Temperature and Isotope Substitution Effects on the Structure and NMR Properties of the Pertechnetate Ion in Water

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Abstract: The uniquely well-resolved ^{99}Tc NMR spectrum of the pertechnetate ion in liquid water poses a stringent test of the accuracy of ab initio calculations. The displacement of the ^{99}Tc chemical shift as a function of temperature has been measured over the range $10-45$ °C for the three isotopomers $Tc(^{16}O)_4{}^-$, $Tc(^{16}O)_3(^{18}O)^-$, and $Tc(^{16}O)_3(^{17}O)^-$ at natural oxygen isotope abundance levels, and in addition the temperature dependence of the Tc$-$O scalar coupling was determined for the $Tc(^{16}O)_3(^{17}O)^-$ isotopomer. Values for these parameters were computed using relativistic spin$-$orbit density functional theory with an unsolvated ion approximation and with treatments of the solvated ion based on the COnductor-like Screening MOdel (COSMO) approach. The temperature and isotope dependence of ^{99}Tc NMR parameters inferred by these methods were in good quantitative agreement with experimental observations. The change in the Tc$-$O bond length associated with the changes in temperatures considered here was determined to be of the order of 10^{-4} Å. Vibrational energies and Tc$-$O bond lengths derived from these models also compare favorably with previous experimental studies.

1. Introduction

An unusually detailed picture of a complex ion's structure and environment in liquid water can be constructed from ^{99}Tc and ^{17}O nuclear magnetic resonance (NMR) spectra of the pertechnetate anion (TcO$_4{}^-$). The ^{99}Tc nuclide's favorable NMR properties, which include a sizable gyromagnetic ratio (9.583×10^6 Hz/T), moderate quadrupolar moment ($Q = -1.29$ barns), large spin angular momentum quantum number ($I = 9/2$), and 100% isotopic abundance, combined with the cubic symmetry of its environment in TcO$_4{}^-$, give rise to a strong, highly resolved ^{99}Tc NMR signal that is sensitive to minute perturbations in the metal atom's environment.

The sensitivity of the pertechnetate ion's NMR parameters is exemplified by the findings of Tarasov et al.[1] in their study of NH$_4$TcO$_4$(aq) containing artificially enriched levels of the ^{18}O isotope. They showed that the ^{99}Tc spectrum consisted of four resolved lines, which they assigned to four isotopomers of TcO$_4{}^-$, corresponding to the ion with zero to three ^{18}O nuclei replacing ^{16}O (the isotopomer with four ^{18}O nuclei was too rare to be detected).

Experimental observations of ligand isotope effects of this magnitude have been limited mainly to those rare instances where a diamagnetic, NMR-detectable metal center occupies a site of high symmetry. Solution-state spin$-$lattice (T_1) relaxation times for metals in sites of perfect cubic symmetry are particularly advantageous for high-resolution measurements of

chemical shifts due to the vanishing of both electric field gradients and the chemical shift anisotropy.[2] Among tetravalent metal oxides, measurable displacements of the metal chemical shift due to oxygen isotope substitution have been reported for ^{55}MnO$_4{}^-$,[3] ^{95}MoO$_4{}^{2-}$,[3] ^{51}VO$_4{}^{3-}$,[4] ^{53}CrO$_4{}^{2-}$,[4] and ^{99}RuO$_4$.[5] The ^{99}Ru chemical shift in RuO$_4$ has also been found to be quite sensitive to temperature.[5] Despite the cubic symmetry of ReO$_4{}^-$, its ^{185}Re and ^{187}Re NMR line widths are too broad[6] for measurement of the isotope or temperature dependence of their chemical shifts. Both rhenium isotopes have substantially larger quadrupolar moments than ^{99}Tc or ^{55}Mn, and in addition ^{99}Tc has a larger spin angular momentum quantum number than ^{185}Re and ^{187}Re. These factors imply that the quadrupolar broadening of the ^{185}Re and ^{187}Re resonances of ReO$_4{}^-$ in the extreme narrowing limit will indeed be greater than that for the ^{99}Tc or ^{55}Mn signal in the analogous species, but the magnitude of the difference is not completely explained by quadrupolar relaxation alone.[6]

Theoretical treatments have been developed[7−11] that interpret such observations in terms of thermally-[12] or isotope-induced[13]

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changes in rotational and vibrational contributions to these NMR properties. Because of the smallness of the energy shifts detected in NMR experiments, a theoretical analysis that quantitatively explains the experimental results requires consideration of extremely subtle features of the metal complex and its interactions with solvent molecules. Various solvation models have been proposed to describe the effect of the molecular environment on NMR properties.[14-22] Mikkelsen et al.[14] demonstrated with a dielectric continuum model that solvation effects are of the same magnitude as rovibrational and electron correlation effects. In this article, we account for solvation by combining the rovibrational treatment with a similar dielectric continuum model.

