# ^{1}H Nuclear Spin Relaxation of Liquid Water from Molecular Dynamics Simulations

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ABSTRACT: We have investigated the nuclear spin relaxation properties of ^{1}H in liquid water with the help of molecular dynamics simulations. We have computed the ^{1}H nuclear spin relaxation times T_1 and T_2 and determined the contribution of the different interactions to the relaxation at different temperatures and for different classical water models (SPC/E, TIP3P, TIP4P, and TIP4P/2005). Among the water models considered, the TIP4P/2005 model exhibits the best agreement with the experiment. The same analysis was performed with Car−Parrinello ab initio molecular dynamics simulations of bulk water at T = 330 K, which provided results close to the experimental values at room temperature. To complete the study, we have successfully accounted for the temperature-dependence of T_1 and T_2 in terms of a simplified model, which considers the reorientation in finite angle jumps and the diffusive translation of water molecules.
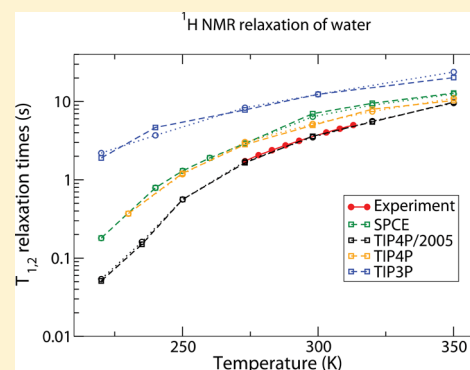
INTRODUCTION

Understanding the relaxation of the nuclear spin in fluids is of fundamental interest and related to important applications such as nuclear magnetic resonance (NMR). The chemical shift spectra and the nuclear spin relaxation times obtained from NMR experiments are among the most reliable quantities to determine the molecular structure and chemical properties of a given substance. In addition, nuclear spin relaxation phenomena can provide valuable information on the molecular dynamics of liquids.[1] Notably, the H nuclear spin relaxation times T_1 and T_2 can be used to obtain information on the molecular dynamics of liquid water in bulk,[2] but also at the interface with biomolecules such as proteins,[3,4] biological membranes,[5] or DNA.[6] The dynamics of the water at interfaces is thought to be influential in processes of paramount importance in biology and materials science such as the hydrophobic interaction between nonpolar solutes in water,[7,8] protein folding,[3] the formation of the enzyme−substrate binding,[9] or ion transport in ionic solutions.[8]

The relaxation of the nuclear spin in fluids is determined by the existence of rapid molecular motions of large amplitude and random character. These include rotational motions of individual and groups of molecules, relative translational motion of molecules, and in rare cases, migrations of atoms from one molecule to another. The longitudinal, T_1, and transverse, T_2, nuclear spin relaxation times of a molecular fluid are determined by dipolar, quadrupolar, and spin-rotation interactions, which fluctuate as a result of the relative motion of the interacting nuclear spins.[1] For the hydrogen atoms of water, the dominant interaction responsible for the nuclear spin relaxation is the magnetic dipolar coupling with the nuclear spin of neighboring hydrogen atoms, both belonging to the same molecule (intramolecular contribution) and belonging to other water molecules (intermolecular contribution). Indeed, the quadrupole interaction with the electronic electric field is nonexistent (only nuclear spins $I \geq 1$ have a quadrupolar interaction with electric gradients), and the spin-rotation contribution to the nuclear spin relaxation can be neglected because of its small magnitude at temperatures below 373 K.[10]

Since the distance between the hydrogen atoms of a water molecule is effectively constant, the time-dependence of their dipole−dipole interactions, and hence the intramolecular contribution to the ^{1}H nuclear spin relaxation, is only due to the rotational motion of the molecules. In contrast, the time-dependence of the relative position of two H nuclei in different water molecules, which determines the intermolecular contribution to the ^{1}H nuclear spin relaxation, depends both on the translational relative motion of the molecules and on their rotational motion. Consequently, the ^{1}H nuclear spin relaxation times in water are only partially related to water rotation.[11−13] In contrast, in the isotope-enriched water $H_2^{17}O$ and D_2O, the nuclear spin of nuclides ^{17}O and ^2H relax through the interaction of the nuclear electric quadrupole with the intramolecular electric field gradient, providing direct information on the rotational motion of individual water molecules[12,13] and, in particular, a direct relation with the second-order

rotational relaxation time (often represented by the symbol τ_2), which can easily be calculated from molecular dynamics simulations.[8,13]

Therefore, the key ingredient needed for an accurate description of the nuclear spin relaxation of ^{1}H in liquid water is a way to faithfully describe the rapid random rotational and translational motions that water molecules undergo due to collisions with other particles. Traditionally, different hypotheses on the nature of such stochastic motions were made to simplify the problem. The most extended treatment assumes that the intramolecular contribution to the nuclear spin relaxation is determined by the rotational motion of molecules, and the intermolecular contribution is given solely by the relative translation of water molecules, on the assumption that nuclei can be considered to be at the centers of spherical molecules. This is an approximation for polyatomic molecules which has been shown to produce significant errors in certain cases.[11] In addition, this treatment assumes that both the molecular rotations and translations can be described by small step diffusive processes, which allows the analytical calculation of the nuclear spin relaxation times.[1] In recent years, D. Laage and J. T. Hynes,[14,15] supported by classical molecular dynamics (MD) simulations, have proposed an alternative model for the reorganization of the hydrogen-bond network based on the reorientation of water molecules by sudden large-amplitude angular steps, which contradicts the accepted paradigm.

