PHYSICAL REVIEW A **80**, 042507 (2009)

Nuclear spin conversion in NH_3

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(Received 9 June 2009; published 14 October 2009)

The nuclear spin conversion (NSC) rate for a gas sample of NH_3 is calculated in the framework of the quantum relaxation model. It is based on the knowledge of the vibration-inversion levels of the lowest vibrational states, the relaxation rates, and the intramolecular magnetic interactions. The magnitudes of the spin-spin and spin-rotation interaction terms have been obtained with the help of *ab initio* calculations. The value of the NSC at 296 K for a pressure of 1 Torr is 3.23×10^{-6} s^{-1} for $^{14}NH_3$ and 9.15×10^{-6} s^{-1} for $^{15}NH_3$. A linear dependence of the NSC rates on the pressure is valid up to 1 atm for $^{14}NH_3$ and up to 30 Torr for $^{15}NH_3$, where quasidegenerate ortho/para pairs are present in the excited $\nu_2=1$ state.

DOI: 10.1103/PhysRevA.80.042507 PACS number(s): 33.15.−e, 31.30.Gs, 34.90.+q

I. INTRODUCTION

The discovery of nuclear spin and the process of the nuclear spin conversion (NSC) in molecules is contemporaneous with the appearance of quantum mechanics and its application to the hydrogen molecule. It was the anomalous behavior of its thermodynamic and optical properties at low temperatures which led to the discovery of the so-called ortho and para spin isomers. The spin isomers differ by the value of the total nuclear spin of the hydrogen nuclei, which can take in H_2 either the value $I=0$ (para-H_2) or $I=1$ (ortho-H_2). Due to the Pauli exclusion principle for fermionic hydrogen nuclei and the consequent symmetry considerations, the para-H_2 can exist only in rotational states with even values of the rotational quantum number J, while the ortho-H_2 only in states with odd values of J. The process of conversion of one spin isomer to the other in pure gaseous hydrogen is very slow because the total nuclear spin is a robust property. It can be, however, dramatically increased by the admixture of paramagnetic impurities. The NSC process can be observed, for example, by measuring the time-dependent evolution of absorption intensities, which carry the information about the spin isomer populations. Such experiments can be therefore used for quantitative studies of the spin conversion rates and molecular properties such as intramolecular magnetic interactions [1]. Besides this fundamental interest, spin isomers can be also used in the astrophysical context. As the relative abundance of nuclear spin isomers can be measured, it is used via specific models to derive the composition and temperature of formation of objects (e.g., dark clouds or comets) of the interstellar medium (ISM) [2,3]. Furthermore, ammonia is a reservoir of nitrogen atoms and thus a key product in the network of chemical reactions in the ISM. Such an approach is reliable if the ortho to para ratio is conserved in time. However, an interchange from one isomer to another, by "flipping" the spin of one of the equivalent atoms, although not very favored in nature, can occur. NSC has been observed in gas phase for CH_3F [1,4], $H_2^{13}CCH_2$ [5], H_2CCH_2 [6], and H_2CO [7]. For all these molecules, NSC mechanism is explained by a quantum relaxation model (QRM) [8], which involves internal magnetic properties of the molecule and nonreactive collisions.

This paper deals with the nuclear spin conversion in ammonia. This molecule has three equivalent hydrogen atoms, like CH_3F, but presents an inversion mode, which requires a specific development of the model specifically described in the following Secs. III and IV. We present a calculation of NSC rates of $^{14}NH_3$ and $^{15}NH_3$ in a gas sample considering self-binary collisions between molecules and excluding reactive processes. The found values are one order of magnitude longer than those calculated and experimentally measured for CH_3F. The calculation is preliminary before setting up an experiment to achieve isomeric enrichment and to measure nuclear spin conversion rate.

II. QUANTUM RELAXATION MODEL

The QRM is based on the existence of pairs of quasiresonant rovibrational levels of different symmetry, playing the role of gates when they may interact through a magnetic interaction able to flip a spin. Let us suppose an ortho molecule reaching by relaxation the energy of such a coupled pair. As the collision does not change the nuclear spin, the wave function describing the molecule at $t=0$ just after the collision has an ortho character. To calculate its evolution in time, the wave function has to be written as a linear combination of the eigenfunctions of the Hamiltonian. Due to the interactions, these eigenstates are themselves combination of

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the unperturbed pure ortho and para states and evolve in time according to their perturbed energies. It is easy to demonstrate that the wave function acquires a para component at time t. Then a nonzero probability exists for the molecule to be projected in to a pure para state at the next collision. This picture of the total spin conversion process has been developed by Chapovsky in the framework of the density-matrix formalism [8]. It is shown that a nonequilibrium excess of concentration of, e.g., ortho molecules $\delta\rho_0(0)$, created at the instant $t=0$, will decay exponentially to zero as

$$\delta\rho_0(t) = \delta\rho_0(0)e^{-\gamma t}, \tag{1}$$

where γ is the conversion rate expressed as

$$\gamma = \sum_{o\in\text{ortho}} \sum_{p\in\text{para}} \frac{1}{\hbar^2} \frac{2\Gamma_{op}|V_{op}|^2}{\Gamma_{op}^2 + \omega_{op}^2}(W_p + W_o). \tag{2}$$

The summation has to be made over all interacting ortho o and para p level pairs. V_{op} is the matrix element of the magnetic interaction expressed in $\hbar$ units. The Boltzmann factors W_o and W_p are the relative population of rotational states in the ortho and para families. ω_{op} is the energy difference between the levels of the pair and Γ_{op} is the collisional decay rate of the off-diagonal element of the density matrix ρ_{op}. Several experimental confirmations of this model have been given [1,9,10].

