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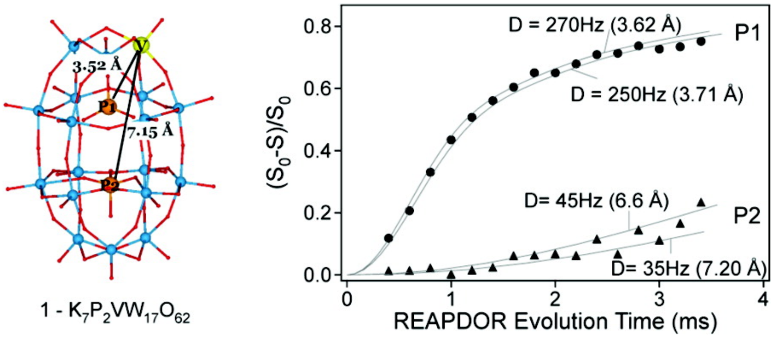

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Internuclear $^{31}P-^{51}V$ Distance Measurements in Polyoxoanionic Solids Using Rotational Echo Adiabatic Passage Double Resonance NMR Spectroscopy

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Abstract: We report the first results establishing rotational echo adiabatic passage double resonance (REAPDOR) experiments for distance measurements between a spin-$^1/_2$ (^{31}P) and spin-$^7/_2$ (^{51}V) pair in a series of vanadium-substituted polyoxoanionic solids from the Keggin and Wells−Dawson families. We have quantitatively measured $^{31}P-^{51}V$ distances in monovanadium substituted $K_4PVW_{11}O_{40}$, 1-$K_7P_2VW_{17}O_{62}$, and 4-$K_7P_2VW_{17}O_{62}$. Numerical simulations of the experimental data yield very good agreement with the averaged P−W/P−V distances determined from the X-ray diffraction measurements in the same or related compounds. REAPDOR is therefore a very sensitive P−V distance probe anticipated to be especially useful in the absence of long-range order. Our results suggest that REAPDOR spectroscopy could be broadly applicable for interatomic distance measurements in other spin-$^7/_2$−spin-$^1/_2$ nuclear pairs.

Introduction

Measurement of interatomic distances by solid-state NMR spectroscopy can provide important structural insight in noncrystalline and insoluble systems intractable by the traditional techniques, such as X-ray diffraction, neutron scattering, and solution NMR.[1−4] Internuclear distances in solid-state NMR are derived from the dipolar interaction. The strength of the dipolar interaction depends on the magnetogyric ratios of the nuclei as well as on the inverse cube of the internuclear distance, r^{-3}, thus providing a direct distance probe. Under magic angle spinning (MAS), the dipolar interaction is averaged to zero over the rotor cycle.[5] Therefore, development of NMR methods that recouple the dipolar interaction yet retain the high resolution under MAS conditions has become an active area of research.[3,5−10]

The recoupling is often achieved by the application of rotor synchronized radio frequency (rf) pulses.[5] Over the past eighteen years a variety of recoupling sequences under MAS have been developed to recover the dipolar couplings in isolated spin pairs. Techniques for homonuclear pairs of spin $^1/_2$ include rotational resonance,[11] dipolar correlation spectroscopy (DICSY),[12] dipolar restoration at the magic angle (DRAMA),[13] dipolar recoupling with a windowless sequence (DRAWS),[14] radio frequency-driven dipolar recoupling (RFDR),[15] and many others, while the method of choice for a heteronuclear pair of spins $^1/_2$ is rotational echo double resonance (REDOR).[16] In the case of a spin $^1/_2$ coupled to a quadrupolar spin REDOR can also be effective provided the quadrupole coupling constant C_Q is not much larger than the rf strength of the recoupling pulses.[4,17,18] However, when C_Q is large, the preferred methods are transfer of populations in double resonance (TRAPDOR)[19] and rotational echo adiabatic passage double resonance (REAPDOR).[20] TRAPDOR has the disadvantage that the dephasing of the signal is sensitive to the asymmetry parameter of the quadrupolar tensor as well as to the orientation of the internuclear vector with respect to the tensor.[21] An accurate distance determination from experimental TRAPDOR data can thus only be performed when the polar angles defining the orientation are known, but these angles are usually not easily accessible. REAPDOR dephasing is generally less sensitive to the orientation of the internuclear vector and the asymmetry parameter of the electric field gradient (EFG) tensor.[4,21]

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(1) Paik, Y.; Yang, C.; Metaferia, B.; Tang, S. B.; Bane, S.; Ravindra, R.; Shanker, N.; Alcaraz, A. A.; Johnson, S. A.; Schaefer, J.; O'Connor, R. D.; Cegelski, L.; Snyder, J. P.; Kingston, D. G. I. *J. Am. Chem. Soc.* **2007**, *129*, 361−370.
(2) Tycko, R. *Q. Rev. Biophys.* **2006**, *39*, 1−55.
(3) Goobes, G.; Stayton, P. S.; Drobny, G. P. *Prog. NMR Spec.* **2007**, *50*, 71−85.
(4) Gullion, T.; Vega, A. J. *Prog. NMR Spec.* **2005**, *47*, 123−136.
(5) Griffin, R. G. *Nat. Struct. Biol.* **1998**, *5*, 508−512.
(6) Schnell, I. *Prog. NMR Spec.* **2004**, *45*, 145−207.
(7) McDermott, A. E. *Curr. Opin. Struct. Biol.* **2004**, *14*, 554−561.
(8) Kristiansen, P. E.; Carravetta, M.; van Beek, J. D.; Lai, W. C.; Levitt, M. H. *J. Chem. Phys.* **2006**, *124*.
(9) Ernst, M.; Samoson, A.; Meier, B. H. *J. Chem. Phys.* **2005**, *123*.
(10) Dusold, S.; Sebald, A. In *Annu. Rep. NMR* 2000; Vol. 41, p 185−264.
(11) Raleigh, D. P.; Kolbert, A. C.; Levitt, M. H.; Griffin, R. G. *Israel J. Chem.* **1988**, *28*, 263−269.
(12) Ok, J. H.; Spencer, R. G. S.; Bennett, A. E.; Griffin, R. G. *Chem. Phys. Lett.* **1992**, *197*, 389−395.
(13) Tycko, R.; Dabbagh, G. *Chem. Phys. Lett.* **1990**, *173*, 461−465.
(14) Gregory, D. M.; Wolfe, G. M.; Jarvie, T. P.; Sheils, J. C.; Drobny, G. P. *Mol. Phys.* **1996**, *89*, 1835−1849.
(15) Bennett, A. E.; Ok, J. H.; Griffin, R. G.; Vega, S. *J. Chem. Phys.* **1992**, *96*, 8624−8627.
(16) Gullion, T.; Schaefer, J. *J. Magn. Res.* **1989**, *81*, 196−200.
(17) Coronado, E.; Gomez-Garcia, C. J. *Chem. Rev.* **1998**, *98*, 273−296.
(18) Katsoulis, D. E. *Chem. Rev.* **1998**, *98*, 359−387.
(19) Grey, C. P.; Vega, A. J. *J. Am. Chem. Soc.* **1995**, *117*, 8232−8242.
(20) Gullion, T. *J. Magn. Res., Ser. A* **1995**, *117*, 326−329.
(21) Kalwei, M.; Koller, H. *Solid State NMR* **2002**, *21*, 145−157.

