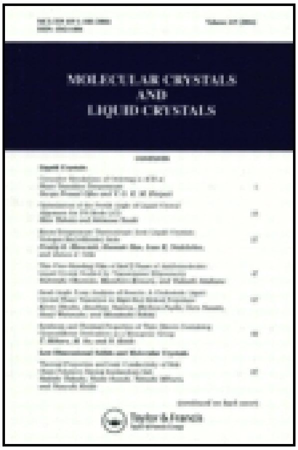

Molecular Crystals and Liquid Crystals

Magnetic Resonance Study of Vanadium Pentoxide Gels

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Version of record first published: 23 Aug 2006

To cite this article: O. R. Nascimento, C. J. Magon, L. V. S. Lopes, J. P. Donoso, E. Benavente, J. Paez, V. Lavayen, M. A. Santa Ana & G. Gonzalez (2006): Magnetic Resonance Study of Vanadium Pentoxide Gels, Molecular Crystals and Liquid Crystals, 447:1, 233/[551]-242/[560]

To link to this article: http://dx.doi.org/10.1080/15421400500377248

Mol. Cryst. Liq. Cryst., Vol. 447, pp. 233/[551]–242/[560], 2006
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400500377248

Magnetic Resonance Study of Vanadium Pentoxide Gels

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This work describes an Electron Paramagnetic Resonance (EPR) and Nuclear Magnetic Resonance (NMR) study of the vanadium pentoxide xerogel $V_2O_5 : nH_2O$ *with* $n \approx 1.8$ *Experiments were performed in the temperature range 65 K–310 K. The EPR spectrum at high temperatures exhibits the typical liquid-like eight lines-hyperfine structure. At low temperatures the EPR spectrum change to a* V^{4+} *anisotropic powder spectra. These two different regimes can be delimited by a transition temperature region centered at 280 K. Numerical simulations of the EPR spectra in the two temperature limits are in good agreement with the experimental data. Proton (*^1H*) NMR lineshapes, as functions of temperature were measured in the range 150–323 K and indicate that nuclear motional narrowing is effective at temperatures above 210 K, with an activation energy of 0.14 eV. The NMR spin-lattice relaxation recovery, associated to protons in the water molecules, was found to be non-exponential throughout the temperature range and described by two different relaxation processes. The slow relaxing component is temperature-independent and was attributed to water molecules located far from* V^{4+} *ions. The temperature dependence of the fast relaxing component shows maximum at*

This work is part of a joint program PRONEX/Fapesp/CNPq, Brazil (Grant 03/09859). The financial support of Capes and Fondecyt are also acknowledged.

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around 260 K, suggesting a relaxation process sensitive to the temperature induced dynamic structural changes in the vanadium oxide matrix.

Keywords: EPR; NMR; vanadium oxide gel; xerogels

INTRODUCTION

Vanadium pentoxide gels V_2O_5:$n$$H_2O$ have attracted considerable attention during the last decade because of their potential importance for electrochemical applications, as antistatic coatings in the photographic industry, electrodes for lithium batteries and electrochromic devices and as conducting matrix in biosensors [1–4]. These gels are composite materials formed by a solvent molecules (H_2O) trapped inside an oxide network (V_2O_5) [1]. The dynamics of the paramagnetic species of the oxide network and the dynamics of the protonic species in nanostructure material constitute an interesting problem [1,5,6]. In this work we examine the solid-to-liquid transition observed in the temperature range 265 K–295 K of the vanadium pentoxide network in the gel V_2O_5:$n$$H_2O$ with $n \approx 1.8$., by Electron Paramagnetic Resonance (EPR) and Nuclear Magnetic Resonance (NMR) spectroscopy. NMR is a well-known experimental technique for the study of molecular dynamics in solids. The temperature dependence of the nuclear lineshapes and spin-lattice relaxation rates allow the determination of motional parameters, as activation energies and correlation times of the molecular motion. Electron Paramagnetic Resonance (EPR) techniques have contributed to the understanding of vanadium oxides gels by determining the coordination environment of the paramagnetic centers and the changes of the EPR spectrum with the water content [1].

EXPERIMENTAL

Preparation of Vanadium Pentoxide Gel

A mixture of 50 ml of t-butyl alcohol (Merck p.a.) and 5 g of V_2O_5 (orthorhombic, Aldrich 99.6%) was refluxed for 6 h. After removing the remaining solid by centrifugation, the clear filtrate was diluted with 250 ml deionised water. Generated t-butyl alcohol and water in excess was then removed under vacuum. To yield a suspension, water was added to the remaining solid. The material was aged at room temperature during 2 month, yielding a red-brown colloidal V_2O_5 (monoclinic). Xerogel was obtained by drying the gel by evaporation in air.