III. CALCULATION OF THE CONVERSION RATE

For the derivation of the conversion rate for ammonia, it is necessary to determine the relevant parameters of the QRM. We consider first the relaxation rates, then we focus our attention on the magnetic interactions, spin-spin (SS), and spin rotation (SR). Taking advantage of tensorial algebra, a straightforward calculation of the matrix elements of the interactions between ortho and para wave functions can be performed. The role of inversion is specific and special care is devoted to extract the selection rules, which apply to identify the pairs in interaction. The strength of the spin-spin dipolar interaction can be calculated using the equilibrium geometry of the molecule, but *ab initio* calculations are necessary to evaluate vibrationally averaged values for the ground state or to calculate the spin-rotation magnetic interaction, which involves the knowledge of electronic structure. All these ingredients are collected to give the nuclear spin conversion rate according to QRM model and to calculate the contribution of the different ortho-para pairs.

Relaxation rates. The magnetic interactions create a coherence between ortho and para states, which is destroyed by collisions at a rate Γ_{op} [cf. Eq. (2)], whose value is usually unknown. As previously shown [11], collisional broadening measurements can be regarded as a quantitative estimation of Γ_{op}. For the estimation of the conversion rate, we neglected the (j, k) rotational dependence of Γ_{op} for the different interacting pairs. For both isotopologues, we used the value $\Gamma=18.7$ MHz Torr^{-1} ($\sim$0.475 cm^{-1} atm^{-1}), which is an average of the values calculated for $^{14}NH_3$ in Ref. [12].

Symmetry considerations and nuclear spin statistics. The equilibrium configuration of ammonia is a symmetric pyramid with three equivalent NH bonds whose symmetry is described by the C_{3v} point group. However, it is not the group of the molecular Hamiltonian because ammonia exhibits a large-amplitude tunneling motion between the two equivalent pyramidal equilibrium configurations. On this tunneling path, it passes through the planar configuration, which corresponds to the top of the potential of the inversion vibration and which has the $D_{3h}(M)$ symmetry. The feasibility of this tunneling motion makes the symmetric bending vibration ν_2 different from the analogous one in, e.g., PH_3, where the inversion motion across the barrier is blocked by its height, or from molecules like CH_3F, where the molecular framework is semirigid due to the CF bond. Therefore all symmetry considerations concerning the dynamics of ammonia are based on the $D_{3h}(M)$ symmetry group. The overall symmetry species of levels are evaluated as a direct product of the electronic, vibrational, rotational, and nuclear spin-wave functions

$$\Gamma_{tot} = \Gamma_e \otimes \Gamma_{vib} \otimes \Gamma_{rot} \otimes \Gamma_{ns}.$$

Since we are considering here the ammonia molecule in its electronic ground state, we have $\Gamma_e=A_1'$. The symmetry of the vibrational wave function is the direct product $\Gamma_{vib} = \Gamma_{\nu_1} \otimes \Gamma_{\nu_2} \otimes \Gamma_{\nu_3} \otimes \Gamma_{\nu_4}$. That corresponds to the four normal modes of the molecule. The ν_1 mode is the symmetric stretching vibration of A_1' symmetry, ν_3 and ν_4 are asymmetric stretching and bending vibrations of E' symmetry. These three modes are the small-amplitude vibrations with wave functions localized around the equilibrium configuration. The inversional mode ν_2 is conceptually different because its wave function is always localized around the two equivalent minima of the potential and connects them dynamically. The feasibility of the tunneling motion makes the two lowest inversional states separated by less than 1 cm^{-1}. They are conventionally taken as the inversional ground-state split into a doublet, with the lower component being symmetric with respect to inversion (A_1' symmetry) and the upper antisymmetric with respect to inversion (A_2'' symmetry). The inversion splitting dramatically increases with excitation of the inversional mode (v_{inv} quantum number) and for the levels with energies above the inversional barrier becomes commensurable with the spacing between vibrational levels in the ν_2 mode. The notation, symmetries, and additional information concerning the inversional levels are summarized in Table I.

In the $D_{3h}(M)$ symmetry group, the symmetry classification of rotational levels differs from the case of C_{3v} in that the effect of the inversion operation E^* on the rotational wave function $|j,k,m\rangle$, whose equivalent rotation in the $D_{3h}(M)$ group is R_z^{π}, is given by

$$E^*|j,k,m\rangle = (-1)^k|j,k,m\rangle, \tag{3}$$

so that the even and odd parity of k plays a role in the symmetry species of rotational function as summarized in Table I. Finally, we combine the symmetries of the rovibronic part of the wave function with the spin-wave function into the complete spin-rovibronic wave function, which has to reflect the general symmetry with respect to permutation of identical nuclei. For the hydrogen nuclei with spin $I=\frac{1}{2}$,

TABLE I. Symmetry species and statistical weight of NH_3 wave functions in $D_{3h}(M)$.

Inversion (v_{inv} [a])	K [b]	$\Gamma_{rot} \otimes \Gamma_{inv}$	Γ_{ns}	Statistical weight[c]
v_{inv} even (symmetric, s)	0	(A_1') [d] (j even)	ortho (A_1')	0
	0	A_2' (j odd)	ortho (A_1')	4
	$6n \pm 1$	E''	para (E')	2
	$6n \pm 2$	E'	para (E')	2
	$6n \pm 3$	(A_1'') [d] $\oplus A_2''$	ortho (A_1')	4
	$6n \pm 6$	(A_1') [d] $\oplus A_2'$	ortho (A_1')	4
v_{inv} odd (asymmetric, a)	0	A_2'' (j even)	ortho (A_1')	4
	0	(A_1'') [d] (j odd)	ortho (A_1')	0
	$6n \pm 1$	E'	para (E')	2
	$6n \pm 2$	E''	para (E')	2
	$6n \pm 3$	(A_1') [d] $\oplus A_2'$	ortho (A_1')	4
	$6n \pm 6$	(A_1'') [d] $\oplus A_2''$	ortho (A_1')	4

[a] The quantum number v_{inv} represents the number of nodes of the inversion wave functions. The numbering of the wave function by v_{inv} can be easily correlated with the usual ν_2 numbering. For $\nu_2=0$ ground state, s and a are associated with $v_{inv}=0$ and 1, respectively, whereas for $\nu_2=1$, s and a corresponds to $v_{inv}=2$ and 3, respectively.

[b] $K=|k|$ and n are positive integers.

[c] Degeneracy including nuclear spin states of hydrogen atoms.

[d] Forbidden by nuclear spin statistics.

