AFRL-AFOSR-JP-TR-2019-0038

134031 QUANTUM PROPERTIES OF MOLECULAR NANOMAGNETS

Stephen Hill
FLORIDA STATE UNIV TALLAHASSEE
874 TRADITIONS WAY
TALLAHASSEE, FL 32306 - 0001

06/04/2019
Final Report

Air Force Research Laboratory
Air Force Office of Scientific Research
Asian Office of Aerospace Research and Development
Unit 45002, APO AP 96338-5002

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
04-06-2019	Final	28 Aug 2013 to 27 Feb 2017

4. TITLE AND SUBTITLE
QUANTUM PROPERTIES OF MOLECULAR NANOMAGNETS

5a. CONTRACT NUMBER

5b. GRANT NUMBER
FA2386-13-1-4031

5c. PROGRAM ELEMENT NUMBER
61102F

6. AUTHOR(S)
Stephen Hill

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
FLORIDA STATE UNIV TALLAHASSEE
874 TRADITIONS WAY
TALLAHASSEE, FL 32306 - 0001 US

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AOARD
UNIT 45002
APO AP 96338-5002

10. SPONSOR/MONITOR'S ACRONYM(S)
AFRL/AFOSR IOA

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AFRL-AFOSR-JP-TR-2019-0038

12. DISTRIBUTION/AVAILABILITY STATEMENT
A DISTRIBUTION UNLIMITED: PB Public Release

13. SUPPLEMENTARY NOTES

14. ABSTRACT
The objective of this collaborative project involving Florida State University (USA), the University of Modena and Reggio Emilia (Italy), and Osaka City University (Japan), is to identify potential molecular spin clusters for qubit encoding and to determine the optimum experimental conditions to fully exploit these systems in information and secure communication technologies. This challenge requires the joint effort of international teams with different skills, instrumentation with specific performances, and theoretical tools to understand the quantum features of this molecular hardware. During the third year of this project, we have focused on key experiments to demonstrate that molecular nanomagnets represent viable candidates for the implementation of quantum technology. Multiple exchanges of personnel (including students) have taken place between the partner institutions, and the project PIs have met on multiple occasions at international conferences and workshops to discuss the outcomes of the research, complete joint publications, and to plan the next steps in the collaboration. Thirteen publications have resulted from the project, including a paper in Nature, and several joint publications involving groups of the project PIs. Several other publications are either under review or in preparation.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			WINDER, SHEENA
Unclassified	Unclassified	Unclassified	SAR		19b. TELEPHONE NUMBER *(Include area code)* +81-42-511-2008

AOARD Scientific Project on Novel Nanomagnetic and Multifunctional Materials

Title: *Quantum Properties of Molecular Nanomagnets (AOARD Project #134031)*

Prof. Stephen Hill
Florida State University and National High Magnetic Field Laboratory (USA)

Collaborative project with:
Prof. Marco Affronte, Università di Modena (Italy)
Prof. Takeji Takui, Osaka City University (Japan)

The objective of this collaborative project is to identify potential molecular spin clusters for qubit encoding and to determine the optimum experimental conditions to fully exploit these systems in information and secure communication technologies. This challenge requires the joint effort of international teams with different skills, instrumentation with specific performances, and theoretical tools to understand the quantum features of this molecular hardware. During the third year of this project, we have focused on key experiments to demonstrate that molecular nanomagnets represent viable candidates for the implementation of quantum technology.

Four publications directly related to the objectives of the project have resulted from the Florida group during the past year; all four publications cite AOARD support.

[1] *Enhancing coherence in molecular spin qubits via atomic clock transitions*, Muhandis Shiddiq, Dorsa Komijani, Yan Duan, Alejandro Gaita-Ariño, Eugenio Coronado, Stephen Hill, Nature **531**, 348-351 (2016); DOI 10.1038/nature16984.

[2] *Coherent Spin Dynamics in Molecular Cr_8Zn Wheels*, Alberto Ghirri, Alessandro Chiesa, Stefano Carretta, Filippo Troiani, Johan van Tol, Stephen Hill, Inigo Vitorica-Yrezabal, Grigore Timco, Richard Winpenny, Marco Affronte, J. Phys. Chem. Lett. **6**, 5062-5066 (2015); DOI: 10.1021/acs.jpclett.5b02527.

[3] *Supramolecular aggregates of single-molecule magnets: exchange-biased quantum tunneling of magnetization in a rectangular $[Mn_3]_4$ tetramer*, Tu. N. Nguyen, W. Wernsdorfer, M. Shiddiq, K. A. Abboud, S. Hill and G. Christou, Chem. Sci. **7**, 1156-1173 (2016), Edge Article; DOI: 10.1039/C5SC02599K.

[4] *A Flexible Iron(II) Complex in which Zero-Field Splitting is Resistant to Structural Variation*, Joseph M. Zadrozny, Samuel M. Greer, Stephen Hill, and Danna E. Freedman, Chem. Sci. **7**, 416-423 (2016), Edge Article; DOI: 10.1039/C5SC02477C.

Two additional publications will be submitted within the next two months; these publications also cite AOARD support.

[5] *EPR Study of Radical-Lanthanide Interaction in a Terbium(III) Bis-Phthalocyaninato Complex*, D. Komijani, A. Ghirri, M. Affronte, S. Klyatskaya, E. Moreno Pineda, M. Ruben, and S. Hill, Phys. Rev. B (in preparation).

[6] *On the Interaction Between an Ensemble of Spins and a Cavity Mode*, Muhandis Shiddiq, and Stephen Hill, Phys. Rev. B (in preparation).

Significant Activities/Achievements

- In June, 2016, the Modena, Osaka and Florida teams met again at a 4th International Workshop on Novel Magnetic and Multifunctional Materials, organized jointly with the French-Korean Meeting on Functional Materials for Organic Optics, Electronics and Devices, Université Pierre et Marie Curie, Paris, France, July 4-8, 2016.
- Takeshi Yamane, a graduate student in the group of co-PI Takeji Takui at Osaka City University, visited the PIs lab at Florida State University for one week in April, 2016. During this period, Takeshi worked together with graduate student, Dorsa Komijani, performing high-field/high-frequency EPR measurements on 3 types of binuclear Re(IV,III) complexes in their mixed valence states. The frequency employed was 600 GHz, and all measurements were carried out at liquid helium temperatures in order to observe the localized high-spin states ($S = 3/2$). The single-crystals were oriented with respect to the static magnetic field. Non-linear shits of the resonance fields of the allowed fine-structure/hyperfine transitions as a function of the microwave frequency were detected for all the three complexes. No additional transitions were identified, suggesting that higher microwave frequencies may be required for direct observation of the zero-field-splitting (ZFS) between the $m_S = \pm^1/_2$ and $\pm^3/_2$ Kramers doublets. However, the non-linear shifts observed in the present experiments give clues to estimate the ZFS parameters and, thus, exact numerical calculations of the resonance fields based on a spin-Hamiltonian approach are underway.
- Research Associate, Alberto Ghirri, and graduate student, Claudio Bonizzoni, from the University of Modena and Reggio Emilia, visited the PIs lab at Florida State University for the month of June, 2016. During this time, they collected a vast amount of High-Field/High-Frequency Electron Paramagnetic Resonance data for a range of molecular spin systems that have been identified by our team as promising candidates for the implementation of Quantum Technologies. These included mono- and bi-nuclear $LnPc_2$ derivatives of different lanthanides (Ln = Tb, Dy, Ho, Er), and the ring shaped Cr_7Ni molecular spin clusters.
- The PI visited Osaka City University in August 2016, where he participated in the Osaka City University International Conference (OCUIC-2016) on Molecular Spins and Quantum Technologies. This visit and a subsequent conference in Sendai, Japan, which was also attended by Co-PI Takeji Takui, provided plenty of opportunities for further discussion related to this project and the joint experiments with Osaka.
- A cooperative agreement is currently being prepared between Florida State University and the University of Modena and Reggio Emilia, aimed at formalizing collaborations and academic/student exchanges between the two institutions. The agreement encompasses the timeframe of this AOARD project and continues beyond, in anticipation of long-term collaboration.
- The PI Chaired the 2016 Gordon Research Conference (GRC) on Conductivity and Magnetism in Molecular Materials, including applying to AFOSR for funds for participant support. The GRC and accompanying Gordon Research Seminar showcased recent work directly related to this AOARD project (see list of presentations below). In addition, Stefano Carretta, University of Parma, Italy, also attended the GRC. Prof. Carretta cooperates closely on this project in the context of the work on Cr_7Ni rings, thereby providing an excellent opportunity for interactions with the Florida team.

