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Nuclear spin conversion in H_2O

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Nuclear spin conversion (NSC) in water molecules has often been investigated in the gas or solid phase. It has not been observed in the former yet because of the difficulty in producing an efficient disequilibrium of the spin isomer populations. Another, again failed, attempt at such an experiment is presented based on the supposed spin-selective adsorption ability of nanoporous materials. To explain the reason for so many failures, the NSC rate has been calculated in the framework of the quantum relaxation model, using the best available values of the energy levels of the vibrational ground state, the intramolecular magnetic interactions, and the collisional relaxation rates. The characteristic time of NSC in the gas phase is of the order of 1 s at ambient temperature. As NSC is observed in low-temperature matrices, the quantum relaxation model can be adapted to estimate the rate in such environments. Finally, some recent experimental results devoted to astrophysical problems are discussed.

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I. INTRODUCTION

Water plays a crucial role in the chemistry of the dense interstellar medium (ISM). The conditions of formation of molecules in space, especially the temperature, must be known for an understanding of the chemical processes involved and even of the thermal history of ISM objects e.g., dark clouds or comets. Radio-astronomical spectra are essential for this purpose by use of the ratio of the line intensities of particular molecules containing half-integer spin atoms, such as hydrogen in H_2O. These molecules exist as several spin isomers, which differ in the value of the total nuclear spin I of the hydrogen nuclei. A water sample is a mixture of ortho water ($I = 1$) and para water ($I = 0$), with spin statistical weights of 3 and 1, respectively, in the high-temperature limit (>50 K). The Pauli exclusion principle requires the total wave functions to be antisymmetric toward proton exchange. Regarding the symmetric character of the vibrational and electronic ground-state wave functions, each rotational state is thus associated with only one of the nuclear magnetic species, and each species can be identified by its own gas-phase rotation-vibration spectrum. The relative abundance, called the ortho-to-para ratio (OPR), of nuclear spin isomers can be measured from the ratio of line intensities of transitions belonging to each spin species and leads via specific models to the composition and temperature of formation in the ISM, e.g. in cometary comae [1–3], in giant molecular clouds [4], or in high-mass star-forming regions [5].

The OPRs are thus believed to be key molecular signatures related to the history of molecules in the universe, providing fundamental links between the kinds of matter observed in different astrophysical media. Such an approach is reliable if the OPR is conserved in time. However, several mechanisms can cause a nuclear spin conversion (NSC) in water molecules by flipping the spin of one of the hydrogen atoms. The first concerns a nonreactive interchange from one isomer to another, as has been observed in the gas phase for CH_3F [6,7], $H_2{}^{12}C^{13}CH_2$ [8], C_2H_4 [9], and H_2CO [10]. For all these molecules, the NSC mechanism is explained by a quantum relaxation model (QRM) [11], which involves internal magnetic properties of the molecule and nonreactive collisions. In astrophysical conditions, we have shown that conversion according to this scheme is highly unlikely (H_2CO [12], NH_3 [13]). Other processes, like interaction with a proton or grain surface, can occur. The present project takes place within a global analysis of the nuclear spin conversion of water that might exist in the gas and solid states and at their interface. To be successful it is necessary to separate intramolecular from collision, proton exchange, surface, and icy contributions.

It is the aim of the present paper to study the first with gas-phase NSC experiments and theoretically within the QRM, i.e., considering self-binary collisions between molecules and excluding reactive processes, using the best current values of the relevant parameters.

NSC measurements require an enrichment of the sample in one of the isomer populations. However, the enrichment duration should be much shorter than the conversion time to be measured. In Sec. II an experiment based on a method developed by Tikhonov and Volkov [14] is presented and discussed. The QRM presented in Sec. III allows an estimation of the conversion rate. The pressure and temperature dependence are studied, and the results are compared to some previous experiments, mainly performed in rare-gas matrices. Use of this model should help in the choice of the proper enrichment method. Furthermore, NSC experimental data, when available, fitted within the QRM provide detailed dynamical information on molecular properties such as very small intramolecular magnetic interactions and collision-induced decoherence of some quantum states [7,15–17].

