

ON THE SINGLE-MOLECULE DYNAMICS OF WATER FROM PROTON, DEUTERIUM AND OXYGEN-17 NUCLEAR MAGNETIC RELAXATION

J.R.C. VAN DER MAAREL, D. LANKHORST, J. DE BLEIJSER and J.C. LEYTE

*Gorlaeus Laboratories, Department of Physical and Macromolecular Chemistry, University of Leyden,
P.O. Box 9502, 2300 RA Leyden, The Netherlands*

Received 5 September 1985; in final form 15 October 1985

Comparison of the nuclear relaxation rates of H, D and ^{17}O shows the isotropic motional model to be adequate for H_2O on the picosecond timescale.

1. Introduction

For several decades the single-molecule reorientational dynamics of water in the liquid state has been a topic of interest. Only a few years ago, an unambiguous value of the reorientational correlation time of the O—H vector was reported [1]. Quite recently Lang et al. have shown the isotropic motional model to be sufficient to predict the temperature and pressure dependence of the spin—spin relaxation times of supercooled water under high pressure [2]. From the observed frequency dependence of the D relaxation rate in water at temperatures near 195 K they concluded that the molecular motion was isotropic on a nanosecond timescale.

In liquid water at 298 K the correlation time shrinks to a few picoseconds and at available field strengths the nuclear relaxation rate is in the extreme-narrowing limit. Therefore, at this temperature, dispersion of the relaxation rate from which correlation times can be calculated is absent.

In the present contribution three relaxation paths in the water molecule are compared to obtain information on the molecular motion: ^{17}O (quadrupolar), D (quadrupolar) and H relaxation due to dipolar coupling with ^{17}O .

The H— ^{17}O dipolar interaction contribution to the H relaxation is a nearly intramolecularly determined process [1]. Both the D and ^{17}O nuclei relax by the quadrupolar interaction mechanism, which is com-

pletely intramolecularly determined. Because not all of the principal directions of the relevant interaction tensors coincide, the symmetry of the molecular motion may be investigated [3].

The ^1H — ^{17}O coupling constant is known from the experimentally determined O—H distance [4–6]. Therefore, τ_{OH} may be calculated from the corresponding rate. Now, τ_{OH} equals τ_{D} within experimental accuracy because the principal axes of the couplings coincide and the asymmetry parameter of the D field gradient is very small. The D relaxation rate then yields the D coupling constant.

From the experimentally observed correlation of the D and ^{17}O coupling constants the latter may now be determined and from the ^{17}O relaxation rate τ_{O} can be calculated. Comparison of τ_{O} and τ_{OH} then shows the isotropic model of the molecular motion of H_2O to be adequate on a picosecond timescale within present experimental accuracy.

2. Theory

The nuclear relaxation rate can be expressed in terms of an interaction constant and an effective correlation time. Because the water reorientation occurs on the timescale of picoseconds, the extreme narrowing condition is fulfilled. The D and ^{17}O relaxation are determined intramolecularly by the quadrupolar interaction, with relaxation rates

$$R_D = \frac{3}{8} (2\pi\chi_D)^2 (1 + \frac{1}{3}\eta_D^2) \tau_D^* \quad (1)$$

for the D nucleus, and for ^{17}O

$$R_O = \frac{3}{125} (2\pi\chi_O)^2 (1 + \frac{1}{3}\eta_O^2) \tau_O^* \quad (2)$$

in which χ_D and χ_O denote the D and ^{17}O quadrupole coupling constants respectively. The correlation times for quadrupolar relaxation τ_D and τ_O still depend on the asymmetry parameters, η_D and η_O respectively, of the electric field gradient experienced by the relaxing nucleus. These correlation times are divided by a factor $1 + \frac{1}{3}\eta^2$ to normalize them under isotropy. This is indicated by the asterisk. The intramolecular part of the H- ^{17}O dipolar interaction contribution to the H relaxation rate is given by

$$R_{\text{OH}}^{\text{int}} = \frac{35}{3} (\gamma_H^2 \gamma_{^{17}\text{O}}^2 \hbar^2 / r_{\text{OH}}^6) \tau_{\text{OH}}, \quad (3)$$

in which r_{OH} denotes the O-H bond distance.

