Isotope Effects on the ^{17}O, ^{1}H Coupling Constant and the ^{17}O–{^{1}H} Nuclear Overhauser Effect in Water

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The NMR spectra of solutions of 30% ^{17}O-enriched H_2O and D_2O in nitromethane display the resonances of the three isotopomers H_2O, HDO, and D_2O. All ^{17}O, ^{1}H and ^{17}O, ^{2}H coupling constants and the primary and secondary isotope effects on $J(^{17}O, ^{1}H)$ have been determined. The primary effect is -1.0 ± 0.2 Hz and the secondary effect is -0.07 ± 0.04 Hz. Using integrated intensities in the ^{17}O NMR spectra, the equilibrium constant for the reaction $H_2O + D_2O \rightleftharpoons 2HDO$ is found to be 3.68 ± 0.2 at 343 K. From the relative integrated intensities of proton-coupled and -decoupled spectra the ^{17}O–{^{1}H} NOE is estimated for the first time, resulting in values of 0.908 and 0.945 for H_2O and HDO, respectively. This means that dipole–dipole interactions contribute about 2.5% to the overall ^{17}O relaxation rate in H_2O dissolved in nitromethane. © 1999 Academic Press

Key Words: isotope effects on coupling constants; NOE ^{17}O–{^{1}H}.

INTRODUCTION

In recent years it has been possible to obtain very good agreement between experimental and calculated values of nuclear spin–spin coupling constants. This is due mainly to substantial progress in calculations of coupling constants (particularly ^{1}H, ^{1}H and ^{13}C, ^{1}H) for small and medium-sized molecules using methods based on the coupled cluster polarization propagator approximation (*1, 2*).

For example, for methane (*2*) recent results show that accurate *ab initio* calculations of $J(^{13}C, ^{1}H)$ and $J(^{1}H, ^{1}H)$ give values which are comparable in accuracy with experimental results. This approach also requires reformulation of coupling constant studies into two distinct areas: (a) the study of small perturbations caused by temperature, pressure, isotope, and solvent effects (*3*) and (b) the study of coupling at equilibrium geometry for the isolated molecule.

According to the general rotational–vibrational description of the former effects (*4*) one calculates derivatives of coupling constants with respect to molecular geometrical coordinates. This permits the construction of a spin–spin coupling surface. Knowledge of the molecular force field including anharmonic

terms then allows the calculation of coupling constants for various isotopomers at any temperature. A parallel approach has been found to be very successful in the case of nuclear shielding (*5–10*).

The water molecule presents an interesting example for comparison of accurate experimental and theoretical study because of its great simplicity and importance. Here we report new experimental data on isotope effects on the ^{17}O, ^{1}H coupling constant in water which can be used to estimate derivatives of the ^{17}O, ^{1}H coupling constant surface. Previous data on water isotopomers obtained during the course of our work include accurate values of the ^{1}H, ^{2}H and ^{17}O, ^{1}H coupling constants in water in dilute solutions in nitromethane (*11*) and also a small but significant isotope effect on proton chemical shifts due to $^{18}O/^{16}O$ substitution (*12*).

In this paper we report new results obtained with mixtures of heavy ($D_2 {}^{16}O$) water and water enriched with the ^{17}O isotope ($H_2 {}^{17}O$). Proton and deuteron exchanges lead to the formation of isotopomers containing the isotope ^{17}O ($H_2 {}^{17}O$, HD^{17}O, $D_2 {}^{17}O$). Since it is possible to see ^{17}O NMR signals of all three isotopomers, the integrated intensities can be used to measure the equilibrium constant K for the classical reaction

$$H_2O + D_2O \rightleftharpoons 2HDO.$$

The equilibrium constant for this reaction has been measured many times for the gaseous phase (see, for example, (*13, 14*)) but data for solutions are scarce. Gold and Tomlinson (*14*) measured the equilibrium constant by using ^{1}H NMR spectra similar to those given in Ref. (*11*) for a mixture of H_2O and D_2O from which the signals of H_2O and HDO were distinctly separated and could be integrated. However, since this approach allows one to observe only H_2O and HDO isotopomers, one needs to know the initial concentrations of H_2O and D_2O.