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REAPDOR has thus far been successfully implemented for distance measurement in spin pairs composed of a spin ${}^1/_2$ and several types of quadrupolar nuclei. For example, the internuclear distance measurement using REAPDOR has been demonstrated in a ($I = {}^1/_2$, $S = 1$) spin pair by Gullion et al.,[22] in a ($I = {}^1/_2$,$S = {}^3/_2$) spin pair by van Wüllen et al.,[23] and in a ($I = {}^1/_2$, $S = {}^5/_2$) spin pair by Gullion et al.[24] Here we report that the internuclear distance between ^{31}P ($I = {}^1/_2$) and ^{51}V ($S = {}^7/_2$) can also be accurately determined from the REAPDOR experiments. We examined a series of monovanadium-substituted polyoxoanionic solids from the Keggin and Wells−Dawson families. We demonstrate that the experimental REAPDOR ^{31}P−^{51}V distance estimates are in close agreement with the average P−W/P−V distances determined from X-ray diffraction measurements. To our knowledge, this is the first demonstration of REAPDOR NMR in a ($I = {}^1/_2$, $S = {}^7/_2$) spin pair, suggesting that this class of experiments can be used as a sensitive P−V distance probe in the absence of long-range order.

Polyoxoanionic solids (polyoxometalates) were discovered in the early 1800s[25] and have been studied extensively ever since.[26] Because of their versatile chemistry and electronic properties, these compounds have found numerous applications as catalysts, dyes, and coatings and more recently have been considered for potential use as nanocomposite molecular devices, luminescent materials, and matrices for actinide separation.[17,18,27,28] In our recent work, we have explored ^{51}V and ^{31}P solid-state NMR spectroscopy for structural characterization of vanadium- and lanthanide-substituted polyoxometalate solids and demonstrated that anisotropic NMR parameters provide a wealth of information about the local geometry and electronic environment in these materials.[29−31] In this work, we illustrate that direct P−V distances in a series of vanadium-substituted Keggin and Wells−Dawson solids can be accurately determined by ^{31}P−^{51}V REAPDOR spectroscopy. We expect our approach to be particularly useful for structural characterization of noncrystalline polyoxometalate solids.

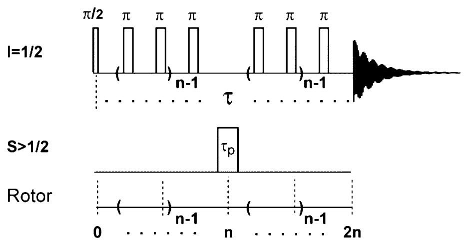

Figure 1. Schematic representation of the REAPDOR pulse sequence. The control and recoupling experiments, yielding the signals S_0 and S, are executed without and with the pulse in the $S > {}^1/_2$ channel, respectively.

Theoretical Background. A detailed description of the REAPDOR experiment can be found in a recent review.[4] Here we briefly introduce the essential points relevant for the ($I = {}^1/_2$, $S = {}^7/_2$) spin pair. The REAPDOR experiment combines two measurements using the pulse sequence shown in Figure 1. In one measurement, a spin echo signal of the $I = {}^1/_2$ spins is generated by a 90° excitation pulse followed by a sequence of refocusing 180° pulses that are applied synchronously with the sample rotation. In this part of the experiment no rf pulses are applied to the quadrupolar nuclei. The combination of the rf pulses and the sample rotation ensures that the signal is not affected by the heteronuclear dipolar interaction with the quadrupolar spins. In the second measurement, the same pulse sequence is repeated with the addition of a “recoupling” pulse applied to the quadrupolar spins at the midpoint of the string of 180° pulses. The objective of the recoupling pulse is to change the magnetic state of the quadrupolar spins such that the dipolar dephasing in the first half of the 180° sequence is not completely refocused in the second half. As a result, the intensity of the echo signal, S, measured in the presence of the recoupling pulse is smaller than that of S_0 measured in its absence. The fractional signal reduction $(S_0 - S)/S_0$, called the REAPDOR fraction, is a function of the size of the dipolar coupling constant D and, hence, of the internuclear distance r through the relationship

$$D = \gamma_S \gamma_I \hbar/(2\pi r^3) \tag{1}$$

where D is expressed in units of Hz and γ_S and γ_I are the magnetogyric ratios of the quadrupolar and observed nuclei, respectively. In practical applications the REAPDOR fraction is measured as a function of the evolution time τ between the excitation pulse and the beginning of the data acquisition (Figure 1). The dipolar coupling constant is then estimated by comparison of the resulting REAPDOR curve and a theoretical curve.

The size of the REAPDOR fraction is also affected by the efficiency of the recoupling pulse to modify the magnetic state of the quadrupolar nucleus. Since the quadrupole interaction in our case is much larger than the interaction with the rf irradiation, the recoupling pulse is not nonselective. Instead, the pulse affects only spins that at the time of its application have a small quadrupole splitting. To describe this process one needs to consider the quadrupolar and rf terms of the Hamiltonian describing the quadrupolar nucleus during the recoupling pulse:

$$H_S(t) = \frac{1}{2}Q(t)\left[S_z^{\,2} - \frac{1}{3}S(S+1)\right] + \omega_{1S}S_z \tag{2}$$

Here $Q(t)$ is the first-order quadrupolar splitting and $\omega_{1S} = 2\pi\nu_{1S}$ is the rf amplitude. The former is given by

$$Q(t) = \frac{1}{2}\omega_Q(3\cos^2\theta(t) - 1 - \eta_Q \sin^2\theta \cos 2\phi(t)) \tag{3}$$

where ω_Q is the quadrupole frequency (in rad/s) and η_Q is the asymmetry parameter of the quadrupolar tensor. The quadrupole frequency in units of Hz ($\nu_Q = \omega_Q/2\pi$) is related to quadrupolar coupling constant C_Q by

$$\nu_Q = \frac{3C_Q}{2S(2S-1)} \tag{4}$$

For $S = {}^7/_2$, $\nu_Q = C_Q/14$. In eq 3, $\theta(t)$ and $\phi(t)$ are the time-dependent polar angles of the magnetic field with respect to

