# Nuclear-Spin Selection Rules in the Chemistry of Interstellar Nitrogen Hydrides

Claire Rist, Alexandre Faure,* Pierre Hily-Blant, and Romane Le Gal

IPAG, Observatoire de Grenoble, Université Joseph Fourier, CNRS UMR5571, B.P. 53, 38041 Grenoble Cedex 09, France

ABSTRACT: Nitrogen hydrides are at the root of the nitrogen chemistry in interstellar space. The detailed modeling of their gas phase formation, however, requires the knowledge of nuclear-spin branching ratios for chemical reactions involving multiprotonated species. We investigate in this work the nuclear-spin selection rules in both exothermic and near thermoneutral ion−molecule reactions involved in the synthesis of ammonia, assuming full scrambling of protons in the reaction complexes. The formalism of Oka [*J. Mol. Spectrosc.* **2004**, *228*, 635] is employed for highly exothermic ion−molecule and dissociative recombination reactions. For thermoneutral reactions, a simple state-to-state statistical approach is suggested, which is in qualitative agreement with both quantum scattering and microcanonical statistical calculations. This model is applied to the seven atom reaction $NH_4^+ + H_2$, of possible importance in the nuclear-spin thermalization of ammonia.
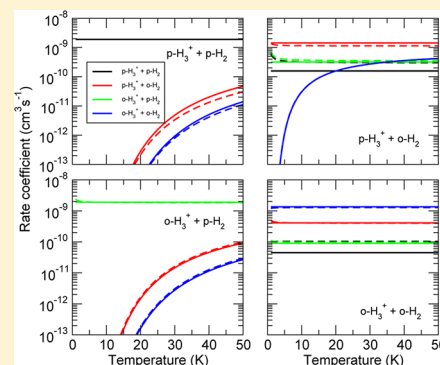
INTRODUCTION

Nitrogen is the fifth or sixth most abundant element in the Universe. Interstellar nitrogen in the gas phase is supposed to be essentially locked in N and N_2, both being difficult to detect in molecular clouds.[1] The determination of the total abundance of nitrogen and its partitioning therefore relies on indirect observations of N bearing species such as CN, HCN, N_2H^+, NH_3, etc.[2,3] These species are also invaluable tracers of the cold gas where major molecules such as CO have frozen on dust grains.[4] Nitrogen hydrides (NH, NH_2, NH_3) are of crucial importance in this context because they are among the simplest and first neutral N-bearing molecules to be formed.[5] Ammonia was the first to be detected via its inversion lines (at cm wavelengths).[6] NH and NH_2 are difficult to detect from Earth-based telescopes but the ground-state rotational transitions, at submillimeter wavelengths, were recently observed at high spectral resolution with the HIFI instrument onboard the Herschel space observatory (see Persson et al.[7] and references therein).

One difficulty in estimating the total abundances of NH_2 (amidogen) and NH_3 (ammonia) comes from the existence of the ortho and para modifications. These modifications reflect the identical-protons permutation symmetry. In the context of weak nuclear magnetic interaction, the total nuclear-spin of the identical protons is a conserved quantum number I. Therefore, radiative or (nonreactive) collisional conversion between nuclear-spin species is very slow. For NH_3 there exists two nuclear-spin species corresponding to $I = 1/2$ (para) and $I = 3/2$ (ortho). For NH_2 and H_2 the nuclear-spin species correspond to $I = 0$ (para) and $I = 1$ (ortho). Observations of both symmetries is needed to understand the detail of their formation. For example, it is usually assumed that the ortho-to-para ratio of ammonia should be equal to 1.0 (i.e., the high temperature statistical value) if it is formed in the gas phase, whereas it should be larger than unity if it is formed at the low temperature (<40 K) of cold dust grains. However, both spin modifications are not necessarily observed in the same astronomical source, especially in the cold gas, and the total abundances with respect to hydrogen usually rely on the estimation of the ortho-to-para ratio (OPR) (see, e.g., Hily-Blant et al.[5]). Recent Herschel observations[5,7] have reported measurements of rotational and hyperfine transitions involving the ground states of NH, o-NH_2, o-NH_3, and p-NH_3 toward cold interstellar gas. The observations of Persson et al.[7] provided the first estimation of ammonia OPR in cold diffuse gas ($T < 50$ K). The derived OPR, ∼0.5−0.7, is incompatible with thermodynamical equilibrium, which requires a value higher than unity. A careful modeling of the chemical processes that drive the OPR of nitrogen hydrides in the cold interstellar gas is therefore critical.

Nitrogen hydrides are thought to be formed from nitrogen-containing ions by hydrogen abstraction from H_2 followed by dissociative recombinations with electrons, starting from $N^+ + H_2$ and ending with $NH_4^+ + e^-$ (see Dislaire et al.[8] and references therein). The production of nitrogen hydrides involves molecules or molecular ions such as NH_n^+ including two or more protons. In these reactions the total nuclear-spin of the identical nuclei is conserved. Moreover, permutation-inversion symmetry constrains the reaction pathways between nuclear spin species, as first formalized by Quack.[9] In cold molecular gas, transitions between nuclear-spin species can be

induced by hydrogen abstraction, proton-exchange and proton-hop reactions with H_2, and dissociative recombinations. Given the predominance of hydrogen in molecular clouds, the OPR of H_2 is expected to influence the OPR of nitrogen hydrides molecules or ions. This points out the need for estimation of branching ratios for all reactions involving species with two or more protons. A first study of the low temperature chemistry of nitrogen-bearing molecules including the relative population of nuclear-spin states was developed by Flower et al.[10] Their model essentially includes the conservation of the total nuclear-spin in key reactions involving species with two or more protons.

To elucidate the production of all nuclear spin forms of nitrogen hydrides, we introduce in this work a simple but consistent scheme to ensure nuclear-spin selection rules and ortho-to-para branching ratios for key reactions involved in the production of ammonia. We assume a complete scrambling of protons in the activated reaction complexes. Although this assumption might be questionable for some reactions, this is the first step toward a consistent nitrogen chemistry reaction network including nuclear-spin selection rules.