TABLE II. Molecular structure parameters. In the molecular frame, the z axis is the axis of symmetry of the molecule, where N is located on negative direction. The xz plane contains H_1 and the projection of the position of H_2 on xy plane lies in the second quadrant.

Bond lengths and angle(Å and °)	Scale factors (kHz)	Spherical tensors
$r_{HH}=1.6278$	$P_{HH}=27.849$	$\widetilde{T}^{(1,2)}_{2,\pm 2}=\frac{3}{2}e^{\pm 2\pi i/3}$, $\widetilde{T}^{(1,2)}_{2,\pm 1}=0$
$r_{NH}=1.011\,39$	^{14}N, $P_{NH}=8.393$	$\widetilde{Q}^{(1)}_{2,\pm 1}=\pm 1.030$
$\angle$H-N-H$=107.17°$	^{15}N, $P_{NH}=-11.773$	$\widetilde{Q}^{(1)}_{2,\pm 2}=-1.295$

the total wave function has to change sign under the permutation of two hydrogen nuclei (12) and remain invariant under a cyclic permutation (123) [13]. From the character table of the $D_{3h}(M)$ group, it follows that the complete wave function must belong either to the A_2' or to the A_2'' species. The proton spin states form the basis of the representation $\Gamma_{ns} = 4A_1' \oplus 2E'$, where the former corresponds to the ortho states with the total spin of the three hydrogen nuclei $I=I_{H_1}+I_{H_2}+I_{H_3}=\frac{3}{2}$ and the latter to the para states with $I=\frac{1}{2}$. The A_2' or A_2'' symmetry of the complete wave function is maintained when

$$\Gamma_{vib} \otimes \Gamma_{rot} \otimes \Gamma_{ns} \subset A_2' \text{ or } A_2'',$$

which means that ortho spin states can combine with rotational states with $K=3n$ and para spin states with $K=3n\pm 1$ in the same manner as in the C_{3v} molecules. The number of the $A_1'(4)$ and $E'(2)$ spin states symmetrically compatible with the particular rovibronic function defines the spin statistical weights of the states so that they become $A_1'(0)$, $A_2'(4)$, $E'(2)$, $E''(2)$, $A_1''(0)$, and $A_2''(4)$.

As written in Eq. (2), the spin conversion rate depends on the square of matrix elements of the magnetic interaction terms between pairs of ortho and para levels. So, only pairs with nonvanishing matrix elements are considered. The previous analysis on the symmetry of the rotation inversion levels is crucial to derive the specific selection rules of nuclear spin conversion and to determine a comprehensive list of ortho-para pairs.

The next section will present the magnetic interactions and their tensorial properties. The specific selection rules will be derived for each interaction, spin-spin, and spin rotation using nonvanishing integral method. *Ab initio* calculations are carried out to derive their strengths. The expected accuracy of the nuclear spin conversion is such that in the calculation of the magnetic strengths we have used the same values for the tensors components of (a) or (s), ground or $\nu_2=1$ excited states. Small variations have been addressed [14] for both spin-spin and spin-rotation constants but are not considered in this paper.

IV. INTRAMOLECULAR MAGNETIC INTERACTIONS

A. Spin-spin interactions

The operator of the SS interaction has been given by Chapovsky for CH_3F [8,15]. For NH_3, we have to consider interactions between the nitrogen nucleus and the hydrogen nuclei $\hat{V}_{NH}$ and those between the hydrogen nuclei $\hat{V}_{HH}$.

The magnetic dipole-dipole $\hat{V}_{12}$ interaction between two particles 1, 2 is generally written in Cartesian coordinates as [8]

$$\hat{V}_{12} = P_{12} \sum_{i,j} \hat{S}_i^{(1)} \hat{S}_j^{(2)} T_{ij}^{(1,2)},$$

$$P_{12} = \frac{\mu_0}{4\pi} \frac{\mu_1 \mu_2}{r_{12}^3 S^{(1)} S^{(2)}}, \quad T_{ij}^{(1,2)} = \delta_{ij} - 3 n_i n_j \quad i,j = x,y,z, \tag{4}$$

where in the scaling factor P_{12}, r_{12} is the distance between the particles, $\mathbf{n}$ is the unit vector directed from the first to the second particle, μ_1, μ_2 are the nuclear magnetic moments, and $\hat{\mathbf{S}}^{(1)}$, $\hat{\mathbf{S}}^{(2)}$ are the spin of particles.

Structure parameters are summarized in Table II.

Introducing the notation $\hat{\mathbf{S}}^{(m)}$ for the spin of the m^{th} hydrogen ($m=1,2,3$) and $\hat{\mathbf{I}}$ for the spin of nitrogen, the operators have the form

$$\hat{V}_{\mathrm{HH}} = P_{\mathrm{HH}} \sum_{m,n} \sum_{i,j} \hat{S}_i^{(m)} \hat{S}_j^{(n)} T_{ij}^{(m,n)},$$

$$\hat{V}_{\mathrm{NH}} = P_{\mathrm{NH}} \sum_{m} \sum_{i,j} \hat{S}_i^{(m)} \hat{I}_j Q_{ij}^{(m)}, \tag{5}$$

where $T_{ij}^{(m,n)}$ and $Q_{ij}^{(m)}$ are the Cartesian components in the laboratory frame of the tensor for H_m-H_n and N-H_m interactions as written in Eq. (4).

To calculate the matrix elements introduced in the QRM, it is convenient to express the interactions in terms of spherical tensor components to benefit of tensorial algebra formalism. From Eq. (4), it is clear that **Q** and **T** tensors are traceless and symmetric ($T_{ij}=T_{ji}$, $Q_{ij}=Q_{ji}$). As a consequence, when we form the nine irreducible spherical tensor operators from the Cartesian one, only remains the rank 2 components $T_{2,q}^{(m,n)}$ and $Q_{2,q}^{(m)}$. $T_{0,0}$ and $Q_{0,0}$ vanish as the traces are 0 as well as $T_{1,q}$ and $Q_{1,q}$ from the symmetric character of the interaction tensors.

