Computational Studies on Vibronic Coupling in Single Molecule Magnets: Impact on the Mechanism of Magnetic Relaxation

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Abstract

In this paper we give an overview of our activities on computations of the electronic structure of single molecule magnets with special emphasis of vibronic coupling as revealed by FIR and Raman spectra of two complexes of Co(II) - [CoL₂]²⁻ (L²=1,2-bis(methanesulfonamido benzoate) (1) and of Co(acac)2(H₂O)₂ (2) subject to two recent publications (Nature communications 2016 [Ref.14] and 2018 [Ref.15], respectively) in close collaboration with several experimental groups. The implications of spin-vibronic coupling for the field dependence of the magnetic relaxation has been discussed in close relation with our analysis of the spin-vibronic coupling in the considered complexes.

1. Introduction

Since the discovery of the Jahn-Teller effect in 1937 [1,2] the concept of vibronic coupling has become a source of inspiration for many researchers—theoreticians and experimentalists, chemists and physicists. Vibronic coupling is manifested in spectroscopy and magnetism of molecules, solids and surfaces, but is often ignored by spectroscopists. In the field of molecular magnetism [3], vibronic coupling is concerned with the mixing of paramagnetic electronic states with nuclear degrees of freedom (normal modes, molecular vibrations, or optical phonons). In molecular complexes vibrations are usually considered as decoupled from the electron spin subsystem. This is only justified if electronic states are well separated from each other and the electronic state under consideration is at minimum of the potential surface (identified as a “geometric structure”), in which case the Born-Oppenheimer approximation is applicable—the total wave function can be set up as a product of electronic and vibrational wavefunctions. [4,5] In the case degenerate or nearly degenerate electronic states a coupling
between electronic states via nuclear displacements takes place which generally leads to a break down of the separability between electronic and nuclear motions.

Single molecule magnets (SMM) are subject of intense research efforts due to the possibility to switch between two distinct states by applying an external magnetic field.[3] Thus, SMM could potentially pave the way to the ultimate miniaturization of magnetic storage devices. SMM are paramagnetic molecules with anisotropic magnetic moments. Magnetic anisotropy is the property of a magnetic moment to align along a preferred direction due to unidirectional orbital moments which couple with the net spin via spin-orbit coupling (SOC). SOC is a purely relativistic effect and, therefore typical for transition 3d, 4d and 5d metals or heavy 4f, 5f elements. The ultimate goal in the field of molecular magnetism is to rationally design molecules that are switchable at room temperature and retain the stored information in long term. However, in practice, interactions of the electron spin with molecular or lattice vibrations (phonons) lead to a „shortcut“ of the relaxation time and consequently to a loss of magnetic information. Understanding of how this happens is of crucial importance in order to explore possible work-arounds. To this end, first principal wave-function based methods based on quantum chemistry provide an invaluable tool for computing and understanding how anisotropy can be created and to what extent and in what directions chemical variations can be used to induce larger magnetic moments and larger anisotropies. Computational tools as implemented in the program ORCA [6,7] allow to study from first principles the electronic structure of large molecular complexes or charge compensated complex ions in solids and interpret magnetic and spectroscopic data on clusters of transition metals with open d- or f-shells. Here we explicitly cite the two basic methods used to study the electronic structures of complexes with open d- and f-shells: the Complete Active Space Self Consistent Field (CASSCF) theory [8] to account for static correlation, and the N-Electron Perturbation Theory to Second Order (CASPT2 [9], or alternatively NEVPT2 [10-13] employed to account for dynamic electron correlation. In this review we will focus on our computational activities taking as examples two Co(II) complexes – a pseudo-tetrahedra14(1) and a pseudo-octahedral one15(2) which we studied computationally in collaboration with several groups of experimentalists[14,15]. This choice was motivated by the following reasons: i) both complexes are in a non-relativistic S=3/2, but different spin-orbit ground states, M_s= ±3/2 in 1 but M_s=±1/2 in 2; ii) both complexes display field dependences in their near IR (for 1) and both IR and Raman spectra (for 2), and therefore, directly detectable spin-phonon couplings; iii) in 1 coupling to one normal mode only is discernible in the field dependent FIR spectra, while in 2, depending on the magnetic field coupling to three normal modes have been detected in the Raman spectra. The importance of the latter providing mechanism for magnetic relaxation will be discussed in close relation with a recent publication on the role of anharmonic phonons (molecular vibrations) in under-barrier relaxation of SMM.[16]

2. Computational Procedures

Calculations on the electronic structures high-spin Co^{2+} complexes subject to this review have been carried out using the implementations of the CASSCF/NEVPT2 methods in the program of ORCA[6,7]. In these computations the ground state geometry is considered as rigid, taken for example from X-ray structural data or approximated using density theory geometry optimizations. This is justified to the extent, that both 1 and 2 are in non-degenerate ground states. In a first step, non-relativistic calculations of all multiplets, the 10 S=3/2 and 40 S=1/2 states(roots) stemming from the d^7 configuration of Co(II) were done averaging the electron density equally over all multiplets. In a second step, spin-orbit coupling has been taken into account using quasi-degenerate perturbation theory (QDPT) [17] and a mean-field spin-orbit coupling operator for the one and two-electron matrix elements.[18,19] From the latter step, both spin-orbit multiplets, including relativistic zero-field splitting (ZFS), and expectation values of the Zeeman operator, yielding anisotropic g-factors, magnetizations and magnetic susceptibilities have been computed. To get insight, we analyzed the numerical results using ab-initio ligand field theory (AILFT) as implemented in ORCA [20-22]. AILFT allows to extract ligand field parameters – one electron ligand field splitting diagrams and two-electron Coulomb repulsion integrals.
using effective Hamiltonian theory from a mapping of the many-particle wavefunctions and energy eigenvalues onto the phenomenological ligand field Hamiltonian. With these parameters at hand, the exploring the relation between the magnetic anisotropy and the electronic and geometrical structure becomes possible. This allows one to deduce magneto-structural correlations and get insight into the relation between the electronic and geometric structure and the magnetic and spectroscopic properties.