An alternative method to account for the molecular dynamics of liquid water is the use of MD simulations. In MD simulations, the interactions among atoms can be computed either from first-principles' calculations (ab initio MD simulations) or employing phenomenological force fields (classical MD simulations). In particular, for classical MD simulations of liquid water, several models have been developed which, in certain ranges of the thermodynamical variables of the system, reproduce with good accuracy both the structural and dynamical properties of bulk water.[16] In addition, in recent years the increase in computer power, the development of new algorithms, and the refinement of force fields have permitted extensive classical MD simulation studies of the properties of hydration water at the interface with large biomolecules[17] and inorganic materials such as graphene,[18] silica,[19] and in the interior of carbon nanotubes[20] to mention just a few examples.

The difficulty of accounting for the polarizability of atoms, the dependence of the analysis on the specific parametrization of the force field employed or the impossibility of treating charge transfer or dissociation processes hinders the predictive power of classical MD simulations. To avoid those limitations, a great effort has been done in the description of liquid water with DFT-based ab initio MD (AIMD) simulation techniques.[21−25] However, the current DFT-based description of liquid water still suffers from important discrepancies with the experiment, mostly due to the difficulty of describing van der Waals interactions.[25]

In ref 13, Qvist et al. used classical MD simulations to understand the NMR relaxation data of nuclides 17O and ^{2}H (in $H_2^{17}O$ and of D_2O, respectively), where the relaxation occurs due to the interaction of the nuclear electric quadrupole with the intramolecular electric field gradient. However, to the best of our knowledge, no systematic investigation exists in which the ^{1}H nuclear spin relaxation properties of water are computed directly from MD simulations. In this article, we perform a comparative study of the nuclear spin relaxation properties of ^{1}H in bulk water at different temperatures, as obtained with the help of classical MD simulations and different water models: SPC/E, TIP3P, TIP4P, and TIP4P/2005. To complete the study, we also investigate the nuclear spin relaxation of ^{1}H in bulk water at room temperature as described by Car−Parrinello ab initio MD simulations. In all cases, we compute the relaxation times T_1 and T_2 taking into account the full molecular dynamics of the modeled water molecules, considering all contributions to the spin relaxation. The relevance of the different contributions to T_1 and T_2 is evaluated a posteriori and its temperature-dependence investigated. The rest of the article is organized as follows. In Theoretical Background, we review the main theoretical results for the nuclear spin relaxation times T_1 and T_2 of water. In Computational Methods, we describe the computational details of the simulations, both classical (Classical MD Simulations) and from first-principles (Ab Initio MD Simulations). In Results, we provide the results obtained from classical and from ab initio simulations. To gain further insight, in Modeling, we present a simplified model of water dynamics which accounts for the obtained results.

■ THEORETICAL BACKGROUND

The theoretical description of the nuclear spin relaxation in fluids adopted in the present study is based on the semiclassical approach introduced by Bloembergen, Purcell, and Pound[1,26] in which the motion of the molecules is treated classically, whereas the nuclear spin is described quantum-mechanically. The nuclear spin of hydrogen is $I = 1/2$, which inhibits the quadrupolar interaction of the nuclear spin with electric field gradients.[1] In addition, the spin-rotation contribution to the nuclear spin relaxation of the hydrogens of liquid water can be neglected due to its small magnitude at temperatures below 373 K.[10] Therefore, the nuclear spin relaxation of the hydrogens of liquid water is dominated by the dipole−dipole interaction.

The dipole−dipole interaction between two spins I and S can be conveniently expressed in terms of second-rank irreducible spherical tensor spin operators $\hat{T}_{2,q}$

$$\mathcal{H}_{\text{dip}} = \sum_{q=-2}^{2} F_q(r, \theta, \phi)\hat{T}_{2,q} \tag{1}$$

with

$$\hat{T}_{2,0} = -\frac{3\gamma_H^2\hbar}{2}\left\{-\frac{2}{3}\hat{I}_z\hat{S}_z + \frac{1}{6}(\hat{I}_+\hat{S}_- + \hat{I}_-\hat{S}_+)\right\}$$

$$\hat{T}_{2,1} = -\frac{3\gamma_H^2\hbar}{2}\{\hat{I}_z\hat{S}_+ + \hat{I}_+\hat{S}_z\}$$

$$\hat{T}_{2,2} = -\frac{3\gamma_H^2\hbar}{4}\hat{I}_+\hat{S}_+, \tag{2}$$

and γ_H being the nuclear gyromagnetic ratio of hydrogen. Due to the stochastic motion of water molecules, $F_m(r, \theta, \phi)$ are random functions of the relative position of the two spins, expressed in terms of the spherical coordinates (r, θ, ϕ),