Electron Paramagnetic Resonance

EPR experiments were carried out at *X*-band frequency (≈9.5 GHz), using a Varian E-109 spectrometer. Temperature was controlled within ±0.1 K by using a continuous flow liquid nitrogen cryostat.

Nuclear Magnetic Resonance

Proton H^1 NMR linewidth and spin-lattice relaxation measurements were carried out in powder samples from 150 to 330 K using a home build pulsed NMR spectrometer operating at 36 MHz equipped with a TECMAG NMR-kit, where a typical non-selective $\pi/2$ pulse length was about 2 µs. Spin-lattice relaxation times were determined using the standard saturation-recovery method. The ^1H lineshape was obtained from the Fourier transform of the free induction decay generated by a $\pi/2$ pulse after 16 accumulations.

RESULTS AND DISCUSSIONS

Electron Paramagnetic Resonance

The paramagnetic V^{4+} ion has a $3d^1$ electronic configuration with electronic spin $S = 1/2$ The nuclear spin for the ^{51}V isotope (natural abundance 99.5%) is $I = 7/2$. Therefore, an eight component hyperfine structure EPR spectra are expected from the dipole-dipole interaction between the magnetic moment of the ^{51}V nucleus and the electronic moment of the paramagnetic V^{4+} ions. The V^{4+} EPR spectrum is usually described by an axial spin Hamiltonian, which includes the hyperfine interaction.

$$H = g_{//}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A_{//} I_z S_z + A_{\perp}(I_x S_x + I_y S_y) \qquad (1)$$

β is the Bohr magneton; H_x, H_y, and H_z are the static magnetic fields; S_x, S_y, and S_z are the spin operators of the electron; I_x, I_y, and I_z are the spin operators of the nucleus; $g_{//}$ and $g_{\perp}$ are the parallel and perpendicular values of the *g*-tensor; A_{ll} and $A_{\perp}$ are the parallel and perpendicular values of the hyperfine *A*-tensor.

Figure 1 shows the X-band EPR spectra of the vanadium oxide gel V_2O_5:$1.8H_2O$ as at different temperatures. The EPR spectrum at high temperatures exhibits the typical liquid-like eight lines-hyperfine structure. At low temperatures the EPR spectrum change to a V^{4+} anisotropic powder spectra. The analysis of the EPR spectra reported in Figure 1 allows an estimate of transition temperature associated with the spectral change. In order to quantify this effect, we have plotted in Figure 2 the temperature dependence of the hyperfine splitting measured between two well-resolved lines in the low field side of

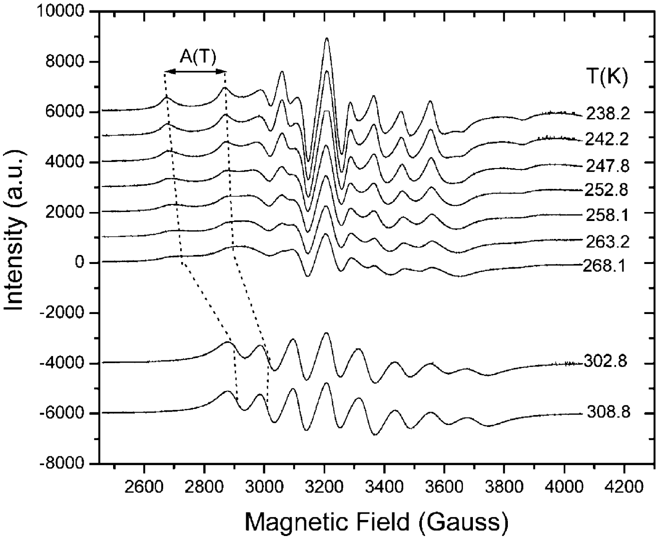

FIGURE 1 X-band EPR spectra of the vanadium pentoxide xerogel, $V_2O_5{:}nH_2O$, recorded as a function of temperature. The dashed lines indicate the field position of the two well-resolved lines in the low field side of the spectrum. The field separation between these two lines, $A(T)$, is a rough estimate of the hyperfine splitting.