2. Experimental Section

Caution. The ^{99}Tc isotope is a β-emitter ($t_{1/2} = 2.1 \times 10^5$ y). All manipulations of solids and solutions were performed in a Category 2 nuclear research facility at the Pacific Northwest National Laboratory in Richland, WA. The NMR solutions were held in capped PTFE/FEP copolymer sleeves (Wilmad) inserted in 10 mm glass NMR tubes, which provided secondary containment of the radioactive liquids.

Preparation of Aqueous ^{99}Tc Standards. NH$_4$TcO$_4$ was prepared by oxidative dissolution of 1 g of TcO$_2$ in 150 mL of ammonium hydroxide and 50 mL of hydrogen peroxide (30 wt % aqueous solution).[23] The solid was recrystallized three times. Ultimately, 1.28 g of NH$_4$TcO$_4$ (100% theoretical yield = 1.38 g) was collected.

KTcO$_4$ was prepared by dissolution of 2.047 g of dry NH$_4$TcO$_4$ in deionized water and passage of this solution through a cation exchange column in the H$^+$ form. The resulting HTcO$_4$ was titrated with 99.999% pure 1.14 M KOH, using phenolphthalein as indicator. The solids were washed with ethanol and ether and were then recrystallized three times. Ultimately, 1.183 g of KTcO$_4$ (theoretical yield = 2.284 g) was collected.

Each solid was dried to constant weight. Stock solutions were made in 10 mL of D$_2$O in volumetric glassware. The standard solutions were sequentially diluted in volumetric glassware with D$_2$O to obtain a set of standards of varying pertechnetate concentrations. Each standard was checked by β-liquid scintillation counting (LSC) by placing a known amount of solution into an Ultima Gold liquid scintillation cocktail.

NMR Spectroscopy. Technetium-99 NMR data were collected at 67.565 MHz on a Tecmag Discovery spectrometer equipped with a 10-mm broadband Nalorac probe. Minor adjustments of the shims using the deuterium lock signal were performed for every sample, but after shimming, the field lock apparatus was put in a hold (unlocked) mode and the Z0 shim was set to the same preselected value for all samples. The uncompensated field drift for the 7.04 T magnet (Oxford Instruments, Inc.) used in these measurements was determined to be negligible ($\sim -4 \times 10^{-4}$ ppm/h).

The temperature of the sample was regulated to within 0.2 K both temporally and spatially by directing dry nitrogen gas at a high flow rate around the NMR tube. Samples were allowed to equilibrate for at least 30 min at the set point temperature of the experiment before the NMR scanning was initiated. The gas temperature was controlled by a refrigerated heat exchanger (Kinetics Thermal Systems) and the NMR probe's heater. The conservative temperature range of this study was dictated at the bottom end by the reduced solubility of pertechnetate salts at low temperatures and at the top end by considerations of radiological safety.

The ^{99}Tc NMR scans were acquired at a rate of one per second, which ensured near-complete recovery of the magnetization between scans for the entire temperature range investigated in this work, according to past T_1 measurements.[24] At natural ^{17}O abundance levels and [TcO$_4^-$] $\geq$ 20 mM, the Tc(^{16}O)$_3$(^{17}O)$^-$ isotopomer's ^{99}Tc sextet was readily detectable after 1000 scans.

3. Computational Approach

Computational studies were performed to elucidate the effects of temperature and isotopic substitution on the NMR properties of pertechnetate in terms of the rovibrational average structure of the molecule. The general theory of thermal and isotope effects has been discussed extensively.[12,13,25,26]

To determine the rovibrational average value of a property, the vibrational force constants and the property derivatives need to be calculated. Both can be derived from calculated potential energy and corresponding property surfaces. The surfaces were calculated on a grid defined in the curvilinear symmetry coordinate system described by Gray and Robiette.[27] Most grid points were selected as outlined by Raynes and co-workers[7,28,29] in their study of similar properties in the methane molecule. These grid points allow for the determination of the linear and quadratic force constants, as well as the cubic force constants F_{111} and F_{222}. In our pertechnetate calculations, we have defined additional two-dimensional grids to obtain the symmetry coordinate force constants F_{1SS} (with $S = 2a, 3x, 4x$). Other combinations replacing S with the symmetric coordinates $2b, 3y$, etc. are related to the ones above by symmetry.[7,28,29] The force constants and property derivatives (calculated on the same grid) were determined by fitting polynomials to the grid points of the calculated potential energy and property surfaces with Mathematica routines.[30]