$$F_0(r, \theta, \phi) = \frac{1 - 3\cos^2\theta}{r^3}$$

$$F_1(r, \theta, \phi) = \frac{\sin\theta\,\cos\theta\,e^{-i\phi}}{r^3}$$

$$F_2(r, \theta, \phi) = \frac{\sin^2\theta\,e^{-2i\phi}}{r^3} \tag{3}$$

The spin operators $\hat{T}_{2,q}$, and the functions F_m satisfy $\hat{T}_{2,q} = \hat{T}^{\dagger}_{2,-q}$, $F_q = F^*_{-q}$.

From this decomposition, we can define the time correlation functions

$$G^{(q,q')}(\tau) = \langle F_q(t) F^*_{q'}(t + \tau) \rangle_T \tag{4}$$

where $\langle\ \rangle_T$ denotes ensemble average, and their corresponding spectral functions

$$J^{(q,q')}(\omega) = \int_{-\infty}^{\infty} G^{(q,q')}(\tau) e^{-i\omega\tau} \, d\tau \tag{5}$$

Within a semiclassical treatment of the problem, with the spin treated quantum-mechanically and the relative positions of spins treated classically, and assuming an isotropic random motion for the relative orientation of the two spins,[27] the following expression for the nuclear spin longitudinal relaxation time T_1 is obtained[1]

$$\frac{1}{T_1} = \frac{9}{8}\gamma_H^4 \hbar^2 [J^{(1,1)}(\omega_I) + J^{(2,2)}(2\omega_I)] \tag{6}$$

Here $\omega_I = \gamma_H B_0$ is the Larmor frequency, with B_0 being the external magnetic field applied. For liquid water in the range of temperatures considered in the present study, the characteristic time of decay of the correlation functions $G^{(q,q')}(t)$ satisfies $\tau_C \ll 1/\omega_I$. Consequently, $J^{(q,q')}(\omega) \approx J^{(q,q')}(0)$ and

$$\Gamma_1 \equiv \frac{1}{T_1} \approx \frac{9}{8}\gamma_H^4 \hbar^2 [J^{(1,1)}(0) + J^{(2,2)}(0)] \tag{7}$$

The nuclear spin transverse relaxation time T_2 is given by

$$\Gamma_2 \equiv \frac{1}{T_2} \approx \frac{9}{24}\gamma_H^4 \hbar^2 [J^{(0,0)}(0) + 10J^{(1,1)}(0) + J^{(2,2)}(0)] \tag{8}$$

We can use the trajectories of water molecules obtained from MD simulations to analyze the evolution of the relative distances and orientations between hydrogen atoms and compute the time correlation functions $G^{(q,q')}(\tau)$ defined in eq 4. From those, the relevant spectral functions $J^{(q,q')}(0)$ can be calculated and the relaxation times computed with the help of eqs 7 and 8.

COMPUTATIONAL METHODS

Classical MD Simulations. We considered four different classical water models, two three-site models, TIP3P and SPC/E, and two four-site ones, TIP4P and TIP4P/2005. For every water model, we prepared a cubic system with periodic boundary conditions of about 2000 molecules and performed an equilibration procedure prior to the production runs. The equilibration consists of a minimization calculation (of 2000 steps) followed by a 100 ps simulation run in the NPT ensemble at $p = 1$ atm. The production runs, of variable length depending on the temperature and water model (from 1 to 50 ns), were performed in the NVT ensemble. However, we made

sure (in some representative cases) that the results obtained were independent of the ensemble used (the same results were obtained for NVT, NVE, and NPT ensembles), as it should be.

Classical MD simulations were performed using the 2.8 version of NAMD[28] simulation packages running in parallel. The Newton equations of motion were solved with a time step of 1 fs, and electrostatic interactions were updated with a 4 fs time step. All bonds between heavy atoms and hydrogen atoms were maintained rigid during all the simulation. The non-bonding Lennard-Jones interactions were cutoff at a distance of 1.2 nm, employing a switching function starting at 1.0 nm. The Ewald summation method was employed with a grid size of 1 Å. Constant temperatures were maintained using a Langevin thermostat with a relaxation constant of 1 ps^{-1}, and constant pressure was attained employing a Nosé−Hoover piston. The simulations of the TIP4P/2005 model were also performed using the 4.05 version of GROMACS[29] simulation package with the simulation parameters specified in ref 30 to ensure robust results.

Ab Initio MD Simulations. AIMD simulations were performed using the Car−Parrinello (ref 31) scheme for propagating the wave functions and the ionic configurations as implemented in the CPMD package.[32] The electronic structure calculations were computed with the help of the BLYP density functional.[33,34] The cutoff for the wave function was set to 80 Ry, the time step was set to 4 au, and the fictitious mass for the orbital was chosen to be 400 a.m.u. A cubic simulation box containing 96 water molecules at the density of 0.997 g cm^3 was used. Periodic boundary conditions were applied.