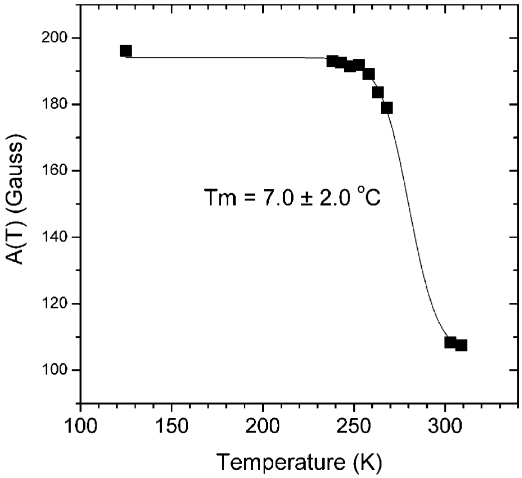

FIGURE 2 Temperature dependence of the hyperfine splitting, $A(T)$, measured according the procedure outlined in Figure 1. The solid-line plot is just a guide for the eyes. From this plot, a transition temperature region can be estimated at around 280 K.

the spectrum, as indicated in Figure 1 as a parameter $A(T)$. In spite of a lack of experimental data in a large temperature range, a rough estimate of a transition temperature of 280 K can be obtained.

The experimental V^{4+} EPR spectrum measured at 65 K was analyzed by numerical simulation of the spin Hamiltonian Eq. (1). The simulated EPR absorption derivative spectra of the $V_2O_5{:}1.8H_2O$ gel in Figure 2 closely reproduce the magnetic field dependence of the experimental spectrum. The best fit of the experimental spectrum is achieved for the spin Hamiltonian parameters $g_{//} = 1.9390$, $g_{\perp} = 1.9810$, $A_{//} = 203.3\ G$, and $A_{\perp} = 75.2\ G$. The best linewidth values needed to fit the experimental spectrum are $\Delta H_{//} = 26.0\ G$ and $\Delta H_{\perp} = 25.4\ G$. The simulated spectrum closely fit the experimental data if a broad lorentzian baseline is added to the V^{4+} ions spectrum, as indicated in Figure 3. We suggest that such broad line

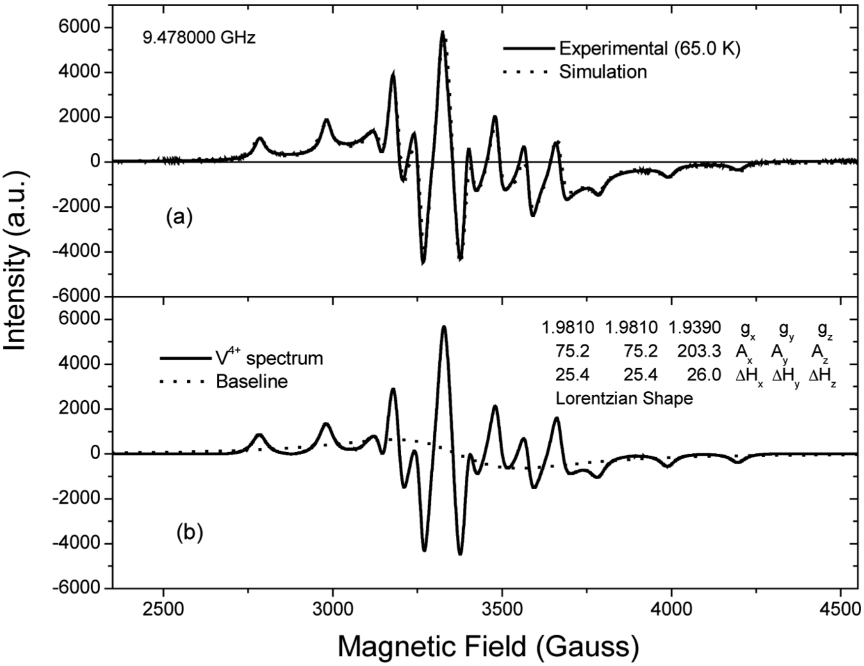

FIGURE 3 Experimental and simulated X-band EPR spectra of the vanadium pentoxide xerogel, $V_2O_5{:}nH_2O$. Experimental data recorded at 65 K (solid line) and simulated signal (dashed line) are shown in (a). The simulated spectrum consists of a structured spectrum due to isolated V^{4+} ions (solid line) added to a broad lorentzian baseline (dashed line) as shown in (b).

