Spectroscopic analysis of vibronic relaxation pathways in molecular spin qubit

$[\text{Ho}(W_{5}O_{18})_{2}]^{9-}$: sparse spectra are key

Avery L. Blockmon,†,‡ Aman Ullah,†,¶ Kendall D. Hughey,‡ Yan Duan,¶ Kenneth R. O’Neal,‡ Mykhaylo Ozerov,§ José J. Baldoví,¶ Juan Aragó,¶ Alejandro Gaita-Ariño,∗,¶ Eugenio Coronado,¶ and Janice L. Musfeldt∗,‡,∥

†These authors contributed equally to this work
‡Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, USA
¶Instituto de Ciencia Molecular, Universitat de Valencia, Paterna 46980, Spain
§National High Magnetic Field Laboratory, Tallahassee, Florida, 32310, USA
∥Department of Physics, University of Tennessee, Knoxville, Tennessee 37996, USA

E-mail: gaita@uv.es; musfeldt@utk.edu

Abstract

Molecular vibrations play a key role in magnetic relaxation processes of molecular spin qubits as they couple to spin states, leading to the loss of quantum information. Direct experimental determination of vibronic coupling is crucial to understand and control the spin dynamics of these nano-objects, which represent the limit of miniaturization for quantum devices. Herein, we measure the vibrational properties of the molecular spin qubit Na$_9$[Ho(W$_5$O$_{18}$)$_2$]·35H$_2$O by means of magneto-infrared spectroscopy. Our results allow us to unravel the vibrational decoherence pathways in combination with ab initio calculations including vibronic coupling. We observe field-induced spectral changes near 63 and 370 cm$^{-1}$ that are modeled in terms of f-manifold crystal
field excitations activated by odd-symmetry vibrations. The overall extent of vibronic coupling in this system is limited by a transparency window in the phonon density of states that acts to keep the intramolecular vibrations and $M_J$ levels apart. These findings advance the understanding of vibronic coupling in molecular magnets, place significant constraints on the pattern of crystal field levels in these systems, and provide a strategy for designing molecular spin qubits with improved coherence lifetimes.

KEYWORDS: mononuclear lanthanide complexes, magneto-infrared spectroscopy, single ion magnets, molecular spin qubits, vibronic coupling, polyoxometalates

**Introduction**

Quantum two-level systems based on spin states known as “spin qubits” are promising building blocks for the development of quantum technologies. In contrast with classical bits that are defined by two states “0” or “1”, qubits exploit quantum behavior by allowing quantum superposition between the basis states. Among different physical platforms, chemistry contributes to this effort via the study of spin states in magnetic molecules, both in the form of molecular spin qubits and molecular nanomagnets. In this context, mononuclear lanthanide complexes provide ideal settings that represent the limit of miniaturization for quantum and classical magnetic memories, respectively.\(^1\)\(^-\)\(^3\) Hundreds of such systems have been characterized so far in an attempt to understand and control their physical properties.\(^4\) A judicious chemical design exploiting magnetic anisotropy and optimizing the molecular structure versus spin-vibrational coupling led to the observation of magnetic bistability up to 80 K and an effective energy barrier of 2217 K in the molecular nanomagnet $[(\text{Cp}^{iPr_5})\text{Dy(Cp}^\ast\text{)}]^+$.\(^5\) Regarding molecular spin qubits, prominent examples include: two vanadium(IV) complexes, namely (i) $[\text{V(C}_8\text{S}_8)_3]^2^-$, which shows a record phase memory time $T_M$ of 0.7 ms\(^6\) and (ii) VOPc, with coherence times up to 1 µs at room temperature;\(^7\) (iii) a Cu$^{2+}$ complex, $[\text{P(Ph}_4\text{)}]_2[\text{Cu(mnt}_2\text{)}]$ ($\text{mnt}^{2^-}=$ maleonitriledithiolate), that preserves coherence up to
room temperature\textsuperscript{8} when diluted in Ni\textsuperscript{2+}; and (iv) a Ln\textsuperscript{3+}-based molecular nanomagnet, [Ho(W\textsubscript{5}O\textsubscript{18})\textsubscript{2}]\textsuperscript{9−}, whose spin qubit dynamics are protected against magnetic noise at optimal operating points known as atomic clock transitions.\textsuperscript{9} In this work, we will focus on the latter, investigating the vibronic relaxation pathways\textsuperscript{10–13} that govern magnetic relaxation. Thus far, these pathways have been largely under-explored. In particular, while transitions between electron-nuclear spin states are protected from quantum decoherence at the atomic clock transitions, this protection of the quantum information is only from magnetic noise. Instead, the system suffers from a reduction of relaxation time $T_2$ by a factor of $1/2$ between 5 and 7 K due to thermal noise, which limits coherence.\textsuperscript{9}