The rovibrational average molecular structure was calculated with the AVIBR code of Lounila et al.[26] Given the force constants, temperature, and atomic isotopes, the AVIBR code calculates the rovibrational average molecular geometry, the deviations from the equilibrium (zero-vibration) geometry, and the average linear and quadratic symmetry coordinate values $\langle S \rangle$ and $\langle S^2 \rangle$. The average symmetry coordinate values and the calculated property derivatives P were used to calculate the rovibrational average property defined in eq 1, with P_e being the value of the property for the equilibrium geometry:

$$\langle P \rangle \approx P_e + P_{S_1}\langle S_1 \rangle + \frac{1}{2}P_{S_1 S_1}\langle S_1^2 \rangle + P_{S_{2a} S_{2a}}\langle S_{2a}^2 \rangle + \frac{3}{2}P_{S_{3x} S_{3x}}\langle S_{3x}^2 \rangle + \frac{3}{2}P_{S_{4x} S_{4x}}\langle S_{4x}^2 \rangle + 3P_{S_{3x} S_{4x}}\langle S_{3x} S_{4x} \rangle \quad (1)$$

All calculations on the pertechnetate molecule were carried out with the Amsterdam Density Functional (ADF 2003.01) code.[31-33] Potential

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energy surface and property surfaces were calculated using density functional theory (DFT) within the VWN local density approach.[34] In some property calculations the Becke88[35] and Perdew86[36] (BP86) generalized gradient approximation (GGA) were used to assess the influence of the exchange-correlation potential on the property values. Both scalar relativistic and spin−orbit effects were included according to the zeroth order regular approximation (ZORA) methodology.[37,38] For the potential energy surface and the shielding surface the standard ADF all-electron ZORA-optimized Slater-type orbital (STO) basis sets TZ2P, triple-ζ with two polarization functions, were used for both technetium and oxygen. The TZ2P technetium basis set was augmented with four steep $1s$ functions, while the double-ζ $1s$ function of the oxygen TZ2P was replaced with the triple-ζ taken from the standard ZORA QZ4P basis set, as has been proposed for the calculation of accurate scalar couplings, especially those involving heavy atoms.[39−41] The numerical integration accuracy parameter INTEGRATION was chosen to be 7.0 throughout. The isotropic ^{99}Tc shielding constant surface was calculated with the NMR program[42,43] with the "Best" option selected. The J_{TcO} spin−spin coupling surface was calculated using the CPL program,[39] including the diamagnetic and paramagnetic orbital terms, and gyromagnetic ratios of 6.046×10^7 rad T^{-1} s^{-1} for ^{99}Tc and -3.628×10^7 rad T^{-1} s^{-1} for ^{17}O.

The effect of the molecular environment, i.e., the solvent, on the rovibrationally averaged properties of the pertechnetate molecule was incorporated using the COnductor-like Screening MOdel (COSMO).[44−46] For ϵ a value of 78.8 was used, whereas the radii defining the cavity surface around the pertechnetate unit were taken as 1.85 for Tc and 1.55 for O and 1.40 for the spherical solvent radius.

4. Results and Discussion

Variable Temperature Studies. The temperature dependence of the ^{99}Tc NMR chemical shift for the Tc(^{16}O)$_4$$^-$ isotopomer is illustrated in Figure 1. Analyses of pertechnetate solutions made with a different concentration ([NH$_4$TcO$_4$] = 0.01 M) or a different cation ([KTcO$_4$] = 0.1 M) revealed no differences of statistical significance.

