Theoretical study of the H-NMR relaxation times in aqueous ionic solutions

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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 relaxation times (T_1 and T_2) obtained from NMR experiments are among the most reliable techniques to determine the molecular structure and chemical properties of a given substance.

In fluid samples, the relaxation properties of the nuclear spin are different from those observed in solids. This is due to the existence of rapid molecular motions of large amplitude and random character. These motions include rotational tumbling of individual and groups of molecules, relative translational motion of molecules and, in some cases, even migrations of atoms from one molecule to another. In molecular fluids, the relaxation time for the nuclear spin is determined by its interaction with other spins through dipolar and quadrupolar coupling and also by the sudden changes of the chemical shift local field due to mechanical rotations. In treating the relaxation of the nuclear spin of the protons of water, quadrupolar interacions are irrelevant, since they are only important for particles with spin $S \geq 1$, and the relaxation due to dipolar coupling is dominant. The relaxation due to dipolar coupling can be decomposed into two contributions: a dominant contribution, determined by molecular reorientation and caused by the interaction with the other hydrogen of the same molecule (intramolecular coupling), and another less important contribution caused by the interaction with hydrogens of other molecules (intermolecular coupling) which is mainly determined by the relative translations between molecules¹.

To compute the NMR relaxation times T_1 and T_2 in a fluid it is necessary to faithfully describe the rapid random motions that particles undergo due to collisions with other particles. Traditionally, assumptions on the nature of the Brownian motions were made to simplify the problem. The most extended treatment, due to Debye, assumes that both the rotations of a molecule and the relative translations of two molecules could be described by a diffusion equation. In that picture, the angular Brownian motion of the water molecules are given by very small regular angular steps. In recent years, however, a combination of theoretical and experimental breakthroughs has provided consistent evidence suggesting a dominant reorientation of water via a mechanism involving largeamplitude sudden angular jumps². Consequently, many of the interpretations of experiments and theoretical predictions based on Debye's picture, in particular those regarding the relaxation properties of nuclear spin of protons in water, need to be revised.

In the present work we have devised a way to calcu-

late the NMR relaxation times T_1 and T_2 for molecular fluids directly from the trajectories of MD simulations, with no assumptions made regarding the nature of the molecular motions. In particular, we have computed T_1 and T_2 for the nuclear spins of protons of bulk liquid water as described by different water models (TIP3P, TIP4P, and TIP4P/2005). Also, we have studied the dependence of such relaxation times on the concentration of different chaotropic and kosmotropic ions, reproducing the behaviour obtained in experiment: an increase (decrease) of the NMR relaxation times as the concentration of chaotropic (kosmotropic) ions is increased³. Furthermore, the mechanisms hypothesized in the literature responsible for such behaviour are quantitively analyzed. Under several simplifying assumptions, we have also obtained analytical results for the NMR relaxation times T_1 and T_2 based on Ivanov's model of water reorientation⁴ and compared them with the results obtained from the MD simulations' trajectories.



FIG. 1. The reorientation of water molecules occurs via large-amplitude sudden angular jumps. Such mechanism governs the time dependence of the different correlation functions which determine the H-NMR relaxation times.

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