

TOWARD UNDERSTANDING OF H_3^+ ISOTOPIC AND NUCLEAR SPIN FRACTIONATIONS IN COLD SPACE

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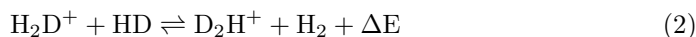
Abstract.

Two levels of statistical theories describing the $\text{H}_3^+ + \text{H}_2$ system and its isotopic variants at temperatures of astronomical interest (~ 10 K) are presented. The canonical approach accounting for the nuclear spins describes the system in a simple and convenient way. The microcanonical approach based on total energy, total angular momentum and total nuclear spin conservations yields state-to-state details. Non-thermal effects and astronomical implications are discussed.

1 Introduction

The cosmic D/H ratio has been determined around 1.5×10^{-5} [1] while deuterium enhancements several orders of magnitude above this value are observed for many species (even triply deuterated species are observed). Deuteration mechanisms are very efficient in cold environments (~ 10 K) like dense molecular clouds where temperatures and thus typical energies, kT , to be significantly smaller than differences in the zero point vibrational energies (ZPVE) of X-H and X-D species, hence favouring incorporation of deuterium atoms in larger and heavier molecules.

The pivotal species and key reactions for the whole deuterium chemical network concern the cation H_3^+ and its isotopomers:



with $\Delta E = 232, 187$ and 234 K for reactions 1, 2 and 3 respectively. Those species drag the deuterium from its reservoir (HD) via proton-deuteron exchange or deuteron transfer reactions with a quasi-collisional efficiency to further spread it to “metallic” species via deuteron transfer reactions. As H_3^+ plays the role of the “universal protonator”, H_2D^+ , D_2H^+ and D_3^+ act as deuterators in reactions like $\text{H}_2\text{D}^+ + \text{X} \rightarrow \text{XD}^+ + \text{H}_2$ with $\text{X} = \text{N}_2, \text{CO}, \text{etc.}$ The deuterium fractionations of N_2H^+ and HCO^+ are thus directly linked to the deuterium fractionation of H_3^+ . Furthermore, as a consequence

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of dissociative recombination, the H_3^+ isotopologues enrich the medium with D atoms and successive to the free deuteron's accretion, they indirectly trigger the deuterium ice chemistry [2].

The growing interest in deuterium chemistry and its H_3^+ parents stimulated by numerous detections [3, 4] led to ever more complex astrochemical models [5, 6, 7, 8, 9, 10, 11] calling for theoretical [12, 13] and laboratory studies [14, 15]. We now understand that high deuterium fractionations of the H_3^+ cations need not only very low temperatures to occur but also significant depletion of heavy-element-bearing species (CO, N_2) on the grains. The H_2 ortho/para ratio which is thought to be not fully relaxed in dense molecular clouds [16] would also limit the level of deuteration of H_3^+ because the extra 170 K internal energy of o- H_2 helps overcoming the endothermicity of reactions (1) to (3) in the reverse direction. Nevertheless detailed rate coefficients for the complete deuteration chain of H_3^+ are still missing and we would like to address this problem here.

We will first introduce two levels of statistical theories to describe the $\text{H}_3^+ + \text{H}_2$ isotopic system: a canonical and a microcanonical approach. Particular focus will be made on the dynamical aspects of the intermediate complex and the constraints imposed by nuclear spins. We will then make use of those results to derive steady-state populations of the H_3^+ system in different H_2 environments. Finally, we will introduce a stochastic method to mend non-thermal effects such as kinetic heating and memory effects when dealing with environments far from thermal equilibrium. In the conclusion, we will discuss the status of our experimental work and possible further developments in astrochemistry.

2 Rate coefficients for the $\text{H}_3^+ + \text{H}_2$ system

2.1 The canonical approach

Up to date, most astrochemical models of the $\text{H}_3^+ + \text{H}_2$ isotopic system are based on canonical rate coefficients which assume the species to be thermalised ensembles meaning that:

- (i) The species are assumed to be kinetically thermalised *i.e.* Maxwell-Boltzmann velocity distribution.
- (ii) The species are assumed to be internally thermalised *i.e.* the rotational levels are populated according to the Boltzmann distribution.