Significant Results

1. Hybrid Electro-Nuclear Clock Transitions. We previously demonstrated [*Nature* **531**, 348 (2016)] that dipolar decoherence can be suppressed in a holmium nanomagnet using so-called atomic clock transitions (ACTs). ACTs are realized at avoided level crossings at which the spin transition frequency is insensitive to variations in the local magnetic field. During the past year, we have observed a new type of electro-nuclear ACT involving coupled dynamics of the electron and nuclear spins. These transitions are formally forbidden in EPR. However, application of a transverse magnetic field mixes m_I and m_{I+1} states, allowing such transitions to occur in the vicinity of avoided level crossings (**see Figure 1**). Our results again suggest an enhancement in the coherence time at these electro-nuclear ACTs. This is significant for applications involving hybrid magnetic qubits, where manipulation of the nuclear spin can be achieved through EPR pulses. In addition, we have found that Electron Spin Echo Envelope Modulation (ESEEM) signals vanish right at the ACTs, providing further evidence that the Ho spins decouple from the surrounding protons. *We expect to submit a manuscript on these results later this year.*

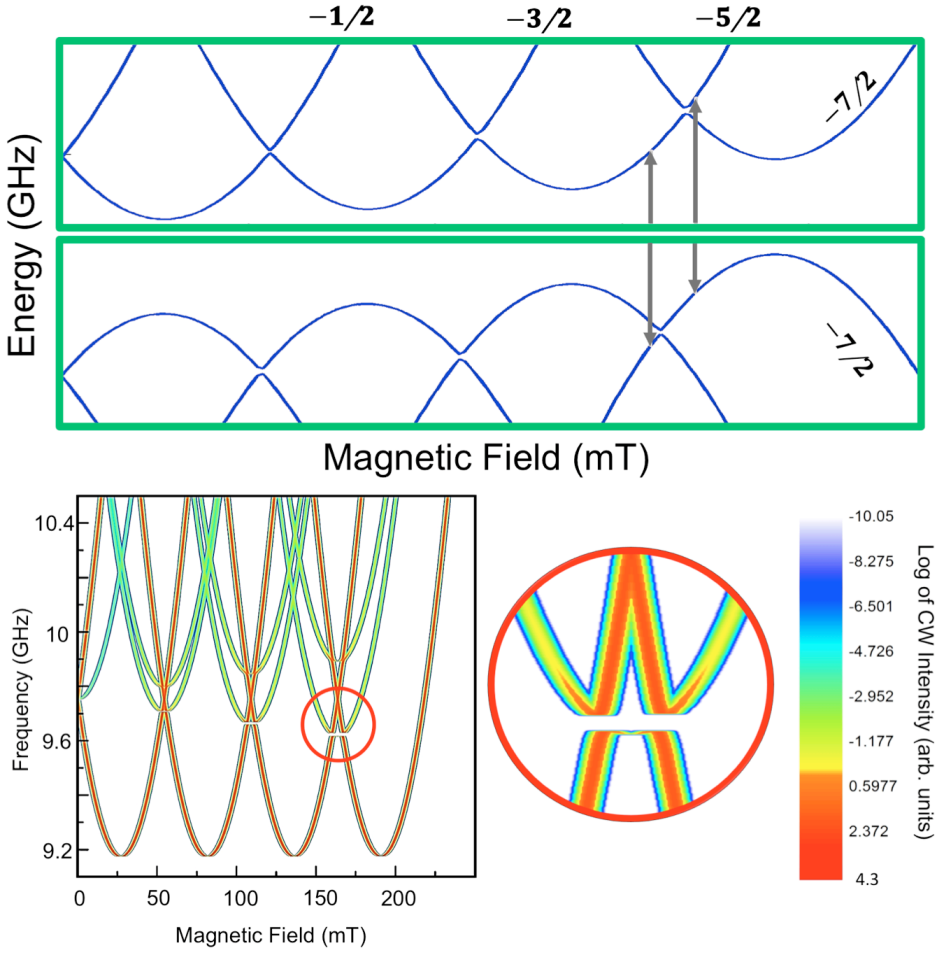


Figure 1. The top panel shows expanded views of the ground and excited electron/nuclear energy states associated with the holmium nanomagnet; the labeling corresponds to the nuclear spin projection, and the gray arrows indicate nominally forbidden EPR transitions that involve both electron and nuclear spin flips. The lower panel is an intensity map of the resultant EPR excitation frequencies, with an expanded view in the vicinity of the electro-nuclear clock transitions. As can be seen, the forbidden and allowed transitions hybridize, giving rise to a strong intensity right at the transition frequency minima/maxima.

2. EPR Studies of Layered Lanthanide Molecular Nanomagnets. In layered rare-earth hydroxide (LLH) compounds with general formula $Ln_2(OH)_5A^- \cdot nH_2O$ (**Fig. 3**), where A^- represents different interlayer anions, the lanthanide cations in the host layer and the anions can be tailored for different applications, offering novel multifunctional materials. We have carried out EPR studies of both pure and doped samples in which the Ln ion is magnetically diluted in a diamagnetic host (LLH: Ln, Ln = Tb, Er, Dy, Ho). To study the magnetic anisotropy, w*ide-band multi-high-frequency* EPR measurements were carried out, yielding components of the effective g-tensor. Furthermore, we used the same method to study the magnetic anisotropy of Er(III) single-ion magnets with two different N,N-donors (**see Figure 2**), $[Er(tpm)_3(bipy)]$ (**1**) and $[Er(tpm)_3(bath)]$ (**2**) (Htpm = 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione, bipy=2,2'-bipyridine and bath = *bathophenanthroline*). These studies clearly indicate an axial anisotropy of **1**, since we only observe the parallel component of the effective g-tensor, while, in the case of **2**, we observe two components of the g-tensor. *A manuscript on these studies is close to submission.*