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(22) Hughes, E.; Gullion, T.; Goldbourt, A.; Vega, S.; Vega, A. J. *J. Magn. Res.* **2002**, *156*, 230−241.
(23) van Wüllen, L.; Jansen, M. *Solid State NMR* **2005**, *27*, 90−98.
(24) Goldbourt, A.; Vega, S.; Gullion, T.; Vega, A. J. *J. Am. Chem. Soc.* **2003**, *125*, 11194−11195.
(25) Berzelius, J. J. *Pogg. Ann. Phys. Chem.* **1826**, *6*, 369−380.
(26) Pope, M. T.; Müller, A. *Angew. Chem. Int.* **1991**, *30*, 34−48.
(27) Chiang, M.-H.; Soderholm, L.; Antonio, M. R. *Eur. J. Inorg. Chem.* **2003**, *2003*, 2929−2936.
(28) Chiang, M.-H.; Williams, C. W.; Soderholm, L.; Antonio, M. R. *Eur. J. Inorg. Chem.* **2003**, *2003*, 2663−2669.
(29) Huang, W.; Schopfer, M.; Zhang, C.; Howell, R. C.; Gee, B. A.; Francesconi, L. C.; Polenova, T. *J. Phys. Chem. B* **2006**, *110*, 12340−12350.
(30) Huang, W. L.; Todaro, L.; Francesconi, L. C.; Polenova, T. *J. Am. Chem. Soc.* **2003**, *125*, 5928−5938.
(31) Huang, W. L.; Todaro, L.; Yap, G. P. A.; Beer, R.; Francesconi, L. C.; Polenova, T. *J. Am. Chem. Soc.* **2004**, *126*, 11564−11573.

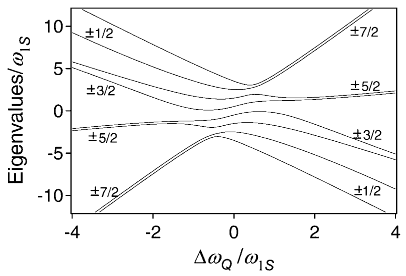

Figure 2. Eigenvalues and eigenstates of a spin $^7/_2$ nucleus in the rotating frame under rf irradiation of 20 kHz as a function of the quadrupole splitting. A small resonance-frequency-offset term $\delta\ S_z(\delta/w_{1S} = 0.05)$ was added to the Hamiltonian of eq 2 to lift the near degeneracy of the $\pm m$ levels.

the principal axis system (PAS) of the quadrupolar tensor. These angles are modulated by sample spinning, causing an oscillatory behavior of the quadrupole splitting around a zero average value. Figure 2 shows a plot of the eigenvalues of the Hamiltonian for the eight spin levels of a spin $^7/_2$ nucleus under rf on-resonance irradiation of amplitude $\nu_{1S} = 20$ kHz, as a function of the quadrupolar splitting. Under magic angle spinning, all quadrupolar spins experience either two or four zero-crossings of the quadrupolar splitting per rotor cycle. The eigenvalues thus repeatedly pass through the avoided level crossing shown in Figure 2. If a passage is sufficiently slow as to be adiabatic, the population of each energy level before the zero-crossing is transferred to the energy level to which it is connected by continuity. This results in the desired change of the magnetic state of the nucleus. However, if the passage is fast, the population transfer is incomplete. Therefore, the efficiency of the population-transfer and, hence, the size of the REAPDOR fraction diminish when the spinning frequency ν_R increases above a certain threshold value. The condition for efficient population transfer has been shown to be that the adiabaticity parameter

$$\alpha = \frac{{\nu_{1S}}^2}{\nu_R \nu_Q} \tag{5}$$

must be larger than a critical value of the order of 1.[32] For REAPDOR measurements of spins 1, $^3/_2$, and $^5/_2$, the critical values of α were found to be 0.25, 0.50, and 0.55, respectively.[4] One of the objectives of the present work is to evaluate the value of α above which the REAPDOR fraction for $S = {}^7/_2$ spins is independent of ν_Q, ν_{1S}, and ν_R.

In a sample with random orientations of quadrupole tensors, the recoupling pulse is most effective when during its application the largest fraction of spins experience one or three zero-crossings of their quadrupole splittings. This is achieved when the pulse duration τ_p equals one-third of a rotor cycle.[33] The fact that only a fraction of the spins participates in the REAPDOR process further implies that the dipolar dephasing depends on the exact time dependence of the dipoar interaction during the rotor cycle. Therefore, the REAPDOR fraction also depends on the asymmetry parameter η of the tensor and on the relative orientations of the internuclear vector and the quadrupole tensor. As commented above in the Introduction, investigations of the $S = 1$, $^3/_2$, and $^5/_2$ spin systems have revealed that the dispersion of REAPDOR curves due to such orientational variations is fortunately quite small.[4] Currently, we extend this investigation to $S = {}^7/_2$.

It is generally assumed that a straightforward application of this numerical procedure for the quantitative analysis of experimental REAPDOR data is only possible provided the two interacting spins form an isolated pair having no appreciable dipolar couplings with other spins of the same kind. In the case of REDOR it has often been noted that the dephasing behavior of a multispin system is a complex result of the magnitudes and orientations of all the internuclear interactions involved, thus necessitating extensive prior knowledge of the atomic geometry as a prerequisite for quantitative distance analysis.[34] Identical complications arise when REAPDOR is applied to a system containing more than two nuclei. Nevertheless, despite the fact that some of the systems studied in this work consist of two spins $I = {}^1/_2$ (^{31}P) and one spin $S = {}^7/_2$ (^{51}V), all REAPDOR results are perfectly interpretable in terms of the isolated ^{31}P−^{51}V pair model, even though the homonuclear $I-I$ dipolar interaction is stronger than the two heteronuclear $I-S$ interactions being analyzed. This fortunate simplification is the result of two favorable circumstances in the present situation. One is that the homonuclear interaction is greatly reduced by the sample rotation. This can be understood if we consider the part of the spin Hamiltonian that describes the spin physics of the $I = {}^1/_2$ nuclei:

$$H_I = \delta_1(t)I_{1z} + \delta_2(t)I_{2z} + \frac{1}{2}d_{12}(t)[3I_{1z}I_{2z} - \mathbf{I}_1\cdot\mathbf{I}_2] + d_{1S}(t)I_{1z}S_z + d_{2S}(t)I_{2z}S_z \tag{6}$$

where δ_1 and δ_2 are the chemical-shift offsets of the two phosphorus sites and d_{12}, d_{1S}, and d_{2S} describe the three pairwise dipolar interactions. The three dipolar coefficients are time dependent under MAS and so are δ_1 and δ_2 if the chemical shift is anisotropic. Since the 180° pulses of the pulse sequence (Figure 1) do not modify the homonuclear term in the interaction representation of the rf, this term is not “recoupled” by the pulses, so that to first order the homonuclear interaction is reduced to its vanishing average under MAS. However, since the homonuclear dipole term does not commute with the other terms in the Hamiltonian, higher-order terms in the Magnus expansion of average Hamiltonian theory[35,36] do contribute to the spin dynamics. Those contributions are however insignificant because the MAS frequency (10 kHz) is much larger than both the dipolar interaction (~0.3 kHz) and the chemical-shift difference. The situation somewhat resembles that of the simple excitation for the dephasing of rotational-echo amplitudes (SEDRA)[37] and RFDR[15] pulse sequences for homonuclear dipolar recoupling. Although the averaging scheme of those sequences is not exactly the same as ours, theirs having one π pulse per rotor cycle instead of two, it is worth noting that the residual dipolar coupling is greatly reduced in SEDRA when the rotor frequency is much larger than d_{12} and $|\delta_1 - \delta_2|$.[15] Moreover, since any signal-intensity reductions that the residual homonuclear dipolar interaction may cause are essentially

