PNNL-31937

Understanding Spin Coherence in Polyoxometalate-Based Molecular Qubits

September 2021

Grant E. Johnson
Patrick Z. El-Khoury

Prepared for the U.S. Department of Energy
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Overview

This research advances the understanding of spin decoherence mechanisms and addresses the grand challenges in quantum information science of generating and stabilizing quantum states that may be manipulated with single-atom precision. It is accomplished using unique capabilities developed at PNNL for ion soft landing and spatially resolved vibrational spectroscopy of well-defined supported molecular qubit (MQ) arrays. It addresses knowledge gaps impeding the development of MQ-based quantum devices by answering two scientific questions: 1) Can we minimize spin-lattice relaxation rates by tuning the substrate-MQ interface? 2) What is the optimum number of spin centers that enables sufficient coherent signal generation prior to decoherence through inter-MQ and MQ-support interactions? The objective is to develop predictive design principles for prolonging spin coherence lifetimes in arrays of optically-addressable MQs for quantum computing applications.

Introduction

MQs have advantages over their solid-state analogues, including reproducible fabrication by scalable chemical synthesis techniques, tailoring of spin centers through chemical design, and control of qubit spatial relationships by interfacial patterning. These favorable properties position MQs as leading candidates with which to form ordered optically-accessible arrays for quantum computing. Despite their advantages, improving the coherence times of MQs remains a long-standing challenge hindering their use in quantum devices. It is appreciated that ensembles of identical weakly-interacting spin centers are favored in this regard. The premise is that there is a fine line between optimum coherent signal generation and the onset of decoherence from spin centers interacting with one another and their surrounding environment. Understanding how the geometric and electronic structure of MQs and underlying supports may be tailored to abate different decoherence mechanisms (*i.e.,* nuclear spin diffusion, electron spin coupling, methyl rotation, spin-lattice relaxation, and spin diffusion barrier) is a challenge in designing MQ arrays with sufficiently long spin decoherence times ($T_2 > 100$ μs) for quantum information science (QIS). In particular, supported molecules undergo spin relaxation through insufficiently understood spin-lattice interactions (spin-phonon coupling), making the substrate-qubit interface an influential parameter.

Despite the control of composition and local environment made possible by inorganic chemistry, identifying and isolating MQs with tailored properties for assembly into arrays remains challenging. This is because molecules are often synthesized and characterized in solution, leading to a distribution of species and aggregation resulting from inactive counterions, solvent, and contaminants when transferred to supports. Consequently, the undefined composition, orientation, and environment of supported MQs makes it difficult to determine which decoherence pathways are dominant. This ambiguity impedes development of predictive structure-property relationships that enable rational design of MQs with improved spin coherence lifetimes. We are addressing this challenge using high-flux ion soft landing (SL), a versatile surface modification technique developed at PNNL that enables controlled delivery of polyatomic ions to substrates in clean vacuum conditions. Self-assembled monolayers are used to control the terminal functionality of the support (*e.g.,* CH_3, CF_3, COOH) to examine the effect of different electrostatic, covalent, and van der Waals interactions on the vibrational characteristics of supported MQs. Nanoscale imaging of the electromagnetic fields surrounding supported MQs is accomplished using spatially resolved nano-infrared (IR) and tip-enhanced Raman spectroscopy (TERS) capabilities developed at PNNL.

SL offers advantages for deposition of selected species, including generation of uniform films that are inaccessible with conventional preparation techniques. SL also enables unmatched “atom-by-atom” selectivity of the deposited species, which is critical to the studies described herein. Polyoxometalates (POMs) have properties that make them particularly amenable for use in supported qubit arrays, including being robust species that maintain their structural integrity in different environments. POMs may also accommodate single or multiple magnetic atoms (*i.e.,* V) in their structures, resulting in magnetic molecules with defined topologies and properties. The exceptional redox activity of POMs also provides an electrochemical route to tuning the strength of exchange coupling and electron delocalization, both of which affect spin coherence lifetimes.