However assumption (ii) can break down because of stringent nuclear spin effects. A non-thermal population of the ortho and para states of H_2 leads to a non-thermal population of the ortho and para states of *e.g.* H_2D^+ and non-thermal isotopic fractionations. To describe those effects, species with different nuclear spin symmetries must be considered as distinct, in the same way isomers are distinguished *e.g.* $\text{HCN} \neq \text{HNC}$. In this frame, assumption (ii) can be valid again.

However, such deeper insight considerably complicates the situation since many more rate coefficients are needed to describe the complete $\text{H}_3^+ + \text{H}_2$ isotopic system. The level of complexity is illustrated in Fig. 1 which organizes the H_3^+ and H_2 reactants by isotopic and nuclear spin symmetry variants. Systems characterized by the same number of H and D atoms are marked in the same color shade. Zero-point energies for each channel are also given relative to their complex' most exoergic channel. There are 45 possible combinations and all reactions within a given complex are possible if not strictly forbidden by nuclear spin conservation. In practice, it is not easy to

measure individually all those rate coefficients therefore it is necessary to have a suitable theoretical treatment providing the numbers of interest.

Complex	H_3^+		H_2D^+		D_2H^+		D_3^+				
	ortho	para	ortho	para	para	ortho	para	meta	ortho		
H_5^+											
H_4D^+	33	0	87	0	50	0	63	43	0	para	H_2
H_3D_2^+	203	170	257	170	220	170	233	213	170	ortho	
D_3H_2^+	265	232	273	187	284	234	63	43	0		HD
D_4H^+	372	339	428	341	205	155	63	43	0	ortho	D_2
D_5^+	457	424	513	426	290	240	148	128	85	para	

Fig. 1. The $\text{H}_3^+ + \text{H}_2$ isotopic system with nuclear spin details. All reactions within a given isotopic complex (color shades) are possible if not strictly forbidden by nuclear spin conservation. The numbers are the channel's zero-point energies (Kelvin) relative to their complex' most exoergic channel. The reactions are globally favoured in the top right direction for energetical reasons. The arrows represent the different processes for an $\text{o-H}_2\text{D}^+ + \text{o-H}_2$ collisions: elastic and inelastic (yellow), nuclear spin reactive (blue) and isotopic reactive (red).

But before going into further discussion, it is important to precise the nomenclature of the four possible collisional events:

elastic collisions: do not affect the internal properties of any reactant.

inelastic collisions: only affect the rotational state of at least one reactant.

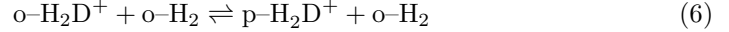
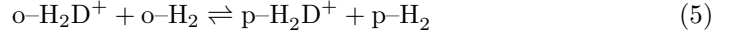
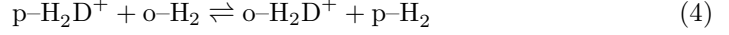
nuclear spin reactive collisions: change the nuclear spin symmetry of at least one reactant (see sec. 2.2.2).

isotopic reactive collisions: affect the mass of both reactants.

As one example, a collision of ortho H_2D^+ with ortho H_2 is considered in Fig. 1. In this particular case, there is enough internal energy available in the reactants such that all six different outcomes are always accessible (only one channel is slightly endothermic). As a result, all outcomes have to be considered but it is difficult to determine their branching ratios on a pure canonical basis (*i.e.* with partition functions) incorporating properly the nuclear spin statistics. Therefore it is necessary to use the branching ratios derived with the microcanonical approach which accounts for conservation of energy, total angular momentum and nuclear spin symmetry as will be described below. Despite these difficulties, the canonical treatment can be formulated in a rather easy way for situations where *nuclear spin species* are approximately internally and kinetically thermalised.