By applying the Wigner-Eckart theorem, it is possible to get an expression for the spin-spin matrix elements involved in $X\mathrm{H}_3$-type molecules. As the other parameters Γ_{op}, ω_{op} involved in the spin conversion calculation [Eq. (2)] does not depend of the projection of j, I, and I_{N} on the Z axis of the laboratory frame, we calculate a summation over these projection quantum numbers M, σ, and σ_{N}, respectively. The result is similar to Eq. (30) of Ref. [8] and can be easily applied to the two isotopologues of ammonia

$$\begin{aligned}\sum_{\substack{M,\sigma,\sigma_{\mathrm{N}}\\ M',\sigma',\sigma'_{\mathrm{N}}}} & |\langle j_o,k_o,I,I_{\mathrm{N}},M,\sigma,\sigma_{\mathrm{N}},v_o|\hat{V}_{X\mathrm{H}} \\ & + \hat{V}_{\mathrm{HH}}|j_p,k_p,I',I_{\mathrm{N}},M',\sigma',\sigma'_{\mathrm{N}},v_p\rangle|^2 \\ & = [j_p][j_o]\begin{pmatrix} j_p & 2 & j_o \\ -k_p & q & k_o \end{pmatrix}^2 \Bigg(\frac{3}{4}[I_X]|P_{\mathrm{HH}}\tilde{T}_{2q}^{(1,2)}|^2 \\ & \quad + \frac{2}{3}|\langle I_X\|\hat{\mathbf{I}}_X\|I_X\rangle P_{X\mathrm{H}}\tilde{Q}_{2q}^{(1)}|^2 \Bigg),\end{aligned} \tag{6}$$

where $q=k_p-k_o$, $(:::)$ stands for the $3j$ symbol, v_o and v_p correspond to v_{inv} quantum numbers and a selection rule will be explained below by symmetry arguments (v_o+v_p+q even).

The symbol $[j]=2j+1$ is used to represent the degeneracy induced by an angular momentum j and $\langle I_X\|\hat{\mathbf{I}}_X\|I_X\rangle$ is the reduced matrix element of the rank 1 spin operator $\hat{\mathbf{I}}_X$. The value of the reduced element is $\sqrt{\frac{3}{2}}$ for $I_X=\frac{1}{2}$ and $\sqrt{6}$ for $I_X=1$ corresponding to $^{15}\mathrm{N}$ and $^{14}\mathrm{N}$, respectively.

$\tilde{T}_{2q}^{(1,2)}$ and $\tilde{Q}_{2q}^{(1)}$ in Eq. (6) are the q components of the spherical tensors of rank 2 $\mathbf{T}^{(1,2)}$ and $\mathbf{Q}^{(1)}$, written in the molecular frame (significance of the $\tilde{}$). Values are given in Table II. Considering the inversion part of the wave function, the vanishing integral method [16] is useful to give selection rules. The only tensors components which appear in the formula are ($\tilde{Q}_{22}$, $\tilde{T}_{22}$) and ($\tilde{Q}_{21}$, $\tilde{T}_{21}$). They are, respectively, of symmetry E' and E'' in the MS group $D_{3h}(M)$ of NH_3. Considering a term like $\langle j_o,k_o,v_o|\tilde{Q}_{22}|j_p,k_p,v_p\rangle$ with v_o and v_p of different parity, $k_p=k_o+2$ follows from the $3j$ symbol rule and then the Table I gives the two possible combinations $A'_2\otimes E'\otimes E''$ or $A''_2\otimes E'\otimes E'$ for the matrix element. This term vanishes as the resulting symmetry is $A''_1\oplus A''_2\oplus E''$ and does not contain the fully symmetric A'_1 species. With the same argument, a matrix element like $\langle j_o,k_o,v_o|\tilde{Q}_{21}|j_p,k_p,v_p\rangle$ also vanishes for v_o and v_p of the same parity. $k_p=k_o+1$ is imposed by the $3j$ symbol rule, then the possible symmetry combinations for the integral (see Table I) are $A'_2\otimes E''\otimes E'$ or $A''_2\otimes E''\otimes E''$, which are both equal to $A''_1\oplus A''_2\oplus E''$. The selection rules are summarized for the spin-spin interaction to be $|\Delta j|\leq 2$ and $|\Delta k|=1$ ($a\leftrightarrow s$) or $|\Delta k|=2$ ($s\leftrightarrow s$ or $a\leftrightarrow a$).

Equation (6) stands for positive values of k_o and k_p. For $k\neq 0$, each $|j,k,v\rangle$ state is doubly degenerate, considering the negative value of k. For each interacting pair with positive value of k_o and k_p, the corresponding $-k_o$ and $-k_p$ has to be considered, this is also valid if k_o is zero. Accounting of this degeneracy, the result of Eq. (6) has to be multiplied by a factor of 2. It can be noticed that this degeneracy is also taken into account in calculating the Boltzmann factors W_o or W_p.

The spin-spin tensor can also be derived with *ab initio* calculations. As evident from the formulation given in Refs. [17,18], the dipolar-coupling tensor is completely determined once the molecular geometry is known, and it does not require any knowledge about the electronic structure of the molecule. However, this strictly applies only to a rigid nonvibrating molecule, and quantum chemistry is thus required for evaluating zero-point vibrational (ZPV) corrections to the equilibrium values. To this end, the perturbational approach described in Ref. [19] is employed. Since all details can be found in this reference, we only recall here that anharmonic effects should be included via cubic force field evaluation. In the latter, the inversion mode is not explicitly taken into account, and thus the vibrational ground state turns out to be an average of the (s) and (a) levels. The coupled cluster method with single and double excitations with a perturbative treatment of connected triples [CCSD(T)] [20] in conjunction with the correlation consistent basis sets [21] has been employed, with all electrons correlated. Best estimates of the interaction terms have then been obtained by adding ZPV corrections, defined as the difference between equilibrium and vibrational averaged values, to the values calculated using the experimental equilibrium structure as reference geometry [22]. The CFOUR program [23] has been employed throughout. The results are summarized in Table III and compared to the available experimental data [24,25]. The chosen level of theory is known to provide very accurate results for vibrational corrections to molecular and spectroscopic properties (see, for example, Refs. [26–28]), as also confirmed by the very good agreement between theory and experiment observed in Table III.

