

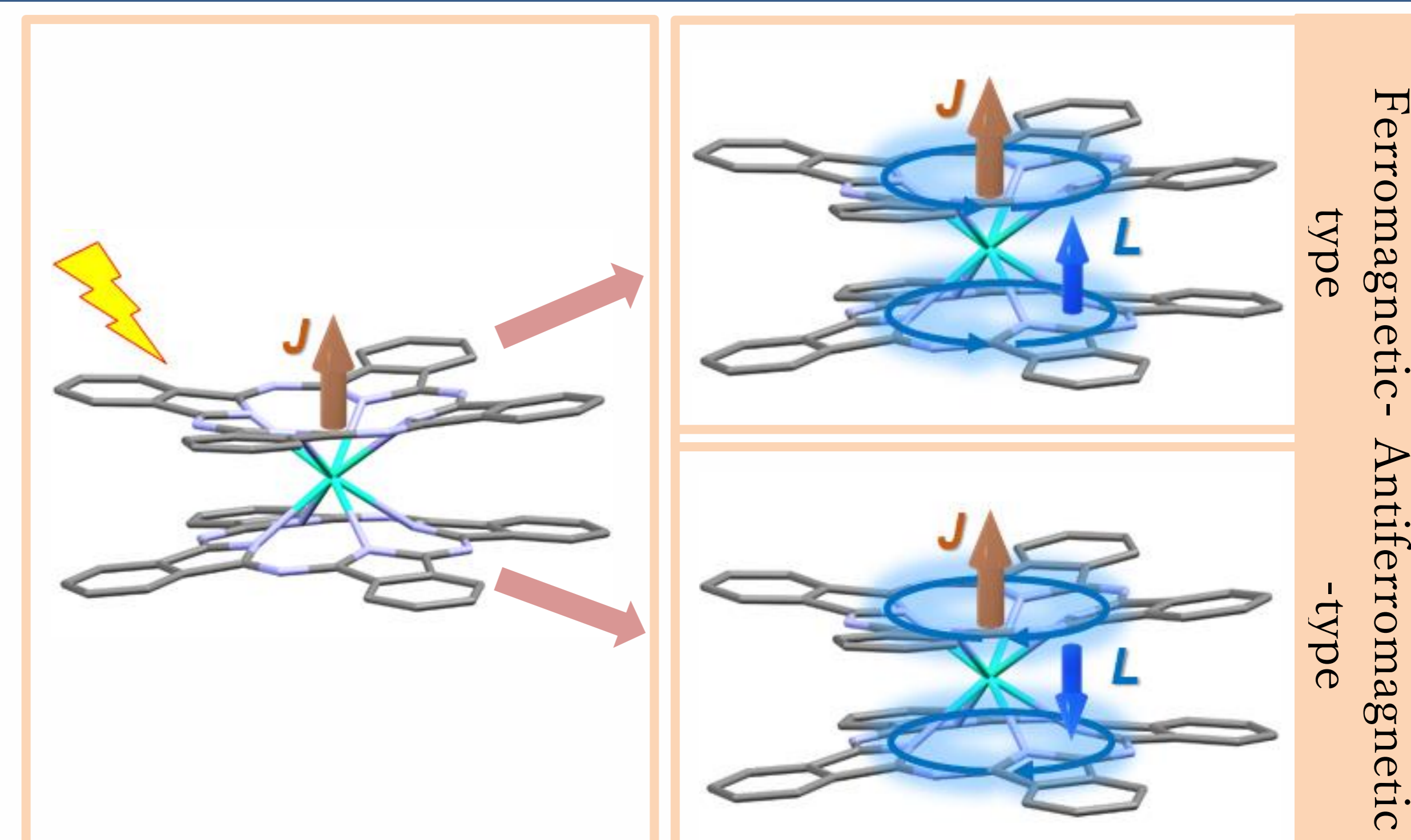
OSAKA UNIVERSITY

Ab Initio Study of An Intramolecular Magnetic Interaction in Rare-Earth-Based Molecular Magnets