In order to discuss such a situation, consider an ensemble of H_3^+ . Collisions with H_2 are much more frequent than with HD so H_3^+ might be considered as equilibrated with its H_2 environment before colliding with HD. A non-thermal ortho/para population of H_2 would lead to a non-thermal population of H_3^+ . Irrespective of the

rotational population of H_3^+ , collisions with HD lead to H_2D^+ at potentially elevated kinetic and internal energies. Then, in collisions with H_2 , either backreaction or relaxation occurs. Assuming that inelastic collisions are fast compared to nuclear spin reactions and backreactions to H_3^+ , para and ortho H_2D^+ individually thermalise with the environment. A further complication arises from the fact that nuclear spin reactive collisions are possible within the H_2D^+ ensemble, i.e. ortho \rightleftharpoons para. These processes are described with the three following nuclear spin reactions:



From which we can derive an equilibrium ortho/para ratio for H_2D^+ :

$$\frac{[\text{o-H}_2\text{D}^+]}{[\text{p-H}_2\text{D}^+]} = \frac{(k_4^+ + k_6^-) \cdot \text{o/p-H}_2 + k_5^-}{(k_5^+ + k_6^+) \cdot \text{o/p-H}_2 + k_4} \quad (7)$$

Here k_4^+ , k_4^- , k_5^+ , k_5^- , k_6^+ and k_6^- denote the rate coefficient of the forward (+) and backward (-) direction of reactions (4),(5) and (6). This simple relationship describes the non-thermal effect of ortho and para H_2 on the o/p ratio of H_2D^+ which propagates to the $\text{H}_2\text{D}^+/\text{H}_3^+$ ratio. To express this isotopic fractionation, one considers all four possible nuclear spin combinations in collisions of H_2D^+ with H_2 (see Fig. 1) and takes into account their respective isotopic reactive rate coefficients:

$$\frac{[\text{H}_2\text{D}^+]}{[\text{H}_3^+]} = \frac{[\text{HD}]}{[\text{H}_2]} \cdot \frac{k_1^+}{k_{oo} \cdot y_o \cdot x_o + k_{op} \cdot y_o \cdot x_p + k_{po} \cdot y_p \cdot x_o + k_{pp} \cdot y_p \cdot x_p} \quad (8)$$

Rate coefficients in the denominator are parts of the backreaction formally described by k_1^- , here the indices o and p indicate the nuclear spin state of the H_2D^+ and H_2 species involved; y_o (y_p) denote the o- H_2D^+ (p- H_2D^+) fractions derived from equation (7) and x_o (x_p) denote the o- H_2 (p- H_2) fractions of H_2 . The deuteration reaction (1) described in the numerator is not blown into its two nuclear spin components because the microcanonical approach yields very similar isotopic reaction rate coefficients for collisions of p- H_3^+ and o- H_3^+ with HD.

Details of this simplified analysis will be given elsewhere. The result is an analytical expression of the equilibrium $[\text{H}_2\text{D}^+]/[\text{H}_3^+]$ ratio which is easy to interpret. A similar behaviour of the $[\text{H}_2\text{D}^+]/[\text{H}_3^+]$ ratio will be found with the microcanonical approach (see Fig. 4) showing a rise when lowering the temperature, then reaching a maximum at a position which depends on the o/p ratio of H_2 and finally drops for lower temperatures. Collisions of the more energetic o- H_2D^+ species with o- H_2 (first term in the denominator of equation (8)) are the dominant route reducing the $[\text{H}_2\text{D}^+]/[\text{H}_3^+]$ ratio. The importance of the o- H_2D^+ ground state has already been discussed by Gerlich *et al.* (2002).

The more sophisticated microcanonical approach has a number of advantages which are not easy to incorporate in the canonical approach or even impossible to take into account. For the latter analysis, several assumptions which had only limited justification were made on the kinetic energy distribution, internal state populations and rate coefficients. As an example it is not clear whether nuclear spin reactive collisions are indeed less frequent than inelastic collisions. Other simplifications might also be questionable.

Therefore the microcanonical approach which considers in details branching ratios on the basis of the number of accessible states will give more quantitative answers to the isotopic fractionation problem. Nevertheless a canonical approach is also able to describe non-thermal effects by splitting conventional species into *nuclear spin species*. In the present example of $\text{H}_2\text{D}^+ + \text{H}_2$ collisions, insight in the dominant physical processes could be derived.

2.2 The microcanonical approach

The idea is to consider the collisional process statistically in detail. This method also known as the Statistical Adiabatic Channel Model (SACM) or more specifically Phase Space Theory (PST), relies on the equiprobability postulate which states that all accessible microstates of the phase space have the same probability to be visited. It gives access to the product state distribution and has proven in the past to be very powerful by its simplicity and successful results [13 and Refs. therein,17].