TABLE III. *Ab initio* spin-spin magnetic interaction terms (kHz) for the vibrational ground state.

	D_{xx}	D_{yy}	D_{zz}	D_{xz}, D_{zx}	D_{xx}	D_{yy}	D_{zz}	D_{xz}, D_{zx}
		$^{14}NH_3$				$^{15}NH_3$		
N-H ($\tilde{Q}$ tensor)								
Reference geometry[a]	−13.348	8.393	4.955	−8.645	18.724	−11.773	−6.951	12.127
Reference geometry[b]	−13.138	8.400	4.738	−8.881	18.429	−11.783	−6.645	12.458
Vibrat. averag.[c]	−12.608	8.014	4.594	−8.386	17.690	−11.244	−6.446	11.764
Best est.[d]	−12.818	8.007	4.811	−8.150	17.985	−11.233	−6.752	11.433
Experiment[e]	−12.759	7.983	4.776	[f]	17.769	−11.045	−6.724	[f]
H-H ($\tilde{T}$ tensor)								
Reference geometry[a]	27.849	−55.698	27.849	0.0	27.849	−55.698	27.849	0.0
Reference geometry[b]	28.305	−56.610	28.305	0.0	28.305	−56.609	28.305	0.0
Vibrat. averag.[c]	27.611	−55.374	27.763	−0.057	27.611	−55.372	27.761	−0.057
Best est.[d]	27.155	−54.463	27.307	−0.057	27.156	−54.461	27.306	−0.057
Experiment[e]	27.539	−55.078	27.539	[f]	27.429	−54.858	27.429	[f]

[a] Values evaluated at experimental equilibrium structure; not dependent of the level of theory, but only on the chosen geometry.

[b] *Ab initio* equilibrium structure optimized at the CCSD(T)/cc-pwCVQZ level.

[c] Vibrationally averaged values at the CCSD(T)/cc-pwCVQZ level.

[d] Equilibrium values at the experimental structure (footnote a) plus ZPV corrections (line c−line b).

[e] Reference [25]: derived from U and T parameters.

[f] Not accessible by hyperfine structure measurement.

B. Spin-rotation interactions

The SR matrix element has been given in Ref. [29]

$$\sum_{\substack{M,\sigma,\sigma_{\mathrm{N}}\\ M',\sigma',\sigma'_{\mathrm{N}}}} |\langle j_o,k_o,I,I_{\mathrm{N}},M,\sigma,\sigma_{\mathrm{N}},v_o|\hat{V}_{SR}| \times j_p,k_p,I',I_{\mathrm{N}},M',\sigma',\sigma'_{\mathrm{N}},v_p\rangle|^2 = 2[I_{\mathrm{N}}]\frac{[j_o,j_p]}{2} \times \left|\sum_l (-1)^l[l]^{1/2}\begin{pmatrix} j_p & l & j_o \\ -k_p & k_p-k_o & k_o \end{pmatrix} C^{(l)}_{k_p-k_o} b_l(j_p,j_o)\right|^2, \quad (7)$$

with

$$b_l(j_p,j_o) = \{j_p(j_p+1)[j_p]\}^{1/2}\begin{Bmatrix} 1 & 1 & l \\ j_o & j_p & j_p \end{Bmatrix} + (-1)^l\{j_o(j_o+1)[j_o]\}^{1/2}\begin{Bmatrix} 1 & 1 & l \\ j_p & j_o & j_o \end{Bmatrix} \quad (8)$$

and selection rule $v_o+v_p+k_o-k_p$ even.

This formulation has been used previously for the calculations of nuclear spin conversion of H_2CO perturbed by molecular hydrogen collisions in astrophysical environments [30]. According to general expression of the NSC given in Eq. (2), a summation is done over the variables M, σ_{N}, σ and M', σ'_{N}, σ' describing the degeneracy of the ortho $\{j_o,k_o,I,I_{\mathrm{N}}\}$ and para $\{j_p,k_p,I',I'_{\mathrm{N}}\}$ states. The difference with Ref. [29] is the presence of the factor $2[I_{\mathrm{N}}]$, which gives explicitly the $\pm k$ and σ_{N} degeneracies.

For the selection rules, the 6j symbols in the $b_l(j_p,j_o)$ lead to $|\Delta j|\leq 1$ and the tensorial components present in the formula give $|\Delta k|=1$ or 2. Contrary to the spin-spin interaction and due to the nature of the interaction, the nine irreductible spherical tensor operators are nonzero. C_0^0 is used in calculating hyperfine structure but has no role in the ortho-para conversion. $C^1_{\pm 1}$ components are linked to the asymmetry of nondiagonal terms of Cartesian tensors (xz and yz). Their symmetry is E'' in the $D_{3h}(M)$ group. For the calculation of matrix elements between ortho and para levels, they follow the same selection rules than $C^2_{\pm 1}$ components. Such rules have been already determined for the spin-spin interaction (see $\tilde{T}^2_{\pm 1}$ and $\tilde{Q}^2_{\pm 1}$). Finally, for spin-rotation interactions, the selection rules are $|\Delta j|\leq 1$ and $|\Delta k|=1(a\leftrightarrow s)$ or $|\Delta k|=2$ ($s\leftrightarrow s$ or $a\leftrightarrow a$) which can also be expressed with $v_o+v_p+k_o-k_p$ even.

Each element of the spin-rotation tensor C has an electronic and a nuclear contribution. Although the latter can be estimated from the structure, the former needs the knowledge of the complete set of rovibronic states and can be obtained as the second derivative of the electronic energy with respect to **J** and **I**. *Ab initio* calculations lead to this determination of the complete spin-rotation second-rank tensor C. For brevity, we refer interested readers to, for instance, Refs. [31,32], for all theoretical details.

For equilibrium values of spin-rotation interaction, a systematic basis set investigation has been performed. More precisely, the cc-pCVnZ ($n=T-6$) and aug-cc-pCVnZ

TABLE IV. *Ab initio* ground-state spin-rotation magnetic interaction terms (kHz) (H) computed at the CCSD(T) level for $^{14}NH_3$ and $^{15}NH_3$. For the seven basis sets, calculation has been performed with experimental equilibrium structure.