Single molecule magnet behavior in Na\textsubscript{9}[Ho(W\textsubscript{5}O\textsubscript{18})\textsubscript{2}]·35H\textsubscript{2}O arises from the magnetic anisotropy of a Ho\textsuperscript{3+} ion ($J = 8$) encapsulated by two polyoxometalate moiety in an eight-fold oxygen coordination environment with local slightly distorted $D_{4d}$ symmetry (Fig. 1).\textsuperscript{14–16} This assignment stabilizes a $M_J = \pm 4$ ground state. In the crystal, the [Ho(W\textsubscript{5}O\textsubscript{18})\textsubscript{2}]\textsuperscript{9−} anions are held together by interactions with Na\textsuperscript{+} ions and free water molecules of crystallization with a space group $P\bar{1}$.\textsuperscript{17} The magnetic properties of Na\textsubscript{9}[Ho(W\textsubscript{5}O\textsubscript{18})\textsubscript{2}]·35H\textsubscript{2}O have attracted significant attention. The out-of-phase ac magnetic susceptibility displays a maximum near 5 K,\textsuperscript{15} and magnetization shows a slow relaxation,\textsuperscript{15} one of the key signatures of single molecule magnets.\textsuperscript{18} Electron paramagnetic resonance sports an eight line spectrum due to the ground $M_J$ level hyperfine coupling to the $I = 7/2$ nuclear spin along with a tunneling gap of approximately 9 GHz ($0.3 \text{ cm}^{-1}$).\textsuperscript{19} Two-pulse electron spin echo measurements at its optimal working points reveal spin coherence times up to $T_2$=8.4 $\mu$s at 5 K when diluted to a 1% concentration in the isostructural diamagnetic matrix of its Y\textsuperscript{3+}-based analog, Na\textsubscript{9}[Ho\textsubscript{0.01}Y\textsubscript{0.99}(W\textsubscript{5}O\textsubscript{18})\textsubscript{2}]·35H\textsubscript{2}O. The high dilution limit for $T_2$ in other molecular spin qubits is usually achieved at concentrations around 0.01%.\textsuperscript{9} Recent results operating at these special points reveal the possibility of quantum magnetoelectric coupling, where voltage control of the crystal field levels can be used to manipulate the spin qubit states.\textsuperscript{20}

Despite the importance of the crystal field levels in this system, spectroscopic information
is limited to the aforementioned 0.3 cm$^{-1}$ tunneling splitting in the ground doublet determined by electron paramagnetic resonance as well as the low energy $M_J$ levels at 41 and 49 cm$^{-1}$ measured by inelastic neutron scattering by Vonci, et al.$^{21}$ A number of authors have attempted to locate the position and determine the order of the rest of the crystal field energy levels in Na$_9$[Ho(W$_5$O$_{18}$)$_2$].$^{21,22}$ While it is very much accepted that the seventeen different $M_J$ levels reside between 0.3 and 400 cm$^{-1}$, the exact pattern and order has been elusive due to the anisotropy of the system along with coupling to the vibrational levels.$^{21}$ Moreover, Ho$^{3+}$ is a non-Kramers ion, so while at first glance, it appears that many of the crystal field levels are doubly-degenerate, there is a very small energy scale that splits the $M_J$ levels and relieves their apparent degeneracies.$^{21}$ Although there is some prior infrared spectroscopy,$^{15}$ the work focused only on the middle infrared and, as a result, did not explore excitations below 400 cm$^{-1}$ which play a key role as they may interact with spin excitations, changes in spin state, and crystal field energy levels.$^{23,24}$ At the same time, the vibrational features in Na$_9$[Ho(W$_5$O$_{18}$)$_2$].$^{35}$H$_2$O are unassigned,$^{15}$ making it difficult to test
the order of the Ho\(^{3+}\) crystal field excitations or model coupling processes. This is important because, as a candidate qubit material, it is crucial to unravel all decoherence mechanisms that emanate from lossy responses in this frequency range.\(^{25,26}\)

