Supplementary Information: Constraints on magnetism and correlations in RuO_2 from lattice dynamics and Mössbauer spectroscopy

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Mössbauer Spectroscopy Analysis

The Mössbauer spectroscopy data were analyzed using various fit parameter settings, including both positive and negative quadrupole splitting (ΔE_Q), as well as zero and non-zero asymmetry-parameters (η). A positive ΔE_Q indicates a positive electric field gradient (V_{zz}), and vice-versa. To determine the correct sign of ΔE_Q – and thus the sign of V_{zz} – we performed fits using positive and negative ΔE_Q values under different parameter settings. As shown in Fig. S1, the best fit corresponds to a negative ΔE_Q. The asymmetry parameter (η) was fixed at 0.74, in agreement with previous NMR results (see main text). Setting η to zero results in a significantly worsened fit, confirming the necessity of a non-zero η. Additionally, fitting with a positive ΔE_Q yields a poor match, particularly failing to reproduce the shape of the doublet tips.

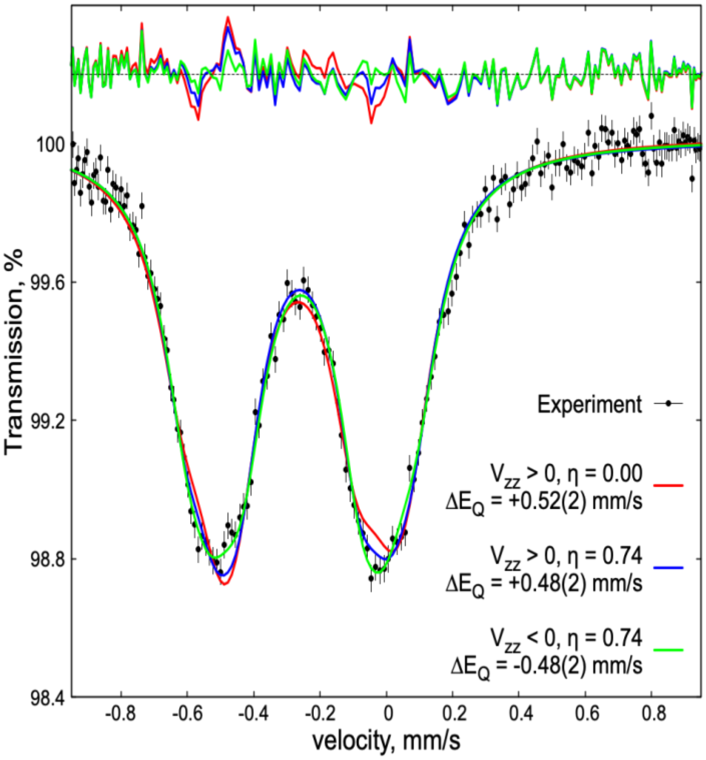

Fig. S1 Mössbauer spectra of RuO_2 with semi-constrained fits. The experimental data is shown as black solid circles with error bars, and the fits are shown as solid-colored curves. The differences of the experimental data and the fits are shown as colored curves above. The hyperfine field was fixed to zero for these fits ($H_{hf} = 0$).

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DFT Calculated Electric Field Gradient

Table S1 Density functional theory calculated electric field gradient (V_{zz}) along three directions, and the asymmetry parameter (η) as computed with different DFT methods. . VASP was used for Method 1 and 2, and WIEN2k was used for Method 3 and 4.

Method	**V_{zz} (10^{21} V/m^2)**			**η**	**Lattice parameters *a*, *c* (Å)**
	[110]	**[1-10]**	**[001]**		
1) r^2SCAN	7.802	3.140	-10.941	0.426	4.492, 3.106 (Berlijn, *et. al.* [S1])
2) GGA+*U* (*U* = 0)	7.134	3.373	-10.510	0.358	
3) GGA+*U* (*U* = 0)	6.384	3.447	-9.831	0.299	4.531, 3.123 (Nowakowski, *et. al.* [S2])
4) GGA+*U* (*U* = 2)	-1.146	8.496	-7.350	0.731	

The DFT calculated electric field gradient (V_{zz}) are highly sensitive to the initial structure, magnetism and the functional used for the calculation [S3]. We used two different initial lattice parameters obtained from experimental results for the V_{zz} calculations as shown in Table S1. Direct comparison of V_{zz} obtained from GGA+*U* (*U* = 0) method with different initial lattice parameters reveal the sensitivity of these calculations in DFT. While the best match of the asymmetry parameter (η) is given by GGA+*U* (*U* = 2 eV) method, the principal axis of the electric field gradient is rotated by 90º.

Dependence of Magnetism and Structure on Functional and Initial Magnetic Moment

Table S2 PBE-GGA+U (with $U = 0$ and 2 eV) and r²SCAN calculations were performed with and without initial magnetic moments (MAGMOM), i.e., $\mu^{\text{initial}} = 0$ and $\mu^{\text{initial}} \neq 0$. The structures were fully relaxed and the computed lattice parameters are given.

Functional	**Type**	**Result**	μ^{relaxed} **(μB/Ru)**	**Computed lattice parameters (Å)**
PBE-GGA+U	$U = 0$ eV; $\mu^{i} \neq 0$	NM	0	$a = 4.520$, $c = 3.118$
	$U = 2$ eV; $\mu^{i} \neq 0$	AFM	~1.179	$a = 4.530$, $c = 3.123$
r²SCAN	$\mu^{i} = 0$	NM	0	$a = 4.472$, $c = 3.114$
	$\mu^{i} \neq 0$	AFM	~0.963	$a = 4.487$, $c = 3.115$

Table S2 presents the magnetic states, moments, energies, and lattice parameters obtained using PBE-GGA+U and r²SCAN functionals under different magnetic initialization settings. While all calculated lattice parameters are within reasonable range of experimental values ($a = b \approx 4.49$ Å, $c \approx 3.11$ Å) [S1,S4], the r²SCAN AFM configuration, with an initial magnetic moment, shows the closest agreement with experiment. PBE+U results are more sensitive to the U value, with $U = 2$ eV favoring an AFM state but overestimating the lattice constants, while $U = 0$ eV gives a non-magnetic state with better structural agreement. Overall, while structural agreement can be achieved in both PBE+U ($U = 0$ eV) and r²SCAN AFM cases, the r²SCAN AFM configuration best captures both the magnetic and structural properties of RuO_2. However, when comparing with experimental phonon spectra (see Fig. 2 in manuscript), a better agreement is observed for the PBE+U ($U = 2$ eV) AFM and r²SCAN NM configurations, indicating that the best structural match does not necessarily correspond to the best dynamical properties. This underscores the subtle interplay among magnetism, structure, and lattice dynamics in RuO_2, reinforcing that the lattice dynamics are primarily driven by electronic correlations.

Supplementary References

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