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1. Introduction

The exploration of electronic interactions in molecular compounds has led to intriguing discoveries in the field of lanthanide complexes. Among these compounds, bisphthalocyaninato lanthanide(III) complexes, Pc_2Ln^- , have exhibited a novel type of interaction. Previous studies have revealed that an interaction arises between the total angular momentum (J) of the lanthanide ion and the orbital angular momentum (L) of the cyclic π system of the ligand.^{1,2} This interaction, called the “ J - L interaction”, can occur in either a ferromagnetic-type or an antiferromagnetic-type manner, as illustrated in Figure 1. Notably, this interaction has the ability to alter the energy ordering of the sublevel structure in the ground state through the photogeneration of L . Consequently, this presents a remarkable opportunity to manipulate the quantum state of molecular magnets via the excitation-deexcitation process.

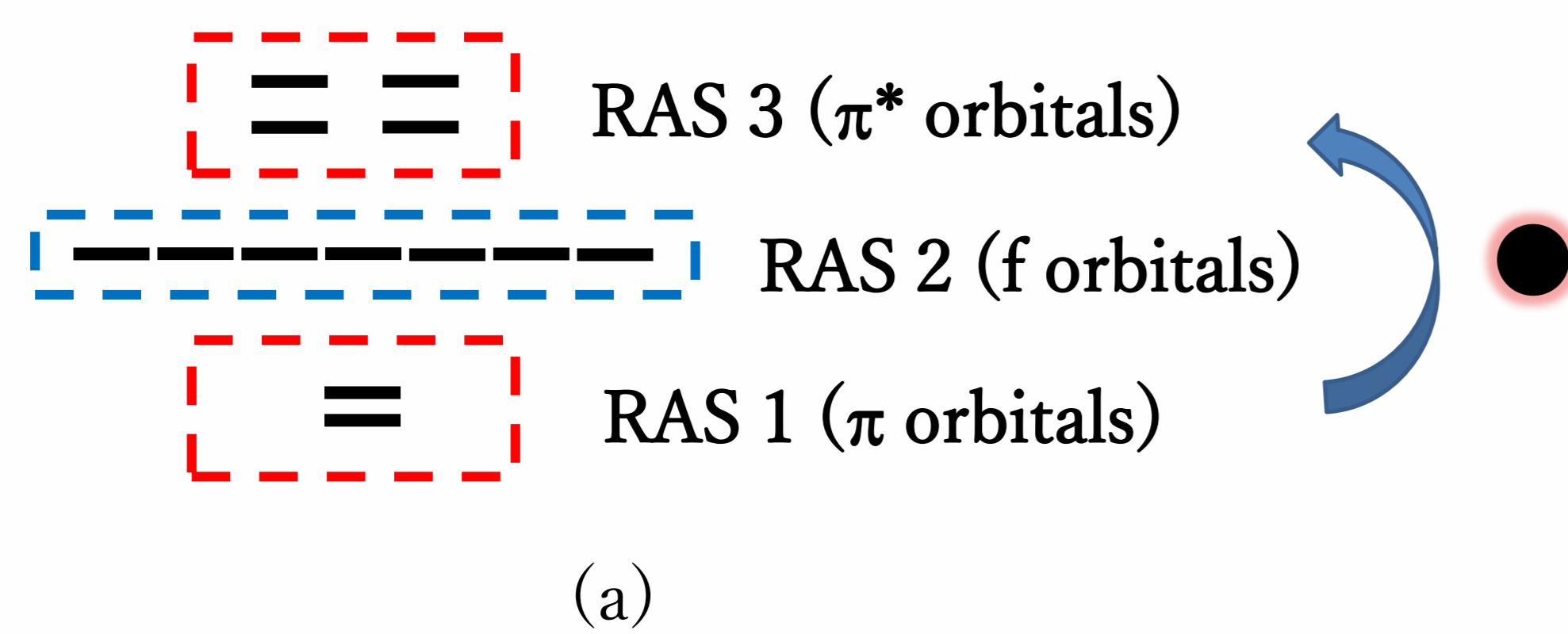
Figure 1. Schematic J - L interaction in Pc_2Ln^- .