We have employed dispersion-corrected atom-centered pseudopotentials (DCACPs) in the Troullier-Martins[35] format for oxygen and hydrogen. These pseudopotentials properly account for London dispersion forces, and it has been shown that simulations employing them faithfully reproduce many dynamical and structural properties of water.[36] The initial configuration of water molecules was obtained from classical MD simulations. As done by Lin et al.,[36] we applied an equilibration NVT run of 3 ps with the temperature set at 330 K prior to the production run of 15 ps in the microcanonical ensemble. The reference temperature was set to 330 K in order to avoid falling into the temperature range where BLYP simulations suffer for nonergodic behavior[37] on timescales shorter than 20 ps.

RESULTS

Results at Room Temperature. We computed nuclear spin relaxation times from the water trajectories of classical and ab initio MD simulations. Prior to such calculations, we verified the basic assumption, implicit in eqs 7 and 8, $G^{(q,q')}(\tau) = \delta_{q,q'} G^{(q,q)}(\tau)$. As shown in Figure 1, the crossed correlation functions $G^{(q,q')}(\tau)$ vanish, and only those with $q = q'$ contribute to the relaxation process.

In Table 1, we show the nuclear spin relaxation times T_1 and T_2 computed from classical MD simulations of liquid water at $T = 298$ K. We have considered four different water models, two three-site models (TIP3P and SPC/E) and two four-site models (TIP4P and TIP4P/2005). We also show the experimental value for the relaxation times at room temperature. In all four models, $T_1 \approx T_2$, as it should be expected for cases in which the characteristic decay time of the correlation functions is much smaller than the inverse of the Larmor frequency, $\tau_C \ll 1/\omega_I$ (see above). The values for the relaxation times computed from classical MD simulations' trajectories are
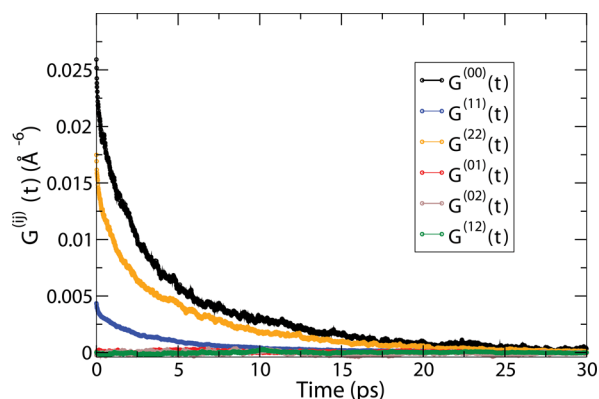
Figure 1. Example of a set of correlation functions for the TIP4P/2005 model at $T = 298$ K: $G^{(00)}(\tau)$ (black), $G^{(11)}(\tau)$ (blue), $G^{(22)}(\tau)$ (yellow), $G^{(01)}(\tau)$ (red), $G^{(02)}(\tau)$ (brown), and $G^{(12)}(\tau)$ (green). The crossed terms, $G^{(q,q')}(\tau)$ with $q \neq q'$, are zero.

Table 1. Nuclear Spin Relaxation Times T_1 and T_2 at Room Temperature Obtained from the Analysis of Water Trajectories of Classical and ab Initio MD Simulations[a]

	T_1 (s)	T_2 (s)	$\Gamma_1^{inter}/\Gamma_1$
TIP3P	12.4	12.4	0.38
SPC/E	7.0	6.9	0.42
TIP4P	5.0	5.2	0.35
TIP4P/2005	3.8	3.7	0.33
ab initio (330 K)	3.9	4.0	0.29
experiment (int.)	3.59	3.59	–

[a]We show the results obtained at $T = 298$ K for four different classical water models (TIP3P, SPC/E, TIP4P, and TIP4P/2005) and the result obtained from ab initio MD simulations at $T = 330$ K. For comparison, we also show the interpolation at $T = 298$ K of the experimental values reported in refs 39 and 40.

in the same order of magnitude as the experimental values for all models, although only the TIP4P/2005 model gives a quantitatively accurate result. Note that water models which exhibit faster dynamics, with faster decaying correlation functions and smaller spectral functions (see eqs 4−8), produce longer nuclear spin relaxation times T_1 and T_2. In particular, the TIP3P model, which is known to greatly overestimate water dynamics,[16,38] produce significantly higher T_1 and T_2 values than the other models and experiment. For the different water models, we have also studied the relative importance to the nuclear spin relaxation of the intramolecular and intermolecular interactions. In Table 1, we show the relative contribution to the relaxation rates arising from intermolecular interactions, $\Gamma_{inter}/\Gamma_{total}$ (the contribution corresponding to intramolecular interactions is $1 - \Gamma_{inter}/\Gamma_{total}$). As expected, the intramolecular contribution dominates.