Spin-vibronic coupling calculations were done using vibronic models as described in the classical monograph by I.Bersuker ([4], see also [5]) applied here to derivatives of the spin-Hamiltonian with respect to the normal mode displacements operating within the Co\(^{11}\)(S=3/2) grounds state manifold. These methods are in principle general but otherwise specific for the two chosen examples and will be elaborated and discussed separately.

3. Spin-phonon coupling to single normal vibrational mode: (HNEt)\(_2\)[Co(pdms)]

3.1. Geometric and electronic structures and magnetic field dependent FIR spectra

[Co(L\(^2\))\(_2\)]\(^2\) (L\(^2\)=1,2-bis(methanesulfonamido benzoate) (1) is a bis-chelate pseudo-tetrahedral complex with two acute (NCoN = 80°) bite angles and a symmetry close D\(_{2d}\) (Figure 1a). In tetrahedral geometry the 3d-centered molecular orbitals split giving rise to the \(\sigma^+\), \(\pi^+\), \(\pi^0\), and \(\pi^-\) antibonding orbitals (Figure 1b). With two extra electrons on the \(\pi^0\) orbital set a \(4A_2(T_0)\) ground state results. The D\(_{2d}\) elongated tetrahedral geometry induced by the two acute L-Co-L chelate angles leads to a large splitting of the \(t_2\) orbitals into \(e(d_{xz},d_{yz})\) and \(b_2(d_{xy})\), with the lowest unoccupied \(b_2(d_{xy})\) orbital just above the \(b_1(d_{x^2-y^2})\) doubly occupied one. The ground state is \(4B_1(D_{2d})\) (electronic configuration \(d_{x^2}^1d_{y^2}^1d_{z^2}^1d_{x^2-y^2}^2\)). The tetrahedral \(4T_2\) excited state splits into the \(4E(d_{xy}^1(d_{xz}^y,d_{yz}^y)^1d_{x^2-y^2}^1)\) and \(4B_2(d_{xy}^2d_{xz}^1d_{x^2-y^2}^1)\) \(D_{2d}\) sublevels, the latter being by only 540 cm\(^{-1}\) above the \(4B_1\) ground state. This energy is comparable with the effective spin-orbit coupling constant of Co\(^{11}\) (446 cm\(^{-1}\)). The mixing of the two states induces a large ground state orbital moment into the S=3/2 spin and magnetic anisotropy quantified by a large and negative zero-field splitting D=−115 cm\(^{-1}\). [14] Magnetic field dependent FIR spectra display an absorption near the energy gap 2D=230 cm\(^{-1}\) separating the ground \(\pm 3/2\) from the lowest excited \(\pm 1/2\) magnetic sublevels of the S=3/2 spin (Figure 1c). In the given spectral range in zero field, four absorptions, at 217, 222, 230 and 237 cm\(^{-1}\) are observed. Of these the one at 217 cm\(^{-1}\) is almost field independent, while the one at 237 cm\(^{-1}\) shows only intensity changes on application of a field. The zero-field features at 221.7 and 229.5 cm\(^{-1}\) shift to higher energies reaching maximal values at the highest field (B=11T, 222.6 and 233.5 cm\(^{-1}\), respectively. The appearance of two rather than only one, \(\pm 3/2\) \(\rightarrow \pm 1/2\) field dependent absorptions points toward intermixing of spin- and vibrational levels made possible when, as in the case considered here, the two states are close in energy and couple vibronically.
Figure 1 (a) Crystallographic structure of the anion 1. The two $\angle$NCoN chelate bite angles are 80.59° and 80.70°. The Co-N bond lengths are very similar and range from 1.998 to 2.013 Å; (b) Ligand field orbital (left) and term (right) energy diagrams from CASSCF/NEVPT2 AILFT calculations for 1. Horizontal lines depict orbital energies, while arrows pointing up or down stand for single electron spins. Promotion of one electron from the b1 ($d_{x^2-y^2}$) orbital of the $^4B_1$ ground state configuration into the lowest singly occupied orbital $b_2(d_{xy})$ leads to a $^4B_2$ lowest excited state computed to be 550 cm$^{-1}$ above the ground state. The two states mix via the z component of the spin-orbit coupling operator inducing a ground state magnetic moment along the complex S4 (D2d) axis. There is no such mixing via the x and y components of the spin-orbit coupling operator, accordingly no components of the magnetic moment perpendicular to the S4 axis are present, magnetic anisotropy is of Ising type; (c) Far infrared transmission spectra recorded on a pressed powder pellet of 1 at T = 4 K and different fields as indicated; inset. The blue and red sticks indicate the calculated 0 T and 11 T excitation energies resulting from the spin-vibronic analysis (see below); adapted with permission from Ref.[14]
3.2. Vibronic Coupling Calculations

The Hamiltonian of a \( S=3/2 \) spin coupling to a single vibrational mode is given by:

\[
H_{\text{eff}} = H_s + H_{\text{vib}} + H_{S-\text{vib}}
\]  
(1)

with \( H_s \) - the static Spin-Hamiltonian, including the zero-field and Zeemann terms and \( H_{\text{vib}} \) - the vibrational Hamiltonian:

\[
H_s = D(\hat{S}_z^2 - S^2/4) + E(\hat{S}_x^2 - \hat{S}_y^2) + \beta_{\text{zz}} \hat{S}_z + \beta_{\text{xy}} \hat{S}_x \hat{S}_y + \beta_{\text{yy}} \hat{S}_y
\]  
(2)

\[
H_{\text{vib}} = \hbar \omega (n + 1/2)
\]  
(3)