The variation in peak heights reflects a broadening of the resonance as the temperature is moved above or below ∼30 °C. Tarasov et al.[24] have found that the ^{99}Tc T_1 of KTcO$_4$ measured at 18.01 MHz passes through a maximum at approximately 320 K, which suggests that the lifetime-broadened resonance should be narrowest at a higher temperature than we have observed. In our own inversion recovery experiments at 67.565 MHz, we observed a broad T_1 plateau at temperatures around 303−318 K for a range of Tc concentrations and for both the potassium and ammonium salts. This is consistent with the observation of a line width minimum at approximately 30
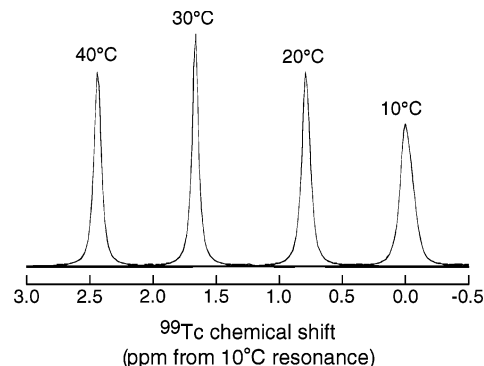
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Figure 1. Temperature dependence of the ^{99}Tc NMR spectrum of a 0.1 M NH$_4$TcO$_4$(aq) solution in a 7.04 T magnetic field (ν_L(^{99}Tc) = 67.565 MHz).
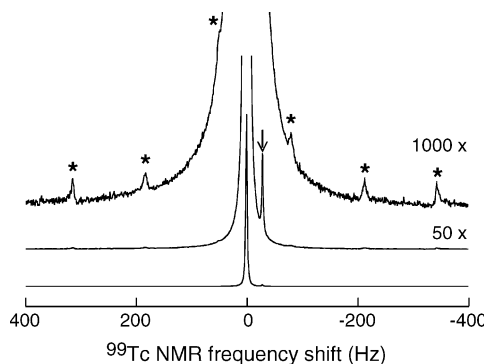

Figure 2. Expansion of the 30 °C ^{99}Tc spectrum from Figure 1, with vertical scaling given on the right. The stars (top spectrum) denote the sextet of the Tc(^{16}O)$_3$(^{17}O)$^-$ isotopomer, and the arrow (middle spectrum) identifies the singlet of the Tc(^{16}O)$_3$(^{18}O)$^-$ isotopomer.

°C. A second factor that potentially contributes to the temperature dependence of the line widths is thermal gradients in the sample. At 67.565 MHz, a temperature spread of only a few tenths of a degree can introduce significant inhomogeneous broadening in these resonances, which have intrinsic line widths of <5 Hz.

Isotope Effects. If it is assumed that a natural oxygen isotope distribution is expressed in an ensemble of pertechnetate ions, the probabilities of the three most common isotopomers, Tc(^{16}O)$_4$$^-$, Tc(^{16}O)$_3(^{18}O)^-$, and Tc(^{16}O)$_3(^{17}O)^-$, will be 99.043, 0.810, and 0.159%, respectively, which implies that the integrated intensities of the ^{99}Tc NMR signals will be in the ratio of approximately 623:5:1. The ^{16}O and ^{18}O isotopes have nuclear spin quantum numbers equal to zero, and therefore, the ^{99}Tc spectra of the Tc(^{16}O)$_4$$^-$ and Tc(^{16}O)$_3$(^{18}O)$^-$ isotopomers are singlets, but since $I = 5/2$ for ^{17}O, the ^{99}Tc spectrum of Tc(^{16}O)$_3$(^{17}O)$^-$ consists of six lines with equal spacings and integrated intensities. These expectations are confirmed in the spectra of Figure 2.

It may be seen from Figure 2 that ^{99}Tc has a different isotropic shift in the three isotopomers. The magnitude of the difference between the resonances of Tc(^{16}O)$_4$$^-$ and the other two isotopomers decreases monotonically with temperature, going from −28.9 Hz (−0.428 ppm) to −28.1 Hz (−0.416 ppm) for $\delta_{Tc(^{16}O)_3(^{18}O)^-} - \delta_{Tc(^{16}O)_4^-}$ and from −16.3 Hz (−0.241 ppm) to −13.6 Hz (−0.201 ppm) for $\delta_{Tc(^{16}O)_3(^{17}O)^-} - \delta_{Tc(^{16}O)_4^-}$ as the temperature was raised from 10 to 45 °C.[47] In experiments

(47) In the case of Tc(^{16}O)$_3$(^{17}O)$^-$, the ^{99}Tc resonance frequency was extracted by averaging the positions of the six lines in its spectrum.