2. Research Purpose

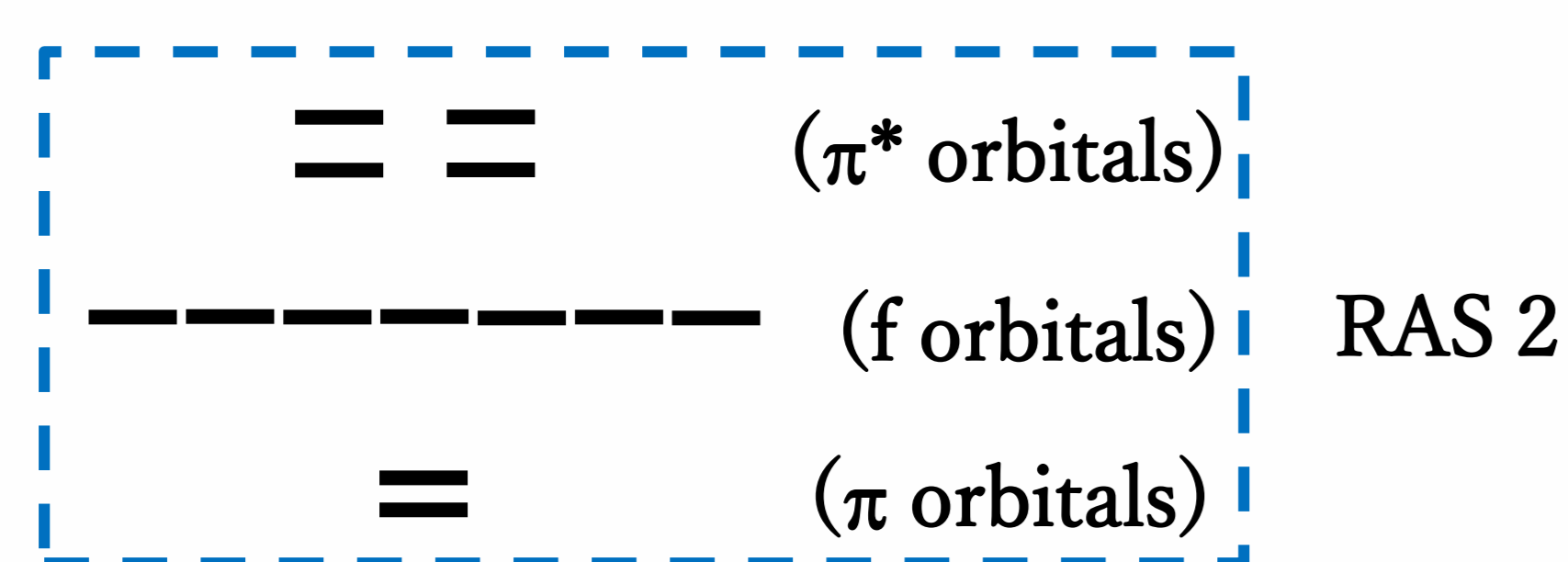
This research aims to study the intramolecular magnetic interaction in the excited state of rare-earth-based molecular magnets and propose a new strategy to control the quantum states of molecular magnets.

3. Methods

This research utilizes three primary software packages: GAUSSIAN, OpenMOLCAS, and ORCA. GAUSSIAN is employed for density functional theory with scalar relativistic effects. OpenMOLCAS and ORCA are used for relativistic *ab initio* wave function calculations with the second-order Douglas-Kroll-Hess scalar relativistic Hamiltonian and ANO-RCC basis sets. State-averaged Complete/Restricted Active Space Self Consistent Field (CASSCF/RASSCF) wave functions are constructed for the f , π , π^* orbitals, as shown in Figure 2. The Restricted Active Space State Interaction (RASSI) and SINGLE_ANISO modules are employed to compute the oscillator strength and spin-orbit coupling states. The magnitude of the J - L interaction is determined from the latter module by referring to our previous report.³ By employing this strategy, the relationship between J and L is expected to be revealed.