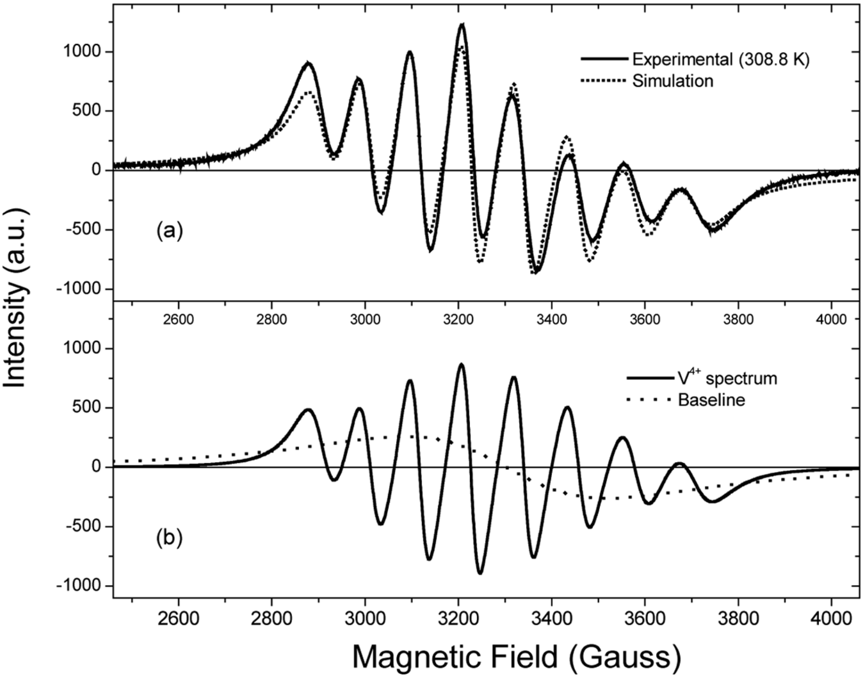

FIGURE 4 Experimental and simulated X-band EPR spectra of the vanadium pentoxide xerogel, $V_2O_5{:}nH_2O$. Experimental data recorded at 308.8 K (solid line) and simulated signal (dashed line) are shown in (a). The simulated spectrum consists of a structured spectrum due to isolated V^{4+} ions (solid line) added to a broad lorentzian baseline (dashed line) as shown in (b). Simulated parameters values written in the text.

could be attributed to vanadium pairs. From the fitting parameters, the values of the isotropic g- and A- factors, are respectively given by $g_0 = (g_{//} + 2g_\perp)/3 = 1.967$ and $A_0 = (A_{//} + 2A_\perp)/3 = 117.9\ G$.

The experimental V^{4+} EPR spectrum measured at 308.8 K was also analyzed by numerical simulation in the limit of high temperature (liquid-like spectra), where all anisotropic interactions are averaged to zero. A broad lorentzian baseline, with identical linewidth as that used for the fitting of the low temperature data, was included. The isotropic linewidth used to convolute with the hyperfine components was taken up to second order in the nuclear quantum number, $\Delta H = A + Bm_I + Cm_I^2$, with A,B, and C taken as adjustable parameters and found to be $A = 44\ G, B = -3\ G$ and $C = 2.8\ G$. The values of the isotropic g- and A-factors were $g_o = 1.971$ and $A_o = 113.5$ G, in good agreement with those obtained for the rigid-lattice spectrum.

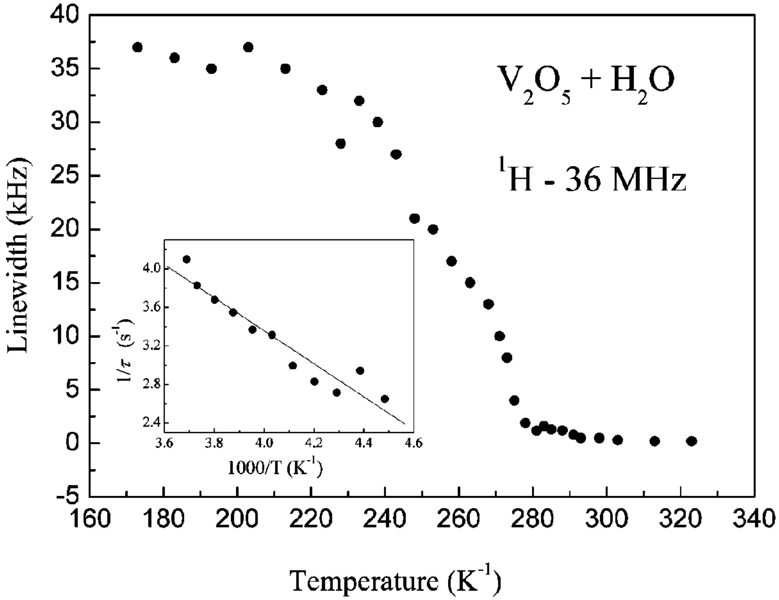

FIGURE 5 Temperature dependence of the ^{1}H NMR linewidth for the vanadium pentoxide gel $V_2O_5{:}nH_2O$. The insert in displays the temperature dependence of the motional correlation time, τ obtained from the line narrowing data.