Ion molecule reactions at low collision energies are usually very well suited for the PST because of the long range charge-(induced) dipole interaction which leads to strongly-bound long-lived complexes. Several classical descriptions of the encounter trajectories of ion-molecule reactants exist with different levels of complexity [18], the simplest being the Langevin model with its practical criteria for complex formation. Once a complex is formed, it explores the potential energy surface (PES) for very long times (ns- μ s) compared to internal motions' timescales (ps) such that it forgets its initial conditions. This complete relaxation of the intermediate complex is called the ergodic hypothesis and it is a requisite for the equiprobability postulate i.e for the PST.

The hypersurface of the accessible microstates is constrained by conservation laws of *e.g.* total energy, total angular momentum and total nuclear spin and also by the accessible regions of the PES. It is therefore important to analyse qualitatively the topology of the PES of the system considered.

2.2.1 H_5^+ PES, internal motions and the full scrambling hypothesis

A schematic view of the PES of the H_4D^+ complex as formed in $\text{H}_3^+ + \text{HD}$ collisions is depicted in Fig. 2 according to calculations on the H_5^+ complex by Xie *et al.*(2005). The minimum energy configuration consist of an H_3^+ triangle entity and an H_2 entity, the charge being localised on the central nuclei. The dissociation energy D_0 is $\sim 2200 \text{ cm}^{-1}$. Three different internal motions are associated to saddle points which are all submerged *i.e.* lower in energy than the dissociative asymptote so *a priori* all formed complexes will have enough energy to overcome those saddle points. Two of those internal motions are relevant with respect to rearrangement of the nuclei. The first relevant internal motion is the central nuclei hop from one H_2 entity to another with an extremely shallow barrier of $\sim 50 \text{ cm}^{-1}$. The second relevant internal motion is the in-plane rotation of the H_3^+ triangle entity so that one outer nuclei takes the central position. The barrier for this motion is $\sim 1550 \text{ cm}^{-1}$ above the minimum configuration but still $\sim 600 \text{ cm}^{-1}$ beneath the dissociation asymptote.

As a consequence, we may assume that at low temperatures when the total energy is close to the dissociation limit, the long-lived complex will explore the full PES by visiting all possible nuclei arrangements forgetting its history. This is called the full scrambling hypothesis. There are in total $5! = 120$ arrangements for five nuclei in

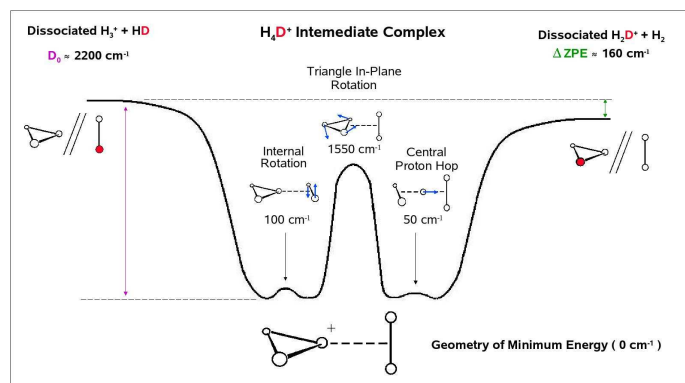


Fig. 2. Schematic of the H_4D^+ PES according to calculations on H_5^+ by Xie *et al.* (2005). The minimum energy configuration consists of an H_3^+ triangle entity and an H_2 entity, the charge being localised on the central nucleus. Saddle points for three internal motions are represented as well as the asymptotes for the two isotopic channels. They differ in energy because of zero-point rotational and vibrational energies.

five distinguishable positions but there are only $5!/3!2! = 10$ different arrangements at the dissociation limits because no distinction is made between the three positions of the H_3^+ product and the two positions of the H_2 product. So there are ten possible nuclei permutations as a result of a collision process among which one is the *identity* permutation, three are *hop* permutations and six are *exchange* permutations. Those dynamical issues are emphasized because they can be very constraining for both isotopic and nuclear spin aspects. Reactions (3) and (5) for example can only occur via *exchange* of two nuclei otherwise they are strictly forbidden.

