore, the activation energy associated to the formation of water from peroxide hydrogen is very low (17 kJ/mol) and can be easily overcome, even under non-energetic conditions. Thus, the formation of water through a reaction pathway involving peroxide hydrogen as an intermediate appears to be an efficient process in the interstellar medium.

Only recently was detected hydrogen peroxide in the interstellar medium (ISM). Indeed, traces of H_2O_2 were only clearly identified in 2011 by the APEX (Atacama Pathfinder Experiment telescope) telescope. [41]

In this work we will be interested mainly in the second reaction of Tielens & Hagen[29] and more particularly in the third stage of the last reaction pathway, the hydrogenation of a saturated bond. This reaction was theoretically investigated by Koussa et al. [35] Slightly different values were proposed in the literature for this reaction. The main theoretically values reported in the literature for the reactivity between hydrogen peroxide and atomic hydrogen are reported in Table 2.

Reaction	Level of theory	Activation energy / ΔH (kJ/mol)	Reference
$H_2O_2 + H \rightarrow H_2O + OH$	MP2//CASSCF/aug-cc-pVTZ	+17.15 / -284.9	Koussa et al. 2006 [35]
$H_2O_2 + H \rightarrow H_2 + HO_2$	MP2//CASSCF/aug-cc-pVTZ	+33.81 / -63.13	Tarchouna et al. 2006 [42]

H_2O_2+H → H_2O+OH	MPW1B95/M3G	+25.94 / -297.90	Ellingson et al. 2007 [43]
H_2O_2+H → H_2 + HO_2	M05-2X/MG3S	+43.51 / -68.62	Ellingson et al. 2007 [43]
H_2O_2+H → H_2O+OH	GRAINOBLE astrochemical model [44]	+20.85 / -281.43	Taquet et al. 2012 [45]
H_2O_2+D → HDO+OH	GRAINOBLE astrochemical model	+19.58 / -289.03	Taquet et al. 2012 [45]

Table 2: Comparison of some theoretical data available in the literature for the reaction of hydrogen peroxide with either H or D atom.

Hydrogen peroxide spontaneously leads to the formation of water. In order to avoid a possible uncertainty between water due to the decomposition of H_2O_2 and water molecules formed during the hydrogenation reaction, deuterium was used for this study. Since it was not possible to work without water, we chose conditions in which water and hydrogen peroxide are formed in similar proportions, in order to reproduce the conditions of astrochemical ices.

II. Experimental technique

Two kinds of experiments were carried out:

- irradiations of hydrogen peroxide trapped in Ne matrix by D/D_2 at 10K,
- and co-condensation of D/D_2 and H_2O_2/Ne at 3K.

For a sake of comparison, three additional experiments were carried out:

- a reactivity study between hydrogen peroxide and molecular D_2,
- a reactivity study between water and D/D_2,
- a reactivity study of a mixed water / hydrogen peroxide ice with D/D_2.

A scheme of the experimental setup is presented in Figure 2, and the experimental method used for the present study has been described previously. [46, 47, 48] The sample holder is a hexagonal copper block on which rhodiated mirrors optically polished are fixed. This block is fixed on the top of a cold head connected to a cryostat (Cryomech PT- 405) operating with a circulating system of liquid helium to the sample. The experimental setup was optimized to be able to reach temperatures as low as 3 K on the surfaces of the mirrors. The sample holder is set in an analysis chamber that is connected to a microwave-driven atomic source, an injection ramp, the infrared spectrometer and a secondary pumping system.