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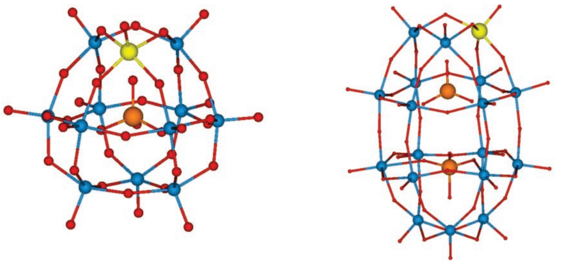
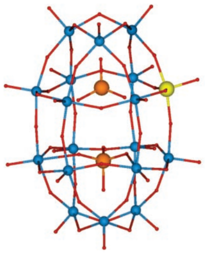
(32) Vega, A. J. *J. Magn. Res.* **1992**, *96*, 50−68.
(33) Ba, Y.; Kao, H. M.; Grey, G. P.; Chopin, L.; Gullion, T. *J. Magn. Res.* **1998**, *133*, 104−114.
(34) Rienstra, C. M. In *NMR Spectroscopy of Biological Solids*; Ramamoorthy, A., Ed.; CRC Press: Boca Raton, 2006; Vol. 1.
(35) Haeberlen, U. *High Resolution NMR in Solids: Selective Averaging*; Academic Press: New York, 1976.
(36) Mehring, M. *High Resolution NMR in Solids*; Springer-Verlag: Berlin, 1976.
(37) Gullion, T.; Vega, S. *Chem. Phys. Lett.* **1992**, *194*, 423−428.



(a) $K_4PVW_{11}O_{40}$ (b) $1\text{-}K_7P_2VW_{17}O_{62}$ (α_2-isomer)



(c) $4\text{-}K_7P_2VW_{17}O_{62}$ (α_1-isomer)

Figure 3. The structures of monovanadium substituted polyoxotungstate anions: (a) $K_4PVW_{11}O_{40}$, (b) $1\text{-}K_7P_2VW_{17}O_{62}\cdot 18H_2O$, and (c) $4\text{-}K_7P_2VW_{17}O_{62}\cdot 17H_2O$. The molecules are depicted in a ball-and-stick representation. In the anion, the tungsten atoms are shown in blue, the central P in orange, and the V atoms in yellow.

identical for the control spectrum (S_0) and the recoupled spectrum (S), it leaves the REAPDOR fraction unaffected. The second simplifying circumstance is that we are dealing with the dipole interactions of two observed nuclei with one recoupled heterospin, in contrast to the often considered case of one observed spin interacting with two recoupled spins. The latter case is complicated because the REAPDOR curve is determined by the simultaneous effects of two distances and an angle between the two internuclear vectors. Extracting these three parameters from a single dephasing curve is obviously problematic. Since in our case each ^{31}P independently sees its own interaction with the ^{51}V, we are not encumbered with a similar complication.

Experimental Section

Materials and Syntheses. All chemicals were obtained from commercial suppliers and used without further purification: sodium tungstate dihydrate ($Na_2WO_4\cdot 2H_2O$), sodium metavanadate ($NaVO_3$), tetrabutylammonium bromide [$(n\text{-}C_4H_9)_4NBr$], cesium chloride (CsCl), and vanadyl sulfate ($VOSO_4$) were purchased from Aldrich Chemicals. Hydrochloric acid, glacial acetic acid, phosphoric acid (85%), sulfuric acid, and bromine were purchased from Fisher Scientific. $\alpha\text{-}K_4PVW_{11}O_{40}$, $1\text{-}K_7P_2VW_{17}O_{62}\cdot 18H_2O$ (α_2-isomer), and $4\text{-}K_7P_2VW_{17}O_{62}\cdot 17H_2O$ (α_1-isomer) were synthesized according to the reported procedures.[38,39] The structures of their anions were reported previously,[31,40] and are presented in Figure 3. Their ^{51}V NMR spectra were reported and analyzed in our earlier work.[41] The resulting quadrupole tensor parameters are listed in Table 1.

Table 1. Experimental ^{51}V Quadrupolar Interaction Parameters of Monovanadium Substituted Keggin and Wells−Dawson Solids Reported in Our Recent Work[31,41]

	$K_4PVW_{11}O_{40}$	$1\text{-}K_7P_2VW_{17}O_{62}$ (α_2)	$4\text{-}K_7P_2VW_{17}O_{62}$ (α_1)
C_Q (MHz)	0.94 ± 0.12	0.88 ± 0.08	1.73 ± 0.01
$\nu_Q = C_Q/14$ (kHz)	67 ± 9	63 ± 6	124 ± 1
η_Q	0.48 ± 0.19	0.75 ± 0.23	0.37 ± 0.04

Solid-State NMR Experiments. The solid-state NMR spectra were acquired on a Tegmag Discovery spectrometer operating at 400.3, 162.0, and 105.2 MHz for ^1H, ^{31}P, and ^{51}V, respectively. A 4-mm triple-resonance Doty XC4 MAS probe was used. REAPDOR experiments were performed using the pulse sequence shown in Figure 1. Radio frequency field strengths of 44 kHz for the observed ^{31}P nucleus and about 45 kHz for recoupling of the ^{51}V nucleus were employed. ^{31}P chemical shifts were referenced externally to 85% H_3PO_4. All REAPDOR data were collected under a spinning frequency of 10 kHz, which was controlled to within ±2 Hz. The recoupling pulse length on the ^{51}V channel was 33.3 μs, corresponding to $\tau_p = \tau_R/3$. It was applied at a frequency close to the center of the ^{51}V spectrum. Spectra were recorded using 30−40 mg of sample. The data for the recoupling and control experiments were collected in an alternating fashion, with each scan using the recoupling pulse followed by a scan without recoupling. This scheme results in efficient cancellation of the effects of long-term fluctuations on the spectrometer performance. Typically, four scans were added for each experiment on $K_4PVW_{11}O_{40}$ and eight scans for $\alpha_2\text{-}1\text{-}K_7P_2VW_{17}O_{62}$ and $\alpha_1\text{-}4\text{-}K_7P_2VW_{17}O_{62}$. The acquisition delays were 570, 430, and 300 s corresponding to five times the ^{31}P spin−lattice relaxation times of $K_4PVW_{11}O_{40}$, $\alpha_2\text{-}1\text{-}K_7P_2VW_{17}O_{62}$, and $\alpha_1\text{-}4\text{-}K_7P_2VW_{17}O_{62}$, respectively.

Numerical Simulations. Numerical simulations of the REAPDOR curves were performed with the SIMPSON program,[42] as described previously.[4,24] Curves were calculated as functions of the product $D\tau$ for specific values of ν_Q, η_Q, ν_{1S}, ν_R, θ, and ϕ. Curves for particular values of D were derived from the $D\tau$ -dependent curves by appropriate adjustment of the τ scale.