To understand further the origin of the nuclear spin relaxation, we have investigated the weight of the contributions to the intermolecular relaxation rate from water molecules at different hydration layers. We have decomposed the intermolecular component of the nuclear spin relaxation into contributions from water molecules within the first hydration shell, second hydration shell, and the rest. The first and second hydration shells are defined by the positions of the first and second minima of the oxygen−oxygen pair correlation function, respectively. The results for the TIP4P/2005 model show (similarly to the other models) that most of the intermolecular relaxation, about 61%, is caused by the interaction with the

water molecules in the first hydration shell. The water molecules in the second hydration shell contribute 25% to the intermolecular relaxation rate and the rest of the water particles 14%. Although the distinction of the different contributions to the nuclear spin relaxation rate is experimentally inaccessible, this knowledge might help understand the ^{1}H nuclear spin relaxation of water under confinement, where the intermolecular term might be partially suppressed, or in the presence of ions, where some rotational degrees of freedom are eliminated.[41]

We have performed a similar analysis with the trajectory of liquid water obtained from the ab initio MD (AIMD) simulations at $T = 330$ K. In this case, the AIMD trajectory was not long enough for a complete decay of the correlation functions, and biexponential fitting functions were used to evaluate the corresponding spectral functions. In Table 1, the values obtained for the ^{1}H nuclear spin relaxation times T_1 and T_2 are given, along with the results from classical simulations and the experimental values. As shown in the table, the relaxation times computed from AIMD simulations at $T = 330$ K are close to the experimental values at room temperature but they are significantly lower than the experimental relaxation times obtained at comparable temperatures (see below). It is well-known that at ambient conditions, there are still serious discrepancies between the results of studies with DFT-based AIMD simulations of liquid water and experiments, regarding both diffusive and structural properties.[23,24,42,43] The cause of such discrepancies with the experimental values[44,45] is still unclear. Nevertheless, it was found that both the structural and dynamical properties of liquid water simulated at a temperature T with the help of AIMD simulations correspond to the properties found in the experiment at lower temperatures.[22] As it was done for the classical MD simulations, in the analysis of the ab initio simulations, we have decomposed the contributions to the relaxation rates originated from intramolecular and intermolecular interactions. As shown in the table, the contribution to the relaxation from intermolecular interactions is similar to the values obtained from classical MD simulations.

Dependence with Temperature. In Figure 2, we represent the temperature-dependence of the ^{1}H nuclear spin relaxation times T_1 and T_2 computed from classical MD simulations of liquid water, as well as the values measured in the experiment.[39] All four models give the correct general
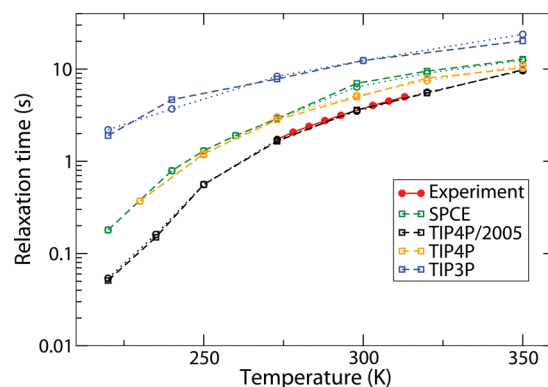

Figure 2. Temperature dependence of the nuclear spin relaxation times T_1 ($\square$) and T_2 ($\bigcirc$) computed from classical MD simulations with different water models: TIP3P (blue), SPC/E (green), TIP4P (yellow), TIP4P/2005 (black). Superimposed, the experimental results for the T_1 relaxation times are also represented (red $\bullet$).

dependence of the relaxation times with temperature, increasing as the temperature increases, although only the TIP4P/2005 model generates nuclear spin relaxation times comparable to the experiment. The SPC/E and TIP4P models give very similar values throughout the range of temperatures investigated, and they both follow the same tendencies (same slope) as the one followed by the TIP4P/2005 model. In contrast, using the TIP3P model not only results in values far from the experimental ones but also gives a much flatter dependence on temperature with respect to the experimental values and the results from the other water models. These results are in accordance with the general observation that, among the water models studied, the TIP4P/2005 model provides the best description of the dynamical properties of liquid water.[16]

For the different water models, we have also studied the temperature-dependence of the relative importance to the nuclear spin relaxation of the intramolecular and intermolecular interactions. In Figure 3, we show the relative contribution to
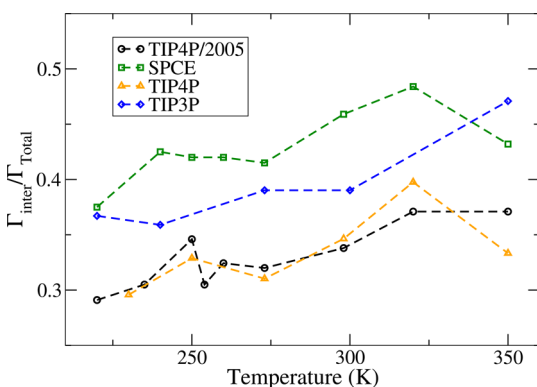

Figure 3. Relative contribution to the ^{1}H nuclear spin relaxation rates from intermolecular interactions, $\Gamma_{inter}/\Gamma_{total}$, as computed from MD simulations with different water models: TIP3P (blue), SPC/E (green), TIP4P (yellow), TIP4P/2005 (black).

the relaxation rates arising from intermolecular interactions, $\Gamma_{inter}/\Gamma_{total}$ (the contribution corresponding to intramolecular interactions is $1 - \Gamma_{inter}/\Gamma_{total}$). As expected,[1] the intramolecular contribution dominates throughout the whole temperature range, although for all the water models, we observe that the relative importance of intermolecular interactions increases with temperature.