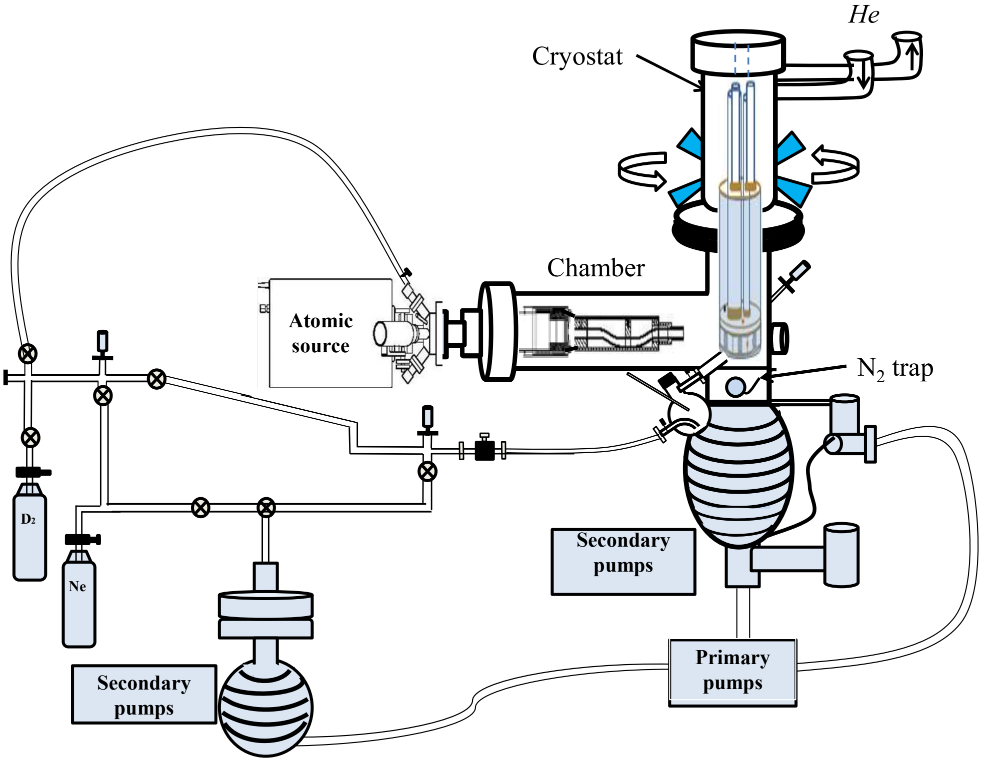

Figure 2: Scheme of the experimental setup used for the present study.[49]

The chamber is maintained at a high vacuum of around 10^{-8} mbar thanks to a diffusion pump (Edwards, Standart Diffstack 160/700/P). The ramp gas, in stainless steel, is connected to a pumping system (Edwards, Standart Diffstack 63/150M). This ramp gas allows the preparation of gaseous mixtures with piezoelectric gauges.

Deuterium atoms were generated from molecular deuterium (Sigma Aldrich), by a microwave-driven atomic source (SPECS, PCS-ECR), whose operation is briefly described herein.

Inside the plasma chamber, electron cyclotron resonance method is used to achieve massive dissociation of molecules in the plasma. Our ECR (electron cyclotron resonance) atomic source has a specially designed aperture which inhibits the release of ions from the plasma while allowing neutral atoms and molecules to effuse out. The particles released are largely thermalized, with an atom flux of about 10^{17} atoms/cm^3/second.

1 bar of D_2 is introduced inside the microwave-driven atomic source and the pressure of the chamber during operation of the atom source is 10^{-5} mbar. The gas leaving the chamber through the apertures is a combination of both atomic and molecular deuterium D/D_2 (15/85).

The ramp gas also allows the introduction of Ne gas inside a round-bottom flask containing the hydrogen peroxide adsorbed on urea.

In the context of laboratory experiments for astrochemically-relevant studies, hydrogen peroxide was extensively studied in rare gas matrix, [50, 51, 52] and a similar approach was used for the present study.

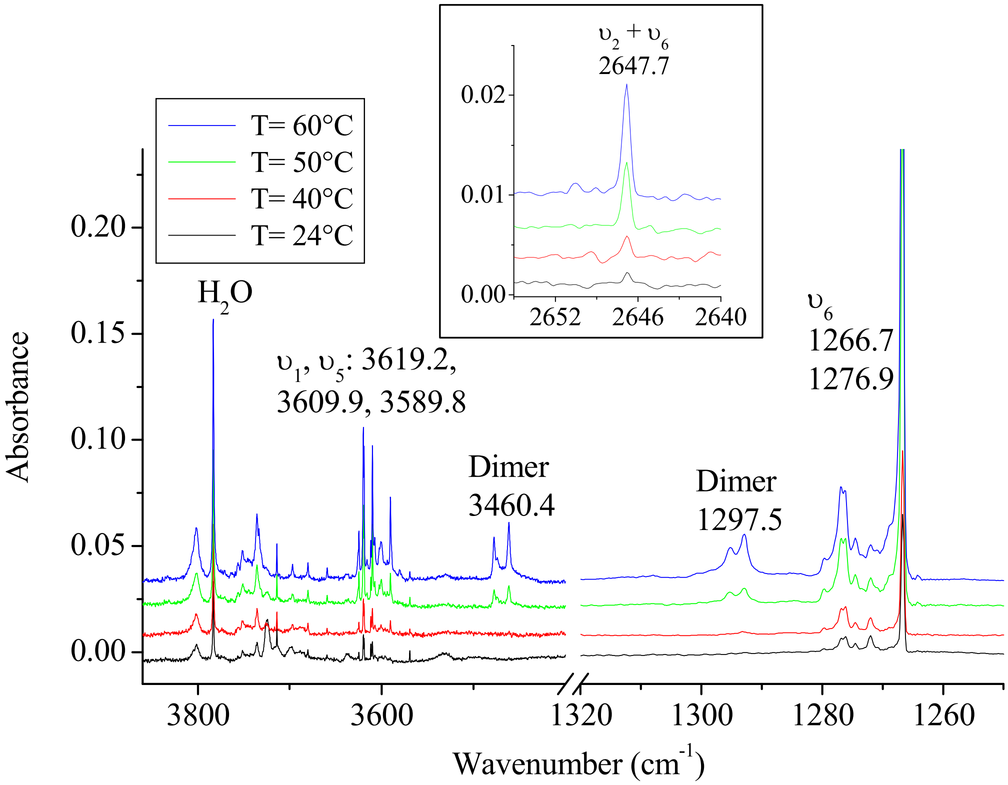

Figure 3: Main IR bands of H_2O_2 observed in Ne matrix from H_2O_2 adsorbed on urea, depending of the heating of the round flask containing the reagent. Except mentioned otherwise, all the attributions are related to H_2O_2.