Calculations of conversion rates in water have been performed previously. Curl *et al.* were the first to model the dynamics of nuclear spin conversion in molecules, considering the specific cases of water, formaldehyde, and methane [18]. Miani and Tennyson estimated the allowed strength of the intensity of radiative perturbation-allowed transitions between ortho and para states [19]. Veber *et al.* [20] tried to reproduce the Tikhonov-Volkov experiment and gave an estimation of the NSC rate. All these works are discussed throughout the present paper.

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II. ATTEMPT AT NUCLEAR SPIN ENRICHMENT

NSC can be experimentally observed only if the possibility exists of creating a disequilibrium, or enrichment, between the populations of the different spin isomers. This is often challenging because of the identical physical and chemical properties of spin isomers. A cryogenic cooling method can be used for hydrogen. Light-induced drift has been used for several polyatomic molecules such as CH_3F [6,7], $H_2{}^{12}C^{13}CH_2$ [8], and C_2H_4 [9]. Isomers of H_2CO can be distinguished by use of laser-based selective photodissociation [10]. These techniques performed in the gas phase are described in detail in Ref. [21], but all of them are inefficient for separation of water spin isomers. More recently, Tikhonov and Volkov proposed an alternative method based on selective physical adsorption onto an aluminum oxide surface [14]. Their achieved enrichment and relaxation time are impressive, and many attempts to reproduce this promising experiment have been made, e.g., by Veber *et al.* [20], but all failed. Instead of that, we started by testing the ability of a nanoporous resin to preferentially adsorb one spin isomer rather than the other. This resin, hyper-cross-linked polystyrene MN200, provided by the Purolite company, was the same as that used by Tikhonov and Volkov. Water vapor was introduced into a cavity cell connected through a valve to a bulb filled with resin grains. The bulb was previously carefully evacuated. A cavity-enhanced absorption technique was used for this measurement, since the intensities of absorption lines of water are around 10^{-22} $cm^{-1}/mol\ cm^{-2}$ in the spectral range around 6770 cm^{-1} . Using two adjacent ortho and para lines, the population of each isomer was simultaneously probed with a near-infrared external-cavity diode laser (New Focus) during the adsorption process. The measurement starts when the valve is opened. After 1 s the pressures between the cell and bulb volumes are equilibrated. A decrease of the pressure is then the result of the adsorption of water on the grains. Figure 1 shows a comparison of the pressures derived from the line intensities and Hitran parameters [22] with the pressures measured with a Baratron gauge. No significant difference between ortho and para populations could be observed during the adsorption process at pressures from 1.5 to 0.12 mbar. In conclusion, this method is definitely ineffective for enrichment of water isomers, and this is confirmed by the theoretical considerations that are now developed.

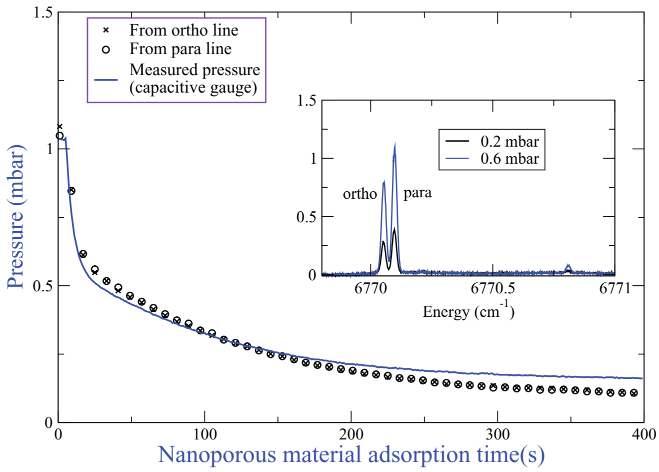

FIG. 1. (Color online) Adsorption of water on nanoporous material: an attempt to observe an enriched sample. Pressures are derived respectively from the capacitive gauge (plain line) and from the intensities of the ortho (crosses) and the para (circles) transitions. No enrichment is visible.

III. QUANTUM RELAXATION MODEL

The QRM was first described by Curl *et al.* [18]. It is based on both the molecules' properties and their environment. The former is the existence of pairs of accidentally quasidegenerate rovibrational levels of different spin symmetries. They play the role of gates if they interact through an intramolecular magnetic interaction able to flip one spin. The latter is revealed by inelastic collisions whose action is to change the energy of the molecules. Let us suppose an ortho molecule reaches 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 combinations of 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 into 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 [11].

It is shown that the relaxation of 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 populations 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 performed [7,21,23].