Results

Keggin phosphotungstate anions ($PW_{12}O_{40}^{3-}$), doped with different numbers of spin-active V atoms, were prepared using a batch solution synthesis method where pre-synthesized $PW_{12}O_{40}^{3-}$ was combined with $NaVO_3$ in predetermined ratios to control the extent of V doping. Negative ion mode electrospray ionization mass spectrometry of the resulting solutions revealed the formation of POMs containing 1-3 spin-active V atoms (*i.e.,* $PVW_{11}O_{40}^{4-}$, $PV_2W_{10}O_{40}^{5-}$, and $PV_3W_9O_{40}^{6-}$). Due to the high charge states of the POMs and the broad isotopic distribution of W, it was necessary to acquire high-mass resolution mass spectra (m/Δm = 60,000) in an Orbitrap mass spectrometer to accurately assign the molecular formula of the anions (**Figure 1**). Following the identification of the V-doped species, the solutions were transferred to a custom-built high-flux ion soft landing system where mass-selected beams of the different V_x-doped POMs (x = 1-3) were deposited onto three self-assembled monolayer surfaces (SAMs) on gold. The kinetic energy of the anions and their coverage on the surface were both optimized to ensure intact deposition of a sufficient quantity of POMs to enable characterization by conventional and spatially-resolved vibrational spectroscopy.

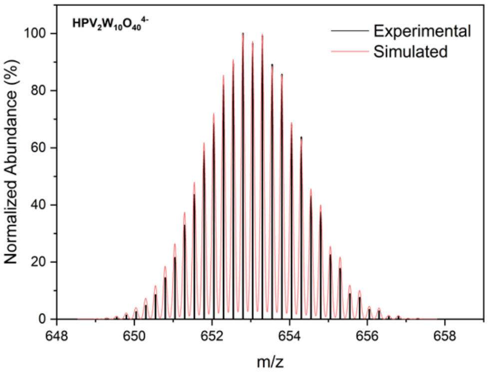

Fig. 1. Representative high resolution negative ion mode electrospray ionization mass spectrum showing excellent agreement between the experimental and calculated spectra of $HPV_2W_{10}O_{40}^{4-}$.

Following soft landing, the supported MQs were removed from vacuum and transferred to a commercial Fourier transform infrared spectrometer (FTIR) to determine how the different vibrational bands of the VWPOMs are influenced by their interactions with the underlying HSAM, FSAM, and COOHSAM supports. In these studies, three different SAMs were used that are terminated with either CH_3, CF_3, or COOH functional groups. Previous studies have shown that HSAM and FSAM surfaces on gold have different interface dipoles and charge transfer properties. In addition, COOHSAMs have been shown to electrostatically bind soft landed cations. POMs have four major vibrational bands that are associated with the central P-O, terminal $W{=}O_t$, and two bridging $W\text{-}O_{a,b}\text{-}W$ bonds of the Keggin structure. As shown in **Figure 2**, the P-O band of the central PO_4 group evolves from a single peak for $PW_{12}O_{40}^{3-}$ to two much broader peaks for $PVW_{11}O_{40}^{4-}$, regardless of the underlying support. This observation is consistent with the loss of symmetry in the single V-doped POM. The terminal $W{=}O_t$ bands exhibit a small shift toward lower wavenumber on the HSAM and FSAM surfaces and a

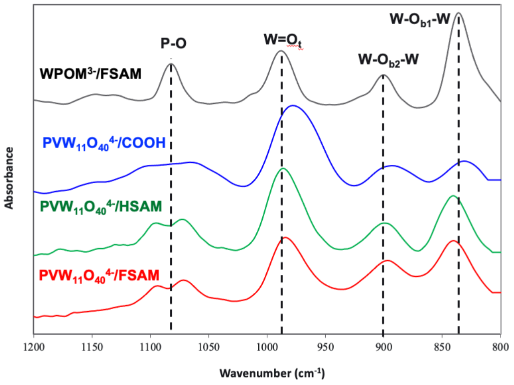

Fig. 2. Representative infrared spectra of $PVW_{11}O_{40}^{4-}$ soft landed on HSAM, FSAM, and COOHSAM supports on Au.

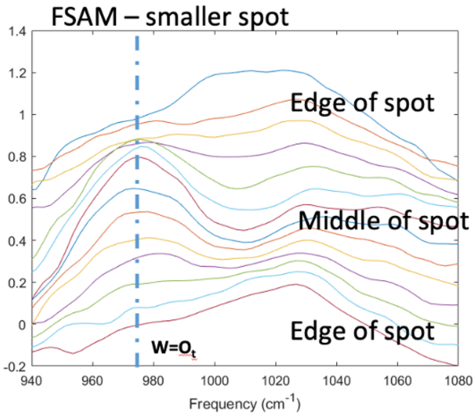

Fig. 3. Representative nano-IR spectroscopy results obtained across the deposited spot of $PVW_{11}O_{40}^{4-}$ on FSAM. The shift in frequency of the $W{=}O_t$ band with position indicates that the coverage and qubit-qubit interactions influence the vibrational modes of the POMs.