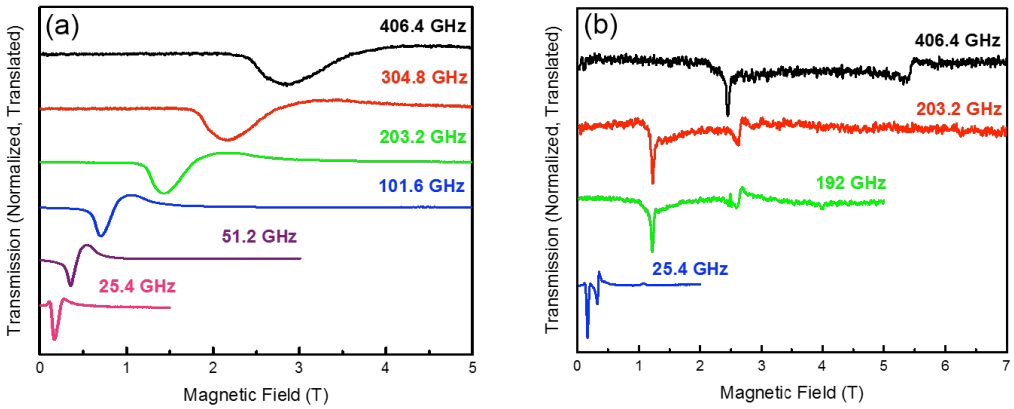


Figure 2. Multi-frequency continuous-wave EPR spectra of **(a)** $[Er(tpm)_3(bipy)]$ and **(b)** $[Er(tpm)_3(bipy)]$ at a temperature of 5 K; the frequencies are indicated in the figure, and the inset to (b) shows the layered structure of $Ln_2(OH)_5Cl \cdot nH_2O$ viewed along the *c*-axis.

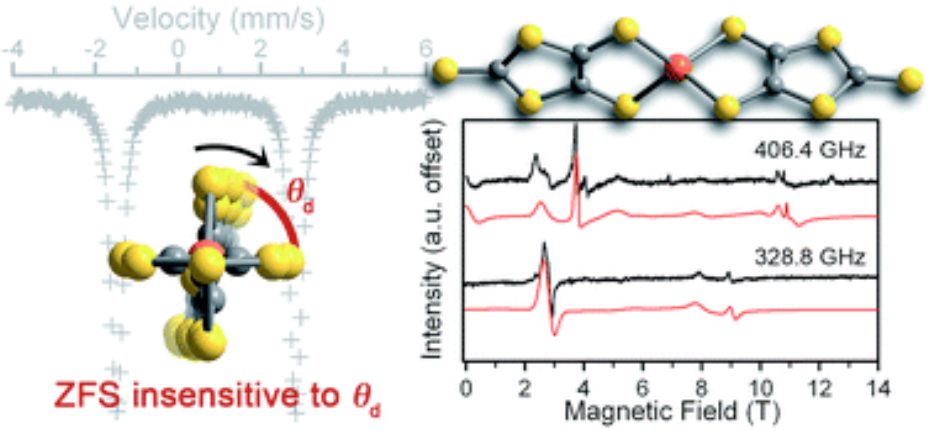


Figure 3. A side-view of the $[Fe(C_3S_5)_2]^{2-}$ molecule is shown top-right, while the lower-left image depicts an end-on view, illustrating the variation in the dihedral angle (θ_d) between the planes of the two $C_3S_5^{2-}$ units that ligate to the Fe(II) ion. The lower-right figure shows multi-frequency high-field EPR spectra obtained for **1**. The upper-left figure in the background depicts Fe(II) Mössbauer data from which information on the energies of the 3*d* orbital states can be obtained.

3. Development of Fe(II) Molecular Spin Qubits. We have studied by EPR three salts of a four-coordinate iron(II) complex $[Fe(C_3S_5)_2]^{2-}$ ($[(18\text{-crown-6})K]^+$ (**1**), Ph_4P^+ (**2**), Bu_4N^+ (**3**)) with a continuous structural variation in a single parameter, the dihedral angle (θ_d) between the two $C_3S_5^{2-}$ ligands (**see Figure 3**). EPR data for **1–3** reveal spin Hamiltonian parameters that are unusually robust to structural variation, representing the first part of a directed effort to understand how spin state energies may be fortified against structural distortions for future applications of qubits in non-crystalline environments. *This work has been published in Chem. Sci.* **7**, 416-423 (2016).

Relevant Presentation citing AOARD support during 3rd year of the award
(Presented by Stephen Hill unless indicated by *)

Keynote Lecture: *Probing Giant Anisotropies in Mononuclear Single-Molecule Magnets Using Very High-Field EPR*, 15th International Conference on Molecule-Based Magnets (ICMM), Sendai, Japan, September 4 to 8, 2016.

Keynote Lecture: *Electro-Nuclear Clock Transitions in Molecular Lanthanide Spin Qubits*, 20th Osaka City University (OCU) International Conference on Molecular Spins and Quantum Technology, Osaka, Japan, August 31 to September 4, 2016.

Invited talk: *Molecular Lanthanide Spin Qubits*, Amherst Workshop on Molecular Magnets, Amherst College, MA, August 19, 2016.

Invited talk: *Molecular Lanthanide Spin Qubits*, 4th International Workshop on Novel Magnetic and Multifunctional Materials, organized jointly with the French-Korean Meeting on Functional Materials for Organic Optics, Electronics and Devices, Université Pierre et Marie Curie, Paris, France, July 4-8, 2016.

Invited talk: *Probing Giant Magnetic Anisotropies in Mononuclear Single-Molecule Magnets Using Very High-Field EPR*, PPHMF-8, Physical Phenomena at High Magnetic Fields, Tallahassee, FL, January 6-9, 2016.

Invited talk: *Controlled Under Pressure: Magnetic Resonance Studies of Molecular Materials*, Pacifichem 2015 – The International Chemical Congress of Pacific Basin Societies, Honolulu, HI, December 15-20, 2015.

Invited talk: *Protecting Molecular Spin Qubits Against Dipolar Decoherence*, Pacifichem 2015 – The International Chemical Congress of Pacific Basin Societies, Honolulu, HI, December 15-20, 2015.

Invited talk: *Terahertz-to-Infrared Spectroscopy in High Magnetic Fields: Application to Molecular Magnetic Materials*, THz to soft X-ray Workshop, BESSY-II, December 7 and 8, 2015, Berlin, Germany.

Summer School Tutorial: *Electron Magnetic Resonance at the MagLab*, Stephen Hill, NHMFL User Summer School, Tallahassee, FL, May 16-20, 2016.

Seminar: *High Field Electron Paramagnetic Resonance Studies of Molecular Nanomagnets*, Centre to Reserche Paul Pascal, Bordeaux, July 1, 2016.

Seminar: *Controlled Under Pressure: Understanding Spin Orbit Coupling and Exchange Anisotropy in Organic Magnets*, Department of Physics, University of Utah, Salt Lake City, Utah, April. 6th, 2016.

Colloquium: *High Field Electron Paramagnetic Resonance Studies of Molecular Nanomagnets*, Department of Physics, Montana State University, Bozeman, Montana, Feb. 26th, 2016.

Seminar: *High Field Electron Paramagnetic Resonance Studies of Molecular Nanomagnets*, Department of Physics, Central Michigan University, Mount Pleasant, Michigan, Feb. 18th, 2016.

Contributed talk: *Electro-Nuclear Clock Transitions in a Ho(III) Molecular Nanomagnet*, Dorsa Komijani,* M. Shiddiq , Y. Duan, A. Gaita-Arino, J M. Clemente-Juan , E. Coronado, S. Hill, presented at the 2016 Gordon Research Seminar on Conductivity and Magnetism in Molecular Materials, Mount Holyoke College, South Hadley, MA, August 13-14, 2016.

Contributed talk: *Probing Giant Magnetic Anisotropies in Mononuclear Single-Molecule Magnets*, Stephen Hill, Lakshmi Bhaskaran, Komalavalli Thirunavukkuarasu, Katie Marriott, Mark Murrie, Mohamed Saber and Kim Dunbar, Rocky Mountain Conference on Magnetic Resonance, EPR Symposium, Breckenridge, CO, July 17-21 (2016).