Modeling. To rationalize the results obtained from MD simulations and to identify the dominant mechanisms inducing the ^{1}H nuclear spin relaxation, we have described in terms of simplified models the rotational and translational motions of TIP4P/2005 liquid water molecules and evaluated their contribution to the spin relaxation. We take the TIP4P/2005 water as a reference because it provides the most accurate account of the experimental results. The dipole−dipole interactions which induce the nuclear spin relaxation of protons in liquid water are mediated by translational and rotational motions of water molecules. Hence, we can decompose the relaxation rates $1/T_{1,2}$ into two contributions,

$$1/T_{1,2} = (1/T_{1,2})_{rot} + (1/T_{1,2})_{trans} \tag{9}$$

corresponding to the rotational and translational components, respectively.

Rotational Contribution. The contribution to ^{1}H nuclear spin relaxation of liquid water due to rotations can be decomposed into a contribution arising from the interaction with the other hydrogen nucleus in the same molecule (intramolecular) and a contribution from the interaction with the rest of hydrogen nuclei in the liquid (intermolecular). Due to the strong distance-dependence of the dipolar interaction, the intramolecular contribution is dominant and we can neglect the intermolecular part of the rotational contribution to the spin relaxation.

Although other simpler models of molecular reorientation exist, one which has recently been successfully employed to describe the reorientation mechanism of the water molecule is the model proposed by Ivanov.[14,46] The isotropic version to Ivanov's model of reorientation considers discrete rotations of finite angles and assumes that rotations through different axes are equally probable. The application of such model to the evolution of the orientation of the HH vector within a water molecule is justified by the jump mechanism of water reorientation described by Laage and Hynes in ref 14. In accordance with this picture, the hydrogen-bond network reorganizes by finite isotropic rotations of water molecules, which break a hydrogen bond with an overcoordinated fist-shell neighbor to form a hydrogen bond with an undercoordinated second-shell neighbor. Further refinements of the reorientation model, such as the one introduced to account for the slower reorientation of water molecules in between switching events, are beyond the precision of our description.

In accordance with Ivanov's model of reorientation, the conditional probability of a molecule reorienting from having Euler angles $\Omega_0 = (\phi_0, \theta_0, \gamma_0)$ at $t = 0$ to $\Omega = (\phi, \theta, \gamma)$ at time t is given by

$$P(\Omega, t|\Omega_0) = \sum_{l,m,n} \left(\frac{2l+1}{8\pi^2}\right) D_{mn}^{(l)*}(\Omega_0) D_{mn}^{(l)}(\Omega) \mathcal{F}^{(l)}(t) \tag{10}$$

where $D_{mn}^{(l)}(\Omega)$ are the Wigner D-matrices, $\mathcal{F}^{(l)}(t) = \exp\{-(1 - \lambda_l)/\tau_R\}$, and $\lambda_l = \sin[(l + 1/2)\theta_0]/((2l + 1)\sin[\theta_0/2])$. The model contains two parameters: the amplitude of the angular jumps (θ_0) (assumed always the same) and the time elapsed between subsequent reorientations (τ_R).

The correlation functions relevant to compute the intramolecular relaxation times are then given by

$$G^{(qq)}(\tau) = \frac{1}{4\pi} \iint d\Omega d\Omega_0 F^{(q)*}(\Omega_0) F^{(q)}(\Omega) P(\Omega, t|\Omega_0) \tag{11}$$

with $q = 0, 1, 2$ and $F^{(q)}$ given by eq 3. In eq 11, it is implicitly assumed that the HH vector of water molecules is initially oriented isotropically. By calculating the corresponding spectral functions and using eqs 7 and 8, we obtain for the relaxation times T_1 and T_2

$$\left(\frac{1}{T_1}\right)_{rot} = \left(\frac{1}{T_2}\right)_{rot} = \frac{3}{2}\frac{\gamma_H^4\hbar^2}{R^6}\frac{\tau_R}{1 - \frac{1}{5}\frac{\sin[5\theta_0/2]}{\sin[\theta_0/2]}} \tag{12}$$