Table 1. Comparison of Experimental[50] and Calculated Vibrational Transition Energies (cm^{-1})

mode	experiment	gas phase	COSMO
$\nu_1(A_1)$	912 ($\pm$1)	942	944
$\nu_3(F_2)$	912 ($\pm$4)	940	903
$\nu_2(E)$	325 ($\pm$2)	317	307
$\nu_4(F_2)$	334 ($\pm$10)	341	319

Table 2. Calculated ^{99}Tc Isotropic Shielding Data (ppm)

isotopomer	temp (K)	gas phase	COSMO	scaled COSMO
Tc(^{16}O)$_4{}^-$	283	−1485.511	−1425.879	−1430.230
	293	−1486.009	−1426.558	−1430.954
	318	−1487.307	−1428.319	−1432.811
Tc(^{17}O)$_4{}^-$	283	−1484.807	−1425.086	−1429.356
	293	−1485.315	−1425.776	−1430.092
	318	−1486.637	−1427.565	−1432.003
Tc(^{18}O)$_4{}^-$	283	−1484.174	−1424.373	−1428.570
	293	−1484.691	−1425.074	−1429.318
	318	−1486.035	−1426.889	−1431.257

performed at a lower field ($\nu(^{99}\mathrm{Tc}) = 18.01$ MHz), Tarasov et al.[1,4] measured a displacement in the ^{99}Tc chemical shift of −0.43 ppm upon each substitution of an ^{16}O atom with ^{18}O. They reported that this isotopic displacement did not change with temperature, but at the lower field of their instrument the small magnitude of the effect may not have been resolvable. Franklin et al.[48] have studied pertechnetate solutions that were artificially enriched in both ^{17}O and ^{18}O and reported finding that the ^{99}Tc chemical shift was displaced by −0.22 ppm upon each increment by one mass unit of one of the oxygens. The temperature dependence of the isotropic shift or the isotopic displacement was not discussed by them.

After Tc(^{16}O)$_3$(^{17}O)$^-$, the next most probable natural abundance isotopomer is Tc(^{16}O)$_2$(^{18}O)$_2{}^-$. Although it represents 0.0025% of the total pertechnetate ion population, or ∼1/64 of the population of Tc(^{16}O)$_3$(^{17}O)$^-$, the ^{99}Tc resonance of Tc(^{16}O)$_2$(^{18}O)$_2{}^-$ is contained in a singlet vs the sextet of Tc(^{16}O)$_3$(^{17}O)$^-$. The expected signal intensity of this single line will therefore be ∼10% of the intensity of a single line in the Tc(^{16}O)$_3$(^{17}O)$^-$ multiplet, well above the detection threshold. However, the separation between the Tc(^{16}O)$_2$(^{18}O)$_2{}^-$ and Tc(^{16}O)$_4{}^-$ resonances will be only 57 Hz in a 7.04 T magnetic field, which positions the Tc(^{16}O)$_2$(^{18}O)$_2{}^-$ line on the shoulder of the much larger Tc(^{16}O)$_4{}^-$ line. Observation of such a signal would be problematic at 67.565 MHz, but in a higher field magnet, the chemical shift difference should be sufficient to detect and separate the signals of the two isotopomers.

The Tc−O scalar coupling was determined from the Tc(^{16}O)$_3$(^{17}O)$^-$ sextet by measuring the separation between the outermost lines and dividing by 5. The measured J_{TcO} was found to decline monotonically with temperature, from 132.5 Hz at 10 °C to 131.9 Hz at 45 °C. Values of 131.6 Hz[49] and 133.3 Hz[1] have previously been obtained from the ten-line ^{17}O multiplet of NH$_4$TcO$_4$ solutions (with ref 49 and without[1] ^{17}O enrichment), in which the ^{17}O line widths were found to be a factor of 6 or greater than the ^{99}Tc line widths of Tc(^{16}O)$_3$(^{17}O)$^-$, while a value of 131.4 Hz was determined at 25 °C from the ^{99}Tc spectrum of ^{17}O-enriched KTcO$_4$.[48]

Computations. The computational approach outlined in the Computational Approach section was evaluated by calculating vibrational frequencies and average bond lengths for comparison with published experimental data. Table 1 shows that the calculated vibrational results are in good agreement with experimental data. The observed near-degeneracy of the ν_1 and ν_3 modes is reproduced by the gas-phase calculations, although overall the calculated frequencies are about 30 cm^{-1} too high. When the COSMO solvation model is included in the calculation, the frequencies of the ν_3, ν_2, and ν_4 are lowered, but the

symmetric stretch mode ν_1 is unchanged. The fact that the ν_1 is not affected by the solvation model can be attributed to the symmetry of this vibration. This mode maintains tetrahedral symmetry and has no dipole or quadrupole moment that could induce a polarization of the solvent. This is in contrast to the other three modes, where the vibration distorts the molecule and the resulting dipole and quadrupole moment induce a polarization of the solvent. A more detailed discussion can be found in a review article by Tomasi and Persico[51] and references therein.