Contributed talk: *A Crystal Field Approach to Orbitally Degenerate SMMs: Beyond the Spin Only Hamiltonian*, Lakshmi Bhaskaran,* Katie Marriott, Mark Murrie and Stephen Hill, American Physical Society March Meeting, Baltimore, Maryland, Mar. 14-18, 2016.

Contributed talk: *Electro-Nuclear Clock Transitions in a Ho(III) Molecular Nanomagnet*, Dorsa Komijani,* Muhandis Shiddiq, Yan Duan, Alejandro Gaita-Ariño, Eugenio Coronado and Stephen Hill, American Physical Society March Meeting, Baltimore, Maryland, Mar. 14-18, 2016.

Contributed talk: *Pushing the Limits of Magnetic Anisotropy in Mononuclear Ni(II) Single-Molecule Magnet*: *A High-Field EPR Study*, Lakshmi Bhaskaran,* Katie Marriott, Mark Murrie and Stephen Hill, Southeastern Magnetic Resonance Conference (SEMRC), Daytona Beach, Florida, Oct. 9-11, 2015.

Student Poster Presentation: *EPR Study of Radical-Lanthanide Interaction in a Terbium(III) Bis-Phthalocyaninato Complex*, Dorsa Komijani,* A. Ghirri, M. Affronte, S. Klyatskaya, E. Moreno Pineda, M. Ruben, and S. Hill, presented at Workshop on Molecular Magnets, Amherst College, Amherst, MA, August 19, 2016.

Student Poster Presentation: *Point Charge Electrostatics in Orbitally Degenerate Mononuclear Single-Molecule Magnets*, Lakshmi Bhaskaran,* Katie Marriott, Mark Murrie, and Stephen Hill, presented at Workshop on Molecular Magnets, Amherst College, Amherst, MA, August 19, 2016.

Student Poster Presentation: *Relating Symmetry to Magnetic Anisotropy in a Trigonal Mn(III) Complex*, Jonathan Marbey,* Pei-Rung Gan, En-Che Yang, Stephen Hill, presented at Workshop on Molecular Magnets, Amherst College, Amherst, MA, August 19, 2016.

Student Poster Presentation: *EPR Study of Radical-Lanthanide Interaction in a Terbium(III) Bis-Phthalocyaninato Complex*, Dorsa Komijani,* A. Ghirri, M. Affronte, S. Klyatskaya, E. Moreno Pineda, M. Ruben, and S. Hill, presented at the 2016 Gordon Research Conference on Conductivity and Magnetism in Molecular Materials, Mount Holyoke College, South Hadley, MA, August 14-19, 2016.

Student Poster Presentation: *Point Charge Electrostatics in Orbitally Degenerate Mononuclear Single-Molecule Magnets*, Lakshmi Bhaskaran,* Katie Marriott, Mark Murrie, and

Stephen Hill, presented at the 2016 Gordon Research Conference on Conductivity and Magnetism in Molecular Materials, Mount Holyoke College, South Hadley, MA, August 14-19, 2016.

Student Poster Presentation: *Relating Symmetry to Magnetic Anisotropy in a Trigonal Mn(III) Complex*, Jonathan Marbey,***** Pei-Rung Gan, En-Che Yang, Stephen Hill, presented at the 2016 Gordon Research Conference on Conductivity and Magnetism in Molecular Materials, Mount Holyoke College, South Hadley, MA, August 14-19, 2016.

Student Poster Presentation: *Electro-Nuclear Clock Transitions in a Ho(III) Molecular Qubit*, Dorsa Komijani,***** M. Shiddiq , Y. Duan, A. Gaita-Arino, J M. Clemente-Juan , E. Coronado, S. Hill, presented at the 2016 Gordon Research Seminar on Conductivity and Magnetism in Molecular Materials, Mount Holyoke College, South Hadley, MA, August 13-14, 2016.

Student Poster Presentation: *Point Charge Electrostatics in Orbitally Degenerate Mononuclear Single-Molecule Magnets*, Lakshmi Bhaskaran,***** Katie Marriott, Mark Murrie, and Stephen Hill, presented at the 2016 Gordon Research Seminar on Conductivity and Magnetism in Molecular Materials, Mount Holyoke College, South Hadley, MA, August 13-14, 2016.

Student Poster Presentation: *Relating Symmetry to Magnetic Anisotropy in a Trigonal Mn(III) Complex*, Jonathan Marbey,***** Pei-Rung Gan, En-Che Yang, Stephen Hill, presented at the 2016 Gordon Research Seminar on Conductivity and Magnetism in Molecular Materials, Mount Holyoke College, South Hadley, MA, August 13-14, 2016.

Student Poster Presentation: *Electro-Nuclear Clock Transitions in a Ho(III) Molecular Nanomagnet*, Dorsa Komijani, Muhandis Shiddiq, Yan Duan, Alejandro Gaita-Ariño, Eugenio Coronado, Stephen Hill, Florida State University, Department of Physics Student Research Showcase, Apr. 14, 2016.

Student Poster Presentation: *HFEPR studies of Zero Field Splitting in a trigonal Mn(III) complex*, Jonathan J. Marbey,***** En-Che Yang, Stephen Hill, Southeastern Magnetic Resonance Conference (SEMRC), Daytona Beach, Florida, Oct. 9-11, 2015.

Student Poster Presentation: *Enhancement in Phase Coherence Time Using Clock Transitions*, Dorsa Komijani,***** Muhandis Shiddiq, Yan Duan, Alejandro Gaita-Ariño, Eugenio Coronado and Stephen Hill, Southeastern Magnetic Resonance Conference (SEMRC), Daytona Beach, Florida, Oct. 9-11, 2015.

Student Poster Presentation: *EPR Studies of Heterometallic Systems Containing Mn^{III} and Rare Earth Ions*, Livia B. L. Escobar,***** Guilherme P. Guedes, Jon Marbey, Stephen Hill, Rafael A. A. Cassaro, Stéphane Soriano, Miguel Novak, Marius Andruh and Maria G. F. Vaz, Southeastern Magnetic Resonance Conference, Daytona Beach, Florida, Oct. 9-11, 2015.

Student Poster Presentation: *Enhancement in Phase Coherence Time Using Clock Transitions*, Dorsa Komijani,***** Muhandis Shiddiq, Yan Duan, Alejandro Gaita-Ariño, Eugenio Coronado and Stephen Hill, 7^{th} Summer School of the European Federation of EPR Groups on Advanced EPR, Berlin, Germany, Aug. 24-31, 2015.

AOARD Scientific Project on Novel Nanomagnetic and Multifunctional Materials

Title: *Quantum Properties of Molecular Nanomagnets (AOARD Project #134031)*

Prof. Marco Affronte
CNR - Institute NanoSciences Modena (and University of Modena e Reggio Emilia), Italy

Collaborative project with:
Prof. Stephen Hill, National High Magnetic Field Laboratory & Florida State University (USA)
Prof. Takeji Takui, Osaka City University (Japan)

Scientific Report for activities 2016.

Coupling molecular spins to superconducting planar resonators.

Recently CNR started to investigate how molecular spins can be coupled to flying qubits such as microwave photons in superconducting circuits. The problem is relevant for Quantum Technologies since it may open the way to exploit molecular spin qubits in hybrid systems and eventually couple them to other superconducting qubits, spins/defects in semiconductors or any other solid state implementation of qubits. To create coherent dynamic, we need to achieve the strong coupling regime for which the coupling between spins and photons is stronger than decay rate of both the spin qubit and photons in resonant cavity. Since, in general, the coupling of magnetic dipole with magnetic component of the electromagnetic wave is weak such condition is hard to achieve. One strategy is to use spin ensemble in such a way that the coupling is effectively enhanced by a factor $\sqrt{N}$, being N the number of spins.