These parameters are collected to derive the nuclear spin conversion rate according to the QRM model and the contributions of the different ortho-para pairs.

A. Intramolecular magnetic interactions

Flipping one spin requires a sufficiently intense gradient of magnetic field at the molecular scale. Intramolecular spin-spin and spin-rotation interactions are *a priori* the most efficient in a dilute phase. The spin-spin (dipole-dipole magnetic) interaction between two particles is generally written as

$$\hat{V}_{12} = P_{12} \sum_{i,j} \hat{I}_i^{(1)} \hat{I}_j^{(2)} T_{ij}^{(1,2)},$$
$$P_{12} = \frac{\mu_0}{4\pi} \frac{\mu_1 \mu_2}{r_{12}^3 I^{(1)} I^{(2)}}, \qquad (3)$$
$$T_{ij}^{(1,2)} = \delta_{ij} - 3 n_i n_j, \quad i,j = x,y,z,$$

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 and μ_2 are the nuclear magnetic moments, and $\hat{\mathbf{I}}^{(1)}$ and $\hat{\mathbf{I}}^{(2)}$ are the spins of the particles. $\hat{V}_{12}$ is a scalar constructed from the product of two symmetric tensors of rank 2 acting on the spatial coordinates and spin variables, respectively. The second-rank tensor $\hat{\mathbf{I}}^{(1)}\hat{\mathbf{I}}^{(2)}$ can be decomposed into the sum of spherical tensors of the zeroth and second orders. Symmetry considerations [12,24] imply that none of these operators can mix the ortho and para H_2O states whose total proton spins are 1 and 0, respectively.

The spin-rotation interaction finds its origin in the coupling of the nuclear spin $\hat{\mathbf{I}}^{(i)}$ of the ith hydrogen atom with the angular momentum of the nuclear and electronic charges in motion. The Hamiltonian is

$$\hat{V}_{\mathrm{SR}} = \sum_i \hat{V}_{\mathrm{SR}}^{(i)} = \frac{1}{2}\left(\sum_i \hat{\mathbf{I}}^{(i)} \cdot \mathbf{C}^{(i)} \cdot \hat{\mathbf{J}} + \mathrm{H.c.}\right), \quad i = 1,2, \qquad (4)$$

where $\mathbf{C}^{(i)}$ is the second-rank spin-rotation tensor for the hydrogen atom i.

The wave functions and matrix elements have been described by Chapovsky for H_2CO [24]. Briefly, the rotational wave functions are written as

$$|J,K_a,K_c\rangle = \sum_K A_K |\{J,K\}\rangle, \qquad (5)$$

where $|\{J,K\}\rangle$ $(0 \leqslant K \leqslant J)$ are defined by the symmetric and antisymmetric combinations of the functions of the symmetric-top molecule $|J,K\rangle$ and $|J,-K\rangle$.

Thus the diagonalization of the Hamiltonian is reduced to the diagonalization of four Wang independent submatrices, each of particular symmetry (A_1,A_2,B_1,B_2). This diagonalization has been performed using the rotational and centrifugal distortion parameters of water in its ground state derived by Matsushima *et al.* [25].

The sum over degenerate quantum numbers (the m and σ projection on the laboratory Z axis of the angular momentum and total spin of the two hydrogen atoms, respectively) associated with an ortho (para) pair ψ (ψ') is given by

$$\sum_{m,\,\sigma} |\langle\psi|V_{\mathrm{SR}}|\psi'\rangle|^2$$
$$= \frac{1}{4}(2J+1)(2J'+1)\left|\sum_{K>0,K'>0} A_K A'_{K'} \Phi(J,K|J',K') + \frac{1+(-1)^{J'+K_c}}{\sqrt{2}} A_1 A'_0 \Phi(J,1|J',0)\right|^2. \qquad (6)$$

The notation used in Eq. (6) refers to the calculation of matrix elements in the spherical-top basis:

$$\Phi(J,K|J',K')$$
$$= \sum_l \sqrt{2l+1}\, \mathcal{C}_q^{(l)} \begin{pmatrix} J' & l & J \\ -K' & q & K \end{pmatrix}$$
$$\times \left[y(J)(-1)^l \begin{Bmatrix} J' & J & l \\ 1 & 1 & J \end{Bmatrix} + y(J') \begin{Bmatrix} J & J' & l \\ 1 & 1 & J' \end{Bmatrix} \right]. \qquad (7)$$