We should point several critics to the full scrambling hypothesis. First of all, the PES considered in Fig. 2 is for zero total angular momentum and it could be distorted for complexes forming with larger orbital angular momentum, *e.g.* at higher collision energy, till the point where the saddle point for the rotation of the H_3^+ entity emerges above the dissociation limit. Associated to the fact that the complex has a shorter lifetime when formed higher above the dissociation limit, the exchange permutation would be hindered since it requires a combination of hop–rotation–hop internal motions. As a result, the *hop* and *identity* permutations would be favoured as inferred from experimental results at 400 K [19]. This statement is also supported by calculations of Xie *et al.* (2005) showing with pure classical trajectories on a complete PES, that for total energies $\sim 1000 \text{ cm}^{-1}$ above the dissociation limit and zero total angular momentum, the in-plane triangle rotation is very improbable. Also pointed out in the same paper is the fact that isotopic symmetry breakdown leads to ZPVE differences not only at the dissociative asymptotes but also within the PES thus favouring certain arrangements. A rotating complex should also favour the heavy hydrogen nuclei in the outer position for centrifugal reasons. Such discussions can also be found in Gerlich *et al.* (2006).

However, only the low temperature range ($< 50 \text{ K}$) is of interest for cold interstellar clouds where H_3^+ isotopologues trigger the deuterium chemistry. Based on published results [14, 20, 21] and on preliminary experimental results performed with a variable

temperature 22-pole ion trap apparatus, we are confident that the full scrambling hypothesis is valid at low temperatures (< 50 K).

2.2.2 Nuclear spin statistics

Once the dynamical constraints are determined, it becomes possible to look at the constraints imposed by the nuclear spins. The fundamental assumption here is that the nuclear spins are good (*i.e.* conserved) quantum numbers because of the lack of significant magnetic perturbation during the collision process. This hypothesis is sometimes referred as the “frozen nuclear spin” approximation [22]. As a consequence, a given set of nuclei conserves its nuclear spin symmetry all along the collision and the only way that nuclear spin changing collisions occur is via rearrangement of the sets of nuclei. That is why these events are called reactive. From such statements, it is a direct step to see that nuclear spin reactions are strictly forbidden for *e.g.* $\text{D}_3^+ + \text{H}_2$ collisions since there is only one possible set for D_3 and H_2 .

The nuclear spins are crucial since they are intimately linked with the energetical aspect by the symmetrisation postulate [23]. Indeed, the permutation symmetry of the nuclear spin wavefunction of a molecule dictates which rotational levels are accessible. Nevertheless, a prerequisite to the complete picture is to understand the nuclear spin statistics only. It is mentioned in the literature as “the high temperature limit” in a sense that all levels are accessible such that the nuclear spins are not constrained by energetical aspects.

There are basically two viewpoints to tackle this problem. On the one hand, we can use the permutation group looking at the symmetry representations of the several identical particles as described in Quack (1977). On the other hand, we can use the K (spatial) rotation group which treats the nuclear spins as angular momenta. The statistics are derived using angular momentum algebra as explained in Oka (2004). He also shows how to decompose the pure nuclear spin statistics according to the different basic nuclei permutations. Both view-points are consistent and can be related by the Clebsch-Gordan coefficients which work on vectorial sums and carry the symmetry information. The rotational group method is simpler but unfortunately, it fails to describe collisional systems *i.e.* complex formation and complex decay, with at least three identical particles of spin greater than 1/2 like D_3H_2^+ while the permutation group method is always correct. This statement can be supported indirectly by the following example: a D_3^+ ion with a total nuclear spin of 1 can be either of A_1 or E nuclear spin symmetry representation so it is not sufficient to say which rotational levels it can access. Despite being a good quantum number, the total nuclear spin is not sufficient to describe the problem while the symmetry is a good and sufficient quantum information. However the problem does not occur for hydrogen (spin 1/2) systems (at least up to 6 hydrogen nuclei) because for each total nuclear spin correlates only one symmetry representation.

As an example, we show in Fig. 3 the pure nuclear spin statistics for the H_4D^+ complex based on the full scrambling hypothesis. Note that some reactions are strictly forbidden such as $\text{o-H}_3^+ + \text{HD} \rightleftharpoons \text{p-H}_2\text{D}^+ + \text{p-H}_2$.