◾ NUCLEAR-SPIN SELECTION RULES

In chemical reactions involving molecules with several identical nuclei, Fermi−Dirac or Bose−Einstein statistics restricts the reaction complex to species antisymmetric or symmetric under exchange of identical particles. In a frozen nuclear-spin approximation these reactions obey restrictive selection rules. A pionnering theoretical description of state-to-state selection rules was presented by Quack[9] using permutation symmetry. In his paper, Quack[9] presents a general method to connect the internal rovibrational states of the reactants and products in a chemical reaction (in the absence of nuclear-spin coupling), according to the irreducible representations of the reaction complex permutation-inversion group.

In the case of large exothermicity and complete scrambling of protons in the reaction complex, Oka[11] derived nuclear-spin selection rules using angular momentum algebra. In contrast to Quack[9] who considers both nuclear-spin and rovibrational states, the approach of Oka[11] is restricted to nuclear-spin states and is only valid for processes in which many rotational states of the products are populated. Branching ratios for a number of reactions involving multiply protonated species were inferred from these angular momentum rules. This formalism is easily generalized to other species with a large number of protons, as discussed in the section below. We note that the approach of Oka[11] was also previously employed to model the OPR abundance ratio of cyclic C_3H_2 in cold molecular clouds.[12,13]

In contrast to highly exothermic reactions, where a large number of product states are populated, in low temperature thermoneutral reactions only a small amount of energy is available for the products because the activated complexes have much smaller excess energy. A state-to-state analysis is required in this case to derive nuclear-spin branching ratios. In practice, the detailed knowledge of the product-state distribution requires a state-to-state full quantum or statistical analysis. A number of results are available for protonic ion-neutral reactions involving H_2. Thus, for $H_2 + H^+$, statistical[14] and quantum[15] state-to-state reaction rates were computed. For $H_3^+ + H_2$, where a full quantum treatment is currently not feasible, theoretical state-to-state reactions probabilities were calculated using microcanonical statistical approaches,[16,17] which ensure conservation of energy together with parity, motional angular

momentum, and nuclear-spin. An extension of this approach, combined with quasi-classical trajectories, was proposed very recently.[18]
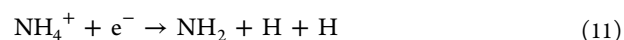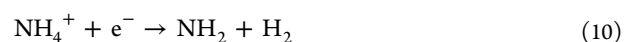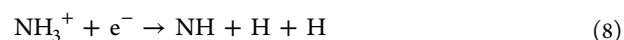
In both exothermic and thermoneutral reactions, one open question is whether proton-exchanges and full scrambling of protons in the reaction complex occur. For highly exothermic reactions such as $H_2^+ + H_2 \rightarrow H_3^+ + H$ or $NH^+ + H_2 \rightarrow NH_2^+ + H$ (respectively 1.7 and 1.9 eV of exothermicity), experiments using deuterated species have demonstrated that the protons are completely scrambled.[19,20] In the case of almost thermoneutral reactions, like in the nuclear-spin thermalization processes $H_2 + H^+ \rightarrow H_2 + H^+$ or $H_3^+ + H_2 \rightarrow H_3^+ + H_2$, the nuclear-spin selection rules and the proton-exchange mechanism have been directly explored experimentally.[14,21−23] Uy et al.[21] were thus the first to experimentally demonstrate the existence of selection rules on nuclear spin modifications in H_3^+ + p-H_2 at ∼400 K. More recently, Crabtree et al.[23] made similar measurements at lower temperature (135 K), where a statistical full scrambling was observed. For more complex systems, very few theoretical studies (e.g., $NH_3^+ + H_2$[24]) are available. Experimental studies at room temperature[25,26] on deuterated isotopologues reactions, however, give some insight on the proton/charge transfer, hydrogen abstraction or exchange mechanisms. There is thus little evidence of protons scrambling for near thermoneutral reactions between ions and molecules containing unlike bonds such as N−H and H−H.[26] At very low temperature, however, we can possibly expect formation of long-lived reaction complexes, in favor of proton exchanges.

◾ INTERSTELLAR AMMONIA CHEMISTRY NETWORK

The formation of ammonia can be understood from a reduced or primary chemistry network (see Dislaire et al.[8] and references therein). The nitrogen bearing ions are formed from N^+ in successive reactions[a] with H_2:

$$N^+ + H_2 \rightarrow NH^+ + H \qquad \Delta H = +10\text{−}20 \text{ meV} \qquad (1)$$

$$NH^+ + H_2 \rightarrow NH_2^+ + H \qquad \Delta H = -1.9 \text{ eV} \qquad (2)$$

$$NH^+ + H_2 \rightarrow N + H_3^+ \qquad \Delta H = -6.2 \text{ eV} \qquad (3)$$

$$NH_2^+ + H_2 \rightarrow NH_3^+ + H \qquad \Delta H = -1.1 \text{ eV} \qquad (4)$$

$$NH_3^+ + H_2 \rightarrow NH_4^+ + H \qquad \Delta H = -1.0 \text{ eV} \qquad (5)$$

Nitrogen hydrides are then formed from highly exothermic dissociative recombinations of nitrogen bearing ions:

$$NH_2^+ + e^- \rightarrow NH + H \qquad (6)$$

$$NH_3^+ + e^- \rightarrow NH_2 + H \qquad (7)$$

$$NH_3^+ + e^- \rightarrow NH + H + H \qquad (8)$$

$$NH_4^+ + e^- \rightarrow NH_3 + H \qquad (9)$$

$$NH_4^+ + e^- \rightarrow NH_2 + H_2 \qquad (10)$$

$$NH_4^+ + e^- \rightarrow NH_2 + H + H \qquad (11)$$

In all these ion−molecule or electron-molecule exothermic reactions, the energy available allows us to treat the product nuclear states statistically. In this so-called "high temperature limit",[23] the nuclear-spin statistical weight (NSSW) was derived for a number of reactions between multiply protonated

species.[11] In the section below, we present the nuclear-spin branching ratio for the above nitrogen chemistry network reactions. We note that the destruction routes of the neutral hydrides NH, NH_2, and NH_3 are not considered here because the total destruction rates (summed over all reaction products) are assumed not to depend on the spin symmetry of the reactants.