Nuclear Magnetic Resonance

Proton NMR lineshapes and spin-lattice relaxation times were measured in the vanadium oxide xerogel ($V_2O_5{:}1.7\ H_2O$) sample in the temperature range between 150 K and 323 K. Figure 5 shows the temperature dependence of the linewidth of the ^{1}H NMR spectrum. Below 210 K the "rigid lattice" nuclear dipole-dipole interaction is the main source of line broadening. Above 210 K, proton mobility average out the inter-molecular dipolar interactions and the line narrows. The motional narrowing of the NMR line takes place when the rate of the fluctuations of the local dipolar fields, which is generally described by a correlation time τ, is of the order of the rigid lattice linewidth (ΔH_{rl}). An estimation of the correlation time for the line narrowing process may be obtained by the relationship [7].

$$\tau = \left(\frac{\alpha}{\Delta H - H_r}\right) \tan\left[\frac{\pi}{2}\left(\frac{\Delta H - H_r}{\Delta H_{rl} - H_r}\right)^2\right] \tag{2}$$

where ΔH is the linewidth at a given temperature, α is a parameter of the order of unity and H_r is the residual linewidth at high temperature

($H_r \sim 0.3\,\mathrm{Hz}$ for our samples). The insert in Figure 5 displays the temperature dependence of τ obtained from Eq. (2). Assuming a thermally activated process following the Arrhenius law, $\tau = \tau_0 \exp(E_A/kT)$, the activation energy E_A and the pre-exponential factor, τ_0^{-1}, can be estimated. The analysis of the line narrowing data in Figure 5 yields an activation energy of 0.14 eV.

Figure 6 shows the temperature dependence of the proton spin-lattice relaxation rates (T_1^{-1}). The relaxation recovery was found to be non-exponential throughout the temperature range. The magnetization recovery curve was fitted by a sum of two exponential functions associated with two different relaxation times. The longer component, $1/T_{1B}$, within experimental error, was found to be relatively temperature-independent, with a relaxation time of 30 ms. The shorter relaxation component, $1/T_{1A}$, shows a more accentuated temperature dependence, with a relaxation maximum at around 260 K. The relaxation data can be interpreted in terms of the motional modulation of the dipolar interactions. In the case of the xerogel studied here the dipole–dipole coupling of the proton nuclear spins (^1H–^1H in H_2O) and the dipolar coupling of nuclear and electronic spins (^1H-V^{4+} in V_2O_5:nH_2O) must be taken into account. The small value of the ^1H

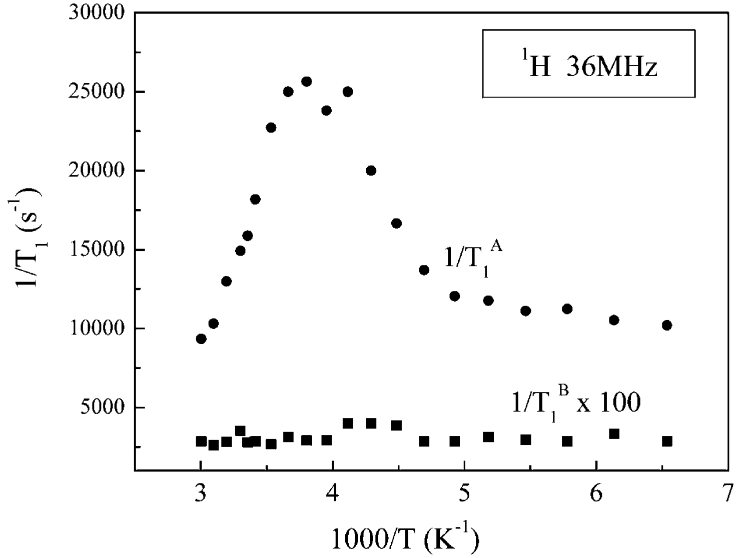

FIGURE 6 Temperature dependence of the ^1H spin-lattice relaxation rates (T_1^{-1}) for the vanadium pentoxide gel V_2O_5:nH_2O with $n \approx 1.7$, measured at the Larmor frequency of 36 MHz.