(a)



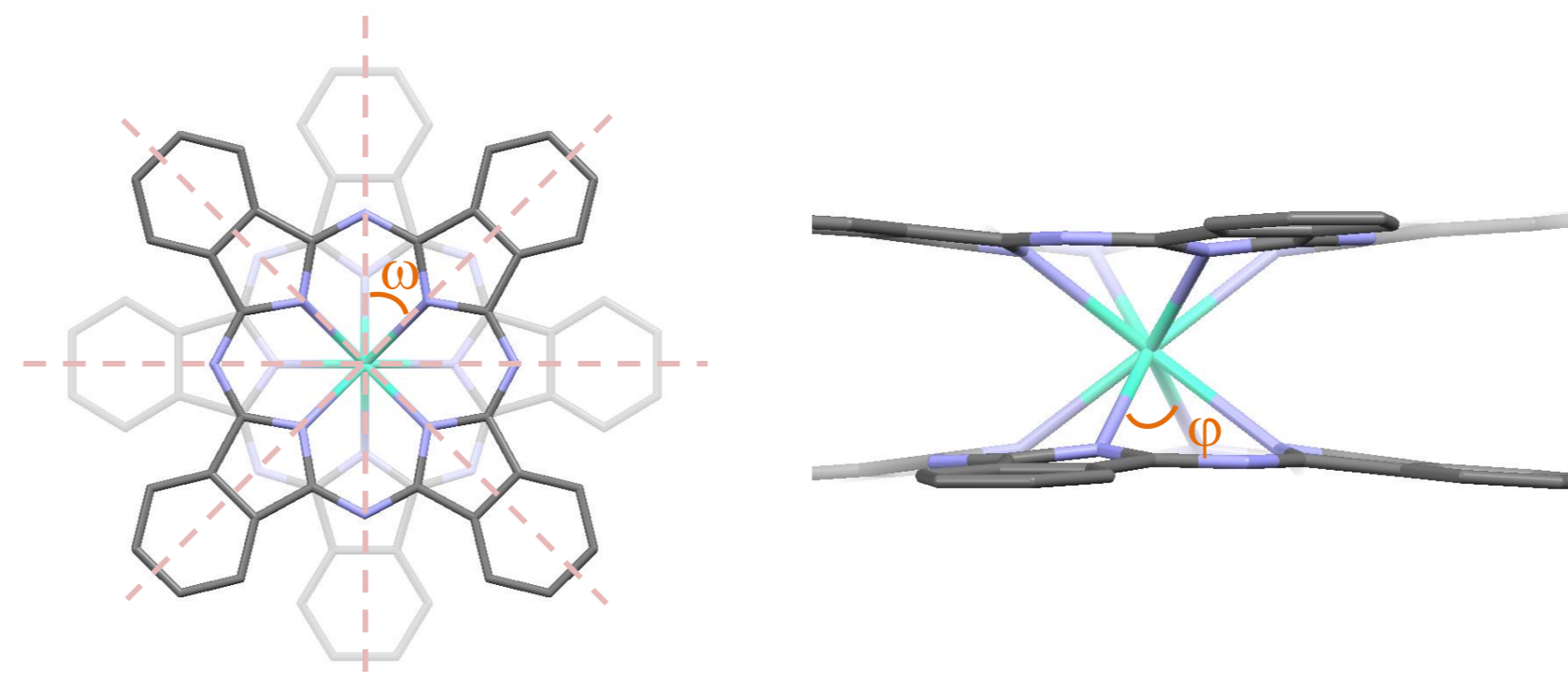
(b)