Results and Discussion

^{31}P Spectra. ^{31}P-observed REAPDOR spectra of the Keggin compound $K_4PVW_{11}O_{40}$ obtained with a dipolar evolution period of $\tau = 2.6$ ms and acquired under adiabatic passage conditions ($\nu_{1S} = 44$ kHz, $\nu_R = 10$ kHz, see later) are shown in Figure 4. The ^{31}P NMR spectra display one single resonance at −14.2 ppm corresponding to the central ^{31}P atom. The bottom trace is the control spectrum S_0, the middle trace is the recoupled spectrum S, and the top trace is the difference ($S_0 - S$). At this spinning speed, no spinning sidebands due to chemical shift anisotropy (CSA) were observed. However, at slower spinning sidebands do appear. An analysis of the CSA tensor components based on the sideband intensities was recently reported for this Keggin structure.[29,41] The CSA components of the presently studied Wells−Dawson compounds were similarly reported elsewhere.[41]

Adiabatic Condition. As discussed earlier, the efficiency of the population transfer in REAPDOR depends on the adiabaticity of the passage of the quadrupole splitting during the rf irradiation of the recoupling pulse. The adiabaticity parameter α, which according to eq 5 depends on the rf strength, the quadrupole frequency, and the MAS frequency, must be of the

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(38) Domaille, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 7677−7687.
(39) Abbessi, M.; Contant, R.; Thouvenot, R.; Herve, G. *Inorg. Chem.* **1991**, *30*, 1695−1702.
(40) Niu, J. Y.; Guo, D. J.; Wang, J. P.; Zhao, J. W. *Cryst. Growth Des.* **2004**, *4*, 241−247.
(41) Huang, W. Ph.D. Thesis, University of Delaware, NJ, 2007.
(42) Bak, M.; Rasmussen, J. T.; Nielsen, N. C. *J. Magn. Res.* **2000**, *147*, 296−330.

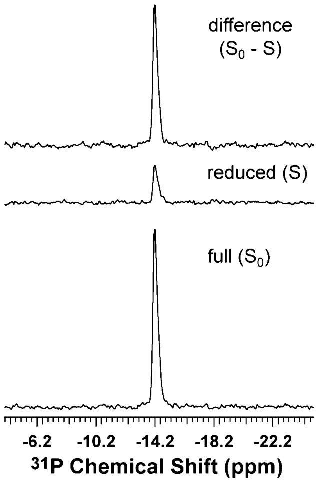

Figure 4. REAPDOR NMR spectra of $K_4PVW_{11}O_{40}$ obtained with a spinning frequency of 10 kHz and an evolution period of 2.6 ms. (Bottom) The control spectrum S_0 with no adiabatic passage pulse applied; (middle) the reduced spectrum S obtained with the adiabatic-passage pulse applied for one-third of the rotor cycle; (top) the difference spectrum ($S_0 - S$).

order of magnitude of at least 1. It has been shown numerically that the exact conditions for adiabaticity are different for quadrupolar nuclei of different nuclear spins ($\alpha > 0.25$ for spin-1 nuclei,[22] $\alpha > 0.5$ for spin-$^3/_2$ nuclei;[4] and $\alpha > 0.55$ for spin-$^5/_2$ nuclei[24]). The following experiments were performed to establish the adiabaticity condition for spin-$^7/_2$ nuclei.

REAPDOR measurements were performed on $K_4PVW_{11}O_{40}$ at a spinning frequency of 10 kHz and recoupling field strengths varying from 12 to 43 kHz. The quadrupole frequency being $\nu_Q = 67$ kHz (Table 1), this corresponds to α ranging from 0.21 to 2.8. Since the recoupling signal, S, decreases as a function of the dipolar evolution time τ, the adiabatic passage can best be observed when the evolution time is large. On the other hand, the signal decreases due to T_2 relaxation when τ gets long. In this study τ was chosen to be 2.6 ms. The result is shown in Figure 5a. The $(S_0 - S)/S_0$ ratio reached its asymptotic value at the field strength of 35 kHz, corresponding to $\alpha = 1.6$. In practice, a higher RF field power of 44 kHz was selected for the ^{31}P−^{51}V distance measurements in $K_4PVW_{11}O_{40}$ to be presented later.

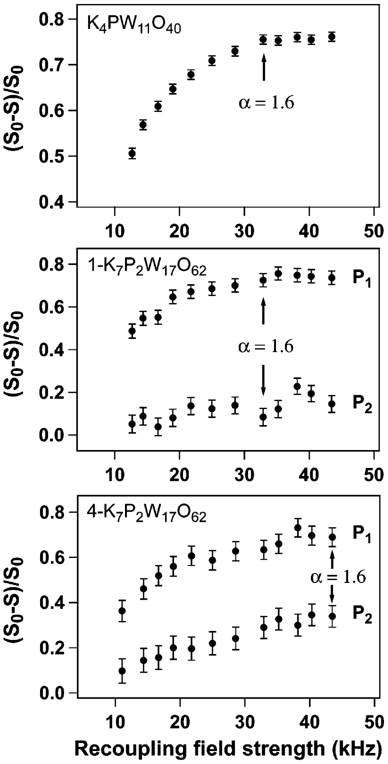

Figure 5. The experimental dependence of REAPDOR $(S_0 - S)/S_0$ values on the ^{51}V rf field strength for (a) $K_4PVW_{11}O_{40}$ ($\alpha = 1.6$ at 35 kHz); (b) 4-$K_7P_2VW_{17}O_{62}$ ($\alpha = 1.6$ at 44 kHz); (c) 1-$K_7P_2VW_{17}O_{62}$ ($\alpha = 1.6$ at 32 kHz). τ_p was 33.3 μs, the spinning frequency τ_R was 10 kHz, and the duration of the dipolar evolution period was 2.6 ms.

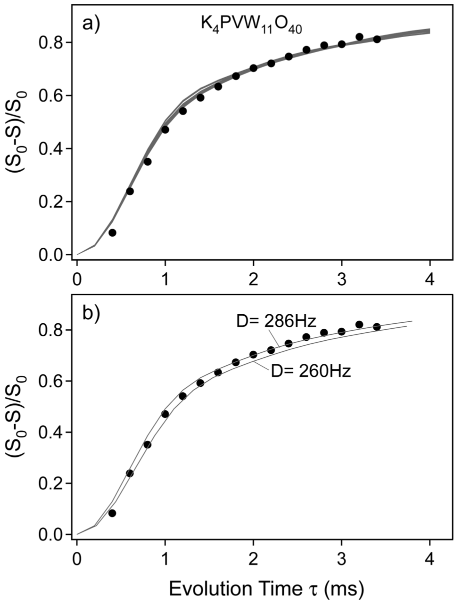

Figure 6. REAPDOR experimental data and simulated curves for $K_4PVW_{11}O_{40}$: (a) 48 simulated curves calculated for $D = 270$ kHz and pairs of polar angles covering the full nonredundant ranges of θ and ϕ. (b) Two simulated curves calculated for $D = 260$ and 286 kHz using the average of the 48 angle dependent curves. Other parameters were $\nu_Q = 67$ kHz, $\eta_Q = 0.48$, $\nu_R = 10$ kHz, $\nu_{1S} = 44$ kHz.