All neutral nitrogen hydrides are formed by dissociative recombination of the ions NH_2^+, NH_3^+, and NH_4^+. Ammonium, NH_4^+, is the direct main precursor of NH_3. As a result, the thermoneutral reaction

$$NH_4^+ + H_2 \rightarrow NH_4^+ + H_2 \tag{12}$$
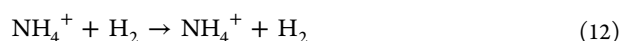
is expected to drive the nuclear-spin thermalization of NH_4^+ and thus the OPR of ammonia, provided that protons are scrambled or exchanged in the complex NH_6^{+*}.

Isotopic studies of this reaction have explored the proton exchange mechanism. Experimental study of the H−D exchange reaction $NH_4^+ + D_2 \rightarrow NH_3D^+ + HD$ at 300 K gives a very low upper limit of 10^{-13} cm^3 s^{-1} for the reaction rate.[25,28] A survey of NH_n^+ reactions at 300 K[26] confirms that the isotopic H−D exchange in $ND_3H^+ + H_2 \rightarrow ND_2H_2^+ + HD$ does not occur with a significant rate. Finally, ion trap study of the similar $CH_4^+ + HD$ reaction down to 15 K[29] also shows very small H−D exchange rates ($\sim 10^{-12}$ cm^3 s^{-1}), in disfavor of an efficient proton scrambling. Although at 300 K proton exchange is unlikely, at very low temperature the ion−molecule complex NH_6^{+*} might survive long enough to enable proton scrambling. In the following we assume a full scrambling of protons and in the absence of any detailed state-to-state analysis for $NH_4^+ + H_2$, we present below a simple statistical model to estimate nuclear-spin branching ratios. This model is an extension of the interpretation of Gerlich[14] for the elementary $H_2 + H^+$ reaction.

NUCLEAR-SPIN BRANCHING RATIOS

In a chemical reaction $R_A + R_B \rightarrow C \rightarrow P_D + P_E$, the total nuclear spin of identical nuclei is conserved. According to Pauli principle, the total wave function should be antisymmetric under exchange of identical protons. Permutation symmetry allows us to infer detailed selection rules between the reactant and product nuclear-spin motional states.[9] For protonated species, the permutation symmetry of the nuclear-spin wave function is completely defined by the nuclear-spin quantum number. Therefore, derivation of nuclear-spin selection rules was obtained from nuclear angular momentum algebra and rotation group representations.[11] Here, we extend this work to the chemistry of nitrogen hydrides.

High Temperature Ortho-to-Para Branching Ratios. For exothermic reactions, the large amount of energy available for the products is sufficient to describe the distribution of states statistically. The nuclear spin selection rules derived by Oka[11] provide NSSW for each nuclear pathway from reactants to products. Full details can be found in the paper by Oka,[11] and we only briefly describe the method below.

The nuclear-spins of protons involved in the reaction complex are determined by conservation of the nuclear-spin angular momentum. For each allowed nuclear spin of the reaction complex, the distribution of product states is deduced from the nuclear-spin conservation for the reverse reaction. This is an analog of Frobenius reciprocity theorem[9,11]

consisting here of tracing the product nuclear-spin states that lead to the complex nuclear-spin.

The reaction branching ratios depend only on the number of protons involved in reactants and products. Oka's generic notation for a reaction is $(n_A, n_B) \rightarrow (n_D, n_E)$ where n_S is the number of protons in molecule S . The reactant and product nuclear-spin species are specified by their nuclear-spin quantum number (I_A, I_B) and (I_D, I_E), respectively. We present in Tables 1 and 2 the branching ratios for hydrogen abstraction and

Table 1. Branching Ratios for Nuclear-Spin Conversion in the Hydrogen Abstraction from H_2 by NH^+, NH_2^+, and NH_3^+ [a]

$(1,2) \rightarrow (2,1)$: $NH^+ + H_2 \rightarrow NH_2^+ + H$			
		branching ratios	
spin species	weight	(0, 1/2)	(1, 1/2)
(1/2, 0)	2	1/2	1/2
(1/2, 1)	6	1/6	5/6

$(1,2) \rightarrow (3,0)$: $NH^+ + H_2 \rightarrow H_3^+ + N$			
		branching ratios	
spin species	weight	(1/2, 0)	(3/2, 0)
(1/2, 0)	2	1	0
(1/2, 1)	6	1/3	2/3

$(2,2) \rightarrow (3,1)$: $NH_2^+ + H_2 \rightarrow NH_3^+ + H$ (see ref 11)			
		branching ratios	
spin species	weight	(1/2, 1/2)	(3/2, 1/2)
(0, 0)	1	1	0
(0, 1)	3	2/3	1/3
(1, 0)	3	2/3	1/3
(1, 1)	9	1/3	2/3

$(3,2) \rightarrow (4,1)$: $NH_3^+ + H_2 \rightarrow NH_4^+ + H$			
		branching ratios		
spin species	weight	(0, 1/2)	(1, 1/2)	(2, 1/2)
(1/2, 0)	2	2/5	3/5	0
(1/2, 1)	6	2/15	21/30	1/6
(3/2, 0)	4	0	3/4	1/4
(3/2, 1)	12	1/15	21/60	7/12

[a]The weight gives the nuclear-spin degeneracy $(2I_A + 1)(2I_B + 1)$ of the reactants. See text for details.

dissociative recombination reactions mentioned in the nitrogen chemistry network above. We assume here full scrambling of protons in all reaction complexes. The listed branching ratios are obtained by summing the combinatorial probabilities of forming the complex in a given nuclear-spin state and subsequently decaying to the product nuclear-spin states.