2.2.3 Phase Space Theory and state-to-state thermal rate coefficients

The mathematical details of the method connecting nuclear spin statistics, energetics and rotational angular momentum will be described elsewhere. It is quite similar to

total scrambling		products						
		H ₂ D ⁺ + H ₂				H ₃ ⁺ + HD		
		(1,1)	(1,0)	(0,1)	(0,0)	(3/2)	(1/2)	
reactants	H ₂ D ⁺ + H ₂	(1,1)	13 / 30	2 / 30	2 / 30	1 / 30	8 / 30	4 / 30
		(1,0)	6 / 30	6 / 30	6 / 30	0	4 / 30	8 / 30
		(0,1)	6 / 30	6 / 30	6 / 30	0	4 / 30	8 / 30
		(0,0)	9 / 30	0	0	9 / 30	0	12 / 30
	H ₃ ⁺ + HD	(3/2)	18 / 40	3 / 40	3 / 40	0	12 / 40	4 / 40
		(1/2)	9 / 40	6 / 40	6 / 40	3 / 40	4 / 40	12 / 40

Fig. 3. Pure nuclear spin statistics for the H₄D⁺ complex assuming full scrambling of the nuclei. For H₂D⁺ and H₂, ortho and para correspond to the total spin 1 and 0 respectively and 3/2 and 1/2 for H₃⁺. The shaded cases are strictly forbidden reactions.

that in Park *et al.*(2007) but we applied it to all isotopic variants. Our results are in good agreement (2% deviation at worst) with their results for the H₃⁺ + H₂ system at 10 K despite the fact that we did not account for tunneling and above-barrier reflexion effects nor charge-quadrupole interactions.

The outcome of this microcanonical treatment is a complete set of state-to-state thermal rate coefficients in the temperature range 5–50 K for collisions from H₃⁺ + H₂ to D₃⁺ + D₂. The rates are consistent with the detailed balance principle, the thermodynamical equilibrium constants and the high temperature statistics based on the Quack (1977) method.

3 H₃⁺ in space and non-thermal effects

3.1 The master equation model

In order to compare our theoretical thermal rate coefficients with our experimental results and to look for astronomical implications, we developed a master equation model (system of ordinary differential equations) based on this set of thermal rate coefficients to probe time evolution and steady-state populations of an ensemble of H₃⁺ ions embedded in a defined and quasi-infinite H₂ environment. The parameters are the kinetic and rotational temperatures of the H₂ environment, assumed to be the same ($T_{kin} = T_{rot}$), the H₂ o/p ratio and the isotopic enrichment [HD]/[H₂]. We can therefore simulate environments with a superthermal spin temperature and check for the consequences on the H₃⁺ ensemble. The environment is considered as quasi-infinite meaning that the H₂ environment is macroscopically quasi-unaffected by the ion-molecule reactions so the very diluted H₃⁺ ensemble reaches a state of pseudo-equilibrium with the environment.

The H₂D⁺/H₃⁺ ratio is shown in Fig. 4 and the detailed nuclear spin and state populations of all isotopologues are also accessed. As explained in Gerlich *et al.*(2002), a superthermal H₂ o/p ratio reduces the isotopic fractionation and enhances the H₂D⁺ o/p ratio but it can also induce rotational heating within the nuclear spin species. Indeed, superthermal quantities of o-H₂ act as a heat reservoir which transfers to the H₃⁺ isotopic ensemble.