H_2O_2 adsorbed on urea (Sigma- Aldrich) was used. This solid powder was introduced in a round bottom flask. Under our experimental conditions, it appears that the best way to condense hydrogen peroxide without destroying it is achieved when the round bottom flask is heated at around 50-60 °C (Figure 3). The gaseous mixture is then carried inside the reaction chamber thanks to a neon flux. These conditions lead to the formation of a neon matrix in which a large amount of hydrogen peroxide, as well as water are trapped.

Infrared absorption spectra of the samples obtained by condensation of gaseous mixtures were recorded in the transmission-reflection mode between 4500 and 500 cm^{-1} with a resolution of 0.5 cm^{-1} using a Bruker 120 Fourier transform infrared (FTIR) spectrometer. Bare mirror backgrounds, recorded from 4500 to 500 cm-1 prior to sample deposition, were used as references in processing the sample spectra. A KBr window is mounted on a rotatable flange separating the interferometer vacuum (10^{-3} mbar) from that of the cryostatic cell (10^{-7}mbar). The signal is then directed to a MCT (HgCdTe) detector. All spectra were recorded at 3K.

The attributions are based on the previous published works. [50, 51, 52, 53, 54, 55]

III. Results

Before presenting our experimental results on the reactivity between H_2O_2 and D atoms, we would like to comment reference experiments that were needed to ascertain the processes described below. Indeed, since the efficiency of the microwave-driven atomic-source, molecular D_2 was introduced in the chamber concomitantly with atomic D. This is the reason why we carried out experiments in which microwave-driven atomic-source was switched off. Under such experiments, similar spectra than the ones obtained when H_2O_2/Ne was condensed alone, were obtained. Thus, without any surprise, hydrogen peroxide do not react with molecular deuterium, and the phenomena described below are indeed due to the reaction between hydrogen peroxide and atomic deuterium.

a. Irradiation of H_2O_2/Ne by D/D_2 at 10K

First, H_2O_2/Ne was condensed at 3K on the surface of the mirror, and this sample was further heated up to 10 K and subjected to a D/D_2 beam. This bombardment was carried out at 10K to avoid the condensation of molecular deuterium on the surface of the sample. Spectra were registered before the D/D_2 exposure and during the exposure every 5 minutes, during 40 minutes. Figure 4 shows the spectra obtained. The spectrum of the initial sample containing hydrogen peroxide in Ne matrix is shown, as well as difference spectra between this spectrum and the ones obtained after the exposures.

The disappearance of H_2O_2 and H_2O_2 dimer are observed, with the concomitant formation of H_2O, HDO and D_2O (Figure 4). Until 40 min. of reaction, this behavior is observed. Furthermore, the formation of D_2O_2 is observed when the initial H_2O_2 sample is bombarded during 5 to 25 min. with a D/D_2 beam. After 25 minutes, the amount of D_2O_2 strongly decreases. Wide bands centered at 2650, 2525 and 2420 cm^{-1}, signature of dangling HDO/ D_2O, are formed during the exposure of H_2O_2 in Ne matrix to a D/D_2 beam. The structure at 2650 cm^{-1} may be due to $(D_2O)_2$, $(HDO)_2$ or OD radicals interacting with a water ice. The formation of such an ice, even after short exposure times, from matrix isolated samples, suggests that exothermic reactions take place.