The correlation times τ_D , τ_O and τ_{OH} are the zero-frequency Fourier components of the correlation functions of the interaction tensors. In other terms, the correlation times are the time-integrals of these correlation functions. These correlation times contain all the dynamical features that can be obtained from NMR, irrespective of the details of the motion. Because the relaxation processes are intramolecularly determined, these correlation times refer only to the reorientational dynamics. Apart from an isotope effect, which will be discussed later, the effective correlation times τ_D^* , τ_O^* and τ_{OH}^* are equal, under isotropic reorientational motion.

However to evaluate these effective correlation times, knowledge is needed about the interaction constants. According to eq. (3) the main factor determining the H- ^{17}O dipolar interaction is the O-H bond distance. Previously a value of 0.958 Å was used (i.e. the gas value), but neutron scattering experiments show that a somewhat larger value should be used for the liquid. A value of 0.98 Å will be used [4-6]. Quantum-chemical calculations show the main factor determining χ_D is the O-D bond length, while the bond angle is of minor importance [7,8]. The ^{17}O quadrupole coupling constant depends more on the charge distribution due to H-bonding than on molecular geometry [7].

In case of both the quadrupole and the dipolar relaxation mechanism the lattice part of the coupling Hamiltonian is given by the second-order spherical

tensor elements $V_k^{(2)}$ [9]. In the principal axis system of the dipolar interaction, one has

$$V_k^{(2)} = \delta_{0k} (3/2)^{1/2} r_{\text{OH}}^{-3}. \quad (4)$$

In the principal axis system of the quadrupole interaction these elements are defined as

$$V_0^{(2)} = (3/2)^{1/2} eq, \quad (5a)$$

$$V_{\pm 1}^{(2)} = 0, \quad (5b)$$

$$V_{\pm 2}^{(2)} = -\frac{1}{2} \eta eq. \quad (5c)$$

To obtain the D quadrupole coupling constant χ_D the following method will be applied. The principal axis of the H- ^{17}O dipolar interaction tensor coincides with the principal axis of the D quadrupolar interaction tensor. The asymmetry parameter of the D field gradient is very small ($\eta_D = 0.135$, gas value). As a consequence the $V_{\pm 2}^{(2)}$ field gradient components are very small with respect to the main $V_0^{(2)}$ component. These two features combined then lead to an approximate equality of the effective correlation times for these relaxation mechanisms, irrespective of the details of the motion. Even if the reorientation motion is described by an axially symmetric diffusion process and the degree of anisotropy (i.e. $D_{||}/D_{\perp}$) does not exceed the value of two, this equality holds within 2% for all orientations of the diffusion tensor. This degree of anisotropy is even a rather high upper limit, because the monovalent cations are not able to induce such a value in their environment, if bulk water is assumed to reorient isotropically [10]. Now from eqs. (1) and (3) and the equality of the effective correlation times one can obtain χ_D as a function of the O-H bond length.

The last problem to be dealt with is the ^{17}O quadrupole coupling constant. For χ_O such a procedure as proposed for χ_D is not possible. However solid-state NQR provides a method to determine the quadrupole coupling constants in crystal hydrates and different forms of ice. Poplett observed a correlation between χ_O and χ_D for crystal hydrates, different forms of ice and water vapor [11]:

$$\chi_O = (38.214 \pm 1.293) \chi_D - (1650 \pm 302) (\text{kHz}). \quad (6)$$

The ^{17}O coupling constant χ_O will be obtained by inserting χ_D into this relation.

3. Results and discussion

The experimental relaxation rates in water at 298 K were previously reported [1]. For the D relaxation rate of HDO in solvent medium H₂O one has

$$R_D = 1.944 \pm 0.004 \text{ s}^{-1}. \quad (7)$$

For the ¹⁷O relaxation rate of H₂¹⁷O in solvent medium H₂O one has

$$R_O = 141.6 \pm 0.5 \text{ s}^{-1}. \quad (8)$$

Both values were obtained by extrapolation of relaxation rates in isotopic mixtures to H₂O. For the intramolecular H-¹⁷O dipolar contribution to the H relaxation one has

$$R_O^{\text{intra}} = 0.270 \pm 0.011 \text{ s}^{-1}. \quad (9)$$

This value was obtained from ¹⁷O enhanced H relaxation in ¹⁷O enriched water.

