

Raman Spectroscopy and Aging of the Low-Loss Ferrimagnet Vanadium Tetracyanoethylene

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Primary CNF Tools Used: GCA 5x stepper, AJA sputtering deposition system, P10 profilometer, Westbond 7400A ultrasonic wire bonder

Abstract:

Vanadium tetracyanoethylene ($V[TCNE]_x$, $x \sim 2$) is a low loss organic-based ferrimagnet with a magnetic ordering temperature $T_C > 600$ K and growth compatibility with many substrates. These properties make it an attractive candidate for coherent magnonics and quantum transduction applications. However, like other organic materials, it is sensitive to air. Encapsulation extends its lifetime in ambient conditions from hours to weeks, but its aging mechanism is not well understood. Here we report micro-focused Raman spectroscopy of $V[TCNE]_x$ as it ages to understand the structural changes accompanying aging and the corresponding changes in magnetism. We also study laser-induced degradation, which enables laser patterning by removing magnetism. These findings enable a local optical probe of $V[TCNE]_x$ quality when local magnetization characterization is impossible, and they enable a new form of patterning.

Summary of Research:

$V[TCNE]_x$ is an organic-based material with low magnetic damping comparable to that of yttrium iron garnet (YIG) at room temperature [1]. It can be grown on a variety of substrates and is an attractive alternative to YIG for coherent magnonics applications. One challenge of working with $V[TCNE]_x$ is its air sensitivity. While encapsulation extends its lifetime from hours to weeks, its aging mechanism is not well understood.

In this work we use a combination of confocal microscopy, micro-focused Raman spectroscopy, ferromagnetic resonance (FMR) and *ab initio* calculations to study $V[TCNE]_x$ and its aging mechanisms [2].

We characterize $V[TCNE]_x$ using Raman spectroscopy to study its structure. By comparing the spectrum with density functional theory (DFT) calculations, we assign the experimental Raman peaks to V-N (336, 457, 543 cm^{-1}), C=C (1308, 1411, 1530 cm^{-1}), C=N (2121, 2194, 2214 cm^{-1}) vibrational modes (Figure 1). These Raman peaks reflect the bonding between vanadium ion and TCNE group and are relevant for magnetism.

Having characterized a pristine $V[TCNE]_x$ film, we next study the effects of aging by laser-induced damage. This allows us to study the effect of aging in the absence of diffused oxygen and water. The response of $V[TCNE]_x$ under high intensity light is particularly relevant for quantum applications requiring coupling between $V[TCNE]_x$ and defect centers [3]. Under focused laser illumination, the sample shows an increase in photoluminescence, which we characterized by a laser damage susceptibility χ_{PL} . This laser damage susceptibility increases with laser power, indicating that the damage is not a single photon process (Figure 2). Instead, this suggests it is a heating effect, where chemical reaction rate increases nonlinearly with temperature.

Next we examine the Raman spectra after the sample has been laser damaged. Raman intensity near 2121 cm^{-1} reduces while intensity near 2202, 2225 cm^{-1} increases. Peaks near 1308, 1530 cm^{-1} increases in intensity and linewidth. Low wavenumber peaks (300-600 cm^{-1}) vanishes. These features

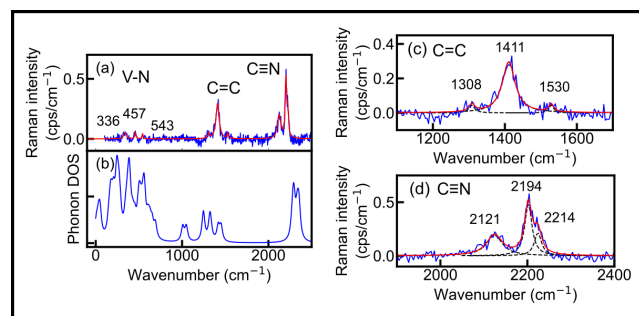


Figure 1: (a) Experimental $V[TCNE]_x$ Raman spectrum. (b) *Ab initio* density functional theory (DFT) calculated density of states where each mode is broadened as a Lorentzian with a full width half maximum (FWHM) of 20 cm^{-1} . (c) C=C, (d) C=N peaks. Individual Lorentzian fits (dashed).

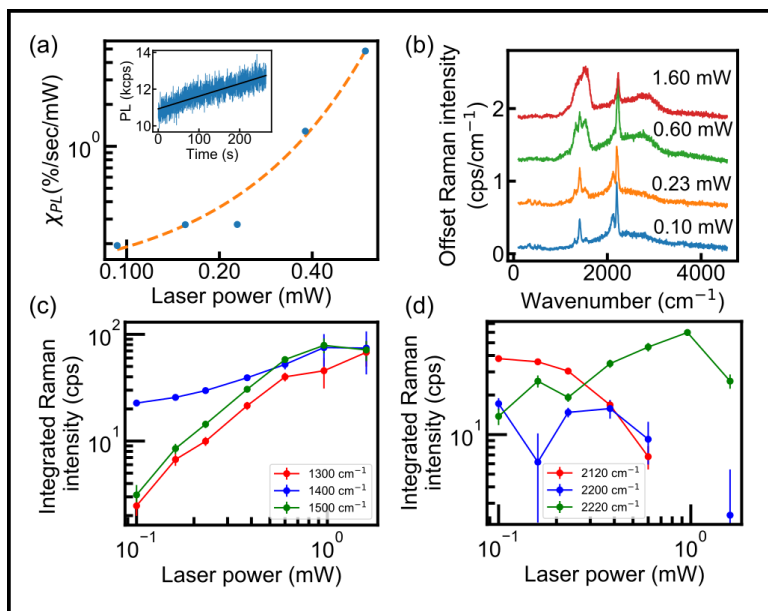


Figure 2: (a) Laser damage susceptibility increases with optical power. (Dashed) A guide to the eye showing an exponential dependence with optical power. (Inset) Photoluminescence over time and a linear fit. (b) Raman spectra at different optical power. (c), (d) Integrated intensity from individual Raman peaks for C=C and C=N peaks.

are clear signatures of aging and suggest a reduction in bonding between vanadium and TCNE. This may reduce spin exchange and magnetization.