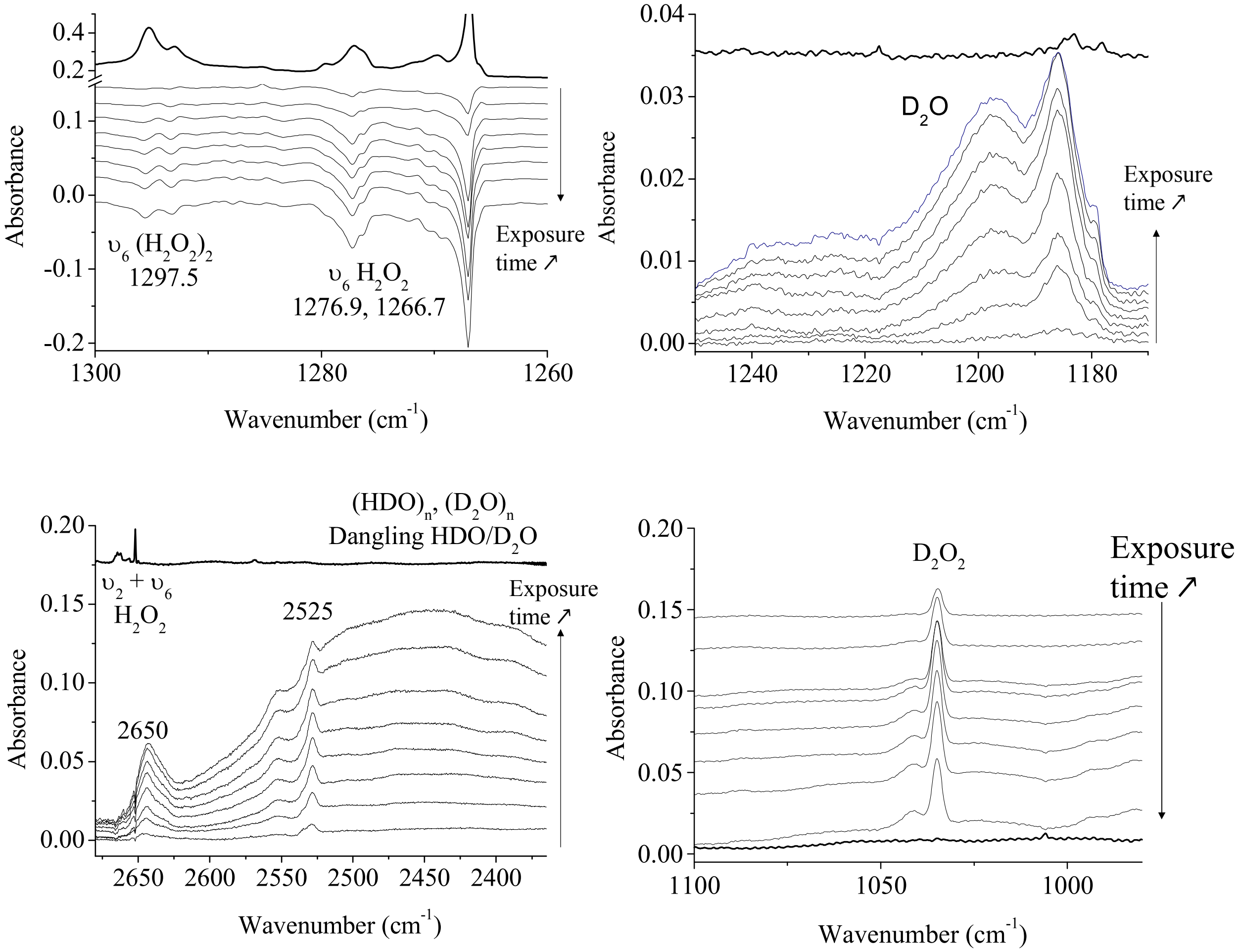

Figure 4: IR spectrum of the initial H_2O_2 sample in Ne matrix (in bold), and difference spectra after exposure to a D/D_2 beam during 5 to 40 min.,

- in the H_2O_2 bending region of hydrogen peroxide (top, left);
- in the ν_2 bending region of D_2O (top, right);
- in the OD stretching regions of D_2O and HDO ices (bottom, left). A wide band centred at 2420 cm^{-1} is observed, as well as two structures at 2650 and 2525 cm^{-1},
- **in the D_2O_2 bending region** (bottom, right).

b. Co-condensation of D/D_2 and H_2O_2/Ne at 3K

These results clearly show that hydrogen peroxide can react with atomic deuterium to form water molecules. However, in this series of experiments that was carried out at 10K, the reaction quickly leads to the formation of a water ice, whereas we were interested in a step-by-step study. This is the reason why we carried out a second reactivity study in Ne matrix, at 3K. In this series of experiments, H_2O_2/Ne and D/D_2 were simultaneously condensed on the surface of the cold mirror. This leads to the formation of a sample containing H_2O_2/D trapped inside a D_2/Ne matrix. Since preliminary experiments have shown that molecular deuterium is inert toward hydrogen peroxide, the presence of D_2 does not affect our experiments. The main species introduced during the condensation of the samples is Ne. As a consequence, we can consider that the samples are obtained in Ne matrix, and the presence of molecular D_2 can be neglected.

In order to further gain some insight on the reaction processes, dark reactions and annealing experiments were carried out. In the former experiments, the sample was maintained at 3K without any radiation. These experiments allow to follow reactions that do not require energy to take place. Typically, tunneling effects can be observed in such experiments. To further allow reagents to react in the neon matrix, the sample was annealed, thus increasing the diffusion of the species in the matrix.

Figure 5 shows the spectra obtained after the co-condensation of hydrogen peroxide and atomic deuterium, as well as the influence of a dark reaction (160 min) and an annealing (up to 9 K), in the OH/OD bending and stretching spectral regions.