Restricting to linear terms of the expansion of the Spin-Hamiltonian in a series of the normal mode \( Q \) we have the spin-vibrational Hamiltonian expressed as:

\[
H_{S-\text{vib}} = (\partial E/\partial Q) \cdot Q(\hat{S}_z^2 - \hat{S}_y^2) + (\partial D/\partial Q) \cdot Q(\hat{S}_x^2 - 5/4)
\]  
(4)

with \((\partial E/\partial Q)\) and \((\partial D/\partial Q)\), the linear vibronic coupling parameters taken at the equilibrium geometry. The basis of the Hamiltonian consists of a set of functions given by products of magnetic of vibrational Hamiltonian expressed as:

\[
\psi_{n, 3/2} = \sum \psi_n \psi_{3/2}
\]

Assuming weak vibronic coupling limit (eq.5,6), the basis functions consist of the ground state manifold – the ground vibronic state \( |3/2,0\rangle \), \( |1/2,0\rangle \), \( |1/2,1\rangle \), \( |3/2,1\rangle \) and magnetic sublevels where one vibrational quantum has been excited, \( |3/2,1\rangle \), \( |1/2,1\rangle \), \( |1/2,0\rangle \), \( |3/2,0\rangle \).

\[
\hbar \omega \gg \langle M_s | \hat{S}_z^2 - \hat{S}_y^2 | M_s \pm 2 \rangle /\langle 0 | Q | 1 \rangle
\]  
(5)

\[
\hbar \omega \gg \langle M_s | \hat{S}_z^2 | M_s \rangle /\langle 0 | Q | 1 \rangle
\]  
(6)

Potentially, both terms of the Hamiltonian of eq.4 contribute to mixing between basis functions of the set. However, considering magnetic resonance transitions only, the first term in eq. (4) can be been taken into account, leading to eq. 7 for the coupling matrix elements:

\[
\langle 3/2 | (\partial E/\partial Q) \cdot Q(\hat{S}_z^2 - \hat{S}_y^2) | 1/2 \rangle = \frac{\sqrt{3}}{2} (\partial E/\partial Q)_{\text{eq}}
\]  
(7)

The representation of the Hamiltonian (eq.1) in this basis takes the form of a two-by-two block form (eq. (8))

\[
H_{\text{eff}} = \begin{bmatrix}
H_s + (\hbar \omega/2) I & H_{S-\text{vib}} \\
H_{S-\text{vib}} & H_s + (3\hbar \omega/2) I
\end{bmatrix}
\]  
(8)

with

\[
H_s = \begin{bmatrix}
D + \frac{3}{2} G_x & \frac{\sqrt{3}}{2} (G_{xx} - iG_{xy}) & \sqrt{3} E & 0 \\
\frac{\sqrt{3}}{2} (G_{xx} + iG_{xy}) & -D - \frac{1}{2} G_x & (G_{xx} - iG_{xy}) & \sqrt{3} E \\
\sqrt{3} E & (G_{xx} + iG_{xy}) & -D - \frac{1}{2} G_x & \frac{\sqrt{3}}{2} (G_{xx} - iG_{xy}) \\
0 & \sqrt{3} E & \frac{\sqrt{3}}{2} (G_{xx} + iG_{xy}) & D - \frac{3}{2} G_x
\end{bmatrix}
\]  
(9)

and
Assigning the zero-field transitions 221.7 and 229.5 cm\(^{-1}\) (B=0) to excitations from the ground state into excited state dominated by vibrational \(0\to1\) and magnetic \(\pm 3/2\to\pm 1/2\) excitations (\([\pm 3/2,0]\to[\pm 3/2,1]\) and \([\pm 3/2,0]\to[\pm 1/2,0]\) respectively, and the features at 222.6 and 233.5 cm\(^{-1}\)) (B=11T) to \([-3/2,2]\to[-3/2,1]\) and \([-3/2,2]\to[-1/2,0]\), we could fix four model parameters: \(D\), \(E'\), \(\hbar\omega\) and the factor \(g\) from a best fit to obtain \(D=-114.5\) cm\(^{-1}\), \(E'=2.98\) cm\(^{-1}\), \(\hbar\omega=223.17\) cm\(^{-1}\) and \(g=1.25\). The low effective g-value is typical for expectation values of electronic Hamiltonians in the regime of the dynamic Jahn-Teller effect (Ham effect, see Section 4.2. and Figure 10). Energy shifts and wave function compositions of the four vibronic levels are illustrated in Figure 2. One should note first, that in all cases, without and with a magnetic field, the ground state is 100% \(|\pm 3/2,0\rangle\)(B=0T) and \(|-3/2,2\rangle\)(B>0) (small yet non-negligible contributions of \(|\mp 1/2,0\rangle\) and \(|1/2,0\rangle\) due to the orthorhombic term \(E\) can be safely neglected). There is a considerable (18%) contribution of a magnetic state (\(|\mp 1/2,0\rangle\)) to the formally vibrational excitation \(|\pm 3/2,1\rangle\) at energy 221.7 cm\(^{-1}\) and (to same amount) a singly excited vibrational state \(|\pm 3/2,1\rangle\) in the excited magnetic state \(|\mp 1/2,0\rangle\) at 229.5 cm\(^{-1}\). The former mixing leads a slight dependence of the lower excitation on the magnetic field detected experimentally as an upward shift of 1 cm\(^{-1}\) at field B=11T. Out of the four transitions two (highlighted in Figure 2 in red) show a non-linear dependence of the field with change of character when going from the low to the high field regions; the field dependent branch of the lower transition (dominated to 82% by a vibrational excitation at zero field) turns to (90%) into \([-3/2,0]\to[-1/2,0]\), formally a magnetic excitation at B=11T, and vice versa, the magnetic peak due to 82% \(|\pm 3/2,0\rangle\to[\pm 1/2,0]\)(B=0T) turns into the mostly forbidden transition to the vibrationally excited (90%) \([-3/2,0]\to[3/2,1]\) state—a typical level anti crossing phenomenon (marked in Figure 1 by red crossing lines) takes place, as is also reflected in the spectrum, Figure 1(c) at the crossing point close to B=5T, E=232.5 cm\(^{-1}\). We should note, that the weak field dependence of a nominally vibrational excitation resembles very much the similar appearance of such a feature in the field dependent Raman transitions of Co(acac)\(_2\)(H\(_2\)O)\(_2\) (2) (and also its deuterated analogues 1-d\(_4\) and 1-d\(_{18}\) as well) (see Section 4 and Figure 8). This will be subject to our analysis in the next Section.
4. Spin-vibronic coupling to three normal vibrations: \( \text{Co(acac)}_2(\text{H}_2\text{O})_2 \)