Figure 5 panels b and c show the dependence of $(S_0 - S)/S_0$ on the rf strength for the two isomers of the monovanadium substituted Wells−Dawson polyoxotungstate at 10 kHz MAS and $\tau = 2.6$ ms. The two distinct phosphorus atoms near the center of each compound exhibit different dephasing signal ratios owing to the different distances between these atoms and the vanadium atom. The P−V distance of one phosphorus (arbitrarily designated P1) is shorter than that of the other (designated P2) and, hence, has a stronger dipolar interaction with the vanadium atom, resulting in a higher $(S_0 - S)/S_0$ ratio for P1 than for P2 at this evolution time. Unfortunately, the data scatter does not allow one to identify a precise beginning point of a horizontal plateau of asymptotic dephasing. However, within experimental error, the data are consistent with the α threshold of 1.6 found above: In the case of 1-$K_7P_2VW_{17}O_{62}$, which has $\nu_Q = 63$ kHz (Table 1) the corresponding rf strength is 32 kHz, while in 4-$K_7P_2VW_{17}O_{62}$, which has $\nu_Q = 124$ kHz (see Table 1), it corresponds to an rf strength of 44 kHz. For distance determinations in the two Wells−Dawson isomers, the REAPDOR experiments were done with rf field strengths of 43 and 45.5 kHz to ensure adiabatic passages.

^{31}P−^{51}V Distance in $K_4PVW_{11}O_{40}$. Figure 6a shows the τ dependence of the experimental $(S_0 - S)/S_0$ values obtained for $K_4PVW_{11}O_{40}$ under adiabatic conditions. To extract the dipolar coupling constant, the experimental data points were matched with theoretical REAPDOR curves. Some results of the simulated curves calculated with the known quadrupolar parameters (Table 1) and the actually used rf strength and rotor frequency are shown as a collection of lines in Figure 6a. Since the data were obtained under adiabatic ^{51}V irradiation, the simulated curves are not sensitive to changes in ν_{1S}, ν_R, and ν_Q. However, as indicated in the Theoretical Background section, the curve is strongly influenced by the dipolar coupling constant D and, to a lesser extent, by the polar angles (θ, ϕ) of the interatomic P−V vector with respect to the quadrupole tensor PAS. The curves in Figure 6a were calculated for a constant value of 270 Hz for D and for a set of 48 pairs of polar angles (θ, ϕ) covering the full range of possible nonredundant orientations ($\theta = 0°, 30°, 60°, 90°$ and $\phi = 0°, 15°, 30°, ..., 165°$). Since the orientation of the quadrupole tensor in the crystal structure is not known, the distribution of these curves introduces an uncertainty in the fitted dipolar coupling constant. To evaluate the error associated with this distribution, we selected the (θ, ϕ) pairs that gave the maximum and minimum curves in the bundle and determined the respective D values that best agreed with the experimental data. In this manner we found $D = 280$ Hz for $(\theta, \phi) = (30°, 0°)$ and $D = 260$ Hz for (90°, 105°) (see Supporting Information for the curve fittings). These values deviate from the average D value (270 Hz) by −3.7% to +3.7%. Hence, the inherent uncertainty in the distance r is ±1.2%.

Another source of inaccuracy is the experimental scatter of the measured data points and their deviation from an ideal theoretical curve shape. To estimate the extent of this error, two theoretical curves forming the upper and lower bounds of the experimental points were simulated, as shown in Figure 6b. The average of the family of curves plotted in Figure 6a was used for this calculation. The dipolar coupling constants of the two curves in Figure 6b are 260 and 286 Hz, corresponding to P−V distances of 3.67 and 3.55 Å, respectively. It is worth noting that the initial portion of dephasing curve is more sensitive to the dipolar coupling than is the plateau region of the REAPDOR curve. Therefore, this initial portion was the focus of the curve fitting. Taking the two sources of uncertainty into account, we conclude that the NMR-determined P−V distance is 3.61 ± 0.07 Å.

The commonly observed positional disorder in substituted polyoxometalates was recently also reported for the vanadium sites in the compounds under investigation.[30,31,43] Because of the random orientational distribution of vanadium atoms in polyoxotungstate anions we could not extract the exact P−V distance from the X-ray structure. Instead, the P−V distance in the monovanadium Keggin polyoxotungstate anion is estimated from the crystallographic coordinates by averaging the distances between the twelve W or V atoms and the P atom. This average P−V distance is 3.55 Å in $[(n\text{-}C_4H_9)_4N]_4PVW_{11}O_{40}$,[31] which has the same anion as $K_4PVW_{11}O_{40}$. The difference between this and the REAPDOR result of 3.61 Å is well within the experimental REAPDOR uncertainty of 0.07 Å.

For the numerical analysis of the REAPDOR results to be valid the interacting ^{31}P and ^{51}V must form an isolated spin pair. An estimate of the distance of a phosphorus atom to the second closest vanadium site can be obtained by comparison with the related Keggin structure $[(n\text{-}C_4H_9)_4N]_5[PV_2W_{10}O_{40}]$ where it is at least 7.5 Å, according to the X-ray structure.[31] Because of the positional disorder of the V's, this distance is larger in most instances. While the packing of vanadium complexes has been shown to depend on the nature of cations,[30,31] we may assume that the intercage distances are similar in structures with identical cations, in this case K^+. The distance from ^{31}P to the next-nearest ^{51}V being at least twice as long as the distance within the cage, the dipolar interaction is at least eight times smaller and can thus confidently be neglected. Similarly, homonuclear ^{31}P−^{31}P dipolar interactions are also negligible because of the long P−P distance exceeding 10 Å.[31]

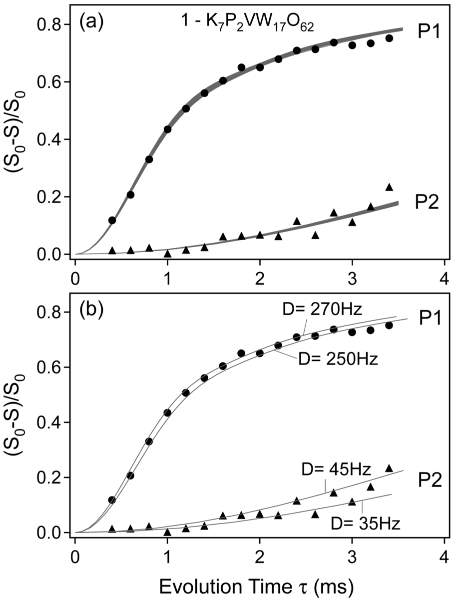

Figure 7. The REAPDOR experimental data and simulated curves for 1-$K_7P_2VW_{17}O_{62}$: (a) 48 simulated curves calculated for $D = 260$ kHz (P1) and 41 Hz (P2) and for pairs of polar angles covering the full nonredundant ranges of θ and ϕ; (b) simulated curves calculated with the indicated D values using the average of the 48 angle dependent curves. Other simulation parameters were $\nu_Q = 63$ kHz, $\eta_Q = 0.75$, $\nu_R = 10$ kHz, and $\nu_{1S} = 44$ kHz.