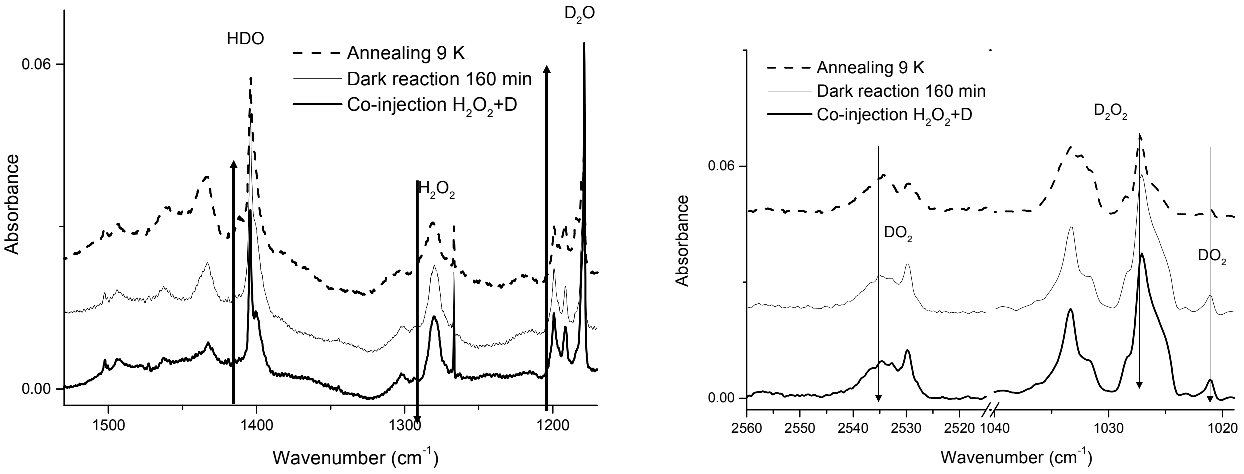

Figure 5: Co-condensation of hydrogen peroxide and atomic deuterium in a Ne matrix. Initial spectrum (in bold), and Spectra registered after a dark reaction of 160 min (solid line) and after an annealing at 9K (dotted line). Left: Bending spectral regions of HDO, D_2O and H_2O_2. Right: Spectral regions of O-D stretching of DO_2 (expected at 2549 cm^{-1} in the gas phase), O-D symmetric bending of D_2O_2 (1029 cm^{-1} in the gas phase), bending of DO_2 (1020 cm^{-1} in the gas phase),

Hydrogen peroxide as well as HDO and D_2O are present in the sample obtained just after the co-condensation of the species. When this sample is maintained in the dark at 3K during 160 min, no dramatic change is observed,. This result clearly indicates that a tunneling effect is involved in the reactions that lead to the formation of water from H_2O_2 and D.

When the sample is further annealed up to 9K, the amount of H_2O_2 is still decreasing, and an additional formation of HDO and D_2O is observed.

The band at 1021 cm^{-1} corresponds to OD_2 species. This species has also a characteristic band at 2529 cm^{-1}. These bands are observed in the sample obtained after the co-condensation of hydrogen peroxide and D atoms in Ne matrix. Then they both decrease during the annealing of the sample. This evolution suggests that the DO_2 radical initially formed, further react with D atoms through tunneling effect.

Two other bands at 1028 and 1033 cm^{-1} are assigned to the OD symmetric bending of D_2O_2. These bands are observed in the sample obtained after the co-condensation of hydrogen peroxide and D atoms in Ne matrix. The intensities of these bands are almost constant during the dark reaction and slightly decrease after the sample annealing.

c. Co-condensation of D/D_2 and H_2O/Ne at 3K

The aim of this experiment was to verify that the formation of HDO and D_2O previously observed is not only due to a hydrogen/deuterium transfer from water molecules (due to partial decomposition of hydrogen peroxide). Figure 6 clearly shows that, under the same conditions as the ones used for the previous experiment, H_2O is almost unreactive toward atomic deuterium. Indeed, only a very small amount of HDO and D_2O is observed after the co-condensation of H_2O/Ne and D/D_2 at 3K. Thus, the formation of HDO, D_2O, D_2O_2 and DO_2 previously observed, was due to the reaction between hydrogen peroxide and atomic deuterium.

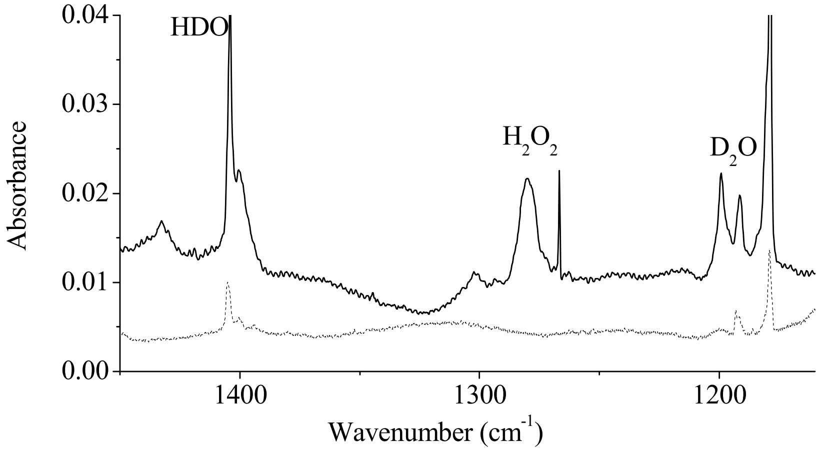

Figure 6: Co-condensation of water and atomic deuterium in a Ne matrix (dotted line). For a sake of comparison, the spectrum obtained after a co-condensation of hydrogen peroxide and atomic deuterium in a Ne matrix is also shown. The absorbances of the two spectra are normalized.

d. Irradiation of a H2O2ice by D/D2 at 10K

A further question was to know whether such a reaction leading to the formation of water from hydrogen peroxide, can also take place in solid phase. Indeed, this point is of primary relevance in the context of chemistry that may take place on the surface of ice grains in the interstellar medium. To determine whether a similar reaction takes place in solid phase, or if other processes occur, hydrogen peroxide was deposited on the surface of the cryogenic mirror maintained at 10K, and then further exposed to the D/D_2 beam. The spectra obtained before and after the exposure are shown in Figure 8. Based on the results above presented and obtained in neon matrix, it is possible to analyze these spectra registered in solid phase. A structural change in the wide band centered at 3200 cm^{-1} concomitantly with the disappearance of the band around 2820 cm^{-1}. Furthermore, the formation of a water ice is observed. It appears that the formation of water from hydrogen peroxide that was previously observed in neon matrix takes place in the same way in solid phase.