Here, R is the distance between the hydrogen atoms within a water molecule. The parameters θ_0 and τ_R can be obtained from the analysis of the MD simulations trajectories of water by analyzing the dynamics of H-bond switches.[14] In Figure 4b, an example of the averaged time-evolution of the H-bond switching event (as described by the TIP4P/2005 model) is
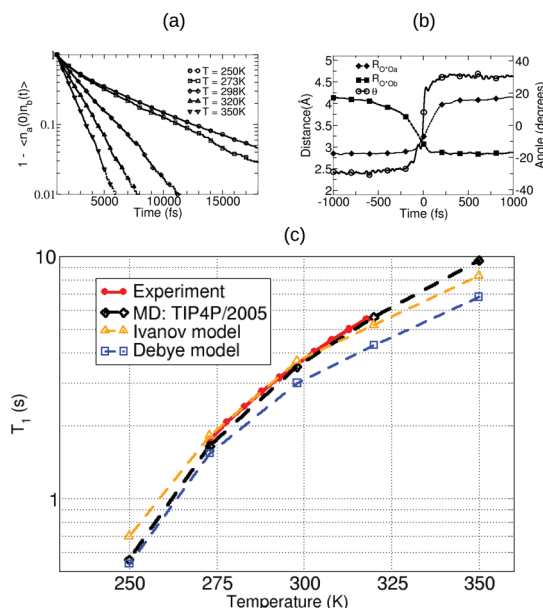
Figure 4. (a) H-bond correlation functions $[1 - \langle n_a(0)n_b(t)\rangle]$ for different temperatures. The slope of the logarithmic plot provides the characteristic time between subsequent reorientations, τ_R. (b) Example (at 298 K) of the ensemble-averaged time evolution of the reorientation process, in which the hydrogen atom ^{1}H switches from being H-bonded to the oxygen O_a to the oxygen O_b by a sudden angular jump θ_0. (c) ^{1}H-nuclear spin relaxation times from the modeling of water dynamics: (orange triangles) results for T_1 obtained by applying eqs 12 and 14 with the parameters extracted from the MD simulations' trajectories of TIP4P/2005 water, provided in Table 2; (blue □) results for T_1 obtained from assuming both diffusive water reorientations and translations (see text). Superimposed, we represent the results for T_1 given by direct analysis of the TIP4P/2005 MD trajectories (black ◇) and the experimental values (red ●).

represented. We can use such parameters to calculate, within Ivanov's reorientation model, the rotational contribution to the relaxation rates via eq 12.

Translational Contribution. Within a water molecule, the variation of the hydrogen−hydrogen distance due to vibrations can be neglected. Therefore, the contribution to the H-nuclear spin relaxation mediated by translations mainly arises from the mutual displacement of water molecules.

We assume that the mutual translation between water molecules can be described by a diffusion equation. Thus, the conditional probability for two molecules to be apart by **r** at time t if they were apart by $\mathbf{r}_0$ at time $t = 0$ is given by

$$P(\mathbf{r}, \mathbf{r}_0, t) = (8\pi Dt)^{-3/2} \exp\left\{-\frac{(\mathbf{r} - \mathbf{r}_0)^2}{8Dt}\right\} \quad (13)$$

From the conditional probability function, we can compute the time correlation functions associated with the functions $F^{(0)}$, $F^{(1)}$, and $F^{(2)}$, resulting from the decomposition of the dipolar interaction Hamiltonian (eq 3). Using eqs 7 and 8, the translational contribution to the nuclear spin relaxation times can be obtained

$$\left(\frac{1}{T_1}\right)_{\text{trans}} = \left(\frac{1}{T_2}\right)_{\text{trans}} = \frac{2\pi}{5} \frac{N\gamma_H^4\hbar^2}{dD} \quad (14)$$

where d is the effective diameter of the water molecule, D its translational diffusion coefficient, and N the density of water

molecules. These expressions are derived under the assumption that the diffusion characteristic time $\tau = d^2/D$ is much smaller than the period of Larmor precession, $\omega_I\tau \ll 1$

Results. We have used the decomposition of eq 9 to compute the nuclear spin relaxation times using eqs 12 and 14. The parameters of the model, the diffusion coefficient D, the amplitude of the angular jumps θ_0, and the time elapsed between subsequent reorientations τ_R, have been obtained from inspection of the MD simulations of TIP4P/2005 water. The effective diameter of the water molecule, d, and the distance between hydrogen atoms within a water molecule, R, are taken directly from the TIP4P/2005 water model.[16] In Figure 4b, we show an example of the ensemble-averaged time evolution of the reorientation process, in which the hydrogen atom H* (which forms a water molecule with the oxygen atom O* and hydrogen atom H′) switches from being H-bonded to the oxygen O_a to the oxygen O_b. Similar to the analysis done in ref 14, θ is defined by the angle formed by the projection of the H′H* vector on the O*$O_a O_b$ plane and the O_aO*O_b angle bisector. From the analysis of the averaged evolution of θ, we extract the amplitude of the angular jump (θ_0). The characteristic time elapsed between subsequent reorientations (τ_R) is obtained from the MD simulations by analyzing the hydrogen-bond correlation function $[1 - \langle n_a(0)n_b(t)\rangle]$, where n_i is 1 when ^{1}H is hydrogen bonded to O_i ($i = a$ and b) and 0 otherwise. In Figure 4a, we represent the evolution of the HB-correlation function for different temperatures. The diffusion coefficient has been obtained from the calculation of the mean square displacement of water molecules from the MD simulations' trajectories.