In order to explore the dynamics of a model molecular spin qubit system, we combined far infrared spectroscopy and magneto-infrared techniques with complementary lattice dynamics and vibronic coupling models to reveal the low energy excitations in Na\(_9\)[Ho(W\(_5\)O\(_{18}\))\(_2\)]·35H\(_2\)O. Strong magneto-infrared effects are observed near 370 and 63 cm\(^{-1}\), which are due to activation of crystal field excitations by molecular vibrations of appropriate symmetry. These structures place significant constraints on the position of several \(M_J\) levels - including the highest energy set - establishing stringent bounds on the entire series of excitations. Our analysis suggests that coherence in Na\(_9\)[Ho(W\(_5\)O\(_{18}\))\(_2\)]·35H\(_2\)O benefits strongly from the limited frequency overlap between the crystal field levels and the phonon manifold. We demonstrate that the limited frequency overlap is due to a large transparency window or “hole” in the phonon density of states. This provides a strategy for the chemical design of molecular nanomagnets and spin qubits in which a full separation of the electronic and vibrational excitations will be likely to entirely eliminate vibronic coupling as a decoherence mechanism.\(^{27-30}\)

**Results and discussion**

**Assigning the low energy excitations in Na\(_9\)[Ho(W\(_5\)O\(_{18}\))\(_2\)]·35H\(_2\)O**

Figure 2 summarizes the far infrared response of Na\(_9\)[Ho(W\(_5\)O\(_{18}\))\(_2\)]·35H\(_2\)O. As a reminder, we focused our efforts on the low frequency regime from 25 - 600 cm\(^{-1}\) because (i) the far infrared contains key vibrations involving the Ho\(^{3+}\) center as well as crystal field levels, and (ii) only the middle infrared was studied in prior work.\(^{15}\) Figure 2 includes a number of important energy levels, predictions, and simulations for comparison. Many of these excitations are vibrational in nature, and with the aid of our lattice dynamics calculations, we
can assign the peaks and model the overall spectrum. For instance, we assign the dominant peak at 365 cm\(^{-1}\) as a rocking motion of HoO\(_4\). This rocking motion is accompanied by minor distortions of the (W\(_5\)O\(_{18}\))\(^{6-}\) cages. The theoretically predicted vibrational response (appropriately broadened) is shown in blue for comparison. The overall agreement with the measured spectrum is satisfactory. Interestingly, our lattice dynamics calculations predict a broad range - from approximately 230 to 330 cm\(^{-1}\) - where the fundamental excitations of the lattice are absent. While less apparent than in the theoretical spectrum, this characteristic of mode clusters below 230 cm\(^{-1}\) and above 330 cm\(^{-1}\) is evident in the experimental spectrum as well. The absence of spectral features in this region is a consequence of a “hole” in the phonon density of states. The implications of this structure will be discussed below. Complete vibrational mode assignments are available in Table S1 of the Supplemental Information.

\(f\)-block elements like Ho\(^{3+}\) also display crystal field levels in the far infrared.\(^{31–33}\) The exact position of the \(f\)-manifold levels varies significantly depending upon the details of the crystal field environment.\(^{13,34,35}\) Previous authors located the \(M_J = \pm 3\) and \(\pm 5\) levels in Na\(_9\)[Ho(W\(_5\)O\(_{18}\))\(_2\)]\(\cdot\)35H\(_2\)O via inelastic neutron scattering.\(^{21}\) These energies are shown in Fig.

Figure 2: Far infrared spectrum of Na\(_9\)[Ho(W\(_5\)O\(_{18}\))\(_2\)]\(\cdot\)35H\(_2\)O at room temperature compared with calculated lattice dynamics and crystal field levels as well as neutron scattering data from Ref 21.
2 in orange and help to define a lower limit to the crystal field manifold. As part of this work, we computed the full set of Ho\textsuperscript{3+} crystal field levels for this system. They are included in Fig. 2 in green for comparison. Our predictions for the position of the $M_J = \pm 3$ and $\pm 5$ levels are consistent with the neutron scattering results.\textsuperscript{21} The upper $M_J$ levels obtained from our model are also in close proximity to various molecular vibrations involving the central holmium atom and coordinated oxygen atoms. These features are on the leading edge of the upper cluster of modes above the 230 - 330 cm\textsuperscript{-1} transparency window or “gap” in the infrared spectrum.