more pronounced shift on the COOHSAM. Because the terminal $W{=}O_t$ bonds are located on the outer shell of the POM structure, it is reasonable that the shifts in the IR peak positions depend on the functionality of the SAM. In a similar fashion, the bridging W-O_{b2}-W bands shift to slightly lower wavenumber on the HSAM and FSAM surfaces but more markedly on the COOHSAM. Interestingly, the W-O_{b1}-W bands show the opposite behavior, with a shift toward higher wavenumber on the HSAM and FSAM and toward lower wavenumber on the COOHSAM. Analogous data has also been obtained for soft landed WPOMs doped with 2 V-atoms We are currently conducting theoretical calculations on the structure and vibrational density-of-states of the supported POMs to better understand the cause of these shifts in the IR spectra. Nevertheless, it is clear that the terminal functional groups of the SAMs perturb the native vibrational modes of the V-doped POMs which has substantial implications for controlling spin-phonon coupling and decoherence rates.

While the FTIR spectra provide insight into how different surface functionality influences the vibrational modes of V-doped POMs, it is a bulk characterization technique that offers an ensemble averaged view of what is occurring at the surface. In addition to interactions between the VPOMs and the HSAM, FSAM, and COOH (MQ-substrate interactions) interactions are also possible between adjacent MQs (MQ-MQ). It is apparent that such interactions depend on the proximity of MQs with respect to one another and, therefore, the surface coverage of the soft landed MQs. Fortunately, the ion beams used to prepare these surfaces by SL have a Gaussian-like radial flux profile that is highest at the center and lower near the edges of the beam. Correspondingly, the VPOMs soft landed on each SAM also have a similar distribution of surface coverage from the center to the edge of the deposited spot. Therefore, using a spatially-resolved nano-IR spectroscopy technique developed at PNNL, it is possible to acquire spectra of VPOMs on SAMs at different surface locations (and coverages) and explore how MQ-MQ interactions influence the vibrational properties of supported VPOMS. As shown in **Figure 3**, the terminal $W{=}O_t$ band of the VPOMs exhibits a pronounced shift in wavenumber from the low coverage edge of the deposited spot (1025 cm^{-1}) to the high coverage center (975 cm^{-1}). Currently, these shifts in $W{=}O_t$ may be interpreted in one of two ways: 1) at the edges of the deposited spot, where the coverage of VPOMs is lower, each isolated VPOM interacts predominately with the underlying substrate without substantial perturbation from nearby adjacent POMs. At the center of the spot, where the coverage is higher, the POMs interact predominately with themselves rather than the underlying SAM; 2) the higher POM coverage at the center of the deposited spot results in reactions between adjacent POMs to form dimeric, trimeric, and possibly larger oligomers of $[(PVW_{12}O_{40}^{4-})_x = 1 - ?]$ when the sample is removed from vacuum. We are currently performing theoretical calculations to better understand which scenario better explains the trends observed experimentally in the vibrational bands. Nonetheless, our experiments reveal the impact of both MQ-substrate and MQ-MQ interactions on the vibrational modes of V-doped POMs which, in turn, determine their spin decoherence rates and suitability for quantum computing applications.

Conclusion

These findings have substantial implications for the immobilization of MQs in optically-addressable arrays for quantum computing applications. As spin-phonon coupling is one of the major contributors to spin decoherence, understanding how different surfaces with specific chemical functionality perturb the native vibrational modes of V-doped POMs is central to: 1) designing MQ-support interactions that minimize spin decoherence rates and; 2) determining the optimum density of MQs that produces coherent signals without triggering MQ-MQ induced spin decoherence. Two scientific manuscripts are currently in preparation based on this work describing: 1) how the different chemical functionality (CH_3, CF_3, and COOH) of SAM supports affects the vibrational modes of singly V-doped WPOMs; and 2) how the presence of multiple V atoms in $PV_xW_yO_{12}^{z-}$ (x = 1-3, y = 11-9, z = 4-6) influences molecular structure, spin-spin coupling, and spin-phonons coupling. Ongoing work includes characterization of these supported POM qubits using spatially-resolved scanning nitrogen vacancy magnetometry and electron paramagnetic resonance spectroscopy. These techniques will allow us to determine the magnetic topology of the qubit arrays and their spin decoherence times. This work is intended to form the foundation of a proposal to be submitted to the DOE Office of Basic Energy Sciences in the area of Quantum Information Science.

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