The $\mathcal{C}_q^{(l)}$ coefficients in Eq. (7) are the spherical spin-rotation components. Veber *et al.* [20] gave only a rough estimation of them, limited to geometrical considerations and the nuclear contribution [26]. Such tensor components can be efficiently derived from *ab initio* Cartesian components $\mathcal{C}_{ab}$ and $\mathcal{C}_{ba}$ including electronic and nuclear contributions:

$$\mathcal{C}_{\pm 1}^{(2)} = \mp \tfrac{1}{2}(\mathcal{C}_{ab} + \mathcal{C}_{ba}), \quad \mathcal{C}_{\pm 1}^{(1)} = \tfrac{1}{2}(\mathcal{C}_{ab} - \mathcal{C}_{ba}). \qquad (8)$$

The *ab initio* Cartesian tensor has been computed by Miani and Tennyson [19], and more recently by Cazzoli *et al.* [27]. The former authors computed at the Hartree-Fock (HF) and multiconfigurational self-consistent field (MCSCF) level of theory using the program DALTON [28], at the experimental geometry of water. The more recent calculation was performed at the coupled-cluster singles and doubles (CCSD) level augmented by a perturbative treatment of triple excitations [CCSD(T)], using the CFOUR program package [29]. The authors used the experimental equilibrium geometry derived by Bak *et al.* [30]. They also showed the importance of including vibrational corrections for quantitative predictions. For these reasons the values $\mathcal{C}_{ab} = 49.31$ kHz and $\mathcal{C}_{ba} = 21.13$ kHz, leading to $\mathcal{C}_{\pm 1}^{1} = 14.09$ kHz and $\mathcal{C}_{\pm 1}^{2} = \mp 35.22$ kHz are used. Note that the total contribution is one order of magnitude greater than Veber *et al.*'s values, where only nuclear terms were considered.

B. Energy difference between ortho and para states and Boltzmann factors

Experimentally derived energy levels of the ground state listed up to $J = 35$ provided by the TAMPA database [31] are used in the calculation. These energies are used for the determination of the energy differences between resonant ortho-para pairs and the Boltzmann factors. For the latter, a complete calculation of the nuclear spin conversion requires consideration of the vibrationally excited states, according to their relative population. This contribution is generally weak and can be evaluated by using the partition function, which is equal to 1.0004 at ambient temperature.

C. Selection rules

The energy levels are labeled with the J, K_a, and K_c quantum numbers, where K_a and K_c refer to the projection of the angular momentum J along the a and c inertial principal axes of the H_2O molecule, whose symmetry axis is labeled b. The ortho or para character of the rotational levels is given by $(-1)^{K_a+K_c}$ [32]. As mentioned in the Introduction, the total wave function must be antisymmetric with regard to proton exchange. The molecule is considered in its symmetric electronic and vibrational ground states. Consequently, para

H_2O nuclear spin wave functions can be mixed with rotational wave functions having even values of the sum $K_a + K_c$. In the same way, ortho H_2O nuclear spin wave functions exist only with rotational states with odd values of this sum. Because of the ortho-para character of interacting pairs, a first selection rule holds in opposite parities of $K_a + K_c$.

The c symmetry axis is perpendicular to the molecular planar frame. As the rotation about this axis is invariant, K_c for both interacting states must be of the same parity.

The last constraint is derived from the definition of the spin-rotation matrix elements: $\Delta J = 0, \pm 1$ and $\Delta K = \pm 1$, K being defined in Eq. (5).

D. Relaxation rates

Magnetic interactions create a coherence between ortho and para states, which is destroyed by collisions at a rate Γ_{op} [see Eq. (2)], whose value is usually unknown. Collisions act similarly to break the coherence created by a radiation field between two levels, inducing pressure broadening of molecular transitions. Thus, by analogy, as previously shown [17], collisional broadening measurements can be regarded as a quantitative estimation of Γ_{op}.