Figure 3 shows the calculated crystal field levels in greater detail along with their evolution under applied magnetic field along the long molecular axis (see the evolution for other directions of the magnetic field in the Supplementary Information). As expected, the Zeeman effect between 0 and 35 T widens the total spread of the crystal field levels, with each level acquiring a slope proportional to its expectation value $< M_J >$. The slopes becoming non-linear as a result of either avoided crossings among crystal field levels or transverse magnetic fields.

![Figure 3](image.png)

Figure 3: Left: Calculated crystal field levels of [Ho(W\textsubscript{5}O\textsubscript{18})\textsubscript{2}]\textsuperscript{9-}. Note that the energies are normalized to the ground $M_J$ state. Right: Double y-axis plot of calculated crystal field levels with magnetic field and vibrational mode intensity times vibronic coupling ($S_n$).

Then we measured the far infrared response of Na\textsubscript{9}[Ho(W\textsubscript{5}O\textsubscript{18})\textsubscript{2}]·35H\textsubscript{2}O as a function of
temperature. As shown in Fig. S2 of the Supplemental Information, the lattice is nearly rigid. These findings were verified by complementary measurements of the non-magnetic analog Na$_9$[Y(W$_5$O$_{18}$)$_2$]·35H$_2$O which reveals a similar lack of temperature effects. Further, the Ho and Y analogs have identical transparency windows in the infrared response (Fig. S1 of the Supplemental Information). The phonon density of states is therefore not radically different than in the diluted case represented by Na$_9$[Ho$_{0.01}$Y$_{0.99}$(W$_5$O$_{18}$)$_2$]·35H$_2$O. Although there are uncoordinated waters in the crystal structure, the slight blue shifting of peaks demonstrates that hydrogen bonding does not strengthen significantly at low temperature.

**Magneto-infrared response of Na$_9$[Ho(W$_5$O$_{18}$)$_2$]·35H$_2$O**

Figure 4 (a,b) displays the magneto-infrared response of Na$_9$[Ho(W$_5$O$_{18}$)$_2$]·35H$_2$O at 4.2 K. The spectra are in the form of absorption differences, $\Delta \alpha (H) = \alpha (H) - \alpha (H = 0 \text{ T})$, which serves to highlight field-induced changes. The latter are not always apparent in the absolute absorption. There are two primary structures that develop systematically under applied field: (i) a set of sharp features centered near 63 cm$^{-1}$, and (ii) several broader, more complex structures between 335 and 400 cm$^{-1}$. Contour plots also show the development of the absorption differences with increasing magnetic field (Fig. 4 c,d). For comparison purposes, we performed similar measurements on the non-magnetic analog Na$_9$[Y(W$_5$O$_{18}$)$_2$]·35H$_2$O. No field-induced spectral changes were observed - as anticipated.

We assign contrast in the absorption difference spectra of Na$_9$[Ho(W$_5$O$_{18}$)$_2$]·35H$_2$O based upon the position of the intramolecular vibrations and $f$-manifold crystal field levels discussed in Fig. 2. The magneto-infrared features centered near 360 cm$^{-1}$ are in close proximity to several different vibrational modes including HoO$_8$ rocking and stretching modes - all of which take place in the center of the cage. Therefore, at first glance, it may seem that the magneto-infrared response in this frequency region may be due to spin-phonon coupling. However, the lack of magnetic order (or change in magnetic order) in the system argues against this interpretation. Other candidate excitations include crystal field levels.
Figure 4: (a,b) Magneto-infrared response of the features centered at 370 and 63 cm$^{-1}$, respectively, at 0, 5, 12.5, 20 and 35 T. The data are shown as absorption differences: $\Delta \alpha(\omega, H) = \alpha(\omega, H) - \alpha(\omega, H = 0 \text{ T})$. (c,d) Contour plots of the absorption difference spectra from panels (a,b) over the full range of magnetic fields. Scale bars are included.