The bond lengths obtained in the calculations are 1.717 Å for the free pertechnetate and 1.714 Å for the solvated molecule, which are in good agreement with the value of 1.711 Å obtained from single-crystal X-ray measurements.[52,53]

Inclusion of rovibrational contributions, which include both zero-point and finite temperature contributions, is found to increase the computed average bond length by 0.004−0.005 Å relative to the ground-state geometry, depending on the model. This bond length increase is accompanied by changes in the ^{99}Tc shielding of ∼−50 ppm (−40 ppm for the gas-phase model) and J_{TcO} by ∼+4 Hz, or approximately 3.5% of its total value.[54] The complete substitution of oxygen isotopes, going from Tc(^{16}O)$_4{}^-$ to Tc(^{17}O)$_4{}^-$, leads to a decrease of the rovibrational average bond length at 283 K of 8×10^{-5} Å (or twice this value when substituting ^{18}O for ^{16}O). The isotope effect is dominated by the symmetric stretch mode. A change in temperature from 283 to 318 K results in an increase of the rovibrational average bond length by 1.5×10^{-4} Å. When the various contributions to the temperature effect are analyzed, one finds that all vibrational modes contribute to the same order of magnitude.

Computed ^{99}Tc isotropic shielding values for a series of temperatures and isotopomers are presented in Table 2. Throughout this article, the definition and sign of the shielding in relation to the chemical shift conform to the standard convention.[55] The values in the scaled COSMO column were obtained by reducing the COSMO F_{11} force constant by 8%. This scaling lowers the vibrational mode ν_1 such that it is degenerate with ν_3, as observed experimentally by Weinstock et al.[50] This scaling thus

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(54) The various contributions of the different terms in eq 1 for the rovibrational averaged Tc(^{16}O)$_4{}^-$ at 283 K are P_e = −1445.031 ppm, $\langle P_{S_1} \rangle$ = −33.899 ppm, $\langle P_{S_1S_1} \rangle$ = −3.111 ppm, $\langle P_{S_2S_2} \rangle$ = −3.498 ppm, $\langle P_{S_3S_3} \rangle$ = 5.983 ppm, $\langle P_{S_4S_4} \rangle$ = −6.020 ppm, and $\langle P_{S_3S_4} \rangle$ = 0.065 ppm. Force constants and property derivatives are provided as Supporting Information.

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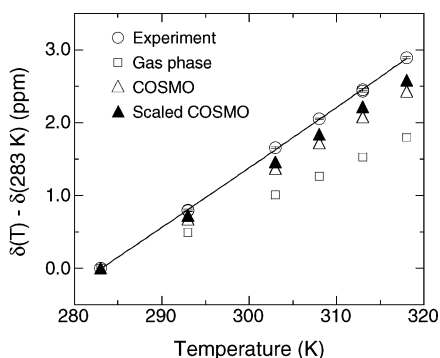
Figure 3. Measured and calculated displacements of the $Tc(^{16}O)_4^-$ isotopomer's ^{99}Tc isotropic chemical shift as a function of temperature ($\delta \equiv 0$ ppm at 283 K). The line is a least-squares fit of a second-order polynomial to the experimental data ($x_0 = -19.05$ ppm; $x_1 = 5.36 \times 10^{-2}$ ppm/K; $x_2 = 4.82 \times 10^{-5}$ ppm/K^2 ($R = 0.9999$)). The sample was 0.1 M NH_4TcO_4(aq).

provides insight into the effect of the symmetric stretch on the calculated properties.

The numbers in Table 2 were obtained using LDA functionals. To assess the influence of the exchange-correlation potential on the property values, additional calculations were performed using the VWN+BP86 functional. Inclusion of the BP86 functional leads to a shift of 8 ppm.

A discussion of chemical shifts usually begins with the definition of a reference molecule, but ^{99}Tc presents a number of special difficulties in this regard. Although the pertechnetate anion would seem to be an obvious choice, the variability of its resonance frequency with temperature, and the sensitivity to the molecule's structure that this implies, makes it questionable both experimentally and theoretically to base a chemical shift scale on TcO_4^-. Only a limited number of technetium-containing compounds have been studied by ^{99}Tc, none of them entirely satisfactory as a standard. The problem of choosing a standard is circumvented, however, by focusing on the thermally- or isotope-induced *changes* in the pertechnetate ^{99}Tc chemical shift rather than the shifts with respect to a fixed reference. The temperature dependence of the ^{99}Tc isotropic chemical shift predicted by the theoretical models of Table 2 is compared to experimental data in Figure 3. The dependent variable in this plot is the displacement of the chemical shift from the position of the resonance at 283 K, i.e.,

$$\Delta_T = \delta(T) - \delta(283\ K) \qquad (2)$$

As this plot shows, the observed direction of the chemical shift displacement (increasing shift with increasing temperature) is correctly predicted by both theoretical approaches. The magnitude of the displacement is underestimated by the gas-phase model, and incorporation of solvent effects is seen to improve the correlation of theory with experiment.[56] The difference between experimental and calculated results for the scaled COSMO approximation, which showed the best correlation, is less than one-third the difference for the gas-phase model.