4.1. Geometric and electronic structures and magnetic field dependent Raman spectra

The electronic structure of \( \text{Co(acac)}_2(\text{H}_2\text{O})_2 \) has been reconsidered in the light of multi reference ab initio calculations in close relation and comparison with two basic experimental studies, the single crystal EPR work by Bencini et al.\cite{23} and, later in a study on the origin of the slow magnetic relaxation by Gómez-Coca et al.\cite{24} Lohr and coworkers have calculated the electronic structure of 2 in terms of crystal fields of descending symmetry from octahedral to orthorhombic and used the results to compute the magnetic properties of the complex.\cite{25} Our results from ab initio calculations on of \( \text{Co(acac)}_2(\text{H}_2\text{O})_2 \) are summarized as follows:

The geometry of the first coordination sphere of Co is of the \( D_{4h} \) type and may be regarded as a tetragonally elongated octahedral with two axial Co-O bonds due to two water molecules (2.199 Å) and four equatorial Co-O bonds (2.05 Å) to the two equatorial acac ligands. The crystallographic symmetry if of \( C_i \) type. In the \( D_{4h} \) point group the \( z \)-axis has been chosen along the oxygen of the aqua ligands, while \( x \) and \( y \) are approximately parallel to the Co-O(acac) bond directions (Figure 3).
**Figure 3.** left: Geometric structure and choice of coordinate axes for Co(acac)$_2$(H$_2$O)$_2$ (2) right: π-anisotropic Co-OH$_2$ bond interactions and their AOM parametrization; adapted with permission from Ref.[15]

The oxygen donors of the H$_2$O and acac ligand are predicted by theory to perturb the $e$(3d)-orbitals of the CoO$_6$ core (O$_h$) by Co σ-antibonding and the $t_2$(3d) orbitals by two types out-of-plane π-interactions of quite different nature. For water there is one electron pair of π-symmetry perpendicular to H$_2$O coordinating in a planar fashion (Figure 3). For acac there is an intrinsic network of π-orbitals which can be classified as in-phase and out-of-phase (Figure 4).

The presence of two different ligands in the coordination sphere of Co(II) and the π-anisotropies of the acac and H$_2$O ligands lead to a splitting of the $t_2$ ($d_{xz}, d_{yz}, d_{xy}$) orbitals and the resulting pattern of this splitting is strongly orthorhombic. This is illustrated by the ab initio ligand field orbital energy diagram (Figure 5) reflected by the almost equal spacing between the orbitals $d_{x'y'}, d_{yz}$ and $d_{x'z'}$ originating from the octahedral $d_{xz}, d_{yz}$ and $d_{xy}$ orbital sets. We should note on passing, that these two sets are related by the following transformation:

\[
\begin{align*}
    d_{x'y'} &= -1/\sqrt{2}(d_{xz} + d_{yz}) \\
    d_{yz} &= 1/\sqrt{2}(d_{xz} - d_{yz}) \\
    d_{xy} &= d_{x'z'} \\
    d_{x'z'} &= d_{x'y'} \\
    d_{x'y'} &= d_{x'z'} \quad (11)
\end{align*}
\]

With the overall tetragonally elongated geometry the order of the σ-antibonding orbitals $d_{z^2} < d_{x'y'}$ is not surprising.
According to the orbital energy diagram, $d_{x'y',z'z'} < d_{x'2-y'2}$ (Figure 5) the $^4T_1$ state of a high-spin octahedral Co(II) complex will undergo a $D_{4h}$ splitting into a non-degenerate $^4A_2$ ground state and a $^4E$ excited state. Due to the symmetry lowering to the orthorhombic $D_{2h}$ symmetry the $^4E(D_{4h})$ state undergoes further splitting. The energies of all ten $S = 3/2$ states and the effect of symmetry lowering are listed in Table 1. The resulting sublevels of $^4T_{1g}$ are well separated from the $^4T_{2g}$ excited ones and the overall splitting of the $^4T_{1g}$ is about twice the effective spin-orbit coupling parameter of Co(II) (530 cm$^{-1}$).
Figure 5. Ab initio (NEVPT2) ligand field 3d-orbital energies of Co(acac)$_2$(H$_2$O)$_2$ (2); reproduced with permission from Ref.[15]

Table 1. Non-relativistic $S = 3/2$ states and their splitting on symmetry lowering from $O_h$ to $D_{4h}$ and $D_{2h}$ (NEVPT2 results).

| $O_h$ | $D_{4h}$ | $D_{2h}$ | Energy/cm$^{-1}$ |
|-------|---------|---------|------------------|
| $^4T_{1g}$ | $^4A_{2g}$, $^4E_g$ | $^4B_{1g}$, $^4B_{2g}$, $^4B_{3g}$ | 0, 707, 1175 |
| $^4T_{2g}$ | $^4B_{2g}$, $^4E_g$ | $^4A_g$, $^4B_{2g}$, $^4B_{3g}$ | 6352, 9152, 9362 |
| $^4A_{2g}$ | $^4B_{1g}$ | $^4B_{1g}$ | 17548 |
| $^4T_{1g}$ | $^4E_g$, $^4A_{2g}$ | $^4B_{2g}$, $^4B_{3g}$, $^4B_{1g}$ | 20806, 21583, 26363 |

Spin-orbit coupling (SOC) along with quasi degenerate perturbation theory accounted for using all 10 $S = 3/2$ and 40 $S = 1/2$ non-relativistic states (roots) of the d$^7$ configuration of Co(II) was used to compute
the ground and excited magnetic sublevels and to access the parameters of the Spin-Hamiltonian (Eq. 12).

$$H_{S=3/2} = D[\hat{S}_z^2 - 5/4] + E(\hat{S}_x^2 - \hat{S}_y^2) - \mu_B \hat{S}gh$$

(12)

The ground $^4A_g$ state splits into two sublevels 169.8 cm$^{-1}$ apart from each other, which in the approximation of an axial system would yield $D = 84.9$ cm$^{-1}$. Diagonalization of the ZFS and the g-tensor yields eigenvalues and eigenvectors which are listed in Table 2.