It is of interest also to compare intensities of both proton-coupled and proton-decoupled ^{17}O NMR spectra in order to search for a possible nuclear Overhauser effect ^{17}O–{^{1}H}. Previously, similar attempts were made, indicating no NOE ^{17}O–{^{1}H} (*15*). However, there were no reported values for dilute solutions of water in organic solvents.

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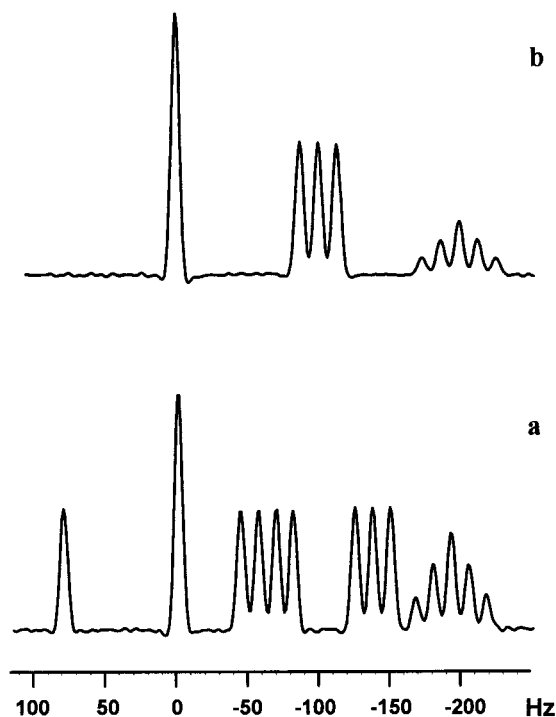
FIG. 1. ^{17}O NMR spectra of a H_2O/D_2O solution in nitromethane-d_3 taken at 67.8 MHz on a Bruker DRX 500. (a) Proton-coupled spectrum and (b) proton-decoupled spectrum.

EXPERIMENTAL

The samples were dilute solutions of water in nitromethane-d_3 prepared in a manner described elsewhere (*12*). Nitromethane-d_3 with deuteration levels of 99.44 ($\pm$0.01)% according to our estimation was purchased from Merck. The proton signal of the residual CHD_2NO_2 was used to determine the water content in the solvent. Nitromethane-d_3 was dried by several freeze–thaw–pump cycles using P_2O_5 as a drying agent under vacuum and passed through a series of traps to eliminate traces of the drying agent. The final water content never exceeded 0.01 mol%. We used doubly distilled $H_2^{16}O$, 30% ^{17}O-enriched H_2O purchased from Isotech, and 99.96% D_2O purchased from Merck. First D_2O and 30% ^{17}O-enriched H_2O were mixed in a special vessel in amounts of about 100 mg in the ratio ca. 1:1. The residual water in nitromethane-d_3 and slow exchange with air affected the ratio slightly but we were able to monitor it from the NMR line intensities. Then the mixture was added to nitromethane-d_3 in amounts resulting in low concentrations of water (of about 1.5 mol%). A small amount of dried TMS was added to control the resolution and the lineshape of the water signal. Addition of TMS and the water mixtures was performed by vaporization into the precalibrated volumes. The final solution was distilled in a 5-mm sample tube and sealed under vacuum.

^{17}O NMR spectra were taken on a Bruker DRX 500 at the Zelinski Institute of Organic Chemistry, Moscow, at a resonance frequency of 67.8 MHz with a sweep width of 34,000

TABLE 1
^{17}O, ^{1}H and ^{17}O, ^{2}D Coupling Constants in Water Isotopomers and the Isotope Effects on the ^{17}O, ^{1}H Coupling Constant (All in Hz)[a]

300 K	343 K
$H_2O\ J(^{17}O, H) = -81.07 \pm 0.05$	$H_2O\ J(^{17}O, {}^1H) = -80.36 \pm 0.02$
$HDO\ J(^{17}O–H) = -81.21 \pm 0.1$	$HDO\ J(^{17}O–H) = -80.43 \pm 0.04$
$J*(^{17}O–D) = -82.2 \pm 0.3$	$J*(^{17}O–D) = -81.38 \pm 0.2$
$D_2O\ J*(^{17}O–D) = -81.7 \pm 1$	$D_2O\ J*(^{17}O–D) = -81.36 \pm 0.4$
$^P\Delta J = -1.13 \pm 0.30$	$^P\Delta J = -1.02 \pm 0.20$
$^s\Delta J = -0.14 \pm 0.11$	$^s\Delta J = -0.07 \pm 0.04$

[a] The signs of all $J(^{17}O, H)$ coupling constants are known to be negative (see Refs. (*20, 22*)).