relaxation time, $T_{1A} \sim 40 - 80\mu s$, of the shorter relaxation component is around three order of magnitude smaller than the T_1 usually observed for H_2O in aerogels (T_1 between 50 and 800 ms) [8]. We attribute this shorter relaxation component in the vanadium pentoxide gel to the strong dipolar coupling of the proton spin with the V^{4+} paramagnetic ion. An elementary approach to describe this mechanism was presented by Slade *et al.*, which assume that the paramagnetic ions are uniformly distributed [9]. The interaction constant of the nuclear spin, I, with the electronic spin, S, is $C \approx \gamma_I^2 \gamma_e^2 \hbar^2 S(S+1)N/r^6$, where $\gamma_I = 2.675 \times 10^4$ Gauss^{-1}seg^{-1} is the gyromagnetic ratio of the ^1H nuclei, r is the closest approach distance between the paramagnetic ions and the proton, $\gamma_e = g\beta/\hbar = 1.77 \times 10^7$ G^{-1}s^{-1} is the electronic gyromagnetic ratio for an EPR signal with $g \approx 2.0$, and N is the number of paramagnetic centers per unit volume. In the case of dynamical processes in a reduced dimensionality, which is relevant in the case of intercalated species in layered structures, the relaxation expression is given by [10–12]:

$$\frac{1}{T_1} \propto C\tau \left[\ln\left(1 + \frac{1}{\omega_o^2 \tau^2}\right) + 4\ln\left(1 + \frac{1}{4\omega_o^2 \tau^2}\right) \right] \tag{3}$$

ω_o is the Larmor frequency and τ is the correlation time of the molecular motion modulating the nuclear spin interactions. Equation (3) predicts a maximum in T_1^{-1} when $\omega_0 \tau \approx 0.3$. Assuming a V–H distance of $\approx 3 - 4$ Å [1] and a V^{4+} paramagnetic ion concentration of the order of 10^{20} (i.e., 1% of the total vanadium ions in V_2O_5), Eq. (3) yields a relaxation rate maximum of $\approx 10^4 s^{-1}$, which is comparable to the value experimentally observed, $(T_1^{-1})_{max} \approx 3 \times 10^4 s^{-1}$ at 260 K (Fig. 6). Therefore, we conclude that the shorter relaxation component in Figure 6 is related to the dipolar coupling of the ^1H nuclear spin with the V^{4+} electronic spins, whereas the longer relaxation component can be attributed to the ^1H of the water molecules far away from the paramagnetic ions.

A remarkable feature of the ^1H relaxation curve in Figure 6 is the broad and asymmetric shape around the relaxation rate maximum (which spans over 120 K interval). The slope of the T_{1A}^{-1} data at the low temperature side of the maximum is smaller than those obtained from the high temperature side reflecting the heterogeneous dynamics of the proton in these temperature range. A satisfactory interpretation of the NMR relaxation data can be achieved by assuming that there are at least two distinct dynamics. Below 280 K the proton NMR is governed by the water dynamics (^1H motional narrowing in Figure 5, and the temperature dependence of the shorter relaxation component in Figure 6). However, above 280 K, it is suggested that the NMR relaxation reflects the structural modifications induced by the temperature in the EPR spectra of the V_2O_5, which change from a liquid-type spectrum to an immobilized one. In light of the EPR results one can build up a scenario in which the ^{1}H relaxation is strongly sensitive to the temperature induced dynamic structural changes in the vanadium oxide. The protons of water molecules far away V^{4+} ions (responsible for the longer ^{1}H relaxation component) are not affected by this dynamics but they can, indeed, contribute to the flexibility of the structure.

CONCLUSION

This paper reports an V^{4+} EPR and ^{1}H NMR study of the vanadium pentoxide xerogel $V_2O_5{:}nH_2O$ with $n \approx 1.8$. At low temperatures the EPR spectrum exhibits a typical V^{4+} anisotropic powder spectra, whereas, at high temperatures the spectrum has well resolved eight lines-hyperfine structure, typical of V^{4+} in liquid samples. By probing the EPR properties as a function of temperature, it was possible to gather information on the transition between these two regimes. Numerical simulations of the EPR spectra in the two temperature limits are in good agreement with the experimental data. Proton NMR lineshapes and relaxation rates are influenced by both the water and vanadium oxide dynamics.

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