^{31}P−^{51}V Distances in 1-$K_7P_2VW_{17}O_{62}$. The Wells−Dawson-type polyoxotungstate anion, $[P_2W_{18}O_{62}]^{6-}$, has a highly symmetric structure D_{3h}. This species has two identical phosphorus atoms located in the center of the anion. Substituting one of the cap tungstens with a vanadium atom yields 1-$K_7P_2VW_{17}O_{62}$, the α_2 isomer of the monovanadium-substituted polyoxotungstate (see Figure 3b), and results in a magnetic inequivalence of the two central phosphorus atoms. ^{31}P MAS NMR spectrum (not shown) of 1-$K_7P_2VW_{17}O_{62}$ acquired at the spinning frequency of 10 kHz exhibits two phosphorus resonances at −11.04 and −13.11 ppm, which are consistent with the corresponding signals observed by solution NMR.[39]

Figure 7 shows two sets of experimental ^{31}P−^{51}V REAPDOR dephasing curves, corresponding to the two phosphorus atoms in the anion core interacting with the vanadium atom. The ^{31}P resonances at −11.04 and −13.11 ppm exhibit fast and slow dipolar dephasing and can thus be assigned to the sites P1 and P2 having the short and long distance to vanadium, respectively. To determine the distances we followed the same procedure as described above. Figure 7a shows the family of curves for the

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(43) Nishikawa, K.; Kobayashi, A.; Sasaki, Y. *B. Chem. Soc. Jpn.* **1975**, *48*, 889−892.

full range of 48 (θ, ϕ) angles, calculated with $D = 260$ and 41 Hz for the phosphorus atoms designated P1 and P2, respectively. Curve fitting to the angle pairs with the highest and lowest simulated curves leads to D-value ranges of +1.9% to −3.1% for P1, and +4.9% to −4.9% for P2. The inherent uncertainties in terms of distance r are thus about ±1.5%. Average curves bracketing the experimental data points (Figure 7b) correspond to $D = 250$ and 270 Hz (3.71 to 3.62 Å) for P1 and $D = 35$ and 45 Hz (7.2 and 6.6 Å) for P2. In conclusion, the REAPDOR-determined P−V distances may be said to be 3.66 ± 0.08 and 6.9 ± 0.3 Å.

As mentioned in the Theoretical Background, this three-spin system consisting of one ^{51}V and two ^{31}P nuclei is allowed to be analyzed quantitatively according to the isolated spin-pair approximation. The P−P distance may be assumed to be about the same as in the parent compound, where it is 4.02 Å.[40] This corresponds to a homonuclear dipole coupling constant of 303 Hz, which is larger than the two ^{31}P−^{51}V dipolar coupling constants (260 and 85 Hz). However, as pointed out above, the ^{31}P−^{31}P interaction has negligible effect on the REAPDOR.

Unfortunately, we cannot make a direct comparison between the distances derived from REAPDOR NMR and those obtained from the X-ray crystal structure of the same compound because crystal structures of this species or its analogues have not been reported. Attempts in our laboratory to generate diffraction-quality crystals have been unsuccessful. For a comparison we therefore resort to the P−W distances in the compound $[\{Ce(DMF)_4(H_2O)_3\}\{Ce(DMF)_4(H_2O)_4\}(P_2W_{18}O_{62})]\cdot H_2O$, the X-ray crystal structure of which was reported by Niu et al.[40] In view of the nearly equal ionic radii of the vanadium and tungsten ions in octahedral coordination,[44] the structures of the parent Wells−Dawson unit $[P_2W_{18}O_{62}]^{6-}$ in this compound and that of the vanadium-substituted anion may be expected to be similar. In the crystal structure of the parent molecule, the distances from P1 and P2 to the tungsten atoms in the cap are 3.52 Å and 7.15 Å, respectively.[40] While the REAPDOR result for the P2−V distance agrees with the X-ray data within experimental uncertainty, we find that the REAPDOR P1−V distance is slightly but significantly larger by about 0.14 Å. One could speculate that this discrepancy is due to V substitution in a cap position, leading to an expansion of the Well−Dawson unit and/or a displacement of the phosphorus atom.

^{31}P−^{51}V Distances in 4-$K_7P_2VW_{17}O_{62}$. The α_1 isomer is formed by the vanadium substitution in the belt of the Wells−Dawson-type anion, as illustrated in Figure 3c. Similar to the α_2 isomer, the vanadium substitution results in two magnetically distinct phosphorus atoms in this species. The isotropic chemical shifts for the two phosphorus atoms are −11.04 and −13.11 ppm, consistent with the solution values.[39]

Figure 8 shows the two sets of experimental ^{31}P−^{51}V REAPDOR dephasing curves of sites P1 (−11.04 ppm) and P2 (−13.11 ppm) at the shorter and longer distances from the vanadium, respectively. The distances were determined as above. Figure 8a shows the family of curves for the full range of polar angles, calculated for $D = 272.5$ Hz (P1) and 85 Hz (P2). Curve fitting to the angle pairs with the highest and lowest simulated curves gives D-value uncertainties of +4.5% to −3.9% for P1 and +4.7% to −2.4% for P2, leading to an over-all inherent uncertainty in r of about ±1.5%. Average curves bracketing the experimental data points (Figure 8b) correspond to $D =$ 280 and 260 Hz (3.52 to 3.67 Å) for P1 and $D = 90$ and 80 Hz (5.22 and 5.43 Å) for P2. In summary, the REAPDOR-determined P−V distances are 3.60 ± 0.10 and 5.32 ± 0.14 Å.

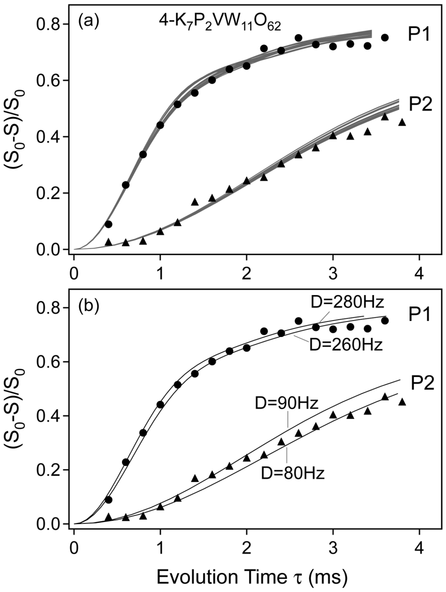

Figure 8. The REAPDOR experimental data and simulated curves for 4-$K_7P_2VW_{17}O_{62}$: (a) 48 simulated curves calculated for $D = 272.5$ kHz (P1) and 85 Hz (P2) and for pairs of polar angles covering the full nonredundant ranges of θ and ϕ; (b) simulated curves calculated with the indicated D values using the average of the 48 angle dependent curves. Other simulation parameters were $\nu_Q = 124$ kHz, $\eta_Q = 0.37$, $\nu_R = 10$ kHz, $\nu_{1S} = 44$ kHz.