Hz, an acquisition time of 0.2 s, and 9000 transients. The FID was processed with resolution enhancement for undecoupled spectra and without resolution enhancement when the nuclear Overhauser effect was measured and it was then Fourier transformed using 128K. Both proton-coupled and proton-decoupled spectra were recorded.

RESULTS AND DISCUSSION

Spectra

^{17}O NMR spectra for the water region are shown in Figs. 1a and 1b. Signals from all three isotopomers are clearly seen as a 1:2:1 triplet for H_2O, a 1:1 doublet of 1:1:1 triplets for HDO, and a 1:2:3:2:1 quintet for D_2O in the proton-coupled spectrum (Fig. 1a) and as a singlet for H_2O, a triplet for HDO, and a quintet for D_2O in the proton-decoupled spectrum (Fig. 1b). Splittings were used directly to measure ^{17}O, ^{1}H and ^{17}O, ^{2}H coupling constants (Table 1). The intensities of proton-coupled and proton-decoupled spectra normalized to the intensity of the D_2O signal are given in Table 2.

^{17}O, ^{1}H and ^{17}O, ^{2}H Coupling Constants and Isotope Effects on the ^{17}O, ^{1}H Coupling Constants

As before (see, for example, Refs. (*3, 16*)) we express our results in terms of the "^{17}O, ^{1}H basis," i.e.,

$$J*(^{17}O, {}^2H) = (\gamma_H/\gamma_D)J(^{17}O, {}^2H), \qquad [1]$$

TABLE 2
Integrated Intensities in ^{17}O NMR of the Mixture H_2O/D_2O at 343 K

	H_2O	HDO	D_2O
Proton-coupled spectrum	1.53	2.37	1.00
Proton-decoupled spectrum	1.39	2.24	1.00

to determine the primary ($^p\Delta J$) and secondary ($^s\Delta J$) isotope effects defined by

$$^p\Delta J = J^*(^{17}O, ^2H) \text{ [HDO]} - J(^{17}O, ^1H) \text{ [H}_2\text{O]} \quad [2a]$$

$$^s\Delta J = J(^{17}O, ^1H) \text{ [HDO]} - J(^{17}O, ^1H) \text{ [H}_2\text{O]}. \quad [2b]$$

In order to obtain accurate values of the isotope effects the magnitudes of $J(^{17}O, ^1H)$ and $J(^{17}O, ^2H)$ must be measured with a very high accuracy (about 0.01 Hz). The crucial factors in obtaining high accuracy are the ^{17}O linewidths and the signal-to-noise ratio in the ^{17}O NMR spectrum.

The first ^{17}O NMR spectrum of a H_2O/D_2O mixture was reported by Klemperer (17) in a reference to a private communication by Mateescu (see also Ref. (18)), who observed signals of all three isotopomers in a solution of water in CH_2Cl_2. However, the signal-to-noise ratio in the spectrum was too low to obtain accurate data for the coupling constants. The next attempt to measure isotope effects for the ^{17}O, H coupling constant was made by Wasylishen and Friedrich (19), who used solutions of water in cyclohexane and managed to obtain a ^{17}O linewidth of about 4 Hz. This is at least twice as good as we obtained with dilute solutions of water in nitromethane (see (11)). Unfortunately the accuracy claimed in Ref. (19) (± 1.3 Hz for $J^*(^{17}O, ^2H)$ and ± 0.2 Hz (± 0.02 Hz in Ref. (19) is probably erroneous) for $J(^{17}O, ^1H)$) was not high enough. The values of the primary and the secondary isotope effects estimated from these data are $^p\Delta J = -0.38$ Hz (± 1.3 Hz) and $^s\Delta J = -0.08$ (± 0.3 Hz), respectively, and are clearly experimentally insignificant.