**Table 2. Parameters of the spin-Hamiltonian of Eq. 12**

|        | $D_{x'x'}$ | $D_{y'y'}$ | $D_{z'z'}$ | $g_x$ | $g_y$ | $g_z$ |
|--------|-----------|-----------|-----------|-------|-------|-------|
| $x$    | -13.13    | -41.12    | 54.26     | 2.574 | 2.846 | 1.889 |
| $y$    | 0.78      | 0.58      | 0.24      | 0.79  | 0.58  | 0.19  |
| $z$    | -0.57     | 0.81      | -0.12     | -0.58 | 0.81  | -0.08 |

* Deduced from NEVPT2 results and a mapping of the lowest four SOC eigenfunctions onto the spin-Hamiltonian of Eq. 12.

From the eigenvalues of the zero-field splitting tensor we deduce $D$ and $E$, $D = 3/2D_z = 81.4$ and $E = (D_{xx} - D_{yy})/2 = 13.995$ cm$^{-1}$ and $E/D = 0.17$. The results show that the magnetic anisotropy reflects a very substantial orthorhombic component. This is in agreement with the metal ligand bonding model and the ligand field orbital pattern (Figure 5). SOC eigenvalues stemming from the excited $^4E_g$ ($D_{4h}$ symmetry notation) states are computed at 884.1, 1144.7, 1481.9, 1616.2 cm$^{-1}$ and show, that, except for the ground state Kramers doublet and second one at 169.8 cm$^{-1}$ above, there are no other excited states close in energy. At the temperatures used to probe the magnetic properties – the magnetic susceptibility and field dependent magnetization and EPR (not specified in the reported data) there is no appreciable population of the lowest lying Kramers doublet. The computed effective g-tensor values of the lowest Kramers doublet are $g_x = 6.846$, $g_y = 3.745$, $g_z = 1.864$. As follows from the eigenvectors (Table 2) the latter are to a good approximation collinear (Figure 6) correspondingly with the easy, intermediate and hard direction of the main values ZFS tensor and the intrinsic g-tensor.

![Figure 6. Effective ground state Kramers doublet principle g-tensor components and their orientation with respect to the molecular frame from NEVPT2/SOC state interaction calculations of Co(acac)$_2$(H$_2$O)$_2$ (2); The smallest g-tensor value is collinear with the z-molecular direction; the g-tensor within the easy equatorial plane is split into a large value of 6.846 containing an angle of only 10° with the bisector of the inter-chelate OCoO angle; the intermediate principle g-value contends an angle of 10° with the direction bisecting each OCoO chelate angle; adapted with permission from Ref.[15]](image)
4.2. Vibronic Coupling Calculations

The Raman spectrum of (2) in dependence of the magnetic field (Figure 7) consist of five branches (denoted by 1 to 5 from left to the right). For each of branches 3 and 4 there are two regions—one at low and one at high fields that show almost no field dependence. These regions must correspond to Raman transitions between vibronic states without change of the magnetic quantum number thus corresponding to the excitation of one vibrational quantum with estimated energies $h\omega_1 = 125$, $h\omega_2 = 129$ and $h\omega_3 = 139$ cm$^{-1}$. At intermediate regions of the magnetic field B the second, third and fourth branch display the slope of a magnetic field induced spin-transition which feature avoided crossings. There are three distinct anti-crossing points between each pair of the upper four branches i.e. between 2 and 3, 3 and 4, 4 and 5 (Figure 7, denoted by x from left to right). These points appear at fields $B = 7.64$, 9.43 and 17.54 T and energies 125.05, 127.99 and 138.71 cm$^{-1}$, respectively. At these points excitation from the ground magnetic level into the excited magnetic level would appear in case no level crossing would be present. The energy of these “missing” magnetic excitations increases with field and happens to cross the three different vibrational levels at the energy positions $h\omega_1 = 125$, $h\omega_2 = 129$ and $h\omega_3 = 139$ cm$^{-1}$. For Co(acac)$_2$(H$_2$O)$_2$ with a positive D and neglecting for the sake of simplicity the orthorhombic term E in the spin-Hamiltonian (actually E/D differs essentially from zero, see below), the only possible magnetic excitation which increases in energy with the field is that corresponding to a transition from the $M_s = -1/2$ split component of the lowest Kramers doublet (KD1) into the upper sublevel of the excited KD2 $M_s = 3/2$. Thus, alone from the slope of the line (the solid line in Figure 7) connecting the three points of level anti-crossing, $\Delta E$(cm$^{-1}$)/ B(Tesla)=1.362, and ignoring anisotropy in g (i.e. setting $E=[3/2-(1/2)]g_{eff}\beta_B B=2g_{eff}\beta_B B$ an effective value of $g_{eff}=1.46$ can be deduced from the experimental data (Figure 7).