The effect of oxygen isotope substitution on the ^{99}Tc isotropic chemical shift is illustrated in Table 3. The experimental results

Table 3. Oxygen Isotope Dependence of the ^{99}Tc Isotropic Chemical Shift (ppm): Comparison of Calculated and Experimental Results for TcO_4^-

single atom substitution	temp (K)	gas phase	COSMO	scaled COSMO	experiment
$^{16}O \rightarrow {}^{17}O$	283	−0.176	−0.198	−0.219	−0.241 (±0.012)
	293	−0.174	−0.196	−0.216	−0.227 (±0.005)
	318	−0.168	−0.189	−0.202	−0.201 (±0.007)
$^{16}O \rightarrow {}^{18}O$	283	−0.334	−0.377	−0.415	−0.428 (±0.015)
	293	−0.330	−0.371	−0.409	−0.427 (±0.006)
	318	−0.318	−0.358	−0.389	−0.416 (±0.009)

are the differences in the chemical shifts of the $Tc(^{16}O)_4^-$ and $Tc(^{16}O)_3(^{17,18}O)^-$ isotopomers, as given by the equation

$$\Delta_{isotope}^{exp} = \delta_{Tc(^{16}O)_3(^{17,18}O)^-} - \delta_{Tc(^{16}O)_4^-} \qquad (3)$$

while the theoretical data were obtained from the expression

$$\Delta_{isotope}^{theory} = \frac{1}{4}[\delta_{Tc(^{17,18}O)_4^-} - \delta_{Tc(^{16}O)_4^-}] \qquad (4)$$

Both the experimental and theoretical results therefore represent the ^{99}Tc chemical shift displacement caused by the substitution of a single ^{16}O atom by either ^{17}O or ^{18}O.

Table 3 shows that the theoretical models successfully account for the observation that the isotopic shift displacement decreases with increasing temperature. The predicted displacement from the gas-phase model is between 17 and 27% less than the experimental measurement over the temperature range considered, and inclusion of solvent effects with scaling reduces the discrepancy between theory and experiment to less than 10%.

The effect of the changes in the property derivatives due to the COSMO solvation model was found to be small. The improved agreement with experiment of the COSMO and scaled COSMO results is predominantly due to changes in the vibrational force constants. Lowering of especially the high frequency vibrational modes has a considerable effect on both the temperature- and isotope-induced chemical shift displacements. Hence, highly accurate vibrational force constants are needed to calculate the temperature and isotopic trends observed in experiment.

The overall accuracy of the calculated temperature and isotope effects is similar to those found in earlier studies on methane,[29] water,[10] and CSe_2.[9] Bühl[18] used molecular dynamics with a one-dimensional symmetric stretch potential to calculate the rovibrational contribution in MnO_4^-, which is isoelectronic to TcO_4^-. The temperature effect observed in our article is 1 order of magnitude larger than that seen by Bühl, which is not surprising as the bending and asymmetric stretching modes have been neglected in the latter case.

By fixing the dielectric constant in the solvation model over the entire temperature range, the effect of temperature on the solvent and the response of the pertechnetate ion to the changed environment are ignored.[14] To assess the effect of the solvent temperature on the shielding, an additional geometry optimization and property calculation were performed with an ϵ value of 67.0. This change from $\epsilon = 78.8$ approximates the change in the dielectric constant of water when heated by 35 °C.[57] On the basis of these calculations, we estimate that a 35 °C

(56) The experimental shift measured for $Tc(^{16}O)_4^-$, going from 283 to 318 K, is 2.894 ppm. The gas-phase, COSMO, and scaled COSMO shifts are 1.796, 2.440, and 2.581 ppm, respectively.

