**NUMERICAL METHODS**

An atomic multiplet cluster model was built for dimerized vanadium (V₂), with each atom surrounded by a roughly octahedral crystal field. The hopping parameter between $d_{||}$ orbitals on paired vanadium atoms was set to $t_{\sigma} = -0.77 \text{ eV}$, similar to the value of $-0.68 \text{ eV}$ from first principles calculations in Ref. [1]. The Coulomb monopole term for the repulsion of electrons on the same atom was set to $U_{dd} = 6 \text{ eV}$, similar to the values in Ref. [1, 2] and other literature. Hopping between the $e_{g}^{\pi}$-orbitals with lobes pointing between the paired V atom was set to $t_{\pi} = -0.2 \text{ eV}$. The crystal field was set by orbital site energies listed below, in which the $e_{g}^{\pi}$-type orbitals are kept degenerate, but the $\sigma$ orbital is placed 0.5 eV lower in energy to match the standard picture of VO₂ orbital energetics.

The inverse lifetimes for XAS and RIXS simulations were obtained by defining a charge transfer threshold from 2.5-4.5 eV above the first resonance state energy. Lifetimes beneath the threshold were set to $\Gamma_{m} = 0.5 \text{ eV}$, and lifetimes within the threshold region increase linearly to 1.2 eV. At higher energies, the lifetime increases linearly to a value of $\Gamma_{m} = 1.5 \text{ eV}$ 8.5 eV above the upper threshold boundary. An artificially small final state inverse lifetime parameter $\Gamma_{f} = 0.1 \text{ eV}$ was used for easy visibility. These modeling parameters are listed in the following table:

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$\Gamma_{f}$</th>
<th>$U_{dd}$</th>
<th>$U_{pd}$</th>
<th>$E_{x_{2}^{-}y_{2}}$</th>
<th>$E_{xy}$</th>
<th>$E_{zy}$</th>
<th>$E_{xz}$</th>
<th>$t_{\sigma}$</th>
<th>$t_{\pi}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy(eV)</td>
<td>0.1</td>
<td>4.0</td>
<td>6</td>
<td>0</td>
<td>1.9</td>
<td>2.2</td>
<td>0.5</td>
<td>-0.77</td>
<td>-0.15</td>
</tr>
</tbody>
</table>

Multipolar Coulomb interactions and spin-orbit coupling energetics were obtained from Hatree-Fock calculations using the Cowan code. Nephelauxetic renormalization from strong hybridization with the oxygen was estimated by calculating the projection of creation and annihilation operators for electrons in vanadium Hartree-Fock orbitals onto the expanded orbitals obtained in an oxygen hybridized model. This model used the Coulomb monopole and orbital energies defined above, disregarded multipolar Coulomb terms, and assigned a ligand site energy of $E_{L} = 2.5 \text{ eV}$. Metal-ligand hopping was set to 2eV for octahedral $e_{g}$ orbitals, and -0.5eV for $t_{2g}$ orbitals. The average renormalization in creation and annihilation operators was then applied to the multipolar terms in the atomic multiplet Hamiltonian. In the ground and final states, Slater-Condon terms were renormalized to 62%. In the intermediate state, the relative strength of the core hole monopole $U_{pd}$ as compared to $U_{dd}$ increased mixing with ligand orbitals and brought the renormalization factor to 56.5% for inter-3d electron multipolar interactions, and 62% for 2p-3d multipolar interactions.

**ADDITIONAL EXPERIMENTAL DETAILS**

The samples used in this study are coherently-strained epitaxial VO₂(001) films deposited on TiO₂(001) substrate, and are known to exhibit compressive strain along the rutile c-axis direction (out-of-plane of the film). This has been confirmed via XRD measurements in our previous studies [3, 4], as well as by several other groups including Cobden et al. [5]. The metal to insulator phase transition is therefore from R to the M1 phase, without involvement of the intermediate M2 phase (see Fig. 1 below from Ref. [5]).

Low resolution incident energy dependence was obtained from a 6nm film with a nearly identical transition temperature to the thicker 10nm film used for high resolution RIXS studies (see Fig. 3). Although the IRIXS spectrograph is designed to achieve high throughput, it was configured as a roll-up endstation on a low resolution beamline (ALS BL8), and data quality was limited by the need to reduce beamline slits to maximize resolution ($\delta E = 0.2 \text{ eV}$). Beam exposure was monitored closely to avoid sample aging during the IRIXS measurement, and data acquisition was performed in a “constant dither” mode that reduced beam exposure per unit area by a factor of 250 during scans. The full IRIXS data set is found in Fig. 2, and is heavily impacted by CCD read noise. Data presented in the main text are integrated over energy loss windows to improve statistics.

FIG. 1: Stress-temperature phase diagram near the MIT from Ref. [5]. Our samples lie below the y=0 dashed line, due to the positive compressive strain along the rutile c-axis (corresponding to negative tensile stress on the plot). Thus, the structural transition is between M1 and R phases.

FIG. 2: Incident energy dependent RIXS spectra: (a) Incident energy dependent RIXS curves measured from (bottom) $h\nu = 514.6$ eV to $h\nu = 516.1$ eV with an 0.25 eV step are plotted with an offset for visibility. The 90° IRIXS scattering geometry causes elastic line intensity to be greatly reduced relative to high resolution measurements in the main paper. (b) (top) Incident energy dependence for energy loss regions highlighted in panel (a) is reproduced from the main text, and compared with theoretical predictions. The theory curves are weighted by the ratio $\Gamma/W$, where $\Gamma$ is the fitted peak width of the corresponding symmetry in Fig. 4 of the main text, and $W$ is the width of the energy loss integration window.

FIG. 3: R-T curve measured with a Quantum Design Dynacool PPMS system in 4 terminal sensing geometry with Aluminum wire bonding directly on the sample.