Figure 2. Schematic RASSCF

4. Research Progress

(a) Geometry Structure Optimization

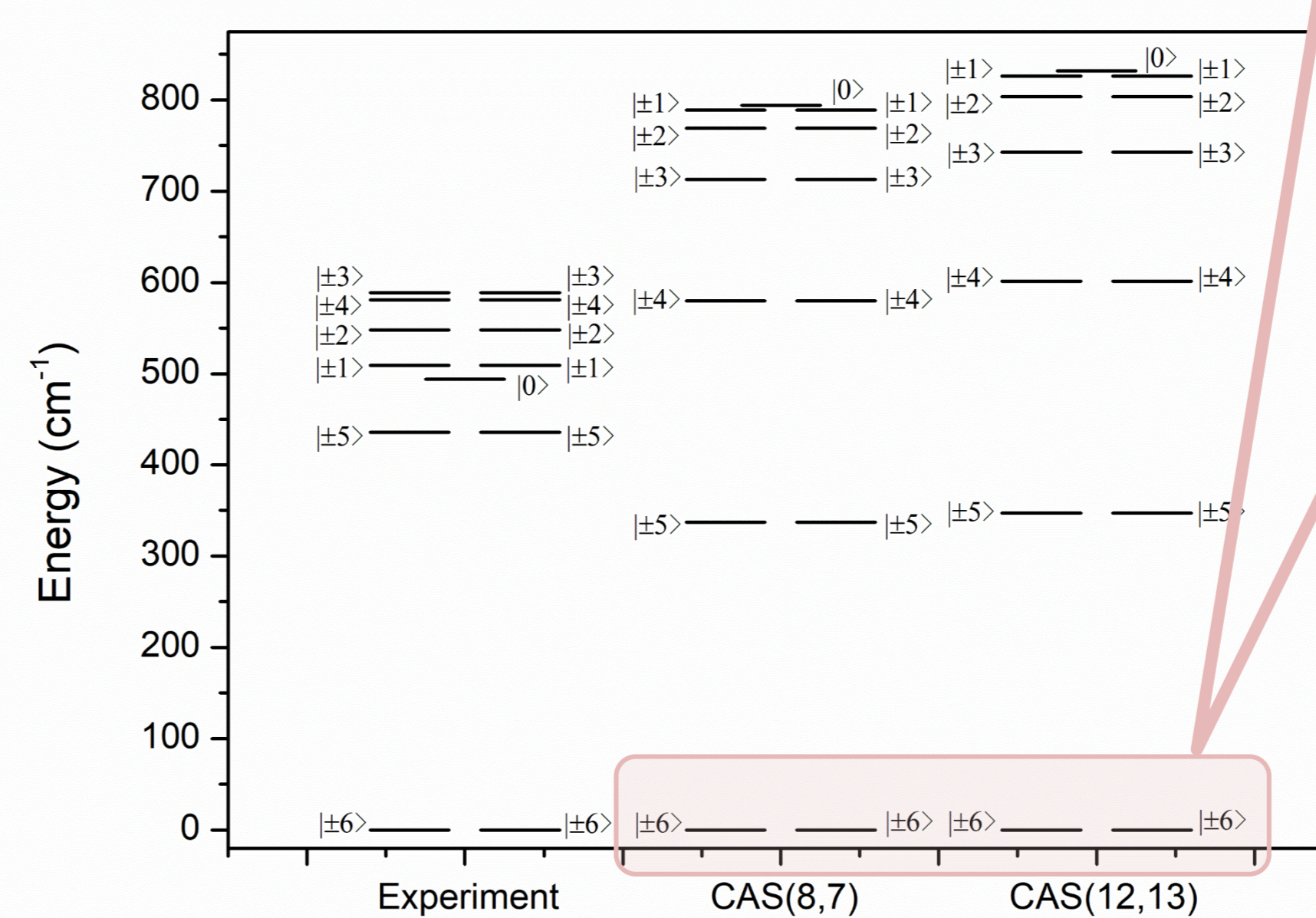
Program : Gaussian 16; Level : B3LYP
Basis set : Stuttgart RSC 1997 (Tb)
6-31G** (C, H, N)