The highest frequency set, $M_J = \pm 7$ are calculated by ourselves and others$^{21}$ to be in this vicinity. This suggests that vibronic coupling - in which the crystal field levels move with applied magnetic field and are amplified by nearby vibrational modes - may be responsible for the magneto-infrared contrast.$^{24,38,39}$ We test both models in this work and establish the vibronic coupling model below. Thus, the assignment of the $M_J = \pm 7$ levels interacting with nearby phonons serves as an upper bound for the entire $f$-manifold of Ho$^{3+}$ excitations.

A similar mechanism can explain the contrast centered near 63 cm$^{-1}$ (Fig. 4b). While our dynamics calculations predict significant intensity for localized vibrational modes starting at 100 cm$^{-1}$ (Fig. 2), Na$_9$[Ho(W$_5$O$_{18}$)$_2$$\cdot$35H$_2$O certainly has librational modes of uncoordinated H$_2$O molecules$^{40,41}$ as well as lattice modes involving asymmetric stretching of
the HoO₈ along with cage tilting. While the details depend upon the precise environment of the uncoordinated water as well as the long-range crystallographic orientation of the polyoxometalates, these vibrations can act as symmetry-breakers for the large number of $f$-manifold excitations in the vicinity. In other words, the contrast centered near 63 cm$^{-1}$ in the magneto-infrared spectra of Na$_9$[Ho(W$_5$O$_{18}$)$_2$]$\cdot$35H$_2$O is due to vibrational modes activating excitations involving nearby crystal field levels - specifically the $M_J = \pm 5$ levels. It is possible that the $\pm 2$ levels contribute as well. This assignment is based upon our detailed calculations of the crystal field levels (Fig. 3). In any case, these crystal field levels also shift with applied magnetic magnetic field and can vibronically couple with appropriate nearby vibrations.

To elucidate the origin of the magneto-infrared response, we simulated the absorption spectra at different fields. In absence of vibronic coupling, the selection rules would mean a trivial simulation that fails to reproduce the experimental behavior. Indeed this would result in the sum of a field-independent purely vibrational spectrum as shown in Fig. 2 and a collection of strongly field-dependent but strongly forbidden transitions among crystal field levels. Instead, we employed a more realistic model to estimate the transition dipole matrix between all possible vibrational and crystal field levels that crucially considers vibronic eigenfunctions, allowing for mixing between the two kinds of excitations (see details in Supplementary Information).

We simulate the magneto-infrared response of Na$_9$[Ho(W$_5$O$_{18}$)$_2$]$\cdot$35H$_2$O employing this approach (Fig. 5). We examined the absorption differences in spectra up to 35 T and find consistent results, with two regions of notable effects at relatively low and high frequencies. They show a wide gap in the spectrum between 200 and 390 cm$^{-1}$ devoid of any significant anti-crossings. Let us discuss first the region above that gap (emphasized in Fig. 5b), which corresponds to the better determined experimental features. In this highest frequency region, the evolution of the spectra with increasing magnetic field is very simple and qualitatively matches the experimental results. In particular, the calculations reproduce the gradual
saturation of the effect of the magnetic field in the absorption intensity, where the linear increase up to 10-15 T is lost and only a minor change is observed between 20 T and 35T (compare with Fig. S4). Overall the agreement is very satisfactory, save for a rigid 40 cm$^{-1}$ blue shift from our experimental features. In the case of the low energy region, where the theoretically estimated effects are also similarly shifted to slightly higher energies, both in the experiment and in the calculations, the behavior is more complex. The region between 80 and 200 cm$^{-1}$ where the calculations predict Zeeman-like displacements of absorptions occur in the experiments by a complex, possibly noisy, pattern. This is, in fact, what we observe (Fig. S3 of the Supplemental Information).

![Graph](image)

Figure 5: Left: Simulated magneto-infrared spectra of $[\text{Ho(W}_5\text{O}_{18})_2]^{9-}$ between 5 and 35 T. Two main regions of interest are denoted. Right: Close-up view of the magneto-infrared simulated response between 390 and 450 cm$^{-1}$.