We can compare the results presented in Tables 1 and 2 to those of Flower et al.[10] We note that both models rigorously include the conservation of the total nuclear-spin angular momentum. In the work of Flower et al.,[10] however, the branching ratios were derived from simple statistical considerations without recourse to the angular momentum rules of Oka.[11] For example, in the case of the reaction $NH^+ + o\text{-}H_2 \rightarrow NH_2^+ + H$ (line $(1/2,1)$ in Table 1), the approach of Oka predicts branching ratios of 1/6 toward $p\text{-}NH_2^+$ and 5/6 toward $o\text{-}NH_2^+$ instead of 1/2 and 1/2 estimated by Flower et al.[10] The reaction $p\text{-}NH_2^+ + o\text{-}H_2 \rightarrow o\text{-}NH_3^+ + H$ is also strictly forbidden in their network whereas our branching ratio is significant, although small. These differences illustrate the importance of the assumptions concerning the decay of the

Table 2. Branching Ratios for Nuclear-Spin Conversion in the Dissociative Recombination of NH_3^+ and NH_4^+ with Electrons[a]

$(3,0) \rightarrow (2,1)$: $NH_3^+ + e^- \rightarrow NH_2 + H$			
		branching ratios	
spin species	weight	$(0, 1/2)$	$(1, 1/2)$
$(1/2, 0)$	2	1/2	1/2
$(3/2, 0)$	4	0	1

$(4,0) \rightarrow (3,1)$: $NH_4^+ + e^- \rightarrow NH_3 + H$			
		branching ratios	
spin species	weight	$(1/2, 1/2)$	$(3/2, 1/2)$
$(0, 0)$	1	1	0
$(1, 0)$	3	2/3	1/3
$(2, 0)$	5	0	1

$(4,0) \rightarrow (2,1,1)$: $NH_4^+ + e^- \rightarrow NH_2 + H + H$			
		branching ratios	
spin species	weight	$(0, 1/2, 1/2)$	$(1, 1/2, 1/2)$
$(0, 0)$	1	1/2	1/2
$(1, 0)$	3	1/3	2/3
$(2, 0)$	5	0	1

$(4,0) \rightarrow (2,2)$: $NH_4^+ + e^- \rightarrow NH_2 + H_2$					
		branching ratios			
spin species	weight	$(0, 0)$	$(0, 1)$	$(1, 0)$	$(1, 1)$
$(0, 0)$	1	1/2	0	0	1/2
$(1, 0)$	3	0	1/3	1/3	1/3
$(2, 0)$	5	0	0	0	1

[a]The weight gives the nuclear-spin degeneracy $(2I_A + 1)(2I_B + 1)$ of the reactants. See text for details.

collision complex. It should be noted in particular that in the case of incomplete scrambling of protons, the hypothesis of an intermediate complex in which all protons are indistinguishable and can easily exchange is no longer valid. Even more restrictive selection rules hold in this case, and the detailed nuclear-spin branching ratios depend on the particular reaction mechanism (hydrogen abstraction, ion capture, etc.) and should be considered carefully for each type of reaction.

Low Temperature Ortho/Para Branching Ratios. In the absence of state-to-state analysis for the thermalization of NH_4^+ by H_2, we consider below a simple statistical model based on the density of states at very low energy. This approach was suggested by Gerlich[14] to interpret dynamically biased statistical cross sections for the thermalization reaction $H_2 + H^+ \rightarrow H_2 + H^+$. For a near thermoneutral reaction $R_A + R_B \rightarrow C \rightarrow P_D + P_E$ at very low temperature, each nuclear-spin species is supposed to lie in its lowest rotational state. The energy gap between the ground state and the first excited state of each nuclear-spin species should be therefore much higher than the kinetic temperature. The reaction pathway is characterized by the reactant and product nuclear-spin and rotation quantum numbers $(I_A j_A)$, $(I_B j_B)$, $(I_D j_D)$, and $(I_E j_E)$, and by the complex nuclear-spin quantum number I_C. The branching ratios $\text{br}(I_A j_A, I_B j_B \rightarrow I_D j_D, I_E j_E)$ reflect both the probability of formation of a reaction complex with nuclear-spin quantum number I_C and the density of product rotation states energetically- and spin-allowed: the reaction must be exothermic (or elastic) for the spin-allowed product rotation states so that energy thresholds can be neglected. As a result, branching ratios for endothermic channels are not calculated but the corresponding rate coefficients can be obtained by

applying the detailed balance principle to the reverse, exothermic, channel. The product nuclear spins must be allowed for a given complex nuclear spin by angular momentum algebra. For protonated species, the permutation symmetry of the total system wave function, as discussed by Quack,[9] is ensured by tracing the *allowed* nuclear-spin-rotation states of the products. We define the nuclear-spin and rotational degeneracies as g_I and g_j. The branching ratios can be expressed as follows:

$$\text{br}(I_A j_A, I_B j_B \rightarrow I_D j_D, I_E j_E) = \sum_{I_C} \frac{g_{I_C}}{g_{I_A} g_{I_B}} \frac{g_{j_D} g_{j_E}}{(\sum_{j'_D, j'_E} g_{j'_D} g_{j'_E})} \quad (13)$$

From phase-space arguments, the first term of eq 13 ($g_{I_C}/g_{I_A} g_{I_B}$) simply reflects the probability of forming a complex of nuclear-spin I_C from the reactant nuclear spin states. The second term gives the probability of decaying from the complex to the state-specific products. The symmetry-allowed nuclear-spin states of products are given by conservation of the total nuclear-spin angular momentum. The symmetry-allowed rotational states of products are determined by the nuclear-spin statistics of each fragment and by checking the exothermicity of the reaction.