It is clear from the results obtained (Table 1) that the use of a 500-MHz spectrometer together with higher concentrations gives a better signal-to-noise ratio and, after using simple deconvolution procedures, gives better accuracy in estimating the ^{17}O, ^1H coupling constants. Indeed, the ^{17}O NMR spectra with linewidths of about 6 Hz and the good signal-to-noise ratio in the spectra given in Fig. 1a allowed us to determine the coupling constants with high accuracy (± 0.02 Hz for $J(^{17}O, ^1H)$ in H_2O at 343 K and about ± 0.04 Hz for $J(^{17}O, ^1H)$ and ± 0.03 Hz for $J(^{17}O, ^2H)$ in HDO at 343 K).

From the measured coupling constants we obtain the isotope effects (see Table 1). The primary effect at 343 K is equal to -1.0 ± 0.2 Hz taking into account the negative sign of the ^{17}O, ^1H coupling constant (20) and the secondary isotope effect is equal to -0.07 ± 0.04 Hz. The data on isotope effects on the ^{17}O, ^1H coupling constant in water can be used to estimate the derivatives $\partial J(^{17}O, ^1H)/\partial R$. The O–D bond length is calculated to be shorter than the O–H bond length by 0.00441 Å (21) which means that $J(^{17}O, ^1H)$ increases with the O–H bond length and the derivative $\partial J(^{17}O, ^1H)/\partial R$ is positive and estimated to be 200 (± 70) Hz/Å. This is close to an *ab initio* calculated value of 269 Hz/Å (22).

It is also interesting to compare the absolute values of the ^{17}O, ^1H coupling constant obtained under different conditions (Table 3). The *ab initio* (SOPPA level) calculations (Ref. (22))

TABLE 3
Comparison of ^{17}O–H Coupling Constants in H_2O

Conditions	^{17}O–H coupling constant	Ref.
Solution in cyclohexane-d_{12}, 0.1%, 293 K	-78.70 (± 0.02)	(19)
Solution in nitromethane-d_3, 0.5%, 323 K	-80.6 (± 0.1)	(11)
SOPPA (CCSD) calculations	-78.22	(22)
Solution in nitromethane, 1.6 mol%		This paper
300 K	-81.07 (± 0.05)	
343 K	-80.36 (± 0.02)	

give the value -78.2 Hz while solutions in cyclohexane give -78.70 Hz and solutions in nitromethane give values from -80.4 to -81.1 Hz. Thus the absolute value of the coupling constant ^{17}O–^1H may show noticeable concentration and solvent dependence (of several percent) but this is not important for the isotope effects which correspond to small deviations from the equilibrated values. It is also worth noting that the ^{17}O, ^1H coupling constant displays a temperature dependence (-81.07 at 300 K, -80.62 at 323 K (11), and -80.36 Hz at 343 K, i.e., a temperature gradient of about $+0.016$ Hz/°C). The theory (22) also predicts the temperature dependence of the ^{17}O, H coupling constant but with a temperature gradient of about $+0.0012$ Hz/°C. Thus although the signs of the experimental and theoretical gradients agree, the experimental value is at least an order of magnitude greater than the calculated value. This suggests the presence of large contributions from intermolecular effects arising from specific water–nitromethane interactions.

Theory also predicts primary and secondary isotope effects on the ^{17}O, ^1H coupling constants. The primary effect was calculated (22) to be -0.982 (in HD^{17}O) at 300 K (compare with the experimental values of -1.13 ± 0.30 at 300 K and -1.02 ± 0.2 at 343 K, Table 1). The secondary effect was calculated (22) to be -0.117 Hz at 300 K while the experimental values are equal to -0.14 ± 0.11 at 300 K and -0.07 ± 0.04 at 343 K. Thus the comparison indeed shows a very satisfactory agreement.