In Table 2, the three parameters D, θ_0, and τ_R extracted from the analysis of the MD simulations of TIP4P/2005 water are

Table 2. Parameters Characterizing the Water Dynamics Computed from the Analysis of the MD Trajectories of TIP4P/2005 Liquid Water

T (K)	D (10^{-5} cm^2/s)	τ_R (ps)	θ_0 (deg)
250	0.4	7.5	54
273	1.1	5.3	57
298	2.0	2.3	58
320	3.5	1.5	60
350	5.7	1.1	59

given for different temperatures. For each temperature, we employ eqs 12 and 14 with the parameters extracted from the simulations to compute the ^{1}H-nuclear spin relaxation time $1/T_{1,2} = (1/T_{1,2})_{\text{rot}} + (1/T_{1,2})_{\text{trans}}$. In Figure 4c, the results are represented along with the experimental results and the values calculated from the classical MD simulations of TIP4P/2005 water. As seen in the figure, the agreement between the results of the model (labeled "Ivanov model") and the experimental values is excellent for all the experimental range but slightly deviates from the results of the simulations of TIP4P/2005 water at high and low temperatures. This might indicate that in the central range of temperatures ($\approx$ 270−330 K), the dominant mechanisms for ^{1}H nuclear spin relaxation are given by the reorientation of water molecules and their mutual diffusive displacement, but other contributions might become significant outside this range (such as finite jump displacements, or the change in orientation of nearby water molecules.) We have also computed $T_{1,2}$ by assuming that the rotational contribution can be modeled as a diffusive process, as it has

been traditionally assumed.[1] As shown in Figure 4c, the results for $T_{1,2}$ of this model (labeled "Debye model"), despite following the general trend in the temperature dependence, significantly deviate from the results obtained directly from MD simulations of the TIP4P/2005 water model, especially at high temperatures.

CONCLUSIONS

Many of the unique properties of liquid water arise from the ability of water molecules to form a dynamical hydrogen bond network, which is constantly reorganizing. Therefore, it is of great interest to develop methods to relate experimentally accessible quantities with the underlying molecular dynamics of water. A measurable quantity which contains information on the dynamics of water is the ^{1}H nuclear spin relaxation time. For example, in ref 3, the ^{1}H nuclear spin relaxation time is used to identify different dynamical regimes of water hydrating lysozyme, which are related to the conformations of the protein. Although a general understanding of the ^{1}H nuclear spin relaxation properties of water exists in terms of simplified models of water dynamics, a quantitative study employing detailed MD simulations is lacking.

In this article, we have characterized the nuclear spin relaxation properties of ^{1}H in bulk liquid water with the help of classical and ab initio molecular dynamics simulations. With classical simulations, we have analyzed four different water models (two three-site models, TIP3P and SPC/E, and two four-site ones, TIP4P and TIP4P/2005) in a wide range of temperatures. The results for the ^{1}H nuclear spin relaxation times T_1 and T_2 compare qualitatively well with the experiment for all models, although only the TIP4P/2005 model gives a good quantitative account of the experimental values. This confirms the general conclusion that, among the water models studied, TIP4P/2005 accounts best for the dynamical properties of liquid water.[16] We have also quantified the intermolecular and intramolecular contributions to the relaxation, concluding that the intramolecular part is dominant ($\approx$70%), with its significance decreasing with increasing temperature. In addition, we have resolved the contributions of water molecules at different hydration layers to the intermolecular component of the relaxation rate, with $\approx$61% arising from the interaction with molecules in the first hydration shell, $\approx$25% with molecules in the second hydration shell, and $\approx$14% from the rest. In spite of being experimentally inaccessible, this knowledge can help understand the ^{1}H nuclear spin relaxation of water under confinement, where the intermolecular term might be partially suppressed, or in the presence of ions, where some rotational degrees of freedom are eliminated.[41] In addition, we have successfully accounted for the values and temperature-dependence of the ^{1}H nuclear spin relaxation times T_1 and T_2 in terms of a simplified model of water dynamics based on the reorientation in finite angle jumps and the diffusive translation of water molecules. We show that this model provides a more accurate account of the $T_{1,2}$ temperature dependence than a model with diffusive reorientation, especially in the experimentally accessible range.

We have conducted a similar analysis from the trajectories of Car–Parrinello ab initio MD simulations of bulk water at $T = 330$ K. The results obtained for the relaxation times T_1 and T_2 are close to the experimental values at room temperature but significantly lower than the experimental relaxation times obtained at comparable temperatures. Such discrepancy is similar to the ones observed in other studies on dynamical and structural properties of liquid water done with DFT-based AIMD simulations.[23,24,42,43]

With our study, we have established a reference calculation to investigate the ^{1}H nuclear spin relaxation properties of water in other, experimentally relevant, systems such as hydration water surrounding macrobiomolecules, ionic solutions, or water under confinement.

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Notes

The authors declare no competing financial interest.

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