To illustrate the relevance and accuracy of the above formula, it was applied to the two astrophysically important thermalization reactions $H_2 + H^+ \rightarrow H_2 + H^+$ and $H_2 + H_3^+ \rightarrow H_2 + H_3^+$, with the total Langevin capture reaction rates $k_L = 2.5 \times 10^{-9}$ cm^3 s^{-1} and $k_L = 1.9 \times 10^{-9}$ cm^3 s^{-1}, respectively. Our results are compared below to the time-independent quantum mechanical (TIQM) scattering calculations of Honvault et al.[15,30] and the dynamically biased statistical calculations of Gerlich[14] for $H_2 + H^+$ (Figure 1) and to the microcanonical statistical calculations of Hugo et al.[17] for $H_2 + H_3^+$ (Figure 2).

For illustration we consider the ortho-to-para conversion of H_2 by H^+ at very low temperature. In this simple case, the reactant and product quantum numbers are o-H_2 ($I_A = 1$, $j_A = 1$), H^+ ($I_B = 1/2$, $j_B = 0$), p-H_2 ($I_D = 0$, $j_D = 0$), and H^+ ($I_E = 1/2$, $j_E = 0$). Energetically, the o-H_2 ground state ($j_A = 1$) is 170 K
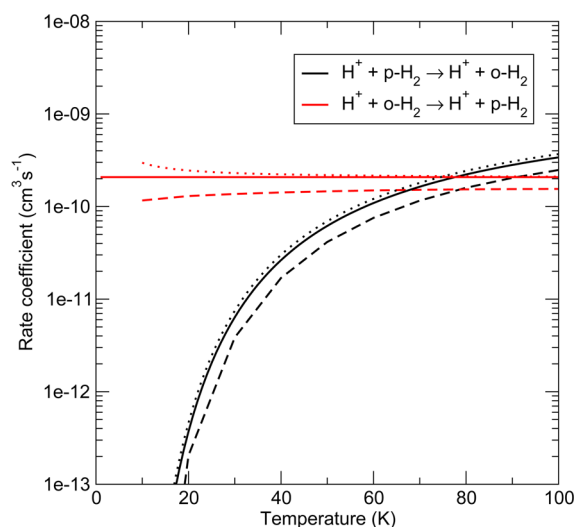

Figure 1. Rate coefficients for the ortho−para conversion of H_2 by H^+ as a function of temperature. The present results, corresponding to eq 13, are denoted by the solid lines. Dashed lines refer to the TIQM calculations of Honvault et al.[15,30] Dotted lines give the dynamically biased statistical calculations of Gerlich.[14]
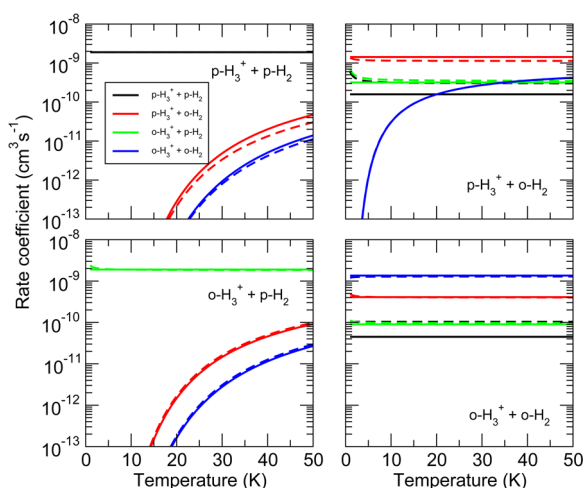
Figure 2. Rate coefficients for the ortho−para conversion of H_2 by o- and p-H_3^+ as a function of temperature. The present results, corresponding to eq 13, are denoted by the solid lines. Dashed lines refer to the microcanonical statistical calculations of Hugo et al.[17] The different product nuclear-spin states are labeled by different colors, as given in the inset of the upper left panel.

above the p-H_2 ground state ($j_A = 0$). From o-H_2 ($I_A = 1$), the complex is either p-H_3^+ with nuclear-spin $I_C = 1/2$ ($g_{I_C} = 2$) or o-NH_3^+ with $I_C = 3/2$ ($g_{I_C} = 4$). Three reaction channels are energetically- and spin-allowed: p-H_2 ($j_D = 0$) and o-H_2 ($j_D = 1$) for the p-H_3^+ complex with $I_C = 1/2$, or only o-H_2 ($j_D = 1$) for the o-H_3^+ complex with $I_C = 3/2$. The decay toward p-H_2 ($j_D = 0$) occurs only for a p-H_3^+ reaction complex with $I_C = 1/2$ nuclear-spin. Therefore, the probability of forming the p-H_3^+ complex from the o-H_2 entrance channel is 2/6. For this p-H_3^+ complex, the number of allowed product rotational states is $g_{j_D} = 1$ for p-H_2 ($j_D = 0$) and $g_{j_D} = 3$ for o-H_2 ($j_D = 1$). The probability of decay into the p-H_2 ($j_D = 0$) channel is then 2/6 × 1/(1 + 3) = 1/12 in the limit of zero temperature.

In Figure 1, it can be noticed that this simple but physically intuitive approach is in very good agreement with the dynamically biased results, as previously discussed by Gerlich.[14] We also observe a good agreement, within a factor of 2, with the TIQM calculations of Honvault et al. As discussed by these authors, this confirms the statistical nature of the reaction, which could be expected from the large potential well of the H_3^+ complex. A similar agreement is observed in Figure 2 for the $H_2 + H_3^+$ reaction, which presents several nuclear-spin

combinations. This good agreement suggests that the simple eq 13 above indeed contains the essential physics of the microcanonical statistical approach.