The D/H-Induced ^{17}O Isotope Shifts in Water

We also obtained new values of ^{17}O isotope shifts due to D/H substitution. These values were measured at 300 and 343 K. In Table 4 they are given in comparison with the data of recent calculations (21) and the data of Wasylishen and Friedrich (19). Experimental results obtained for nitromethane at 300 K and the calculated results for 300 K are in excellent agreement. It is worth noting that the more accurate data obtained for 343 K reveal a small nonadditivity effect. If we define the nonadditivity as (23)

$$\eta = (1/2)\Delta_{isot}(D_2/H) - \Delta_{isot}(D/H), \quad [3]$$

where $\Delta_{isot}(D_2/H)$ and $\Delta_{isot}(D/H)$ are the D/H-induced isotope

TABLE 4
D/H-Induced ^{17}O Isotope Shifts in Water

Isotope shift in HDO (in ppb)	Isotope shift in D$_2$O (in ppb)	Conditions	Nonadditivity (in ppb)[a]	Ref.
-1550 ± 5	-3090 ± 5	In cyclohexane, 293 K	5 ± 6	(*19*)
-1385.5 ± 1	-2763.5 ± 1	In nitromethane, 300 K	4 ± 2	This study
-1420.0 ± 0.1	-2832.4 ± 0.3	In nitromethane, 343 K	4.0 ± 0.3	This study
-1356	-2697	Calculated for 300 K	7.5	(*21*)

[a] See Eq. [3].

shifts due to two and one deuterium atom, respectively, we obtain the following values of η: 4 (± 0.3) ppb for the experimental data obtained in nitromethane at 343 K and 7.5 ppb for the calculated value at 300 K. The results obtained in the solvents cyclohexane and nitromethane at 300 K are not sufficiently accurate. Thus the D/H nonadditivity in H$_2$O is positive both experimentally and theoretically in contrast to the D/H nonadditivity for ^{13}C isotope shifts in halomethanes which turn out to be negative and equal to about 1–4 ppb (*23*). In any case it is clear that an accuracy of the order ± 0.5 ppb is necessary to detect nonadditivity effects.

Equilibrium in Water Mixtures

The integrated intensities for H$_2$O, HDO, and D$_2$O (see Fig. 1a) in the proton-coupled spectrum (not perturbed by a possible nuclear Overhauser effect, see below) are proportional to the molar concentrations of the corresponding isotopomers, i.e., m_{1eq}, m_{2eq}, and m_{3eq}, respectively. They are equal to 1.53, 2.37, and 1.00 (Table 2) which correspond to molar fractions m_{1eq}, m_{2eq}, and m_{3q} of 0.312, 0.484, and 0.204, respectively. These values can be used to calculate the equilibrium constant K using

$$K = m_{2eq}^2/(m_{1eq}m_{2eq}). \qquad [4]$$

This gives a K value of 3.68.

To estimate the experimental error in the K value we used the standard theory of errors (see, e.g., (*24*)). This shows that a 1% error in the molar fraction leads to an error of about 5% in the equilibrium constant when m_{10} and m_{30} are near 1:1. Assuming an error of 1% in the molar fraction data we obtain an equilibrium constant of 3.80 ± 0.2 at 343 K. This result is in good agreement with the value reported in Ref. (*14*) which is 3.95 ± 0.12. The latter accuracy seems to us to be unreasonably high taking into account possible incorporation of water from the solvent. NMR estimates seem to be less accurate than those obtained using mass spectroscopy (3.82 ± 0.05 at 295.6 K, see Ref. (*13*)) but they refer to reactions in the liquid phase.

Furthermore, one can find the initial concentrations of H$_2$O and D$_2$O and so check whether the residual water in the solvent does indeed mix with the dissolved water. From the data on

molar fractions m_{1eq}, m_{2eq}, and m_{3q} one finds that the starting concentrations m_{10} and m_{30} are equal to 0.554 and 0.446, respectively. This shows that the small amount of residual water in nitromethane has added to the water mixture since m_{10} and m_{30} were chosen in the ratio ca. 1:1.

Nuclear Overhauser Effect $^{17}O–\{^1H\}$

The data on the integrated intensities of proton-coupled and proton-decoupled spectra (Table 2) allow one to estimate the nuclear Overhauser effect $^{17}O–\{^1H\}$ using

$$NOE = I_{(dcpl)}/I_{(cpld)}, \qquad [5]$$

where $I_{(dcpl)}$ and $I_{(cpld)}$ are the intensities of the X signal for the cases of proton-decoupled and proton-coupled spectra, respectively.