The effective correlation time τ_{OH} , calculated by inserting the experimental intramolecular H-¹⁷O dipolar relaxation rate (eq. (9)) into eq. (3), is displayed in fig. 1 as a function of the O-H bond distance. Values obtained with the gas and ice value were previously reported [1]. For an O-H bond length of 0.98 Å one obtains

$$\tau_{OH} = 1.95 \pm 0.08 \text{ ps}. \quad (10)$$

As discussed in section 2, the effective correlation times τ_{OH} and τ_D^* have to be nearly equal. This equality is exact when η_D is neglected, leaving only

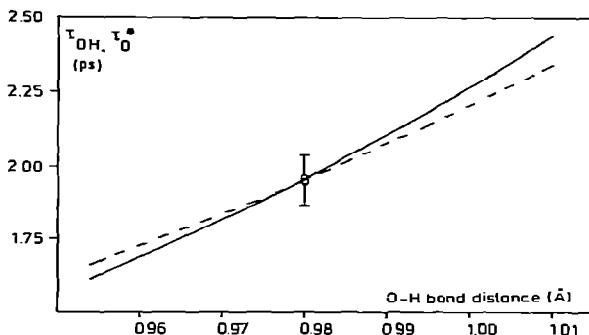


Fig. 1 Effective correlation times as a function of the O-H bond distance. Solid line, intramolecular H-¹⁷O dipolar interaction; dashed line, ¹⁷O quadrupolar interaction.

the D solute isotope effect to be taken into account [1]:

$$\tau_D^* = (1.05 \pm 0.02)\tau_{OH}. \quad (11)$$

This solute isotope effect is the effect on the reorientational correlation time due to the molecular species involved. In the liquid state the O-H and O-D bond lengths are equal within the experimental accuracy of the neutron and X-ray scattering experiments [12]. Therefore a possible D isotope effect on the O-H bond length is neglected. By inserting the calculated H-¹⁷O effective correlation time into eq. (11), one obtains the effective correlation time for D relaxation. The D quadrupole coupling constant χ_D , calculated by inserting the experimental D relaxation rate (eq. (7)) and the effective correlation time for D relaxation into eq. (1), is a nearly linear function of the O-H bond distance in the small range of 0.96 to 1.01 Å. Values calculated with the gas and ice O-H bond distance were previously reported [1]. For $r_{OH} = 0.98 \text{ \AA}$, one obtains

$$\chi_D = 253 \pm 6 \text{ kHz}. \quad (12)$$

This value agrees with the result of quantum-chemical calculations [7]. However, for $r_{OH} = 0.98 \text{ \AA}$ these calculations were only performed on an isolated water molecule and a pentamer. The isolated water molecule calculation slightly overestimates χ_D , while the pentamer calculation gives a somewhat lower value. To calculate the exact value the distribution of the number of H-bonds should be known.

The ¹⁷O quadrupole coupling constant can now be obtained by inserting χ_D into the relation of Poplett (eq. (6)). Taking $r_{OH} = 0.98 \text{ \AA}$, one obtains

$$\chi_O = 8.0 \pm 0.2 \text{ MHz}. \quad (13)$$

By inserting χ_O , the experimental ¹⁷O relaxation rate (eq. (8)) and the commonly used gas value for the ¹⁷O asymmetry parameter (0.75) into eq. (2), one obtains the effective correlation time for ¹⁷O relaxation. The ¹⁷O solute isotope effect on the correlation time will be neglected. This correlation time is also displayed in fig. 1 as a function of the O-H bond length. Particularly if $r_{OH} = 0.98 \text{ \AA}$, one obtains

$$\tau_O^* = 1.96 \pm 0.11 \text{ ps}. \quad (14)$$

Fig. 1 shows that the effective correlation times for H-¹⁷O and ¹⁷O relaxation are equal within the

estimated experimental accuracy in the range of the expected liquid water O—H distance, i.e. 0.98 Å.

The equality of the effective correlation times for ^{17}O and H— ^{17}O relaxation is necessary but not sufficient to prove the reorientational motion to be isotropic. The effect to anisotropy of the reorientational motion may be obscured for certain orientations of the diffusion tensor which cause an equality of the effective ^{17}O and H— ^{17}O correlation times [3]. However, the range of these orientations is very narrow and does not include intuitively expected preferred orientations such as the molecular symmetry axis. Therefore it may be concluded that, within present experimental accuracy the isotropic dynamical model describes the reorientational motion of the water molecule on a picosecond scale at 298 K.

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