Of course, the applicability of any statistical approach relies on the formation of long-lived complexes (here H_3^{+*} and H_5^{+*}) with a complete randomization of the internal energy. A statistical behavior is therefore expected to be valid only at temperatures well below the potential well of the complex. Zero-point energy (ZPE) effects are also very important in this context. A detailed discussion about the importance of ZPE efects in H_5^{+*} can be found in Gomez-Carrasco et al.[18]

We have applied eq 13 to the thermalization of ammonium by H_2. The nuclear-spin rotation spectroscopy of ammonium NH_4^+ can be deduced from the spectroscopy of methane CH_4.[31,32] If I and j are the nuclear-spin and rotation quantum numbers, the spin-rotation states can be identified by I_j. NH_4^+ exists in three nuclear-spin states: para ($I = 0$), meta ($I = 1$), and ortho ($I = 2$). Fermi−Dirac statistics forces the total spin-rotation wave function to be antisymmetric in proton exchange. Therefore, in the $j = 0$ ground rotational state only the ortho nuclear form exists. The lowest nuclear-spin-rotation states I_j and their nuclear-spin degeneracy g_{I_j} are (2_0, $g_{20} = 5$), (1_1, $g_{11} = 3$), (1_2, $g_{12} = 3$), and (0_2, $g_{02} = 2$). We label these ammonium spin-rotation states respectively o-NH_4^+, m_1-NH_4^+, m_2-NH_4^+, and p-NH_4^+. Similarly, the hydrogen H_2 nuclear-spin-rotation states (I_j, g_{I_j}) = (1_1, 3) and (I_j, g_{I_j}) = (0_0, 1) correspond to o-H_2 and p-H_2. To trace all energetically allowed pathways, we have to take into account the rotational energy of both reactants and products. The rotation constant of ammonium was measured to be 5.8 cm^{-1}.[33] The ammonium $j = 1$ and $j = 2$ rotation states lie respectively at 17 and 51 K above the ground state whereas the hydrogen $j = 1$ o-H_2 rotation state is 170 K above the $j = 0$ p-H_2 ground state. In Table 3 we present the low temperature branching ratios between nuclear-spin-rotation states computed from eq 13.

As an example and to clarify the numbers in Table 3, we provide the detailed branching ratios calculation for the nuclear-spin conversion of o-NH_4^+ by o-H_2: the reactant and product rotation energies E_{AB}, E_{DE}, the nuclear-spin probabilities, the density of allowed rotational states, and the sum for the branching ratios are resumed in Table 4. The reactants and products can be described in terms of their quantum numbers I_j.

It can be noticed in Table 3 that the vast majority of nuclear-spin conversions of ammonium are endothermic or strictly forbidden when p-H_2 is the reactant. Thus, a non-negligible amount of o-H_2 is required to convert the four lowest nuclear-

Table 3. Branching Ratios for Nuclear-Spin Conversion of NH_4^+ by H_2^{a}

products		reactants: (NH_4^+ H_2)							
(NH_4^+ H_2)	weight	(2_0 0_0)	(1_1 0_0)	(1_2 0_0)	(0_2 0_0)	(2_0 1_1)	(1_1 1_1)	(1_2 1_1)	(0_2 1_1)
(2_0 0_0)	5	1	×	×	×	0.083	0.043	0.198	×
(1_1 0_0)	3	×	1	0.375	×	0.055	0.050	0.029	0.060
(1_2 0_0)	3	×	−	0.625	×	0.091	0.083	0.048	0.100
(0_2 0_0)	2	×	×	×	1	×	0.040	0.019	×
(2_0 1_1)	15	−	−	−	×	0.771	0.178	0.088	0.060
(1_1 1_1)	9	−	×	×	−	−	0.606	0.299	0.180
(1_2 1_1)	9	−	×	×	−	−	−	0.497	0.300
(0_2 1_1)	6	×	−	−	×	−	−	−	0.300

^{a}Crosses × correspond to strictly forbidden channels whereas − correspond to endothermic channels. The nuclear-spin-rotation states are labeled I_j, where I and j are the nuclear-spin and rotation quantum numbers. The weights are the nuclear-spin degeneracies.

Table 4. Branching Ratios for Nuclear-Spin Conversion of o-NH$_4^+$ in Reactions with o-H$_2$[a]

reactants	$2_0 + 1_1$	E_{AB} = 170 K	I_C allowed	I_C = 1	I_C = 2	I_C = 3	br
			$g_{I_C}/g_{I_A}g_{I_B}$	3/(5 × 3)	5/(5 × 3)	7/(5 × 3)	
products	$I_{Dj_D} + I_{Ej_E}$	E_{DE}(K)	I_C allowed	$g_{j_D}g_{j_E}/(\sum_{j_D',j_E'}g_{j_D}g_{j_E})$			$\sum_{I_C}$
o-NH$_4^+$ + p-H$_2$	$2_0 + 0_0$	0	2	×	1/(1 + 3)	×	0.083
m_1-NH$_4^+$ + p-H$_2$	$1_1 + 0_0$	17	1	3/(3 + 5+3)	×	×	0.055
m_2-NH$_4^+$ + p-H$_2$	$1_2 + 0_0$	51	1	5/(3 + 5+3)	×	×	0.091
p-NH$_4^+$ + p-H$_2$	$0_2 + 0_0$	51	×	×	×	×	×
o-NH$_4^+$ + o-H$_2$	$2_0 + 1_1$	170	1, 2, 3	3/(3 + 5+3)	3/(1 + 3)	3/(3)	0.771

[a]Crosses × correspond to strictly forbidden channels whereas − correspond to endothermic channels. See text for details.

spin-rotation states of ammonium. We note in this context that the OPR of H$_2$ is not necessarily thermalized in the low temperature (T < 30 K) of interstellar clouds.[34] As a result, we can expect a nonequilibrium distribution of the three nuclear-spin symmetries of ammonium in cold interstellar clouds.

To conclude, it should be noted that the nuclear-spin-rotation branching ratios presented in Table 3 can be employed to derive nuclear-spin branching ratios by averaging and summing over the two meta states (m_1-NH$_4^+$ and m_2-NH$_4^+$), assuming for instance a thermalized distribution of the two meta levels. However, as we have considered only levels with j = 0, 1, and 2, our calculations are restricted to very low temperatures: indeed, the level j = 3 lies only 100 K above the ground state j = 0. Thus, in practice, nuclear-spin branching ratios based in Table 3 can be derived for kinetic temperatures up to ∼1/3 × 100∼30K. This cold regime is still of great relevance to study the thermalization of ammonium, and therefore ammonia, in dense and diffuse interstellar clouds. This will be investigated in future works.