We next study V[TCNE]_x aging at room temperature in ambient atmosphere. One clear visual signature of aging is the film turning from opaque to transparent, as shown in Figure 3 where the transparency front advances from sample edges to the center, which we attribute to diffused oxygen and water across the encapsulation epoxy. In comparison, the central region does not show a strong color change, suggesting it has not been oxidized. We observe similar changes in Raman spectra for both a laser damaged sample and a naturally aged sample, indicating similar reactions are happening in both processes. A more drastic signature of aging is the increase in laser damage susceptibility χ_{PL} , which increases exponentially in time while the effective magnetization reduces over time. This establishes a link between optical properties and magnetic properties and show that optical measurement can be a local probe of V[TCNE]_x film quality.

With the findings of V[TCNE]_x laser damage, we explore using it for patterning by selectively damaging V[TCNE]_x to remove magnetism. We show a proof-of-concept demonstration by writing the collaboration's affiliations on a V[TCNE]_x film (Figure 4). Laser damaged regions have a higher photoluminescence. This also turns the material transparent which appears bright in the optical micrograph.

This work shows optical measurement can be used to assess V[TCNE]_x film quality. In the future, we plan to study the anisotropy and spin wave modes of patterned V[TCNE]_x.

References:

- [1] H. Yu, et al. "Ultra-Narrow Ferromagnetic Resonance in Organic-Based Thin Films Grown via Low Temperature Chemical Vapor Deposition" *Applied Physics Letters* 2014, 105, 012407.
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- [3] D. R. Candido, et al. "Predicted Strong Coupling of Solid-State Spins Via a Single Magnon Mode" *Materials for Quantum Technology* 2020, 1, 011001.

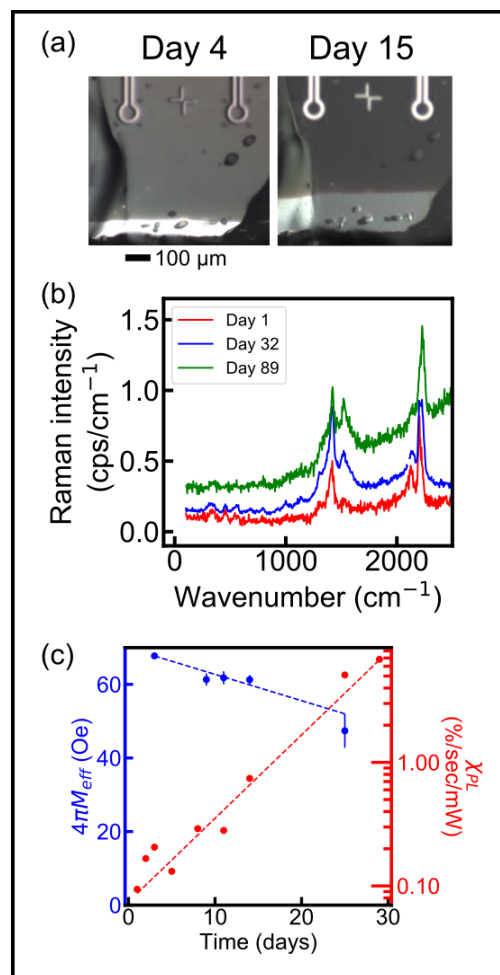


Figure 3: (a) Visual indication of aging, where the transparency front advances from sample edges to the center, revealing the underlying reflective aluminum layer. (b) Raman spectra without baseline subtraction at the central region. Fluorescence background increases and peaks at 1300, 1500 cm⁻¹ (C=C) increases. Low wavenumber (300-600 cm⁻¹, V-N) and 2120 cm⁻¹ (C=N) peaks vanish. (c) A reduction in the effective magnetization $4\pi M_{eff}$ and an increase in laser damage susceptibility. Fitted decay rate of 0.72 Oe/day and laser damage susceptibility increases with a $1/e$ time constant of 6.4 days.

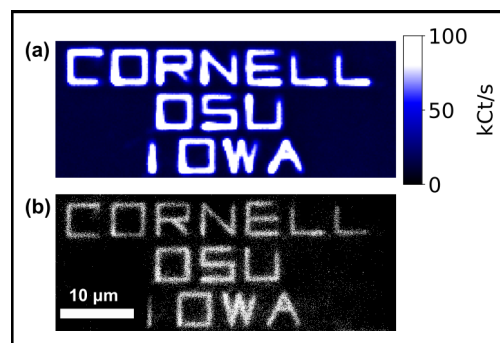


Figure 4: Laser patterning of a 400 nm V[TCNE]_x film. (a) Photoluminescence map of the patterned sample. High photoluminescence regions are laser damaged. (b) Optical micrograph. Laser damaged regions are more transparent and appear brighter in this image.