	C_{zz}	C_{xx}	C_{yy}	C_{zx}	C_{xz}
			$^{14}NH_3$		
Basis set					
CVTZ	20.13	5.00	33.76	−12.46	−7.15
CVQZ	19.86	4.49	33.27	−12.21	−7.01
CV5Z	19.79	4.23	33.03	−12.14	−6.99
CV6Z	19.76	4.14	32.97	−12.12	−6.96
aCVTZ	20.24	4.22	33.96	−12.42	−7.14
aCVQZ	19.90	4.15	33.27	−12.21	−7.01
aCV5Z	19.80	4.12	33.06	−12.16	−6.97
Reference geometry[a,b]	19.96	4.94	33.28	−12.43	−7.25
Vibrat. averag.[c,b]	18.82	4.25	31.83	−11.78	−6.76
Best est.[d]	18.66	3.43	31.61	−11.51	−6.48
Experiment[e]	19.01	3.28	32.26	[f]	[f]
		$^{15}NH_3$			
Basis set					
CVTZ	20.13	4.99	33.68	−12.43	−7.15
CVQZ	19.86	4.48	33.18	−12.18	−7.01
CV5Z	19.78	4.22	32.95	−12.11	−6.99
CV6Z	19.76	4.13	32.89	−12.10	−6.96
aCVTZ	20.24	4.21	33.88	−12.39	−7.14
aCVQZ	19.90	4.14	33.19	−12.18	−7.01
aCV5Z	19.80	4.11	32.97	−12.12	−6.97
Reference geometry[a]	19.96	4.92	33.19	−12.40	−7.25
Vibrat. averag.[c]	18.82	4.23	31.75	−11.75	−6.76
Best est.[d]	18.66	3.42	31.53	−11.47	−6.48
Experiment[e]	19.05	3.28	32.26	[f]	[f]

[a] *Ab initio* equilibrium structure optimized at the CCSD(T)/cc-pwCVQZ level.

[b] Reference [33].

[c] Vibrationally averaged values at the CCSD(T)/cc-pwCVQZ level.

[d] CCSD(T)/augCV5Z values plus ZPV corrections (line a−line b).

[e] Reference [34]: derived from S parameters.

[f] Not accessible by hyperfine structure measurement.

($n=T-5$) hierarchic series of bases [21,35,36] have been considered. In all cases, all electrons have been correlated and the reference geometry chosen as the experimental equilibrium structure [22].

To calculate vibrational corrections, the same approach and level of theory used for spin-spin interaction constants have been employed. It should be noted that these calculations for $^{14}NH_3$ have already been published [33]. Data for $^{15}NH_3$ are new.

As for the spin-spin interaction, the best estimates of spin-rotation constants were obtained by adding to the best equilibrium values [i.e., those computed at the CCSD(T)/aug-cc-pCV5Z level] the corresponding ZPV corrections. Furthermore, from Table IV, it is evident that by augmenting the cardinal number n of the basis set, the absolute constant values decrease, the convergence of the equilibrium values is monotonic and smooth, and the two series of basis sets employed provide almost equivalent results. Components of the Cartesian tensor of spin-rotation interaction are presented in Table IV. Let us mention that some authors [14] have addressed small variations for both spin-spin and spin-rotation constants with the inversion quantum number v_{inv}. The difference is less than 0.1% for 0^+ ($v_{inv}=0$) and 0^- ($v_{inv}=1$) states. On the other hand, larger variations (up to a few %)

TABLE V. Main first ortho-para pairs involved in the nuclear spin conversion of $^{14}NH_3$ at a temperature of 296 K.

Level pairs $j_o\ k_o\ v_o - j_p\ k_p\ v_p$	$\omega/2\pi$ (GHz)	Boltzmann factor W_o+W_p	γ/P (s^{-1}/Torr)
$4\ 0\ a-4\ 2\ a$	441.9	9.01×10^{-4}	1.90×10^{-7}
$5\ 0\ s-5\ 2\ s$	440.8	5.58×10^{-4}	1.90×10^{-7}
$6\ 0\ a-6\ 2\ a$	438.0	3.13×10^{-4}	1.63×10^{-7}
$3\ 0\ s-3\ 2\ s$	444.2	1.33×10^{-3}	1.58×10^{-7}
$1\ 0\ s-1\ 1\ a$	87.7	2.09×10^{-3}	1.38×10^{-7}
$7\ 0\ s-7\ 2\ s$	436.1	1.60×10^{-4}	1.22×10^{-7}
$2\ 0\ a-2\ 2\ a$	444.5	1.77×10^{-3}	1.00×10^{-7}
$8\ 0\ a-8\ 2\ a$	432.8	7.42×10^{-5}	8.03×10^{-8}
Total rate (3472 pairs)			$\mathbf{3.09\times10^{-6}}$

are expected for the excited $\nu_2=1$ ($v_{inv}=2,3$) vibrational states. Such variations have not been considered in the *ab initio* treatment and are not included in the conversion rates calculation.

V. RESULTS

For the ground state of $^{14}NH_3$, energy levels ($j<25$, $k\leq j$, $v_{inv}=0$, or 1) have been calculated with the molecular parameters obtained by Urban *et al.* [37]. From this list of 625 levels, ortho-para pairs have been identified with the selection rules corresponding to spin-spin and spin-rotation interactions. Let us recall the rules obtained in previous section: they are $|\Delta j|\leq 2$, for the spin-spin interaction, and $|\Delta j|\leq 1$ for the spin-rotation one, and for both $|\Delta k|=1(a\leftrightarrow s)$ or $|\Delta k|=2$ ($s\leftrightarrow s$ or $a\leftrightarrow a$). All the possible pairs (3472) have been considered in the calculation and sorted according to their contribution to nuclear spin conversion rates by both interactions. The matrix elements of the spin-spin and spin-rotation interactions required for the application of the QRM have been computed by means of quantum-chemical techniques; the best estimates of Tables III and IV have been used in the calculation. The beginning of the list is given in Table V.