Veber *et al.* used a constant value equal to $\Gamma = 1 \times 10^8\ \mathrm{s}^{-1}$/Torr. As a consequence of the selection rules given in Sec. III C, the main pairs of interactive levels are for J values between 7 and 17. A graph of the self-broadening coefficients given in the HITRAN database [22] versus J exhibits a rapid variation as J increases, for $J > 10$. Such a J dependence has been analyzed by Trappeniers and Elenbaas-Bunschotten for CH_3F [33]. A least-squares fit valid up to $J = 30$ gives $\Gamma(J) = 2.478 \times 10^8 \times (1.0 \times 10^{-5}\ J^2 + 0.4548) \times e^{-0.00397 J^2}$, expressed in s^{-1}/Torr.

When the temperature dependence of the nuclear spin conversion rate is calculated, the temperature dependence of the relaxation rates is taken into account. The effective power-law model given by Birnbaum is used with a one-term intermolecular potential [34]:

$$\Gamma(T) = \Gamma(T_0)\left(\frac{T_0}{T}\right)^n. \tag{9}$$

In this model T_0 is the ambient temperature and n is the temperature exponent, equal to 1 if dipole-dipole interactions are considered. This model is consistent at first order for temperatures higher than 200 K.

IV. RESULTS

As the first result, the calculation made at room temperature for pressure from 0 to 200 Torr is presented on Fig. 2. All the possible pairs (about 15 000) have been considered in the calculation. Nevertheless it should be noted that the quasidegenerate pairs $J, K_a = 0$ and $K_a = 1, K_c = J$ dominate the result. Figure 2 shows that the pressure dependence is not linear at low pressure ($\Gamma_{op}^2 \ll \omega_{op}^2$) as observed for CH_3F [6] and H_2CO [10]. This is explained by the fact that for these two molecules the rates are essentially given by the contribution of one or two specific pairs which represents 99% of the nuclear spin conversion of the state, whatever the pressure range is. For water the most efficient pairs change with the pressure regime: below 5 Torr, the pair $(J_o K_{a,o} K_{c,o},\ J_p K_{a,p} K_{c,p}) =$ (16 1 16, 16 0 16) is predominant due to the quasidegeneracy (<1 MHz) of levels; above this value the contribution is spread over different pairs with decreasing J values as pointed out in Table I. This leads to the variation shown as a broken curve in the inset of Fig. 2. Above 200 Torr, the regime is such that $\Gamma_{op}^2 \gg \omega_{op}^2$, and the conversion is inversely proportional to Γ_{op} [see Eq. (2)] and thus to pressure. Thus the curve is to be extrapolated to a value of the conversion rate at atmospheric pressure of about 0.39 s^{-1}. The explanation of such behavior has been given by Nagels *et al.* as an inhibition, or quantum Zeno effect, of the conversion by collisions [35]. Because the saturated pressure of water is 28 hPa (21 Torr) at 296 K (see Fig. 2), it is not possible to think about experiments with pure gaseous water at higher pressure. The only possibility is to add a buffer gas to increase the pressure and thus the number of collisions.

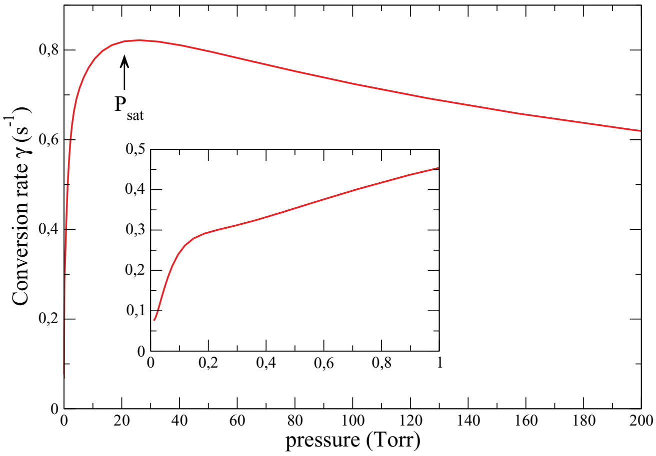

FIG. 2. (Color online) Nuclear spin conversion of water at room temperature.

Within this model, the variation of the nuclear spin conversion rate with the temperature can be calculated. In addition to Γ_{op} [see Eq. (9)], the partition function also changes with the temperature, and the Boltzmann factors W_o and W_p have to be recalculated. The role of low energy levels is emphasized as the temperature decreases. For a gas-phase situation, the saturated pressure rapidly decreases with decreasing temperature, the value at 200 K being less than 3 mTorr. Figure 3 represents the temperature dependence of the saturated pressure in the range 190 to 296 K and the value of the nuclear spin conversion rate for that specific pressure. These curves show that gas-phase experiments at low temperature require high sensitivity and a stable setup. A way to accelerate the conversion would be again to add a foreign gas as mentioned above.