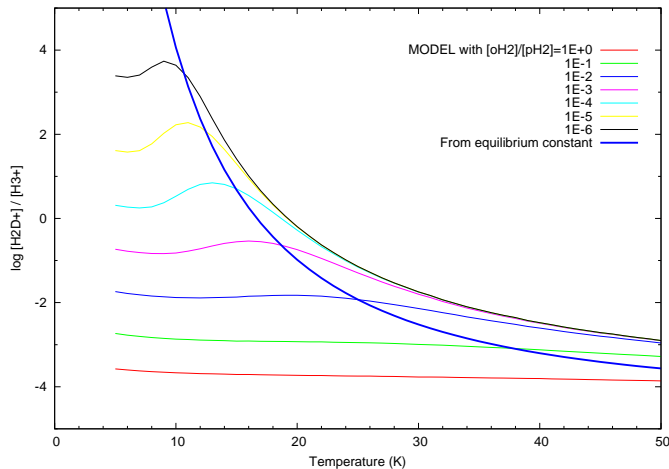


Fig. 4. Steady-state $[\text{H}_2\text{D}^+]/[\text{H}_3^+]$ of an H_3^+ ensemble embedded in a H_2 environment according to the master equation. The temperature $T_{kin} = T_{rot}$ of the environment ranges from 5 to 50 K. The isotopic enrichment was set to $[\text{HD}]/[\text{H}_2] = 3.2 \times 10^{-5}$. The different curves correspond to an H_2 o/p ratio ranging from 1 to 1×10^{-6} . Results are compared to the thermal isotopic fractionation (thick curve).

3.2 The stochastic model

The master equation model used above is based on thermal rate coefficients *i.e.* cross sections averaged over a Maxwellian collision energy distribution which implies both reactants being kinetically thermalised. This condition should breakdown for environments very far from thermal equilibrium *e.g.* $n\text{-H}_2$ at 10 K. Indeed, an H_3^+ ion in such conditions would keep colliding with $o\text{-H}_2$ thus constantly facing the 170 K internal energy of $o\text{-H}_2$ such that all its kinetic and internal degrees of freedom would be excited at mean energies much higher than 10 K. The ions would be kinetically heated hence thermal rate coefficients are incorrect for such environments.

This pure statistical mechanical problem can be solved mathematically as a continuous-time stochastic process. It can be shown that the thermal state-to-state master equation is describing a Markovian (memoryless) process in the restricted phase space of the internal states only at kinetic thermal equilibrium. The Markovianity in this restricted phase space breaks down when departing from a thermal environment by revealing memory effects on the kinetic degrees of freedom and inconsistencies with the first principle of thermodynamics. These problems can be mended by introducing the kinetic degrees of freedom in the phase space of consideration. Propagation of ions in this extended phase space can be performed in an analytical manner using fluxes of distributions but it is rather complicated so we prefer a single-walker stochastic method which is easy to settle and sufficient to obtain the steady-state solution.

The parameters which define the H_2 environment in this approach are the same as for the master equation model ($T_{kin} = T_{rot}$, o/p- H_2 , HD fraction). An initial ion state is chosen and we let the ion (walker) evolve in the complete (internal + kinetic) phase space by repeating collision events until satisfying convergence with

the steady-state is reached. The simplicity of the model lies in the fact that effective Langevin rate coefficients are independent of the ion's kinetic energy. A collision event consists of a succession of steps: (i) pick randomly among the environment a state specific colliding partner according to their number density and collisional cross sections (ii) pick randomly the 3 dimensional laboratory frame kinetic energy components of the colliding partner according to the environment's temperature (iii) calculate the collision energy and the center of mass velocities in the laboratory frame (iv) calculate the state-to-state probabilities according to the reactant states and collision energy using the PST with an extra kinetic energy phase space density term (v) pick randomly a product channel among the calculated probabilities (vi) pick randomly a decay direction within an isotropic distribution (vii) calculate the new ion velocities in the laboratory frame from the center of mass velocities, decay directions and ion velocities in the center of mass frame.

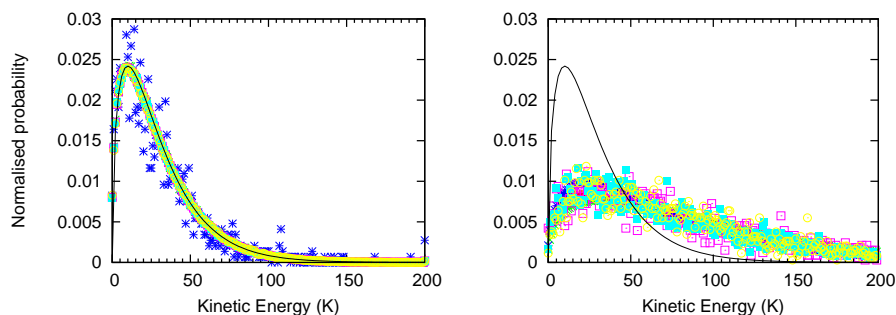


Fig. 5. Simulation of a virtual system after 10^7 collisions (see text). The colors correspond to different internal states. Left graphic: The environment is thermal. The ions' kinetic energy distributions are Maxwellian (solid line), their levels' populations follow the Boltzmann distribution and the isotopic fractionations are consistent with thermodynamical equilibrium constant. Right graphic: The environment is internally non-thermal. The ions' kinetic energy distributions are not Maxwellian and their levels' populations are non-thermal. Note that some states are more scattered because less visited during the simulation