A complete calculation of the nuclear spin conversion requires to consider the vibrationally excited states, according to their relative population. The contribution is generally weak and can be evaluated by using the partition function. On Table VI, we recall the energy position of the first vibrationally excited levels [38] and their corresponding contribution.

TABLE VI. Vibrational contribution to partition function.

Level		Energy[a] (cm^{-1})	Z_v/Z_{tot}
Ground state	$(s)v_{inv}=0$	0.00	0.495
Ground state	$(a)v_{inv}=1$	0.79	0.493
ν_2	$(s)v_{inv}=2$	932.43	5.6×10^{-3}
ν_2	$(a)v_{inv}=3$	968.12	4.7×10^{-3}
$2\nu_2$	$(s)v_{inv}=4$	1598.47	2.3×10^{-4}
$2\nu_2$	$(a)v_{inv}=5$	1882.18	5.9×10^{-5}
ν_4	(s) sym. stretch.	1626.30	2.0×10^{-4}
ν_4	(a) sym. strech.	1627.30	2.0×10^{-4}

[a] Reference [38].

TABLE VII. First ortho-para pairs of the ν_2 state involved in the nuclear spin conversion of $^{14}NH_3$.

Level pairs $j_o\ k_o\ v_o - j_p\ k_p\ v_p$	$\omega/2\pi$ (GHz)	Boltzmann factor W_o+W_p	γ/P (s^{-1}/Torr)
$8\ 3\ s-8\ 4\ a$	23.6	8.87×10^{-7}	6.50×10^{-8}
$9\ 3\ s-9\ 4\ a$	41.4	3.74×10^{-7}	1.03×10^{-8}
$7\ 3\ s-7\ 4\ a$	86.6	1.91×10^{-6}	8.75×10^{-9}
$6\ 3\ s-6\ 4\ a$	146.3	3.76×10^{-6}	4.81×10^{-9}
$3\ 3\ s-2\ 2\ a$	146.3	1.66×10^{-5}	4.28×10^{-9}
$6\ 6\ a-6\ 5\ s$	195.0	5.25×10^{-6}	3.73×10^{-9}
$5\ 3\ s-5\ 4\ a$	200.9	6.72×10^{-6}	3.31×10^{-9}
$11\ 3\ a-11\ 2\ s$	24.0	4.54×10^{-8}	2.50×10^{-9}
$4\ 3\ s-4\ 4\ a$	249.2	1.09×10^{-5}	1.98×10^{-9}
$7\ 6\ a-7\ 5\ s$	259.8	2.67×10^{-6}	1.98×10^{-9}
Total rate (3472 pairs)			$\mathbf{1.37\times10^{-7}}$

It can be noticed that the $\nu_2=1$ represents only 1% of the population at room temperature (296 K). As the energies of this state have been obtained with high accuracy by fitting the experimental data [39], we have made the complete calculation of the real contribution of the $\nu_2=1$ level to the nuclear spin conversion rate. From the energy levels [$j<30$, $k\leq j$, $v_{inv}=2$ (a) or $v_{inv}=3$ (s)], we derived the possible ortho-para level pairs needed for the calculation. The first pairs are listed in Table VII with their contributions to the conversion rate. One can notice that the $\nu_2=1$ state is responsible of 4% of the nuclear spin conversion of $^{14}NH_3$ to be compared to the 1% population.

The calculation for $^{15}NH_3$ has been done using the same approach and the results are given in Table VIII for the

TABLE VIII. First ortho-para pairs of the ground state involved in the nuclear spin conversion of $^{15}NH_3$ at a temperature of 296 K.

Level pairs $j_o\ k_o\ v_o - j_p\ k_p\ v_p$	$\omega/2\pi$ (GHz)	Boltzmann factor W_o+W_p	γ/P (s^{-1}/Torr)
$5\ 0\ s-5\ 2\ s$	437.8	8.38×10^{-4}	1.68×10^{-7}
$4\ 0\ a-4\ 2\ a$	439.0	1.35×10^{-3}	1.61×10^{-7}
$6\ 0\ a-6\ 2\ a$	435.0	4.70×10^{-4}	1.49×10^{-7}
$3\ 0\ s-3\ 2\ s$	441.2	1.99×10^{-3}	1.27×10^{-7}
$7\ 0\ s-7\ 2\ s$	433.1	2.41×10^{-4}	1.14×10^{-7}
$1\ 0\ s-1\ 1\ a$	88.1	3.13×10^{-3}	9.03×10^{-8}
$8\ 0\ a-8\ 2\ a$	429.8	1.12×10^{-4}	7.64×10^{-8}
$2\ 0\ a-2\ 2\ a$	441.5	2.65×10^{-3}	7.44×10^{-8}
$3\ 0\ s-3\ 1\ a$	89.0	1.94×10^{-3}	7.14×10^{-8}
$9\ 0\ s-9\ 2\ s$	427.2	4.76×10^{-5}	4.50×10^{-8}
$5\ 0\ s-5\ 1\ a$	90.5	8.15×10^{-4}	4.29×10^{-8}
Total rate (5158 pairs)			$\mathbf{2.72\times10^{-6}}$

TABLE IX. First ortho-para pairs of the ν_2 state involved in the nuclear spin conversion of $^{15}NH_3$.

Level pairs $j_o\ k_o\ v_o - j_p\ k_p\ v_p$	$\omega/2\pi$ (GHz)	Boltzmann factor W_o+W_p	γ/P (s^{-1}/Torr)
11 3 a − 11 2 s	0.5	7.04×10^{-8}	5.11×10^{-6}
8 3 s − 8 4 a	5.4	1.37×10^{-6}	1.24×10^{-6}
7 3 s − 7 4 a	56.2	2.94×10^{-6}	2.07×10^{-8}
6 3 s − 6 4 a	114.8	5.77×10^{-6}	7.73×10^{-9}
5 3 s − 5 4 a	168.5	1.03×10^{-5}	4.60×10^{-9}
9 3 s − 9 4 a	68.9	5.77×10^{-7}	3.74×10^{-9}
6 6 a − 6 5 s	226.5	8.04×10^{-6}	2.74×10^{-9}
4 3 s − 4 4 a	216.0	1.67×10^{-5}	2.53×10^{-9}
Total rate (5158 pairs)			$\mathbf{6.43\times10^{-6}}$

ground state and in Table IX for the $\nu_2=1$ excited state. They reveal a completely different behavior since two quasidegenerate pairs are present in the excited state.