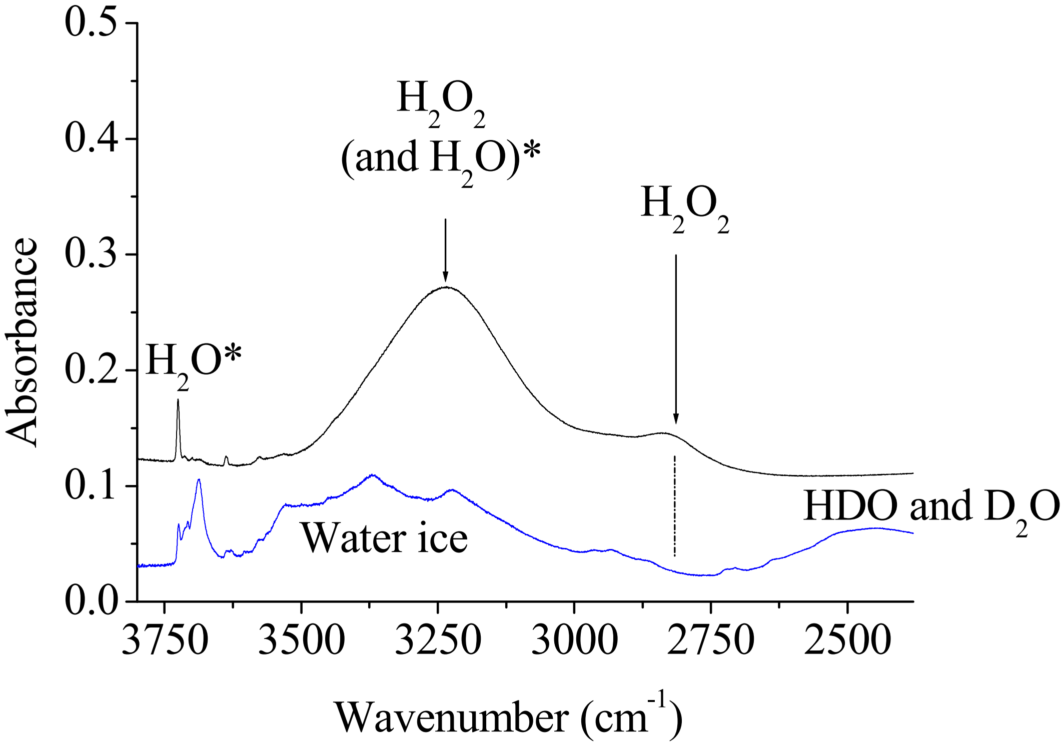

Figure 7: Irradiation of a H_2O_2 ice by a D/D_2 beam. The disappearance of H_2O_2 with the concomitant formation of a water ice is observed. The star indicates a small amount of water present in the initial sample because of a natural decomposition of hydrogen peroxide molecules.

IV. Discussion

The results presented below clearly show that, as proposed in the literature, hydrogen peroxide can react with atomic hydrogen to form water, even in neon matrix, at a temperature as low as 3K, from reagents in their fundamental state. Thus, if hydrogen peroxide is formed in the interstellar medium, it may react spontaneously with atomic hydrogen to form water molecules. This may explain, at least partially, why hydrogen peroxide is not present in abundant proportions in the interstellar medium.

This is consistent with what we expected. Indeed, the reaction

$$H_2O_2+D \rightarrow HDO+OH \quad (8)$$

is expected to have an activation barrier of about +19.58 kJ/mol. [45]

Thus, under our non-energetic conditions, this reaction is not supposed to take place. However, two hypotheses can be proposed to explain the reactivity observed:

i. either the reaction (8) proceeds via a quantum tunneling process,

- ii. or the exothermicity of the reaction favors further reactions after a first initial and slow process.

i. Let us first consider the occurrence of quantum tunneling process under our experimental conditions. Quantum tunneling processes may play a fundamental role in the chemical processes occurring on the surface of dust grains in molecular clouds.[56, 57, 58] As an example, it was proposed that O atoms can diffuse by quantum mechanical tunneling. [59] Such a tunneling can lead to the formation of interstellar CO_2 on the surface of dust grains, from CO molecules.[60, 61] The importance of tunneling in the formation of molecular hydrogen on interstellar grains was also investigated, both experimentally [62] and theoretically. [63] H-atom tunneling may also be involved in the hydrogenation processes of CO, leading to the formation of methanol,[64, 65] as well as in the isomerization processes of small radicals. [66] As far as reactions involving the formation of water and/or hydrogen peroxide, quantum tunneling processes may also be involved. [14, 40, 67, 68] If a quantum tunneling process occurred under our experimental conditions, a reaction would have been observed during experiments in the dark (Figure 5), as it was in the case of reaction between hydrogen atoms and carbon monoxide [69] for instance. This result suggests that the reaction observed under our experimental conditions is not governed only by a quantum tunneling mechanism.