**Developing molecular design criteria**

The main goal for the rational design of longer-lived molecular spins is decoupling spin energy levels from vibrational excitations. Our experimental and theoretical work confirms that the key towards this goal is two-fold. First, one needs a sparse low-energy crystal field spectrum, resulting from a very strong crystal field as in dysprosocenium, from a bunching of crystal field levels at higher energies as in Tb bis-phthalocyaninato sandwiches or from
incorporating U as a magnetic center.\textsuperscript{43} This can be combined with the optimization via chemical design of different coordination environments that will displace the $M_J$ levels to other regions of the spectra. Second, one needs an effectively sparse low frequency vibrational spectrum, resulting from a molecular environment for the spin that is either very simple, like in small molecules, with fewer degrees of freedom,\textsuperscript{6,8} or very rigid, as in fully aromatic ligands,\textsuperscript{7} where vibrations are pushed to higher frequency or engage in exceptionally limited vibronic coupling. The point is that by placing these features off-resonance, thermal routes to decoherence may be weakened and potentially curtailed.

In terms of decoherence pathways in the system Na$_{9}$[Ho$_{x}$Y$_{(1-x)}$(W$_{5}$O$_{18}$)$_{2}$]/35H$_{2}$O, our analysis allows the qualitative rationalization of the strong thermal dependence of the coherence time $T_2$ in the so-called atomic clock transitions. $T_2$ was experimentally determined to be $T_1$-limited up to concentrations of $x = 0.01$ and down to temperatures of 5 K.\textsuperscript{9} In the present work we demonstrate that there is a relatively dense population of energy levels, both crystal field and vibrational, in the region below 100 cm$^{-1}$, and these present significant vibronic coupling, as evidenced both experimentally and theoretically. This means that even a small population of these levels at relatively low temperatures is expected to have a significant detrimental effect on the coherence. In contrast, there is a limited frequency overlap between the crystal field levels and the phonon manifold in the window between 200-330 cm$^{-1}$. Should it be possible to alter the coordination to place this large “hole” in the phonon density of states at lower energies, it would render many of the vibronic pathways in this system ineffective in terms of generating decoherence. The transparency window in the phonon density of states renders some pathways ineffective even now. A full separation of the electronic and vibrational excitations is likely to entirely eliminate vibronic coupling as a decoherence mechanism.
Concluding remarks

We combined far infrared spectroscopy and magneto-infrared techniques with complementary lattice dynamics and vibronic coupling models to unveil the low energy excitations in Na$_9$[Ho(W$_5$O$_{18}$)$_2$]·35H$_2$O and gain insight into the spin dynamics of a model qubit system. We found strong magneto-infrared effects near 370 and 63 cm$^{-1}$ due to the activation of crystal field excitations via molecular vibrations of appropriate symmetry. Specifically, the $M_J = \pm 7$ crystal field levels couple to the various HoO$_8$ rocking and stretching modes. On the other hand, the $M_J = \pm 5$ levels near 63 cm$^{-1}$ (and very likely the $M_J = \pm 2$ levels) are activated by nearby phonons (such as H$_2$O librations and asymmetric HoO$_8$ stretching with cage tilting). At the same time, we report the first direct evidence for a transparency window in the phonon density of states in a robust molecular spin qubit. Besides exploring the consequences of this “hole” on vibronic coupling, we use our findings to propose new design rules aimed at mitigating thermal decoherence pathways such as those involving vibronic coupling in the next-generation of molecular spin qubits for quantum technologies. Both the site-specific spectroscopic technique and the first-principles theoretical approach demonstrated herein can be generally applied to identify crystal field excitations in other $f$-block complexes, regardless of the coordination environment. This approach paves the way toward a high temperature frontier for molecular nanomagnets where first-principles prediction and experimental optimization advance the development of molecular spin qubits with improved lifetimes and high operating temperatures.

Methods

Crystal growth and sample preparation: Single crystals of Na$_9$[Ho(W$_5$O$_{18}$)$_2$]·35H$_2$O were grown by solution techniques. The non-magnetic Y$^{3+}$ analog was prepared as well. In order to control the optical density, we combined the crystals with a paraffin matrix which is transparent in the far infrared region.
**Far infrared spectroscopy:** We employed a Bruker 113v Fourier transform infrared spectrometer equipped with a bolometer detector to reveal the far infrared response of Na$_9$[Ho(W$_5$O$_{18}$)$_2$]·35H$_2$O. The measured transmittance $T(\omega)$ was converted to absorption as $\alpha(\omega) = -\frac{1}{nd} \ln(T(\omega))$. Here, $n$ is the loading, and $d$ is the thickness. An open flow cryostat was used for temperature control. Magneto-infrared work was performed at the National High Magnetic Field Laboratory in Tallahassee, FL using a Bruker 66V/S spectrometer and a 35 T resistive magnet. Absorption differences are ideal for revealing small field-induced spectral changes. They are calculated as: $\Delta \alpha(\omega, H) = \alpha(\omega, H) - \alpha(\omega, H = 0 \, \text{T})$. Here, $H$ is applied magnetic field, and $\omega$ is the frequency.