The nuclear spin conversion rate of the $\nu_2=1$ state is essentially given by the contribution of two specific pairs $(j_o\ k_o\ v_o-j_p\ k_p\ v_p)=(11\ 3\ a-11\ 2\ s)$ and $(8\ 3\ s-8\ 4\ a)$, which represents 99% of the nuclear spin conversion of the state.

Although the population of this state only represents 1% of the total, its contribution is dominant compared to the contribution of the ground state.

VI. DISCUSSION

With the values described in the preceding sections, the conversion rate is calculated for 1 Torr and assuming a linear dependence on pressure, the total contribution is found to be 3.23×10^{-6} s^{-1} $Torr^{-1}$ at 296 K for $^{14}NH_3$ and 9.15×10^{-6} s^{-1} $Torr^{-1}$ for $^{15}NH_3$. The linear dependence remains valid as the approximation $\Gamma^2 \ll \omega^2$ is fulfilled. For $^{14}NH_3$, the validity is conserved up to 1 atm, whereas a limit of 30 Torr could be given for $^{15}NH_3$, where two quasidegenerate pairs are present. Above these limits, the real value of the rate is lower than described by the linear dependence.

These NSC rates are one or two orders of magnitude lower than those observed up to now for H_2CO. This corresponds to the characteristic conversion time of 86 h and 30 h for $^{14}NH_3$ and $^{15}NH_3$, respectively, at a pressure of 1 Torr.

These values suggest that if we are able to perform an isomeric enrichment, the sample at a typical pressure of few Torrs can be kept for hours and that conversion time will be experimentally accessible by measuring the kinetics of the recovering of the statistic equilibrium distribution.

(a) Astrophysics. As the approximation $\Gamma^2 \ll \omega^2$ remains valid in Eq. (2) up to 1 atm, the conversion rate stays proportional to the collisional decoherence rate Γ and thus to the pressure. This argument is convincing to claim that although not strictly forbidden, the conversion rate of NH_3 in ISM conditions is far too low for gaseous phase with mechanism involving nonreactive collisions. Nevertheless, other mechanisms have been proposed as a potential source of nuclear spin conversion. They involve chemical reaction, such as proton exchange with interstellar proton, but also the adsorption-desorption process on grains since it has recently been shown with CH_3F and H_2CO that surfaces may induce a dramatic acceleration of the conversion [40,41].

(b) Temperature dependence. The temperature dependence of the conversion rate is also important for astrophysical media. It has not been considered in this paper, but as a consequence of the calculation, some remarks can be made. The temperature dependence is different for the two isotopologues: a small variation is expected for $^{14}NH_3$, whereas a rapid decrease (factor 3) with decreasing temperature will appear for $^{15}NH_3$, due to the role of specific pairs of excited $\nu_2=1$ state. Such values can be compared to the conversion rates measured for NH_3 in Ar matrices at typical temperature of 5 K [42]. The conversion is mainly due to magnetic intermolecular interaction between molecules in the concentration range of 1/200–1/1000. The intramolecular process is considered as a limit of high dilution and the value found is 2×10^{-5} s^{-1}. Here, the relaxation rate to consider for an isolated molecule is the collision with the matrix environment described by interaction with phonons of the lattice. A theoretical value (0.67 cm^{-1}) is given considering the infrared profile of the $\nu_2=1$ band of NH_3 trapped in Ar matrix [43]. One can see that this is comparable with a broadening in gas phase at a typical pressure of 1 atm.

Nuclear spin conversion was suggested to take place in the case of a molecular beam of NH_3, to explain the different population of states during the expansion [44]. As conversion is forbidden during collisional process, the population ratio between ortho and para levels is expected to be maintained to a value of 1, valid at room temperature. It is the case for different beam conditions, except for 10% NH_3 seeded in Ar, where an overpopulation is measured in para $(j,k)=(1,1)$ state. As the lower state $(j,k)=(0,0)$ is of ortho character, such result is very surprising, even if conversion could be partially allowed. The authors gave a tentative explanation involving a specific $\Delta K=1$ doorway conversion. But, our calculated values considering a pressure of few bars remain too small to allow such conversion during the expansion process.

(c) Enrichment. The main difficulty to study experimentally NSC remains the lack of techniques allowing this enrichment of the medium in one of the nuclear spin configurations. Light-induced drift technique has been used for H_2CO [9] and H_2CCH_2 [5,6]. Some attempts on NH_3 were not successful. Other techniques have to be tested using selective adsorption and desorption on surfaces as demonstrated on H_2O [45].

Another promising method has been proposed [46,47] using the excitation of the molecule from the ground state with low conversion rate in an excited vibrational or electronic state, where the rate is significantly higher. The conversion occurs when the molecule is excited and is quenched when it returns back in the fundamental state. Our calculations reveal that $^{15}NH_3$ is a good candidate to test this possibility, using the existence of two quasidegenerate pairs in interaction in the $\nu_2=1$ state.

Performing an enrichment has also a spectroscopic interest, especially for the analysis of the manifold vibrational combination and overtone bands, which are difficult to be assigned, for instance, in the 1.5 μm spectral region [48]. The enrichment is an enhancement of the population of one spin isomer compared to the other. As a consequence, relative intensity of lines gives a way to sort them according their spin symmetry.

ACKNOWLEDGMENTS

This work is part of the scientific program of the Centre d'Études et de Recherches Lasers et Applications (CERLA), which is supported by the Ministère de la Recherche, the Région Nord-Pas de Calais, and the Fonds Européen de Développement Économique des Régions. The support from the Grant Agency of the Academy of Sciences of the Czech Republic (Project No. IAA400400706) is also gratefully acknowledged.

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