In 2015, CNR has demonstrated that electron spin ensembles of radicals coherently couple to microwave photons in high Tc YBCO planar resonator up to 50K and in finite magnetic field (APL2015). This new research line has been pursued by CNR in 2016 in two ways:

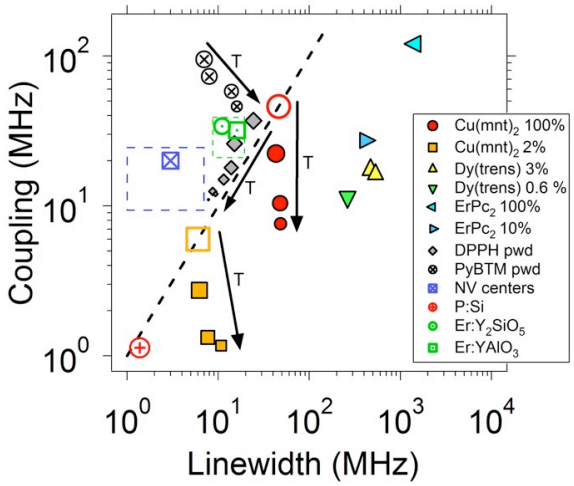


Figure 1 Plot of coupling rate and spin linewidth parameters obtained by fitting the experimental data. Black arrows with T and the size of symbols represent the temperature evolution, from 2K (larger symbols) to 50 K (small symbols). Open circles display the parameters extrapolated to 0.3 K by means of Eq. 4. The dashed line represents the threshold above which strong coupling regime is achieved. The parameters of DPPH and PyBTM organic radicals (measured between 2 and 70K) are taken form [APL] and [PyBTM] respectively. The rectangles show the typical values obtained for NV centers [spin_impurities] and Er:Y_2SiO_5 [Er_doped] at 10-50 mK.

In a preliminary work (ref. Dalton Trans.) we have carried out systematic spectroscopic measurements looking for the coherent coupling between molecular magnetic centers and microwave photons. The aim was to find the optimal conditions and the best molecular features

to achieve the strong coupling regime for which coherent dynamics of hybrid photons-spin state take place. To this end we used a high critical temperature YBCO superconducting planar resonator working at 7.7 GHz to investigate three molecular mononuclear derivatives, namely $Cu(mnt)_2$, $[ErPc_2]^-TBA^+$ and Dy-*trensal* and different organic radicals. Results are summarized in Fig.1. The strong coupling regime was achieved for dense organic radical but not for diluted mono-nuclear samples. These results provide several hints on how to design molecular magnetic centers to be integrated into hybrid quantum circuits.

- In February 2016, Prof. T. Takui and Prof. Nakaza from OCU spent one week in Modena starting a new series of spectroscopic measurements on nitronil nitroxides radicals by YBCO planar MW resonators. Systematic investigation include sample of both simple radical and bi-radical of different concentration. Data analysis which may account for the zero field splitting of the ground triple is still under way but these preliminary experimental spectra show that strong coupling regime can be achieved with non-concentrated samples, suggesting that exchange narrowing effect may significantly contribute at obtaining coherent spin photon states.

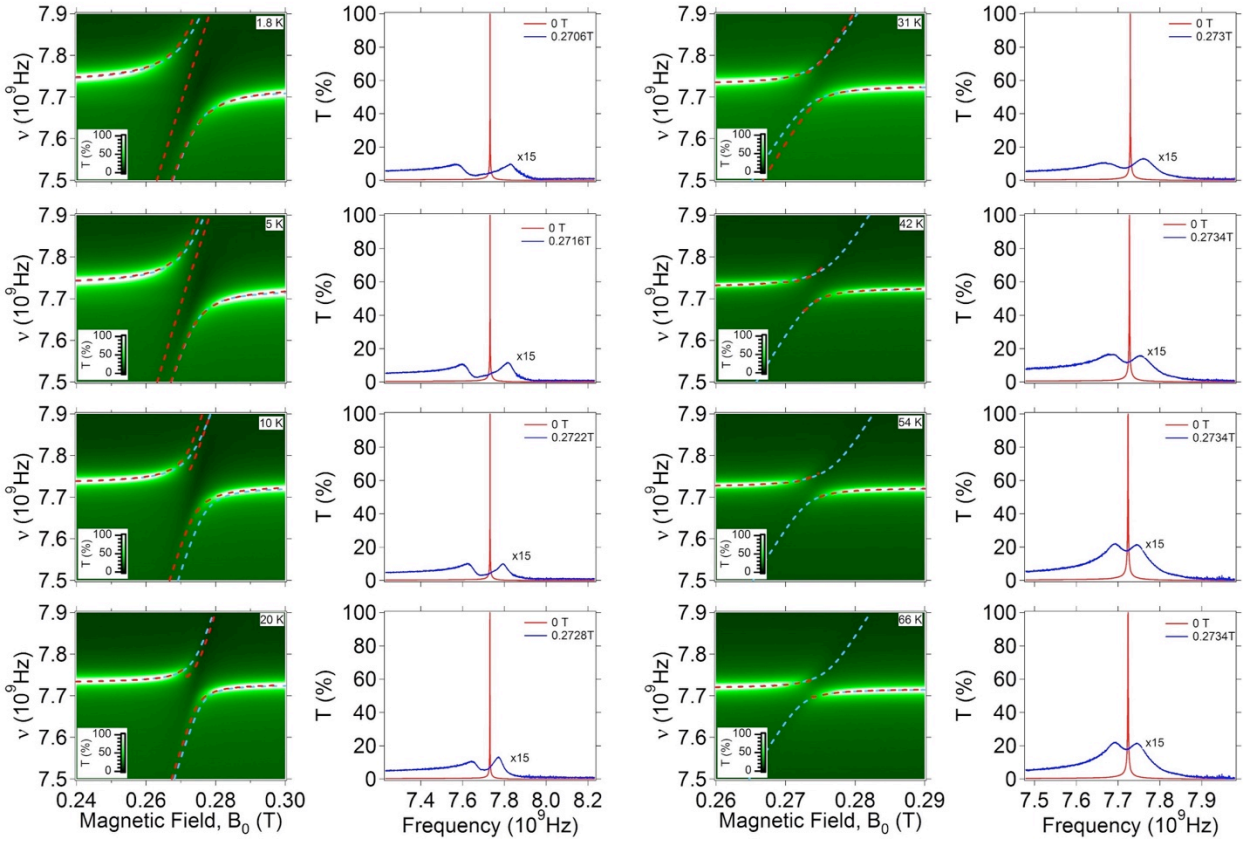


Figure 2 Transmission spectral map for the IN-NO bi-radical measured at 2K and Pin = -15 dBm and coparison with simulated curves at the level anti-crossing.

In a further work we revisited the problem of coupling distinct ensembles of two level systems through photons in a quantum box by using organic radicals (spin 1/2) and a high T_c superconducting coplanar resonator with which an exceptionally strong coupling is obtained. Up to three spin ensembles are simultaneously coupled and are made physically distinguishable by

chemically varying the Landé g factors and by exploiting the inhomogeneities of the applied magnetic field. The observed multiple anticrossing, along with the simulations performed within the input-output formalism, demonstrate the coherent coupling.