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Table 4. Comparison of Calculated and Experimental $^{99}Tc-^{17}O$ Scalar Coupling Data (Hz)

temp (K)	gas phase[a]	COSMO[a]	scaled COSMO[a]	experiment[b,c]
283	−120.286	−131.242	−130.836	132.5 (±0.2)
293	−120.235	−131.183	−130.772	132.1 (±0.1)
318	−120.102	−131.028	−130.615	131.9 (±0.1)

[a] Theoretical results for the $Tc(^{17}O)_4^-$ isotopomer. [b] Experimental results for the $Tc(^{16}O)_3(^{17}O)^-$ isotopomer. [c] The sign of J_{TcO} cannot be determined from the experimental spectra.

temperature increase of the solvent will increase the temperature-induced shift displacement by 0.1 ppm, which improves the correspondence with experiment.

Calculated and experimental values for the Tc−O scalar coupling are compared in Table 4. In contrast to the chemical shift, not only the temperature and isotope displacements but also the scalar coupling constant itself can be compared to experimental data. The scalar coupling values for the (COSMO) solvated pertechnetate ion seem to be in good agreement with those observed in experiment. This agreement might be somewhat fortuitous as the value of J_{TcO} depends on the exchange-correlation functional chosen. For example, for the VWN+BP86 functional the scalar coupling is reduced by 5 Hz. The theoretical models correctly predict the trend that the absolute value of the scalar coupling decreases with increasing temperature. The predicted changes due to temperature are smaller than those observed in experiment.[58] A solvation model involving explicit water molecules could improve the overall accuracy of both the scalar coupling value and the predicted trend, since the direct interaction of the oxygen with the water molecules will affect its electronic density and thereby J_{TcO}.

Although not presented here, the calculations predict the isotopic displacements to be in the order of 0.01 Hz. This change is 1 order of magnitude smaller than the displacement due to temperature changes and is smaller than the experimental uncertainty in the measurement of J_{TcO}.

5. Conclusion

The theoretical analysis presented suggests that most of the temperature and oxygen isotope dependence of the pertechnetate molecule's ^{99}Tc NMR parameters can be accounted for by accurate thermal averaging over rovibrational states. The ^{99}Tc resonance remained narrow over the entire temperature range, which implies that the ion maintained its tetrahedral symmetry despite changes in temperature. The primary modification in structure was thus in the Tc−O bond length, which can be calculated to be on the order of 10^{-4} Å. Inclusion of solvent effects in the theoretical treatment lowers the calculated vibrational frequencies and thereby improves the correspondence of the calculated and experimental values.

Strong sensitivity of a metal's solution state NMR parameters to temperature or surrounding isotope has been noted in a large number of cases.[59] Past explanations have identified thermally activated exchange phenomena as a common source of this sensitivity. In systems with low-lying electronic excited states, changes in the splitting of the ground state and the excited states

have also been proposed as a cause of strong temperature and isotope dependences.[60,61] On the other hand, among metal-containing molecules in the solution state TcO_4^- is a comparatively rare example in which the observed sensitivity can be mainly attributed to rovibrational corrections and effects within the electronic ground state. Because of the need to consider the effects of bonding and the small magnitudes of the NMR energies, the theoretical analysis involves a demanding computational effort.

Although temperature changes of as little as 1 °C can cause the pertechnetate ^{99}Tc peak to shift by an amount exceeding its line width, to our knowledge the observation of temperature-induced displacements of the chemical shift and scalar coupling has never been reported. While oxygen isotope effects have been studied in the past with isotopically enriched samples, we have shown that it is feasible to detect and resolve three, and perhaps four, pertechnetate isotopomers with oxygen isotope populations at natural abundance levels and to discern differences in their response to changes in temperature. For the $Tc(^{16}O)_3(^{17}O)^-$ isotopomer, an added interest is the possibility of measuring the Tc−O scalar coupling from the multiplet pattern of its ^{99}Tc spectrum. The scalar coupling has been determined from the ^{17}O NMR spectrum, but the ^{17}O lines are significantly broader than the ^{99}Tc peaks, and hence the ^{99}Tc-derived value can be considered more accurate. These findings suggest that the pertechnetate ion, in addition to being a useful test case for ab initio calculations, can serve as a sensitive model probe for solvent−ion interactions.

Supporting Information Available: NH_4TcO_4 solubility in water as a function of temperature (0−70 °C), temperature dependence of the ^{99}Tc chemical shift of 0.01 M NH_4TcO_4 and 0.10 M $KTcO_4$, ^{99}Tc inversion recovery T_1 measurements of 0.01 M NH_4TcO_4 and 0.10 M $KTcO_4$ at 10, 30, and 45 °C, and calculated force constants and property gradients from gas-phase and COSMO solvation calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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