CONCLUSION

We investigated in this work nuclear-spin selection rules in the low temperature chemistry of interstellar nitrogen hydrides. We introduced a simple but consistent scheme to ensure nuclear-spin selection rules and ortho-to-para branching ratios for key reactions involved in the production of ammonia, assuming a full scrambling of protons in the activated reaction complexes. Both exothermic and near thermoneutral reactions were considered. The formalism of Oka,[11] based on angular momentum algebra, was employed for highly exothermic systems including ion−molecule and dissociative recombination reactions. For thermoneutral reactions, a simple state-to-state statistical approach was proposed. This approach consists in a generalization of the interpretation of Gerlich[14] for the elementary reaction H$_2$ + H$^+$, which was shown to have a statistical behavior. This method was additionally tested on the five atom reaction H$_2$ + H$_3^+$ and was found to have a factor of 2 accuracy, with respect to microcanonical statistical calculations. The numerous branching ratios for the key thermalization (seven atom) reaction NH$_4^+$ + H$_2$ were derived. Strong differences between p-H$_2$ and o-H$_2$ were observed.

A number of experiments on purely protonic systems, i.e., H$_n^+$ with n = 3, 4, and 5, actually demonstrated that the scrambling of protons does occur in both highly exothermic and near thermoneutral reactions. In contrast, for NH$_n^+$ systems like NH$_3^+$ + H$_2$ or NH$_4^+$ + H$_2$, involving unlike bonds, proton exchanges were not observed at room temperature. It is unclear whether scrambling is more efficient at lower temperature, where the lifetime of the reaction complexes NH$_n^{+*}$ is longer. Ab initio quantum chemistry calculations, e.g.,

for NH$_4^+$ + H$_2$ systems, are required to investigate the topology of the interaction potential energy surface and the height of eventual exchange barriers. Experimental isotopic studies at very low temperature would also clarify whether protons are scrambled or not.

In any case, the branching ratios determined in this work will help to study the impact of the nuclear-spin selection rules in the synthesis of interstellar ammonia. In future works, these new branching ratios will be used in models of interstellar nitrogen with the aim of interpreting the observed NH$_2$ abundances and the unexpected ortho-to-para ratios observed in NH$_3$. Extension to secondary reactions, like e.g., H$_3^+$ + NH, and to other hydride families (carbon and oxygen), is also under progress.

AUTHOR INFORMATION

Corresponding Author
*E-mail: afaure@obs.ujf-grenoble.fr.

Notes
The authors declare no competing financial interest.

ADDITIONAL NOTE

[a]We note (i) that it is not clear if reaction 1 is really endothermic or whether it is hindered by a barrier[27] and (ii) that reaction 5 is exothermic but possesses an activation energy of about 90 meV.[24]

REFERENCES

(1) Knauth, D. C.; Andersson, B.-G.; McCandliss, S. R.; Moos, H. W. Potential Variations in the Interstellar NI Abundance. *Astrophys. J. Lett.* **2003**, *596*, L51−L54.
(2) Maret, S.; Bergin, E. A.; Lada, C. J. A Low Fraction of Nitrogen in Molecular Form in a Dark Cloud. *Nature* **2006**, *442*, 425−427.
(3) Daranlot, J.; Hincelin, U.; Bergeat, A.; Costes, M.; Loison, J.-C.; Wakelam, V.; Hick-son, K. M. Elemental Nitrogen Partitioning in Dense Interstellar Clouds. *Proc. Natl. Acad. Sci.* **2012**, *109*, 10233−10238.
(4) Hily-Blant, P.; Walmsley, M.; Pineau Des Forêts, G.; Flower, D. Nitrogen Chemistry and Depletion in Starless Cores. *Astron. Astrophys.* **2010**, *513*, A41.
(5) Hily-Blant, P.; Maret, S.; Bacmann, A.; Bottinelli, S.; Parise, B.; Caux, E.; Faure, A.; Bergin, E. A.; Blake, G. A.; Castets, A.; et al.

Nitrogen Hydrides in the Cold Envelope of IRAS 16293−2422. *Astron. Astrophys.* **2010**, *521*, L52.

(6) Cheung, A. C.; Rank, D. M.; Townes, C. H.; Thornton, D. D.; Welch, W. J. Detection of NH3 Molecules in the Interstellar Medium by their Microwave Emission. *Phys. Rev. Lett.* **1968**, *21*, 1701−1705.

(7) Persson, C. M.; De Luca, M.; Mookerjea, B.; Olofsson, A. O. H.; Black, J. H.; Gerin, M.; Herbst, E.; Bell, T. A.; Coutens, A.; Godard, B.; et al. Nitrogen Hydrides in Interstellar Gas. II. Analysis of Herschel/HIFI Observations towards W49N and G10.6 - 0.4 (W31C). *Astron. Astrophys.* **2012**, *543*, A145.

(8) Dislaire, V.; Hily-Blant, P.; Faure, A.; Maret, S.; Bacmann, A.; Pineau Des Forêts, G. Nitrogen Hydrides and the H_2 Ortho-to-Para Ratio in Dark Clouds. *Astron. Astrophys.* **2012**, *537*, A20.

(9) Quack, M. Detailed Symmetry Selection Rules for Reactive Collisions. *Mol. Phys.* **1977**, *34*, 477−504.

(10) Flower, D. R.; Pineau Des Forêts, G.; Walmsley, C. M. The Abundances of Nitrogen-Containing Molecules During Pre-Protostellar Collapse. *Astron. Astrophys.* **2006**, *456*, 215−223.

(11) Oka, T. Nuclear Spin selection Rules in Chemical Reactions by Angular Momentum Algebra. *J. Mol. Spectrosc.* **2004**, *228*, 635−639.

(12) Park, I. H.; Wakelam, V.; Herbst, E. Modeling the Ortho-to-Para Abundance Ratio of Cyclic C_3H_2 in Cold Dense Cores. *Astron. Astrophys.* **2006**, *449*, 631−639.