This phenomenon of spin-phonon entanglement can be rationalized employing a model of one magnetic excitation from the $M_s = -1/2$ ground state (induced by the field B) into the $M_s = 3/2$ excited state, $|{-1/2,0,0,0}\rangle \rightarrow |3/2,0,0,0\rangle$ (both levels in their ground vibrational state) into three singly excited vibrational states within the same magnetic ground state $M_s = -1/2$: $|{-1/2,0,0,0}\rangle \rightarrow |{-1/2,1,0,0}\rangle, |{-1/2,0,1,0}\rangle, |{-1/2,0,0,1}\rangle$. Please notice, that the magnetic transition $M_s = -1/2 \rightarrow 3/2$ is magnetically dipole forbidden, but the three vibrationally excited ones are (in the approximation of the Harmonic oscillator) Raman allowed. Employing a representation of the five basis functions $|M_s,n_1,n_2,n_3\rangle$, $M_s = -1/2,3/2$, $n_i = 0,1,i = 1,2,3$ as simple product $|M_s,n_1,n_2,n_3\rangle = |M_s\rangle |n_1\rangle |n_2\rangle |n_3\rangle$ the following Hamiltonian matrix of the problem results:

$$
\begin{pmatrix}
-1/2,0,0,0 & 3/2,0,0,0 & -1/2,1,0,0 & -1/2,0,1,0 & -1/2,0,0,1 \\
3/2,0,0,0 & -1/2,0,0,0 & 3/2,1,0,0 & -1/2,0,1,0 & -1/2,0,0,1 \\
-1/2,1,0,0 & 3/2,1,0,0 & -1/2,0,0,0 & 3/2,0,1,0 & -1/2,0,0,1 \\
-1/2,0,1,0 & 3/2,0,1,0 & -1/2,0,0,0 & 3/2,0,0,0 & -1/2,0,0,1 \\
-1/2,0,0,1 & 3/2,0,0,1 & -1/2,0,0,1 & -1/2,0,0,1 & -1/2,0,0,0
\end{pmatrix}
$$

Figure 7. Magnetic and phonon positions vs. magnetic fields in Raman spectra: 2; adapted with permission from Ref.[15]
converts to a vibrational excitation $| -1/2,0,0,0\rangle \rightarrow |3/2,0,0,0\rangle$. There is twice a change in character of branch 3 where the low-field region due to $| -1/2,0,0,0\rangle \rightarrow | -1/2,1,0,0\rangle$ becomes replaced by $| -1/2,0,0,0\rangle \rightarrow |3/2,0,0,0\rangle$, while the latter in turn converts to $| -1/2,0,0,0\rangle \rightarrow | -1/2,1,0,0\rangle$ at the anti-crossing point $x$ on the right.

In branch 3, $| -1/2,0,0,0\rangle \rightarrow | -1/2,1,0,0\rangle$ becomes converted to $| -1/2,0,0,0\rangle \rightarrow |3/2,0,0,0\rangle$ at the third anti crossing point $x$, but the second change to $| -1/2,0,0,0\rangle \rightarrow | -1/2,0,0,1\rangle$, expected to appear at higher field falls outside the range of field values. Finally, in branch 5, initially (zero-field) a $| -1/2,0,0,0\rangle \rightarrow | -1/2,0,0,1\rangle$ excitation goes to $| -1/2,0,0,0\rangle \rightarrow |3/2,0,0,0\rangle$ at the highest field $B=17.54$ value. As was stated above, in the approximation of a purely axial anisotropy the $| -1/2,0,0,0\rangle \rightarrow |3/2,0,0,0\rangle$ is magnetically dipole forbidden. It only appears in the spectra if significant mixing with a Raman active vibration in the vicinity of an anti crossing point takes place. Thus, in branch 2 at low field values far from the avoided crossing point mixing between $| -1/2,0,0,0\rangle \rightarrow |3/2,0,0,0\rangle$ and $| -1/2,0,0,0\rangle \rightarrow | -1/2,1,0,0\rangle$ is small which readily explains the absence experimental points at low field.

As was stated above, the orthorhombic $E$ term (eq.12) is large, such that a more precise consideration of the data of Figure 7 needs to be done. In order to analyze in more quantitative terms the phenomenon of this spin-phonon (vibration) entanglement we extended the model of eq.13 to a Hamiltonian matrix taking a complete basis set $| M_s,n_1,n_2,n_3\rangle$ ($M_s=3/2,1/2,-1/2,-3/2$, $n_1,n_2,n_3=0,0,0;1,0,0;0,1,0;1,0,0$) into account. This leads to the four-by-four block form of eq. (15)

$$H_{eff} = \begin{bmatrix} H_S & H_{S-vib1} & H_{S-vib2} & H_{S-vib3} \\ H_{S-vib1} & H_S + \hbar\omega_1 I & 0 & 0 \\ H_{S-vib2} & 0 & H_S + \hbar\omega_2 I & 0 \\ H_{S-vib3} & 0 & 0 & H_S + \hbar\omega_3 I \end{bmatrix}$$

The same expressions for the spin-Hamiltonian matrix $H_S$ (eq.2) and the spin-vibrational coupling sub-diagonal matrices $H_{S-vib1}, H_{S-vib2}$ and $H_{S-vib3}$ of the form of eq.10 apply, now referring to the coupling of the spin $S$ with the three normal modes $Q_1$, $Q_2$ and $Q_3$. The Hamiltonian has been diagonalized under the following simplifying assumptions:

- The parameters of the spin-Hamiltonian $D$, $E$, $g_s$, $g_s'$ and $g_s''$ are not reliably known – four different sets of these parameters which reproduce the experimental ground state KD1 values (with a preferred set $g_s=6.84, g_s'=2.74$ and $g_s''=1.88$ [24]) equally well have been reported. Here...
we rely on field dependent IR spectra (see Ref.15 for more details) which allow to set with confidence the energy separation $\Delta E$ (expressed as $2\sqrt{D^2 + 3E^2}$) between the ground KD1 and excited KD2 at 115 cm$^{-1}$. We have chosen the ab initio (NEVPT2) ratio $\lambda$=E/D=0.17 to derive $D$=55.16 and $E$=9.38 cm$^{-1}$. Furthermore, we applied eqs.16 [26] along with the preferred set of g-factor values for KD1 values to deduce the spin-Hamiltonian parameters $g_x$=2.793, $g_y$=1.864 and $g_z$=2.047.

$$g_x = g_x \left(1+ \frac{1+3\lambda}{\sqrt{1+3\lambda^2}} \right)$$

$$g_y = g_y \left(1- \frac{3\lambda}{\sqrt{1+3\lambda^2}} \right)$$

$$g_z = g_z \left(-1+ \frac{2}{\sqrt{1+3\lambda^2}} \right)$$

- Mixing between wavefunctions corresponding to magnetic and vibrational levels in zero field has been neglected. This allows identifying fundamental quanta for the three vibrational levels with the zero-field energies of Raman transitions (but see below): $\hbar \omega_1 = 125$, $\hbar \omega_2 = 129$ and $\hbar \omega_3 = 139$ cm$^{-1}$.