**DFT calculations:** The structural optimization of the crystallographic coordinates (in vacuum) and the vibrational modes calculations were carried out at DFT level using the Gaussian16 package in its revision A.03. Vibrational frequency calculations were performed using both the fully optimized structure and the X-ray crystal structure with no optimization. The PBE0 hybrid exchange-correlation functional was used for both optimization and frequency calculations in combination with Stuttgart RSC ANO basis set with effective core potential (ECP) for the Ho$^{3+}$ cation. CRENBL basis set have been used for W with corresponding ECP potential and 6-31G(d,p) basis set had been used for oxygen. An ‘ultra-fine’ integration grid and ‘very tight’ SCF convergence criterion were applied. Dispersion effects were taken into account using the empirical GD3BJ dispersion correction.

**Ab initio calculations:** The time-independent electronic structure was computed using the multireference Complete Active Self-Consistent Field Spin-Orbit (CASSCF-SO) method as implemented in the OpenMOLCAS program package (version 18.09). The molecular geometry was extracted from the crystal structure determined by Single Crystal X-ray diffraction and was fully optimized at density functional theory (DFT) level (vide infra). In addition, the electronic structure of the molecular geometry with no prior optimization was calculated. Scalar relativistic effects were taken into account with the Douglas–Kroll–Hess
transformation using the relativistically contracted atomic natural orbital ANO-RCC basis set with VDZP quality for all atoms. The active space consisted of 10 electrons on the 7 f-orbitals of Ho\(^{3+}\) ion. The molecular orbitals were optimized at the CASSCF level in a state-average (SA) over 35 quintets of the ground state term \((L = 6\) for Ho\(^{3+}\)). The wave functions obtained at CASSCF were then mixed by spin-orbit coupling by means of the RASSI approach. The combined effect of the crystal field and the spin orbit coupling were computed using SINGLE-ANISO module.\(^{46}\)

**Vibronic coupling:** For vibronic-coupling-dependent IR absorption spectra, we defined an effective Hamiltonian described as:

\[
\hat{H}_{\text{eff}} = \hat{H}_S + \hat{H}_{\text{vib}} + \hat{H}_{S-\text{vib}}
\]

where \(\hat{H}_S\), \(\hat{H}_{\text{vib}}\) and \(\hat{H}_{S-\text{vib}}\) correspond to the system, the vibration (bath) and the spin-vibration Hamiltonian, which can be written as:

\[
\hat{H}_S = \sum_{k=2,4,6} \sum_{q=-k} B_{k}^{q} \hat{O}_{k}^{q}(J)
\]

\[
\hat{H}_{\text{vib}} = \sum_{j} \hbar \omega_{j} (n_{j} + 1/2)
\]

\[
\hat{H}_{S-\text{vib}} = \sum_{j} \sum_{kq} \hat{Q}_{j} \left( \frac{\partial B_{k}^{q}}{\partial Q_{j}} \right) _{0} \hat{O}_{k}^{q}(J)
\]

where \(B_{k}^{q}\) and \(\hat{O}_{k}^{q}(J)\) correspond to the crystal field parameter and the Stevens operator, respectively. \(j\) is an index running over the vibrations and \(n_{j}\) correspond to the vibrational level of mode \(j\). \(\hat{Q}_{j}\) denotes the vibrational coordinate and the term \(\left( \frac{\partial B_{k}^{q}}{\partial Q_{j}} \right) _{0}\) is the vibronic coupling for a given vibrational mode \(j\). To compute this term, we carried out \textit{ab initio} calculations at CASSCF-SO level. The introduction of vibronic coupling is key to compute the IR absorption spectra, since due to the mixing more transitions will be optically allowed.
Complete details can be found as Supplementary Information.

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