Assuming that there is no NOE for the D$_2$O signal (thus normalizing to the intensity of D$_2$O as in Table 2) one obtains the following results: NOE (H$_2$O) = 0.908 and NOE (HDO) = 0.945.

It is known from relaxation theory that the NOE is connected to that part of the relaxation which is due to dipole–dipole interactions as follows (*25*),

$$NOE = 1 + (1/2)(\gamma_H/\gamma_X)(T_1/T_{1dd}), \qquad [6]$$

where γ_H and γ_X are gyromagnetic ratios for H and X nuclei, and T_1 and T_{1dd} are the total relaxation time and the dipole–dipole relaxation time, respectively. Thus one can obtain the contributions of dipole–dipole relaxation to overall spin–lattice relaxation.

Using Eq. [6] with γ_X equal to γ_{17O} ($(\gamma_H/\gamma_{17O}) = -7.37$) and experimental data for NOE, one obtains $T_1/T_{1dd} = 0.026$ for H$_2$O and $T_1/T_{1dd} = 0.015$ for HDO. We can now estimate the contributions of dipole–dipole (R_{dd}) and quadrupole (R_{quadr}) relaxation mechanisms to the total relaxation rate R

$$R = R_{quadr} + R_{dd}, \qquad [7]$$

with R_{dd} contributing about 2.5 and 1.5% in H$_2$O and in HDO, respectively, confirming an expected decrease of NOE in the

case of HDO where only the proton effectively contributes to the dipole–dipole relaxation.

From the theoretical point of view the possibility of significant dipole–dipole contribution to the total relaxation rate can be related to the intramolecular contribution to ^{17}O relaxation ($R_{^{17}O-H,\,intra}$) from the protons of the same molecule.

To estimate the intramolecular dipole–dipole contribution to the spin–lattice relaxation rate of ^{17}O one can use known estimates of the intramolecular contribution to the T_1 relaxation of the proton in water $R_{H-H,\,intra}$ (see, e.g., Ref. (*26*), where $R_{H-H,\,intra}$ was estimated to be about 0.2 s^{-1} in pure water $H_2{}^{16}O$ at ambient temperatures) and then transform $R_{H-H,\,intra}$ into $R_{^{17}O-H,\,intra}$.

Assuming the same correlation times τ for the relaxation of ^1H in $H_2{}^{16}O$ and ^{17}O in $H_2{}^{17}O$ one can write for the case of extreme narrowing

$$R_{H-H,\,intra} = (3/2)(\gamma_H^4 h^2 / 4\pi^2 r_{HH}^6)\tau \qquad [8a]$$

$$R_{^{17}O-H,\,intra} = 2(\gamma_H^2 \gamma_{^{17}O}^2 h^2 / 4\pi^2 \, r_{OH}^6)\tau. \qquad [8b]$$

Here the factor $(\frac{3}{2})$ corresponds to relaxation in systems of like spins $\frac{1}{2}$, and the factor 2 in the case of ^{17}O relaxation takes into account both protons for the relaxation of ^{17}O in $H_2{}^{17}O$. Thus

$$R_{^{17}O-H,\,intra}/R_{H-H,\,intra} = (2\gamma_{^{17}O}^2/r_{OH}^6)/(\gamma_H^2/r_{HH}^6) = \sim 0.33$$

since $r_{HH} = \sim 1.51$ Å and $r_{OH} = \sim 0.96$ Å. The latter values were taken from a recent theoretical study of the water molecule (*22*). Thus $R_{^{17}O-H,\,intra} = 0.33 \times 0.2$ s$^{-1} = \sim 0.066$ s^{-1}. These estimates indeed show that the dipole–dipole contribution to the ^{17}O relaxation is very small but not negligible.

ACKNOWLEDGMENTS

Note added in proof. V. Denisov (Lund, Sweden) has pointed out to the authors that it is probably not correct to use the same correlation time in Eqs. [8a] and [8b] as that for R_{H-H} is based on data for pure liquid while that for R_{O-H} is taken from data for dilute solutions.

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