- Vibronic matrix elements coupling the excited state $|3/2,0,0,0\rangle$ with $|-1/2,1,0,0\rangle$, $|-1/2,0,1,0\rangle$ and $|-1/2,1,0,0\rangle$ $E_1$, $E_2$ and $E_3$ were set to their values deduced from experiment, 1, 1 and 2 cm$^{-1}$, respectively, while vibronic coupling with participation of other magnetic sublevels: $M_s=1/2$ with $M_t=3/2$ have been neglected.

- The parameters $D_1$, $D_2$ and $D_3$ for the three vibrations were set to zero.

Under these assumptions magnetic and phonon positions with magnetic fields oriented parallel to the z, x and y canonical axes have been computed and plotted in Figure 8. Inspection of the plots allow to identify sets of data points which strictly follow a linear B vs E dependence (denoted using filled black circles) and such that undergo avoided crossing reflecting spin-phonon entanglement. The B||z plot reproduces the three anti crossing regions with values of the field and the crossing points comparing well with the experimental points. Given no parameter adjustment has been done (see Ref.15 for a best fit) agreement between theory and experiment is satisfactory. Field directions parallel to x and y lead to resonances at higher fields in agreement with the observed trends. Field directions along x and y (particularly the latter) explains the large tail seen in branch 4, shifted toward significantly higher energies compared to what the B||z plot shows.

Experimental data set for magnetic and phonon positions (Figure 7, branch 1, black points) allow to identify an excitation dominated by a vibration which shows a curvature toward higher energies in high field. We analyzed this using the single mode model of Section 3.2. In this model, a phonon at 114 cm$^{-1}$ interacts with the magnetic excitation at 115 cm$^{-1}$ with an off-diagonal element $E$=1 cm$^{-1}$ which mixes the two wavefunctions in zero field. Due to this mixing, the vibrational state acquires some magnetic character and this is responsible for the high-field-high-frequency shift of the resonance. As shown in Figure 9, the single mode coupling model nicely reproduces this feature for all three field directions $B||z$, $B||x$ and $B||y$.

Finally, one may argue, that vibronic coupling affects ground and excited g-factors in a way that may lead to a departure from the usual spin-Hamiltonian description. To check this point we employed the Hamiltonian of eq.15 accounting for the three modes by computing the ground and excited KD g-factors in dependence of E/D in a field of B=0.025 T in all three directions x, y, z and comparing the results with simple calculations using the usual static spin-Hamiltonian of eq.2 only. In Figure 10 results obtained using the latter approximation (solid lines) have been compared with the ones accounting for vibronic coupling (black points). As far as the ground state KD1 g-factors are concerned, results from
the two descriptions are identical; this is not surprising since it was assumed that there are no vibrations in the vicinity of the ground state KD1. For the excited state Kramers doublet (KD2) deviations are present, but at least for E/D smaller than 0.25 they are not significant. At E/D values above E/D=0.25 smaller values of $g_z$ and $g_y$ resulting from the vibronic calculation are obtained. The trend of these changes follows Frank Hams theorem of vibronic reduction of the expectation values of electronic operators (the Ham effect)[27-28, see also Ref.4].

**Figure 8**: Magnetic and phonon positions vs. magnetic fields in Raman spectra for 2 computed using the vibronic coupling model of eq.15 along with parameters specified in the text and field directions with respect to magnetic canonic axes: parallel to z (top, right), x (top, left) and y (bottom), notations of vibronic states refer to dominant contributions to wave functions which take full account for the orthorhombic ligand field.
Figure 9. Magnetic and phonon positions computed employing a model of two nearly degenerate states, lower one due to a phonon at energy $\hbar \nu = 114$ cm$^{-1}$, upper one due to a magnetic excitation at energy 115 cm$^{-1}$, coupled in zero magnetic field. Parameters employed in the plot are: $D=55.2$ cm$^{-1}$; $E/D=0.17$; $E_1=1$ cm$^{-1}$, $D_1=0$; adapted with permission from Ref.[15]

Figure 10. Rhombograms showing the effect of vibronic coupling on the ground KD1 g-tensor (left) and the excited KD2 g-tensor (right). Parameter set from NEVPT2 spin-orbit calculations used to
simulate the plot are: D=55.2 cm$^{-1}$, E/D=0.17, gx=2.793, gy=1.864, gz=2.047; vibrational frequencies: $\hbar \omega_1 = 125$, $\hbar \omega_2 = 129$ and $\hbar \omega_3 = 139$ cm$^{-1}$; spin-vibronic coupling parameters $E_1=D_1=E_2=D_2=1.0$ cm$^{-1}$; $E_3=D_3=2.1$ cm$^{-1}$; the field was set at B=0.025T; reproduced with permission from Ref.[15]

5. Implications for the Magnetic Relaxation

Paramagnetic relaxation in complexes of Co(II) takes place via coupling to vibrations (molecular, or lattice – phonons) or due to hyperfine interactions of the electron spin with the $I=7/2$ Co nuclear magnetic moment. The latter coupling is week and already small magnetic fields are able to overcome the electron-nuclear spin entanglement.