ii. To the best of our knowledge of the literature, the effect of exothermicity in reactions that take place on interstellar grains was taken into account only recently. Until then, it was considered that the grain surface processes are memoryless. However, a new kinetic Monte Carlo model that takes into account a non-Markovian behavior of species formed during an exothermic reaction was proposed. [70] The simulations that were carried out with this model have shown that the exothermicity may play a fundamental role in some cases, such as the reaction between H and HO_2.[70]

Under our experimental conditions, the exothermicity is clearly of primary importance in the reactivity observed. Indeed, the quick formation of water ices during the exposure of a H_2O_2/Ne sample to D atoms is clearly due to an exothermic process. Additionally, the formation of D_2O DO_2 and D_2O_2 suggests that the products observed during these experiments are not only due to the reaction (8). A more complex process should be involved.

The reaction (8) corresponds to a very exothermic process (ΔH = -289.03 kJ/mol) [45]. If one hydrogen peroxide molecule reacts with one atomic deuterium to form a water molecule and an hydroxy radical, a large amount of energy will be released. As a consequence, the products of the reaction will be able to diffuse a little bit in the sample (even in a neon matrix), such as (2) and (5).

$$OH+D \rightarrow HDO \qquad (2)$$

$$OH+D_2 \rightarrow HDO+D \qquad (5)$$

Furthermore, another reaction between hydrogen peroxide and atomic hydrogen may lead to the formation of hydroperoxy radical (reaction 9):

$$H_2O_2+H \rightarrow H_2 + HO_2 \qquad (9)$$

The activation energy associated to this exothermic reaction (-63.13 -68.62 kJ/mol) [42, 43] is rather high (+33.81 kJ/mol or +43.51 kJ/mol). [42, 43] Thus, under our experimental conditions, this reaction can proceed either via a quantum tunneling mechanism, or from hot species.

The exothermicity of the reaction (8), in combination with quantum tunneling mechanism, and in combination with reactions due to the diffusion of species, may explain the various species observed under our experimental conditions. As an example, a scheme of consecutive process that may take place is proposed in Figure 7.