Finally, calculation of the conversion rate at lower temperature can be considered in the general situation where relaxation is enabled by the interaction with the molecular environment. In such cases Γ_{op} is no longer linked to the water pressure but has to be regarded as a variable parameter given by the environment. Rare-gas matrix experiments are given as an example in the following section. We just note that the dependence of γ is linear with Γ_{op} at very low temperature.

TABLE I. Nuclear spin conversion rate at $T = 296$ K. The table gives for selected pressures the main contributions in % of each ortho or para pair. For each pressure P, the maximum contribution to the total rate is emphasized by emboldened numbers.

Pairs		P (Torr)				
(ortho, para)	ω_{op} (MHz)	0.1	0.5	5	20	200
(6 1 6, 6 0 6)	16 672					3.80
(7 0 7, 7 1 7)	−7068.1			0.32	1.11	12.49
(8 1 8, 8 0 8)	2970.7	0.06	0.21	1.06	3.64	25.50
(9 0 9, 9 1 9)	−1247.9	0.18	0.61	3.06	10.14	**25.54**
(10 1 10, 10 0 10)	533.1	0.44	1.50	7.43	21.49	15.55
(11 0 11, 11 1 11)	−227.1	0.95	3.30	15.55	**28.75**	7.57
(12 1 12, 12 0 12)	100.8	1.72	5.92	23.57	19.87	3.25
(13 0 13, 13 1 13)	−33.9	4.81	16.34	**28.81**	9.21	1.26
(14 1 14, 14 0 14)	17.7	5.01	16.45	13.15	3.31	
(15 0 15, 15 1 15)	6.3	9.99	25.91	4.84	1.07	
(16 1 16, 16 0 16)	0.9	**74.19**	**27.25**	1.46	0.32	
(17 0 17, 17 1 17)	4.8	0.82	2.11	0.38		
Total (%)		98.17	99.61	99.65	98.92	94.95
γ (s^{-1})		0.2447	0.3538	0.7072	0.8183	0.6195

V. DISCUSSION

This section is focused on the analysis of the possibility of experimental enrichment of one particular water isomer population, on the explanation of some results obtained in rare-gas matrices, and finally on some proposals about nuclear spin conversion in the ISM.

A. Possibility of enrichment in the gas phase

In Sec. II the failure of water enrichment via the adsorption mechanism was described. Either the adsorption is not sufficiently spin selective, or conversely a fast spin conversion occurs due to the possible magnetic influence of the surface. Whatever the explanation is, the huge enrichment announced by Tikhonov and Volkov [14] seems to be affected by some experimental artefacts. Veber *et al.* arrived at the same conclusion, with however an underestimation of the conversion rate by four orders of magnitude as calculated at room temperature and with a gas pressure of 760 Torr [20]. The reasons for this underestimation are that (i) their spin-rotation constants are one order of magnitude smaller than those used for the present work, (ii) their assigned pairs giving the largest contributions are at lower J values, and (iii) the levels with energies up to 2000 cm^{-1} only were taken into account, whereas many important pairs are at higher energies. At ambient temperature, conversion times are of the order of 1 s and is likely shorter in the condensed phase due to additional intermolecular interactions. This means that faster enrichment techniques have to be developed. Kravchuk *et al.* recently showed the possibility of spatial enrichment of a sample in ortho water [36]. A slow and cold molecular beam of water diluted in a carrier gas of krypton can be magnetically focused when it passes through a hexapole magnetic field. Such a setup is spin selective, and only ortho ($I = 1$) molecules are focused, whereas the trajectory of para molecules diverges. A small aperture cuts the beam, which becomes enriched in ortho molecules. Because of the short time of flight (about 5 ms) after the magnet and the highly diluted sample, we can conclude from our results that no conversion occurs. The authors of Ref. [36] propose several applications like NMR experiments, with the proviso that they are realistic only if the lifetime of spin polarization of water is long enough. According to our calculations, this may be achieved when the experiment is conducted with a sample at low temperature. In the gas phase, a high sensitivity of detection is required since the vapour pressure is low. The discussion now deals with the condensed phase.