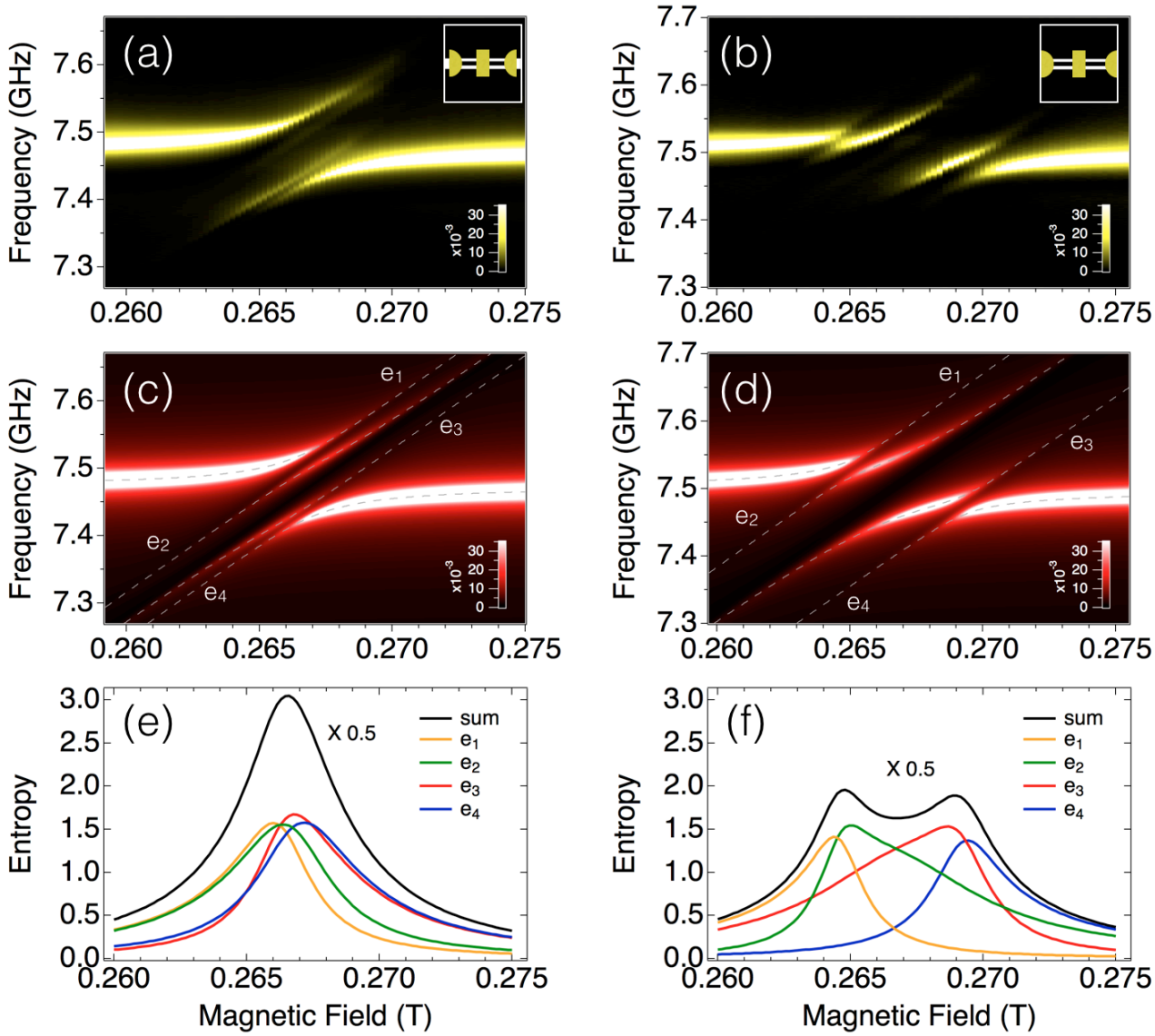


Figure 3 Transmission spectroscopy experiments with three spin ensembles. One ensemble is positioned at the center of the resonator, while the two external ensembles are placed on the edge of the central electrode (left column) or on the gap between the central strip and the external box (right column). In each column we display the experimental results obtained for a given geometry (a,b) and the corresponding simulations performed through the input-output formalism (c,d). Panels (e,f) show the entropic measures S_k, and their sum S calculated for the hybrid spin-photon modes, as a function of the magnetic field.

Electron Spin Resonance Experiments on Ln-Pc double and triple decker.

Lanthanide centers are appealing for electron spin manipulation since they have high and very anisotropic Landé *g*-factors. However, considering the ground state of most Ln, the intra-multiplet transitions are not allowed by conventional EPR selection rules. Few ESR experiments have been reported in literature on the molecular bricks, namely the bis(phtalocyaninato)

lanthanide double-decker complexes ($LnPc_2$, Pc=phtalocyanine). In their neutral form, $LnPc_2$ complexes comprises an additional radical spin 1/2 delocalized onto the Pc molecules, which influences the low temperature magnetic properties and plays an important role when the molecule is coupled to our spintronic devices or deposited on a magnetic surface. The open question is to see whether the spin radical, which provides quite accessible EPR transitions, may give useful information when coupled to Ln in double and triple decker.

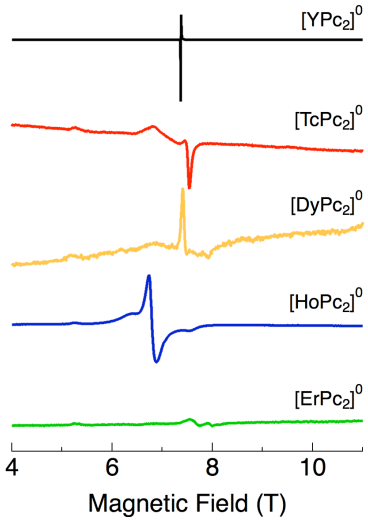


Figure 4 Comparison between the EPR spectra (frequency ≈210 GHz) taken on the series of $LnPc_2$ double-decker complexes at 2K.

We (CNR) decided to get more insights on the role of this this spin radical by performing high frequency high field EPR experiments at National High Magnetic Field Laboratory in Tallahasse (FL, USA) exploiting the collaboration with group of Prof. S. Hill. Dr Alberto Ghirri (CNR researcher) and Claudio Bonizzoni (PhD student from University of Modena) have spent one month in June 2016 at NHMFL in Tallahasse. With the group of Prof S. Hill, they have carried out a systematic study by means of high frequency Electron Paramagnetic Resonance (EPR) spectroscopy on the series of $LnPc_2$ neutral compounds, where Ln=Tb, Dy, Ho and Er. Powder samples of $LnPc_2$ molecules were investigated by means of a multi-frequency transmission spectrometer operating at several frequencies in the range 25-400 GHz. The comparison with the EPR spectrum of YPc_2 shows that the resonances with *g*-factor near 2 are influenced by the presence of each Ln(III) ion (see Figure 2). We have investigated the frequency dependence of the resonance fields and compared these results with a theoretical model that includes the Ln-radical exchange interaction. For $TbPc_2$ the experimental results evidence that the coupling is ferromagnetic with an exchange constant of about 0.5 cm^{-1}. This outcome is also corroborated by ab-initio calculations. These results provide hints for non conventional manipulation of Ln spins.

Related Publications.