Preliminary results to test the method were obtained on a virtual toy system apparent to the $\text{H}_3^+ + \text{H}_2$ isotopic system in terms of masses, energetics and angular momenta but neglecting the nuclear spins. In this virtual system, the ions consist of two isotopologues with three rotational levels each and the neutral environment consist of two isotopologues with two rotational levels each. As shown in Fig. 5, for a thermal environment, the model renders kinetically and internally thermalised ions showing an isotopic fractionation consistent with the thermodynamical equilibrium constant and the environment's isotopic fractionation. For kinetically thermal but internally non-thermal environments (like n-H_2 with $T_{kin} = 10\text{K}$), the kinetic energy distributions of the ions deviate from the Maxwell Boltzmann distribution, their internal states' populations deviate from the Boltzmann distribution and their isotopic fractionation is not in agreement with the thermodynamical equilibrium constant and the environment's isotopic fractionation. During the simulation, we can also record the effects on the neutral colliding partners and may determine in this way internal relaxation efficiency and kinetic heating rates for the environment. Yet we plan to

apply this model to the real $\text{H}_3^+ + \text{H}_2$ isotopic system and determine ortho-to-para relaxation rates for the H_2 environment.

4 Conclusions

Two statistical theories with increasing level of complexities and exactness were presented: (i) a canonical approach for rate coefficients between *nuclear spin species* and (ii) a microcanonical approach for thermal state-to-state rate coefficients. The two methods rely on dynamical issues for which the full scrambling hypothesis is assumed valid at low temperatures. We showed that nuclear spin modifications and statistics need to be accounted for in theoretical calculations, experimental studies and astrochemical modelling of systems like $\text{H}_3^+ + \text{H}_2$ or $\text{H}^+ + \text{H}_2$. We also propose a stochastic method to overcome statistical mechanical problems occurring in H_2 environments far from thermal equilibrium. Note that those same methods can straightforwardly be applied to $\text{CH}_3^+ + \text{H}_2$ which is a twin system of the $\text{H}_3^+ + \text{H}_2$ system i.e. five protons scrambling during the complex's lifetime.

In order to validate those results, we are carrying out extensive measurements using a variable temperature 22-pole ion trap apparatus. To enlight those nuclear spin dependances, a p- H_2 generator which provides purities better than 99% was built. The experiments turn out to be difficult because of isotopic preferential freezing between H_2 and HD in the range 10–20K [26] and problematic accurate temperature estimation. We also use lasers to gain state specific informations like populations or state specific rate coefficients. Preliminary results are in good agreement with the calculated thermal rate coefficients [27] and further systematic studies are still in progress.

From the astronomical point-of-view, competition between radiative processes and collisional processes in non-thermal H_2 environments is a most exciting subject and it will probably have to be treated in a stochastic way. Detections of the o- H_2D^+ ($1_{11}-1_{10}$:372GHz) and p- D_2H^+ ($1_{01}-1_{10}$:692GHz) transitions can already give a good constraint on the H_2 o/p ratio and further line detections like p- H_2D^+ ($0_{00}-1_{01}$:1.37THz) with the CONDOR detector on APEX or SOFIA or o- D_2H^+ ($0_{00}-1_{11}$:1.48THz) with Herschel (see Table 3 in [28]) would constrain this parameter even better. Because of their ability to release the internal energy of the o- H_2 by exchanging protons(deuterons), H_3^+ and its isotopologues are certainly the most sensitive tracers for the H_2 o/p ratio. It would also be interesting to study the energy budget of the $\text{H}_2(\text{H}_3^+ \text{'s}, \text{H}^+)$ thermodynamical system considering the different degrees of freedom as heat sinks, the peculiar role of the H_3^+ isotopologues and H^+ as dissipative structures as well as the radiative cooling power of H_2D^+ and D_2H^+ in the coldest environments we know.

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