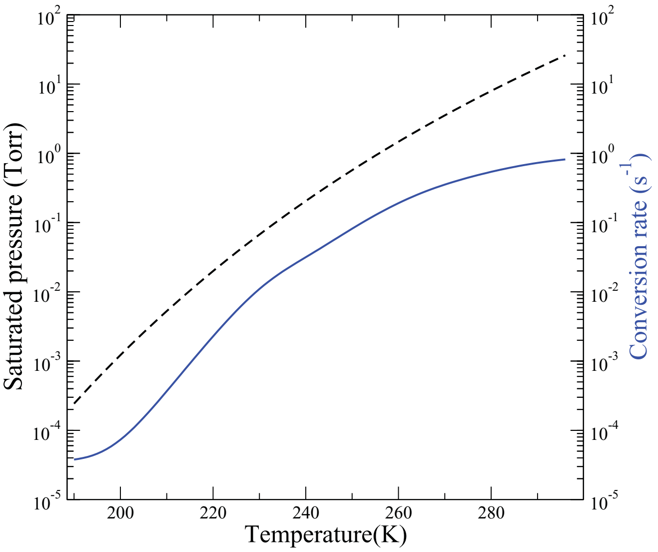

FIG. 3. (Color online) Temperature dependence of nuclear spin conversion of water in the gas phase: the dotted line corresponds to saturated pressure, and the full line to the corresponding NSC rate (see text).

B. Low-temperature matrices

Up to now, NSC in water molecules has been observed in cryomatrices only. Experiments have been performed at low temperatures in the range 4–20 K for different concentrations of water in rare-gas matrices [37,38] or in solid parahydrogen

TABLE II. Decoherence Γ_{op} parameters derived from experimental conversion rates within the quantum relaxation model and compared to IR self-broadening coefficients Γ_{sb}.

Matrix	γ (s^{-1})	Γ_{op} (cm^{-1})	Γ_{sb} (cm^{-1})
Ar (4.2 K)	2.56×10^{-5} [37,38]	0.04	0.46[a]–0.75[b] [40]
Ne (4.2 K)	1.67×10^{-4} [37]	0.26	0.88[a]–1.59[b] [40]
Kr (4.2 K)	3.33×10^{-5} [37]	0.05	0.78[a]–0.63[b] [40]
Xe (4.2 K)	1.67×10^{-4} [37]	0.26	1.56[a]–2.40[b] [40]
Para H_2 (2.4 K)	5.23×10^{-4} [39]	0.81	1.60[b] [39]

[a] From ortho $1_{1,0} \longleftarrow 1_{0,1}$ IR transition.

[b] From para $1_{1,1} \longleftarrow 0_{0,0}$ IR transition.

at 2.4 K [39], γ varying from 1.5×10^{-4} to 2.5×10^{-5} s^{-1} depending on the matrix and more specifically on the lattice parameter.

As suggested in Ref. [37], the quantum relaxation model, which has been validated for the gas phase, could also be used for highly diluted matrices, with the two following differences. The first one is the hindering of the molecular rotation in the cage of the matrix, leading to a narrowing of the gap ω_{op} between interacting levels of the order of 13%, whatever the matrix is. The second is the nature of the interaction with the environment, which might be revealed by the decoherence parameter Γ_{op}. As already mentioned, this parameter is analogous to the broadening coefficient observed in the gas-phase rovibrational spectra [17]. In a matrix, interactions with the cage and phonon exchanges have to be considered. Table II gives the Γ_{op} parameters derived using experimental conversion rates within the framework of the QRM. The density of phonons strongly depends on the matrix temperature. So, to be close to low interaction rates like those in the gas phase and because of available NSC rates, calculations have been performed at 4 and 2.4 K for rare-gas and solid-hydrogen matrices, respectively. For such a range of temperatures, NSC is supposed to be mainly gouverned by intramolecular interactions and the only significant pairs are (101,111) and (110,000). The sum of the Boltzmann factors appearing in Eq. (2), $W_p + W_o$, is one order of magnitude larger for the first pair, whereas $|V_{op}|^2$ is one order of magnitude larger for the second pair. But the product of both terms is the same since their difference is only about 2.5%. The main (>90%) contribution to the total rate comes from the first pair since the levels are separated by about 13 cm^{-1}, whereas the separation is 40 cm^{-1} for the second pair. So the conversion can be regarded as entirely due to the first pair (101,111).