(13) Morisawa, Y.; Fushitani, M.; Kato, Y.; Hoshina, H.; Simizu, Z.; Watanabe, S.; Miyamoto, Y.; Kasai, Y.; Kawaguchi, K.; Momose, T. Correlation between Nuclear Spin Ratio of Cyclic C_3H_2 and Chemical Evolution in TMC-1 Cores. *Astrophys. J.* **2006**, *642*, 954−965.

(14) Gerlich, D. Ortho-Para Transitions in Reactive H^++H_2 Collisions. *J. Chem. Phys.* **1990**, *92*, 2377−2388.

(15) Honvault, P.; Jorfi, M.; González-Lezana, T.; Faure, A.; Pagani, L. Ortho-Para H_2 Conversion by Proton Exchange at Low Temperature: An Accurate Quantum Mechanical Study. *Phys. Rev. Lett.* **2011**, *107*, 023201.

(16) Park, K.; Light, J. C. Microcanonical Statistical Study of Ortho-Para Conversion in the Reaction H_3^++H_2→$(H_5^+)^*$→H_3^++H_2 at Very Low Energies. *J. Chem. Phys.* **2007**, *126*, 044305.

(17) Hugo, E.; Asvany, O.; Schlemmer, S. H_3^++H_2 Isotopic System at Low Temperatures: Microcanonical Model and Experimental Study. *J. Chem. Phys.* **2009**, *130*, 164302.

(18) Gómez-Carrasco, S.; González-Sánchez, L.; Aguado, A.; Sanz-Sanz, C.; Zanchet, A.; Roncero, O. Dynamically Biased Statistical Model for the Ortho/Para Conversion in the H_2+H_3^+→H_3^++ H_2 Reaction. *J. Chem. Phys.* **2012**, *137*, 094303.

(19) Hierl, P. M.; Herman, Z. Crossed Beam Study of the Reaction H_2 + D_2 → D_2H^+ + H. *Chem. Phys.* **1980**, *50*, 249−254.

(20) Wittemann, A.; Sadílek, M.; Polách, J.; Teloy, E.; Schlier, C.; Herman, Z. Crossed Beam Scattering Studies of the Dynamics of the Reaction NH^+(D_2; H,D) NHD^+, ND_2^+. *Z. Phys. Chem.* **2001**, *215*, 749−764.

(21) Uy, D.; Cordonnier, M.; Oka, T. Observation of Ortho-Para H_3^+ Selection Rules in Plasma Chemistry. *Phys. Rev. Lett.* **1997**, *78*, 3844−3847.

(22) Cordonnier, M.; Uy, D.; Dickson, R. M.; Kerr, K. E.; Zhang, Y.; Oka, T. Selection Rules for Nuclear Spin Modifications in Ion-Neutral Reactions involving H3+. *J. Chem. Phys.* **2000**, *113*, 3181−3193.

(23) Crabtree, K. N.; Kauffman, C. A.; Tom, B. A.; Beçka, E.; McGuire, B. A.; McCall, B. J. Nuclear Spin Dependence of the Reaction of H_3^+ with H2. II. Experimental Measurements. *J. Chem. Phys.* **2011**, *134*, 194311.

(24) Herbst, E.; Defrees, D. J.; Talbi, D.; Pauzat, F.; Koch, W. Calculations on the Rate of the Ion−Molecule Reaction between NH_3^+ and H_2. *J. Chem. Phys.* **1991**, *94*, 7842−7849.

(25) Huntress, W. T., Jr. Laboratory Studies of Bimolecular Reactions of Positive Ions in Interstellar Clouds, in Comets, and in Planetary Atmospheres of Reducing Composition. Astrophys. *J., Suppl. Ser.* **1977**, *33*, 495−514.

(26) Adams, N. G.; Smith, D.; Paulson, J. F. An Experimental Survey of the Reactions of NH_n^+ Ions (n = 0 to 4) with Several Diatomic and Polyatomic Molecules at 300 K. *J. Chem. Phys.* **1980**, *72*, 288−297.

(27) Gerlich, D. Experimental Investigations of Ion−Molecule Reactions Relevant to Interstellar Chemistry. *J. Chem. Soc, Faraday Trans.* **1993**, *89*, 2199−2208.

(28) Kim, J. K.; Theard, L. P.; Huntress, W. T., Jr. ICR Studies of some Hydrogen Atom Abstraction Reactions: X^+ + H_2 → XH^+ + H. *J. Chem. Phys.* **1975**, *62*, 45−52.

(29) Asvany, O.; Savíc, I.; Schlemmer, S.; Gerlich, D. Variable Temperature Ion Trap Studies of CH_4^+ + H_2, HD and D_2: Negative Temperature Dependence and Significant Isotope Effect. *Chem. Phys.* **2004**, *298*, 97−105.

(30) Honvault, P.; Jorfi, M.; González-Lezana, T.; Faure, A.; Pagani, L. Erratum: Ortho-Para H_2 Conversion by Proton Exchange at Low Temperature: An Accurate Quantum Mechanical Study [Phys. Rev. Lett. 107, 023201 (2011)]. *Phys. Rev. Lett.* **2012**, *108*, 109903.

(31) Bright Wilson, E., Jr. The Statistical Weights of the Rotational Levels of Polyatomic Molecules Including Methane, Ammonia, Benzene, Cyclopropane and Ethylene. *J. Chem. Phys.* **1935**, *3*, 276−285.

(32) Herzberg, G. *Infrared and Raman Spectra of Polyatomic Molecules*; Krieger Publishing Co.: Malabar, FL, 1991.

(33) Crofton, M. W.; Oka, T. Infrared Studies of Molecular Ions. I - The v_3 Band of NH_4^+. *J. Chem. Phys.* **1983**, *79*, 3157−3158.

(34) Flower, D. R.; Pineau Des Forêts, G.; Walmsley, C. M. The Importance of the Ortho:Para H_2 Ratio for the Deuteration of Molecules During Pre-Protostellar Collapse. *Astron. Astrophys.* **2006**, *449*, 621−629.