The REAPDOR distances can again be compared with those of the X-ray structure of the parent compound $[\{Ce(DMF)_4(H_2O)_3\}\{Ce(DMF)_4(H_2O)_4\}(P_2W_{18}O_{62})]\cdot H_2O$, where the distances of P1 and P2 to the W atoms in the belt were reported as 3.55 and 5.25 Å, respectively.[40] The discrepancies with the corresponding REAPDOR distances are well within the experimental uncertainties.

Outlook and Applications to Other Systems. We envision the possibility of wider applications of REAPDOR and other dipolar recoupling methods for interatomic distance determinations involving spin-$^7/_2$ nuclei in areas ranging from materials to biological solids. Besides ^{51}V, spin-$^7/_2$ nuclei amenable to NMR investigations and important in biological systems and technologically include ^{45}Sc, ^{49}Ti, ^{59}Co, and ^{133}Cs. Of these, ^{45}Sc, ^{51}V, ^{59}Co, and ^{133}Cs have a desirable natural abundance of 100%. The nuclear properties of ^{45}Sc, ^{51}V, and ^{59}Co are similar with resonance frequencies at 9.4 T of 97.3, 105.2, and 94.9 MHz, respectively, and with typical quadrupole coupling constants C_Q ranging between 2 and 27 MHz.[45−50] The C_Q values of the compounds studied in this work are somewhat smaller than those reported for less symmetric molecular environments. ^{133}Cs has a lower resonance frequency, 52.46

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(44) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751−767.

(45) Medek, A.; Frydman, V.; Frydman, L. *Proc. Natl. Acad. Sci. U.S.A.* **1997**, *94*, 14237−14242.

(46) Medek, A.; Frydman, V.; Frydman, L. *J. Phys. Chem. B* **1997**, *101*, 8959−8966.

(47) Rossini, A. J.; Schurko, R. W. *J. Am. Chem. Soc.* **2006**, *128*, 10391−10402.

(48) Pooransingh, N.; Pomerantseva, E.; Ebel, M.; Jantzen, S.; Rehder, D.; Polenova, T. *Inorg. Chem.* **2003**, *42*, 1256−1266.

(49) Pooransingh-Margolis, N.; Renirie, R.; Hasan, Z.; Wever, R.; Vega, A. J.; Polenova, T. *J. Am. Chem. Soc.* **2006**, *128*, 5190−5208.

(50) Nielsen, U. G.; Jakobsen, H. J.; Skibsted, J. *J. Phys. Chem. B* **2001**, *105*, 420−429.

MHz at 9.4 T; however, its typical C_Q values are much smaller than 1 MHz in inorganic and organometallic solids,[51−53] making it a favorable isotope for distance measurements by dipolar recoupling. In this case, the more robust REDOR method can be applied, which employs a π-inversion pulse instead of an adiabatic-passage pulse to achieve dipolar recoupling.[54] ^{49}Ti is a challenging nucleus with low natural abundance (5.51%), low resonance frequency (22.04 MHz at 9.4 T), and large C_Q, ranging from 2.75 to 24 MHz in inorganic titanates.[55] Nevertheless, with isotopic enrichment dipolar recoupling experiments might be feasible in the ^{49}Ti-containing solids with more symmetric environments.

If RF amplitudes as large as 80 kHz are available and the C_Q has a large value of 13 MHz, one can achieve the adiabaticity of $\alpha > 1.6$ required for quantitative REAPDOR measurements, provided the sample rotation speed does not exceed 4.3 kHz (eq 4 and 5). For a smaller C_Q of 5 MHz, an rf-amplitude of 60 kHz combined with a rotation speed of 6.3 kHz is adequate. The results presented in this work indicate that dipolar coupling constants as small as 40 Hz can readily be measured. When ^{15}N or ^{31}P serve as the observed nucleus, this corresponds to atomic distances as large as 4.3 or 7 Å, respectively. The ^{13}C, ^{23}Na, and ^{79}Br resonance frequencies are very close to those of ^{45}Sc, ^{51}V, and ^{59}Co, thus preventing easy double-resonance studies with these nuclei. Nevertheless, it was demonstrated that a ^{23}Na−^{51}V TRAPDOR experiment can be readily conducted in a single-resonance probe with frequency and amplitude switching applied during the pulse sequence,[56] suggesting feasibility of other dipolar recoupling methods under similar hardware conditions.

Conclusions

We have introduced REAPDOR for the measurement of dipolar interaction and internuclear distances in spin-$^1/_2$ - spin-$^7/_2$ nuclear pairs. The ^{31}P−^{51}V distances in monovanadium substituted polyoxotungstates were measured with REAPDOR. The shapes of the experimental REAPDOR curves follow very closely those of the simulated curves, so that distances can be estimated with high confidence. Four of the distances ranged from 3.6 to 5.3 Å and were determined with an experimental uncertainty of less than ±3%. A fifth longer distance of 6.9 Å could be determined within ±4% uncertainty. The REAPDOR distances are in excellent agreement with X-ray structures of the same or closely related compounds. An advantage of the REAPDOR method in vanadium-substituted tungsten POM's is that it directly measures the P−V distance, in contrast to X-ray determinations, which can only yield the average of the P−V and P−W distances because of positional disorder of the substitution sites. Our results also suggest that REAPDOR spectroscopy could be broadly applicable to other spin-$^7/_2$ nuclei in inorganic and biological solids.

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Supporting Information Available: Figure 1S, experimental data, and the simulated REAPDOR dephasing curves; error analysis of REAPDOR fraction. This material is available free of charge via the Internet at http://pubs.acs.org.

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(51) Ashbrook, S. E.; Whittle, K. R.; Le, Polles, L.; Farnan, I. *J. Am. Ceram. Soc.* **2005**, *88*, 1575−1583.
(52) Wong, A.; Sham, S.; Wang, S. N.; Wu, G. *Can. J. Chem.* **2000**, *78*, 975−985.
(53) Skibsted, J.; Vosegaard, T.; Bildsoe, H.; Jakobsen, H. J. *J. Phys. Chem.* **1996**, *100*, 14872−14881.
(54) Hughes, E.; Jordan, J.; Gullion, T. *J. Phys. Chem. B* **2001**, *105*, 5887−5891.
(55) Padro, D.; Jennings, V.; Smith, M. E.; Hoppe, R.; Thomas, P. A.; Dupree, R. *J. Phys. Chem. B* **2002**, *106*, 13176−13185.
(56) van Wüllen, L. *Solid State NMR* **1998**, *10*, 235−240.