YBCO microwave resonators for strong collective coupling with spin ensemble A. Ghirri, C. Bonizzoni, D. Gerace, S. Sanna, A. Cassinese, and M. Affronte ***Applied Physics Letters*** 106, 184101 (2015); doi: 10.1063/1.4920930

Coherently coupling distinct spin ensembles through a high-Tc superconducting resonator A. Ghirri, C. Bonizzoni, F. Troiani, N. Buccheri, L. Beverina, A. Cassinese, and M. Affronte, **PHYSICAL REVIEW** A **93**, 063855 (2016)

Coupling molecular spin centers to microwave planar resonators: towards integration of molecular qubits in quantum circuits C. Bonizzoni, A. Ghirri, K. Bader, J. van Slageren, M. Perfetti, L. Sorace, Y. Lan, O. Fuhr, M. Rubene, and M. Affronte *Dalton Transactions (2016)* DOI: 10.1039/c6dt01953f

AOARD Scientific Project on Novel Nanomagnetic and Multifunctional Materials

Title: *Quantum Properties of Molecular Nanomagnets (AOARD Project #134031)*

Prof. Takeji Takui
Department of Chemistry & Molecular Materials Science, Graduate School of Science, Osaka City University, Osaka

Collaborative project with:
Prof. Marco Affronte, Università di Modena (Italy)
Prof. Stephen Hill, National High Magnetic Field Laboratory & Florida State University (USA)

Milestones of The Project:
(1) Identification of molecular systems with optimal performances as qubits. The design of spin clusters with suitable features needs to be combined with the synthesis of molecules.

(2) Identification of molecular spins coupled to one another or to other quantum systems. Control of spin entanglement at (supra-) molecular level is a fundamental step towards implementation of quantum gates. "Quantum Control" challenges chemists/materials scientists to implement quantum-control mediated gate operations for realistic matter spin qubits.

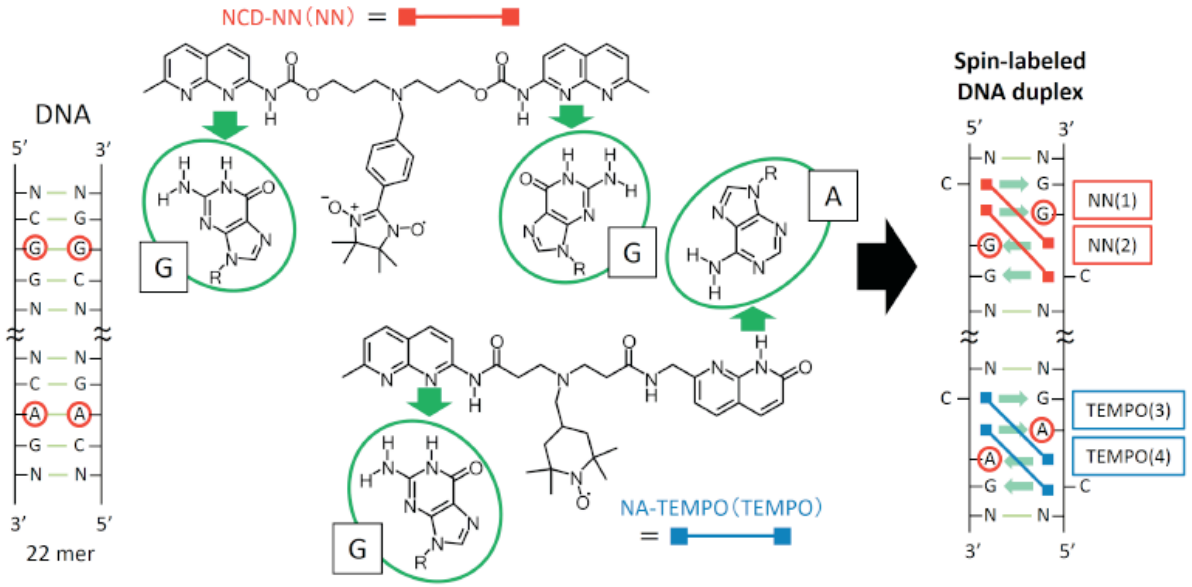
(3) Key spin resonance experiments. Here, there are several technical challenges to be overcome in combining high power microwave pulses with low temperature and high sensitivity in detection.

From the theoretical side, a breakthrough in practical quantum algorithms for quantum chemistry (or quantum chemical calculations) is expected.

1. Significant Achievements
The aim of Collaborative Scientific Project is to identify molecular nanosystems/entities composed of molecular spins or any open shell molecular systems in 0-3 dimension and to optimize their molecular magnetic properties suitable for molecular spin qubits of quantum computers/simulators (QCs/QSs) and quantum information processing systems. Quantum control has been emerging in the field of QCs/QSs, and relevant molecular optimization challenges chemists/materials scientists to implement quantum control by the use of molecular spin qubits. We emphasize that the objectives are closely relevant to implementing highly sophisticated pulse-based microwave spin technology which can afford "quantum control" among the qubits as the key spin technology. This quantum control is novel and generally termed "Molecular Spin Quantum Cybernetics", which is essential for spin-qubit based quantum computing and quantum information processing. Our theoretical basis for quantum control is underlain by Lie-group theory/Lie-algebra. In the context above, we have executed this collaborative project along the four main lines as follows:

(1) Molecular Optimization for Matter Spin Qubits:
One is to optimize molecular spins for realistic matter spin qubits which are composed of electron bus-qubits and nuclear client-qubits in molecular frames. Thus, in this project our theoretical work has always included realistic molecular spins, with which we have implemented "Adiabatic Quantum Computing", for example during the basic 2013/2014 (- Mar., 2015) years. We also have developed quantum chemical calculations to evaluate accurate spin-orbit

interactions in zero-field splitting tensors of both open shell metallic ion complexes and organic spin-triplet molecular systems with sizable fine- structure parameters. It has turned out that the introduction of bromine atoms in the pi electronic network enables us to tune the magnitude of the fine-structure parameters of the organic triplet molecules. The tuning capability is useful to couple the triplet molecules in ensemble (quantum spin memory) with superconducting qubits (gate operations).



A quest for a Lloyd model of electron spin qubits as scalable qubits is of extreme importance in terms of molecular spin qubit design and optimization. We have extended our helical symmetry approach to DNA-based double-stranded helical oligomers, whose specific sites are labeled with stable radical qubits (termed g-tensor engineering) (see Fig. 1). Characterization/identification of the magnetic properties of the radical qubits embedded in the oligomer's helical structure is essential for the Lloyd model of the electron spin version. Thus, we have characterized the detailed magnetic properties of the four radical qubits embedded in an DNA oligomer (22-mer) by using PELDOR spectroscopy and MM calculations ([0-1] submitted to Journal of Physical Chemistry, B and under review). Based on the acquired results, relevant synthetic work is in progress in collaboration with Prof. Schiemann's group, Univ. of Bonn.

(2) Quantum Control of Molecular Spin Qubits: Methodological Establishment.
The second is to implement quantum control technology applicable to few-qubit molecular spins in the solid state (single crystals) from both the theoretical and experimental side. We have applied a Lie-Algebra based control theory to realistic molecular spins and tested our quantum control approach, in which high fidelity and total computation time required to implement Controlled-NOT gates between the two client nuclear qubits by use of microwave GRAPE (Gradient Ascent Pulse Engineering) pulses are simulated. We have checked the anisotropic behavior of the quantum control occurring in the realistic molecular spins adopted in this project and found physical meanings behind the behavior, which serve for the molecular optimization. In this project, we have adopted the molecular spins of three-spin qubits, i.e., the systems with one electron bus-qubit and two nuclear client spin qubits which are indirectly connected through hyperfine couplings.