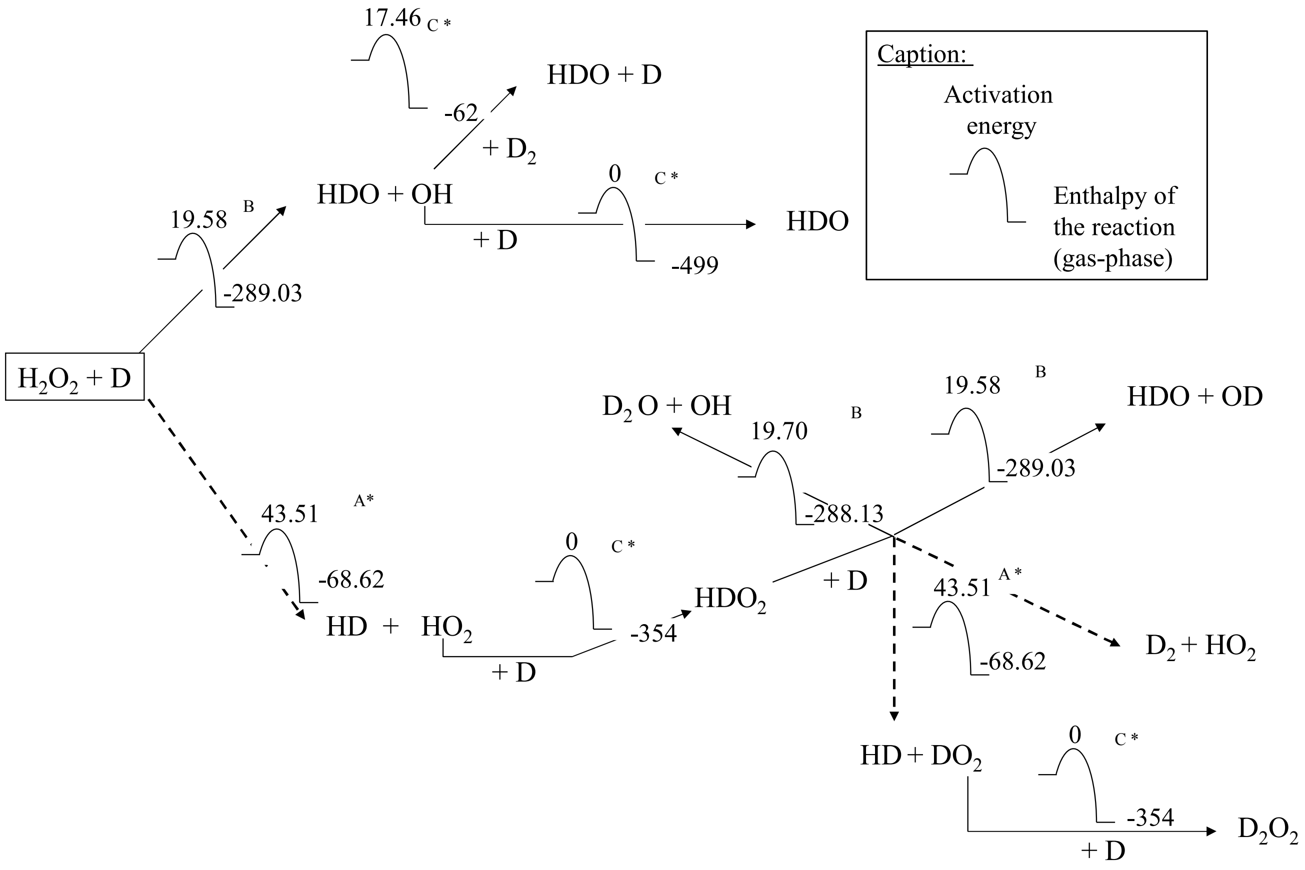

Figure 8: Main reactions proposed to explain the formation of the different products observed during the reaction between hydrogen peroxide and atomic deuterium (see the text). Solid lines correspond to hydrogenation processes, whereas dotted lines correspond to de-hydrogenation processes. For each reaction, the activation energy as well as the enthalpies of the reaction in the gas phase are indicated in kJ/mol., according to the literature. A: see ref. 43; B: see ref. 45; C: see ref. 58. When the values quoted correspond to a similar process involving non-deuteriated species, a star was added.

V. Conclusion

The conversion of hydrogen peroxide to water in the interstellar medium may explain the relative abundances of these two species in dense and molecular clouds. To investigate this point, we carried out experiments in neon matrix in order to follow the hydrogenation of hydrogen peroxide step by step, using atomic deuterium. The formation of mixed $D_2O/HDO_2/H_2O_2/D_2O_2$ ices, demonstrates that the hydrogenation of hydrogen peroxide is indeed an efficient way to produce water. Furthermore, our results clearly show that this hydrogenation reaction is exothermic.

In order to further characterize this hydrogenation reaction, experiments in which H_2O_2/Ne was co-condensed with atomic deuterium, were carried out. The initial formation of water molecules suggest that almost no activation energy is needed for this reaction. A progressive reaction is observed during the dark reaction, as a consequence of the diffusion of deuterium atoms. These results are in total agreement with the theoretical data (activation energy and enthalpy of formation) known for the H_2O_2/H reaction.

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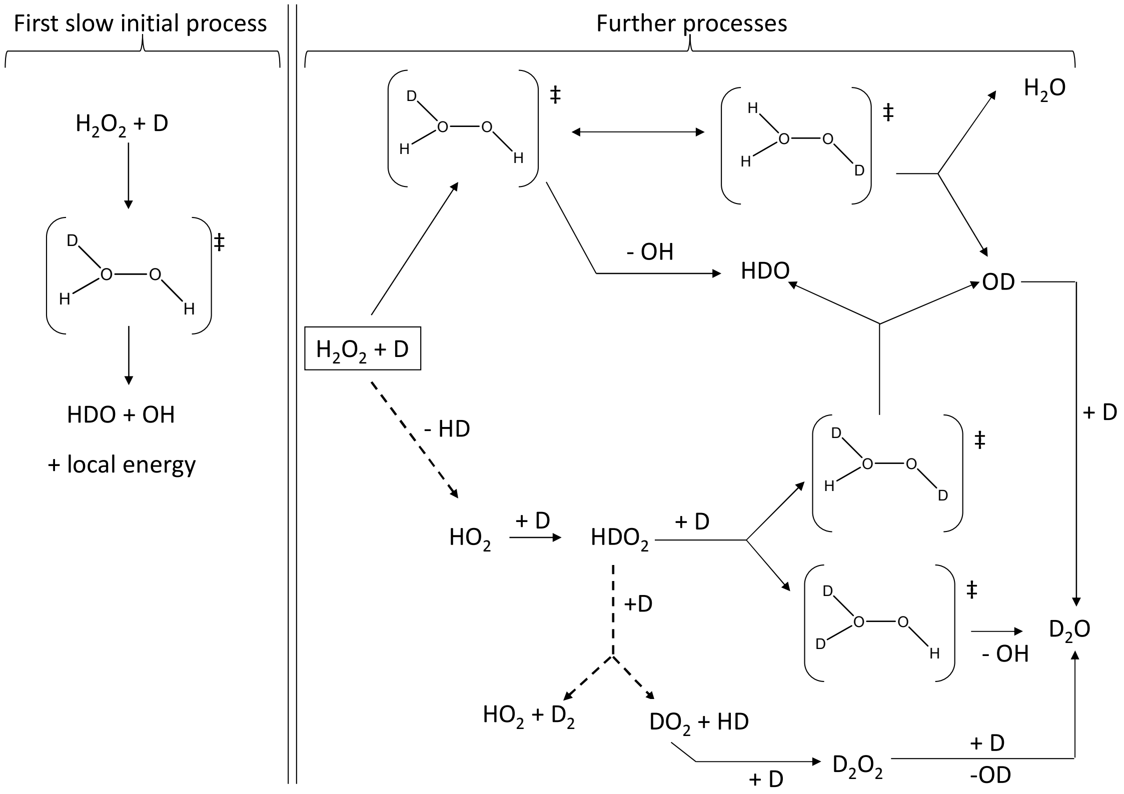

Graphical abstract: Hydrogenation processes of hydrogen peroxide leading to the formation of water