The temperature (T) and field (H) dependence of magnetic relaxation time (τ) in single molecule magnets is typically described by the expression

$$
\tau^{-1} = \frac{A_1}{1 + A_2 H^2} + DH^4 T + CT^n + \tau_0^{-1} \exp(-U/kT)
$$

where the four terms represent quantum tunneling, direct, Raman, and Orbach relaxation processes, respectively.[3] In this expression $A_1, A_2, D, C$ – are material constants, while $U$ is the barrier for Orbach relaxation of the magnetization – the energy separation between the ground (KD1) and excited (KD2) Kramers doublets. Frequently, it turns out that it is impossible to fit magnetic relaxation data to the total sum of contribution of the four processes. Moreover, it is usually found, that Arrhenius plots of the relaxation rate at elevated temperatures where the Orbach term dominates (the linear range in a ln($\tau^{-1}$) vs 1/kT plot) are characterized by a smaller slope $U_{\text{eff}}$ than $U$ estimated either theoretically or spectroscopically ($U$=230 and 115 cm$^{-1}$ extracted directly from the field dependent IR and Raman spectra of complexes 1 and 2, respectively). This finding points toward a mechanism of under barrier relaxation. Such a mechanism has recently been proposed [16], wherein specific vibrations facilitate relaxation through a direct doublet transitions, where both phonon- and magnetic excitations are simultaneously involved. The two examples presented here and our vibronic calculations suggest, that spin-vibronic coupling may be responsible for such a relaxation process. It was experimentally and theoretically shown using the two examples, that a variable magnetic field can tune the vibronic mixing between a spin-excited state, here focusing on the excited Kramers doublet (KD2) and the singly excited vibronic states. This mixing is maximal (50:50) in the vicinity of the anti-crossing point where the two states are of the same energy and the vibronic coupling constant $V$ is small yet different from zero. When applied to the ground Kramers doublet (KD1) an external magnetic field tends to stabilize the lowest component of the ground state Kramers doublet thus increasing its energy separation to any excited vibronic state – here the vibronic excitation. This lowering of energy due to magnetic Zeeman terms tends to reduce vibronic mixing, and therefore to decrease of the relaxation rate. In a sense this mechanism acts in the same direction as the tunneling term of eq.1 which at lower field values tends to reduce vibronic mixing, and therefore to decrease of the relaxation rate. In a sense this mechanism acts in the same direction as the tunneling term of eq.1 which at lower field values tends to reduce vibronic mixing, and therefore to decrease of the relaxation rate. In a sense this mechanism acts in the same direction as the tunneling term of eq.1 which at lower field values tends to reduce vibronic mixing, and therefore to decrease of the relaxation rate.

When switching on the field, the energy gap energy $\Delta E = \hbar \omega_1$ has to be corrected by the Zeeman stabilization (destabilization) of the lower(upper) magnetic sublevel ($M=-M_s$,ground,$M=M_s$), vibronically...
excited magnetic sublevel, Figure 11), resulting in a eq.19 with a sign +/- for the upper/lower vibronic level:

$$\Delta E = \hbar \omega \pm \beta_B H | M |$$  \hspace{1cm} (19)$$

A numerical simulation shows, that at lower fields the relaxation time increases with field being dominated by the vibronic coupling term of eq.18. At higher fields the D,B^+T starts dominate the relaxation process, leading to a decrease of the relaxation time. The $\tau$ vs $B$ curve of Figure 12 looks very much alike the tunneling term (the first term in eq.17) but is of a different physical origin.

![Figure 11](image)

**Figure 11.** (left) Vibronic model for magnetic relaxation in a field. The model is an extension of the model put forward by Lungi et al [16] where tuning of the energy separation between the ground and excited vibronic levels by a magnetic field (eq.19) was taken into account. The vibronic Hamiltonian accounts for terms in the Taylor expansion of the Zeeman operator along a single normal mode $Q$ with frequency $\hbar \omega _{Q}$:

$$H_{vb} = (\frac{\partial H}{\partial Q})_Q Q_S + (\frac{\partial^2 H}{\partial Q^2})_Q Q_S^2$$

leading to a matrix element $V$ mixing the ground and lowest excited vibronic levels; (right) simulation of the dependence of the relaxation rate on the applied magnetic field accounting for the vibronic and direct relaxation mechanisms. Parameters used in the simulations are: $\hbar \omega _{Q}=7 \text{ cm}^{-1}$, $g=2.00$, $M_z = \pm 1/2$, $T=3.5K$, $D$ (eq.17, second term)=$0.5 \text{ s}^{-1} \text{K}^{-1} \text{T}^{-4}$, $V=2 \text{ cm}^{-1}$.

6. Conclusions and outlook

In this review we summarized computational results dedicated to rationalize magnetic field dependent IR and Raman spectra of two Co(II) complexes subject to detailed analysis in two recent publications[14,15] in a close collaboration with several groups of experimentalists:

1) Correlated calculations on two single molecule magnets, 1 and 2 allow to characterize their non-relativistic ground states as orbitally non-degenerate, but with an energy separation to the lowest excited state of T symmetry, split in the D_2d(1) and C2(2) symmetries, respectively. Spin-orbit coupling induces a mixing of these states leading to large $S=3/2$ zero-field splitting of the Co(II) metal centered ground state being negative for 1 and positive in 2 with a large orthorhombic distortions superimposed in the
latter case. Using the CASSCF/NEVPT2 methods along with QDPT for spin-orbit coupling we could successfully reproduce the spectroscopic and magnetic data for the two complexes in agreement with reported experimental spectroscopic data.

2) Vibronic models have been employed to rationalize the field dependent FIR (1) and Raman (2) spectra of the two complexes allowing one to extract by comparison between simulated and reported spectra spin-vibronic coupling parameters $V$. In spite of the quite different nature of the two complexes spin-vibronic constants $V$ in a very narrow range between 1 and $3 \text{ cm}^{-1}$ have been deduced from the interpretation and best fit to the experimental data. The same parameters can in principle be computed from first principle CASSCF/NEVPT2 SOC calculations which is a rewarding task to carry out in future studies.

3) Expanding on a recent model for magnetic relaxation put forward by A. Lungi et al [16] we have shown, that spin-phonon coupling in combination with high quality quantum chemical calculations can be used to shed light on the mechanism of relaxation in SMM, particularly the field dependence of the relaxation time in complexes with Kramers ground states, deemed in literature to be due quantum tunneling of the magnetization.

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