(3) Pulse-Based Microwave Spin Control Technology: Establishment of NMR-paradigm Based ESR Spectroscopy.
In order to implement quantum control in the systems of molecular spin qubits from the experimental side, NMR-paradigm based electron spin resonance techniques as highly sophisticated electron magnetic resonance spin technology are required. We have designed and established such pulse-based microwave spin technology operating at X-band, in which an AWG (Arbitrary Wave Generator) is the heart of the setup. Quantum computing experiments for implementing Controlled-NOT gates by use of stable organic radicals in the solid state are underway.

(4) Quantum Chemical calculations/Quantum Chemistry on Quantum Computers (QCC/QC-on-QCs) and Development of Adiabatic Quantum Computing (AQC) by the use of Molecular Spin Qubits.
Since Shor's quantum algorithm appearing in 1993 for the factorization as an NP problem, there has been no disruptive approach to the issues of the factorization from both the theoretical and experimental sides. Putatively, there are required a vast number of addressable qubits to tackle intractable subjects that modern "classical computers" cannot deal with. We emphasize that there is another way to methodologically develop quantum computing besides the standard gate operation/circuit model approach. Adiabatic Quantum Computing (AQC) is one of the counterparts, which can afford reduction of the number of the addressable qubits. We have shown for the first time that molecular spins are computing resources which can afford CPU 500-1000 times faster than NMR QC experiments for the factorization with three spin qubits.

Considerable advance in applications of QCs to quantum chemical calculations has been made from both the theoretical and experimental sides, until recently. We have implemented a quantum algorithm which enables us to construct configuration state functions (CSFs) for Full-CI calculations on QCs for vector space-demanding open shell molecular systems such as single molecule magnets, the first and typical example of nanomagnets. A notorious difficulty in QC applications to electronic structure theories in quantum chemistry has been relevant to the antisymmetrization of electronic wavefunctions. Full-CI for sizable molecules demands exponential CPU time, and it is intractable on any modern classical computers. A relevant paper is under review ([0-2] in 3. Publications, submitted to Journal of American Chemical Society).

2. Significant Activities of Collaboration with the Other PIs
In the following are exchange meetings to initiate collaborative researches, noting that in order to conduct AOARD Scientific Collaborative Project a university-level cooperative agreement between Osaka City University and Florida State University was executed in November, 2014. Prior to the formal conclusion, mutual understanding of terms and conditions in detail was made in every level for five months after July, 2014. A similar agreement between Graduate School of Science, Osaka City University and Department of Physics, University of Modena and Reggio Emilia was concluded in Aug., 2014.

(1) Dr. Stefano Pittalis and Dr. Carlo Rozzi (CNR-Modena) of the Modena team were invited to OCU and gave their lectures at the departmental seminar, hosted by PI of OCU.

(2) The Modena, Florida and Osaka teams met at Workshop on Molecular Electron Spin Qubits at the University of Manchester, UK. Multiple members of each team were present at the WS,

allowing us to have extensive discussions of the scientific results and outlining of manuscripts. In addition, several other researchers who have collaborated on this project and co-authored joint publications with Prof. S, Hill, PI of the Florida team were at the meeting (Freedman, Carretta, Timco and Winpenny).

(3) Several members of the collaboration met and discuss the latest results and further collaborative plans in September 15-18, 2015, Warsaw at the European Materials Research Symposium on Molecular Materials for Quantum Computing: Hill (Florida); Ghirri and Troiani (Modena); Takui (Osaka); Ruben (Karlsruhe); Freedman and Graham (Northwestern); and Santini (Parma).

(4) Prof. Freedman, a collaborator of the Florida team was invited to AWEST 2015, an intn'l WS on Electron Spin Science and Technology: Biological and Materials Science Oriented Applications, Awaji Island, Japan, organized by PI, Takeji Takui, and discussed future collaboration in view of theoretical calculations of zero-field tensors with her.

3. Publications

Publications relevant to the objectives of AOARD Scientific Project are listed in the following: The publications cite the financial support from AOARD Scientific Project.

The following are book chapters (reviewed and written in English, ones in Japanese not included) relevant to the objectives of the Project. The first publication of the book chapters is an account article, and the rest is all original and reviewed.

(1) "Molecular spin qubits: Molecular optimization of synthetic spin qubits, molecular spin AQC and ensemble spin manipulation technology", ed. by Y. Yamamoto, K. Semba, Chapter 28, Principles and Methods of Quantum Information Technologies, Lecture Notes in Physics 911, DOI 10.1007/978-4-431-55756-2_28, 2016.

(2) "Exploiting quantum effects in electron-nuclear coupled molecular spin systems" in Electron Spin Quantum Computing: Electron Spin-Qubit Based Quantum Computing and Quantum Information Processing, Robabeh Rahimi Darabad, Kazunobu Sato, Patrick Carl, Peter Höfer, Raymond Laflamme, Takeji Takui, Chapter 2, Biological Magnetic Resonance, Vol. 31 (2016), in press.

(3) "Adiabatic quantum computing on molecular spin quantum computers", in Electron Spin Quantum Computing: Electron Spin-Qubit Based Quantum Computing and Quantum Information Processing, Satoru Yamamoto, Shigeaki Nakazawa, Kenji Sugisaki, Kazunobu Sato, Kazuo Toyota, Daisuke Shiomi and Takeji Takui, Chapter 4, Biological Magnetic Resonance, Vol. 31 (2016), in press.

The following are article papers under review:

0-1."Structural determination of a DNA duplex oligomer/oligonucleotide with double pair-wise molecular spins by MM calculations and PELDOR spectroscopy: toward a DNA-based Lloyd model of electron spin qubits for QC/QIP", Satoru Yamamoto, Shigeaki Nakazawa, Kenji Sugisaki, Kensuke Maekawa, Kazunobu Sato, Kazuo Toyota, Daisuke Shiomi, Takeji Takui

Journal of Physical Chemistry B (under review).

0-2. "A superpolynomial quantum algorithm for the preparation of constructing the wavefunctions of open shell molecules: Quantum chemistry on quantum computers, Kenji Sugisaki, Satoru Yamamoto, Shigeaki Nakazawa, Kazuo Toyota, Kazunobu Sato, Daisuke Shiomi, Takeji Takui Journal of Physical Chemistry A (under review).

The reviewed published papers are listed below:

1. "Hyperfine spin qubits in irradiated malonic acid: heat-bath algorithmic cooling", Daniel K. Park, Guanru Feng, Guanru, Robabeh D. Rahimi, Stephane Labruyere, Taiki Shibata, Shigeaki Nakazawa, Kazunobu Sato, Takeji Takui, Raymond Laflamme, Jonathan Baugh, Quantum Information Processing, Volume 14, Issue 7, Pages 2435-2461 (2015). Published: JUL 2015. DOI: 10.1007/s11128-015-0985-1

2. "Probing an untouchable environment for its identification and control", Masaki Owari, Koji Maruyama, Takeji Takui, Go Kato, Physical Review A. Volume 91, Issue 1, Article Number 012343 (2015). Published: JAN 30 2015. DOI: 10.1103/PhysRevA.91.012343

3. "Adiabatic quantum computing with spin qubits hosted by molecules", Satoru Yamamoto, Shigeaki Nakazawa, Kenji Sugisaki, Kazunobu Sato, Kazuo Toyota, Daisuke Shiomi, Takeji Takui, Physical Chemistry Chemical Physics, Volume 17, Issue 4, Pages 2742-2749 (2015). Published: JAN 28 2015. DOI: 10.1039/c4cp04744c