The last column of Table II gives self-broadening [full width at half maximum (FWHM)] coefficients Γ_{sb} derived from some ν_2 infrared lines of H_2O in annealed matrices [39,41]. There is only one order of magnitude difference between the two Γ values, except for the para H_2 case, showing that the QRM could be useful in predicting the order of magnitude of NSC rates in matrices. It is necessary to recall that the use of Γ_{sb} instead of Γ_{op} comes from the facts that no value exists for the latter, and that there is an analogy between both environment-induced decoherence processes. In the gas phase, the collision impact approximation assumes that (i) the perturbers are statistically independent and only binary collisions between a perturber and the active molecule are important; (ii) the time during collision is short compared to the time between collisions. The larger value of Γ_{sb} obtained for the matrix environment suggests that long-distance effects exist and that the interaction time between the water molecule and the cage is longer, for instance through rotation-translation coupling. This is obviously due to the permanent position of the molecule on a substitution site in the matrix. This could also explain the much smaller difference between the Γ's for the para H_2 matrix since it is known that the molecule rotates almost freely in the cage, i.e., the interaction is weak. These arguments are supported by the result obtained by Fry *et al.*, who observed the pure rotational far-infrared $1_{1,1} \longleftarrow 0_{0,0}$ transition of water embedded in an argon matrix [41]. The Γ_{sb} is 0.31 cm^{-1}, which is close to that of the IR lines.

C. Astrophysics

Figures 2 and 3 show that, as expected, there is no chance that NSC occurs in the gas phase. But, in comets and in the ISM, icy grains or dust surfaces might be active. The major difficulty is to understand what occurs in these solids whereas information can be obtained only from gas-phase studies. Buntkowsky *et al.* [42] and Konyukhov [43] independently proposed a reactionless mechanism of conversion inside an icy nucleus. It requires an intermolecular interaction within two water neighbors and an intramolecular magnetic dipolar interaction in one partner of this water dimer. Since the molecule is in the solid phase, this latter interaction is supposed to be rotation independent, and the energy difference between ortho and para states is very small. In addition to the work mentioned above [38], recent experiments may confirm this model. It has been recently shown that NSC occurs within intermediate clusters formed in molecular beams [44]. This validates the idea that a water monomer cannot change its total spin when alone; it is necessary to have partners, at least one other molecule as given in the above-mentioned model. However, it must be noted that the experiment is not a proof of the model since a reactive process might also be an explanation of the conversion. Sliter *et al.* [38] showed that conversion in water clusters observed in an argon matrix occurs within a few minutes at the temperature of comets (about 30 K), leading to the conclusion that all molecules in ISM ice are converted.

Molecules, when leaving an ice or dust surface, are sensitive to the electric and magnetic fields produced by this surface. The strength of these fields changes with the distance to the surface. This creates level crossings between ortho and para states and thus an enhancement of the conversion. Such behavior has been shown with CH_3F under a Stark electric field [7]. The mechanism described by Buntkowsky *et al.* [42] also depends on the speed with which the efficient zone above the surface is crossed. Hama *et al.* presented an experiment dealing with the desorption of H_2O molecules from amorphous solid ice [45]. Ice samples were prepared with different methods at 8 K, but heated up at 150 K in the same way at a rate of 4 K/min. The spin temperatures derived from Resonant Enhanced Multi-Photon Ionization (REMPI) spectra of desorbed H_2O were different from the sample temperatures. From their experimental results, the authors were not able to determine whether NSC occurs in the solid phase or not. They suggest other desorption methods like vacuum-ultraviolet photodesorption [46]. Sliter *et al.* tried to observe a splitting of the dimer line into two components of equal intensities and separated by 7.5 cm^{-1} [38]. One line corresponds to para-para and ortho-para dimers, and the other line to the ortho-ortho dimer. Such a doublet has been assigned in an environment of He droplets [47]. Only the first component has been observed in an argon matrix, suggesting a fast conversion of the ortho-ortho dimer on the scale of a few minutes. As such doublets are observed in He droplets and could possibly be detected in solid parahydrogen, a first step would be to desorb the dimers and analyze whether their respective line intensities are conserved. This would give information about eventual surface-induced conversion. A further step would be the breaking of the dimer and a check of the OPR of the monomers.

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