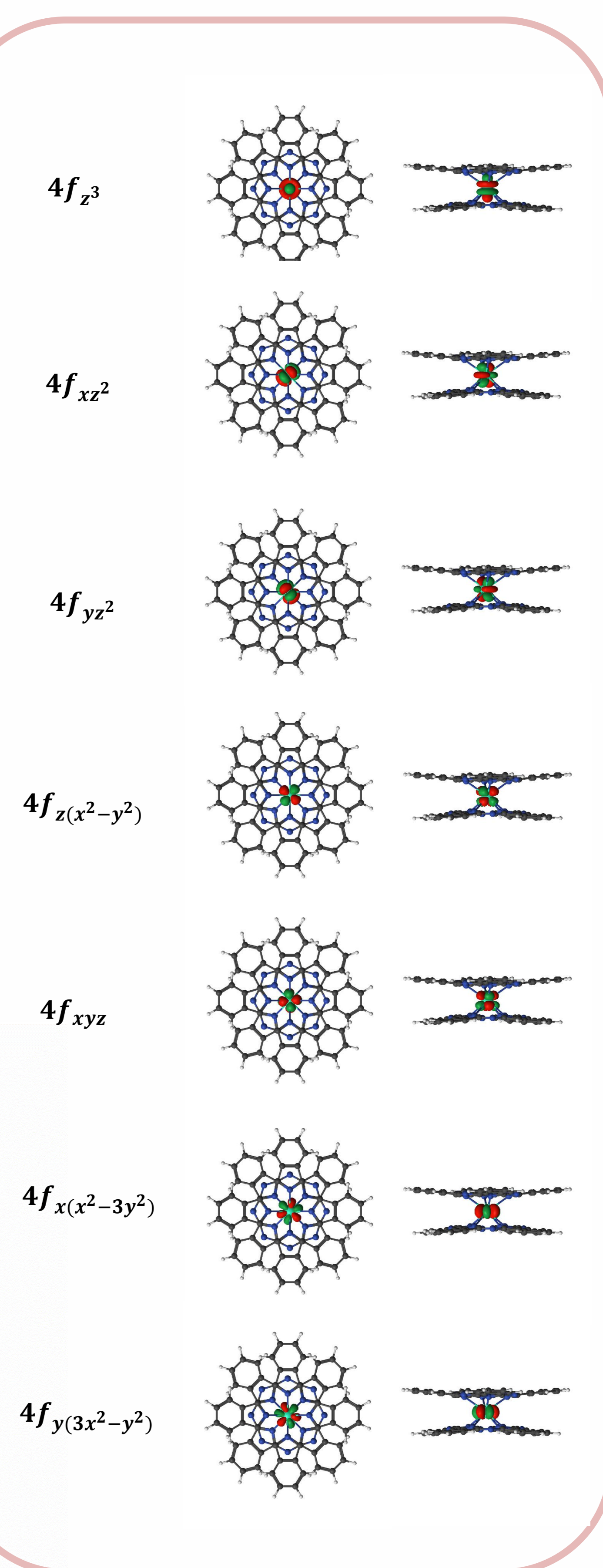
	Calc.	Exp. ⁴
Tb-N(average)	2.45 Å	2.44 Å
Interplanar distance (d_N)	2.86 Å	2.83 Å
Skew angle (ω)	44.97°	45.00°
Opening angle (ϕ)	108.73°	108.86°

(b) Ground Multiplet State of Pc_2Tb^-

Program : OpenMOLCAS V.20.06
Basis set : ANO-RCC-VTZP (Tb)
ANO-RCC-VDZ (C_{close} , N_{close})
ANO-RCC-MB ($C_{distant}$, $N_{distant}$, H)



(c) The 4f orbitals



5. Conclusions

At this stage, the ground multiple states of the terbium complex have been determined using the CASSCF calculations, followed by RASSI and Single Aniso modules. Expanding active space in calculations can influence the energy gap between two states in the ground state. Nevertheless, the two lowest substates for the complex remains the same, with the lowest J_z state is ± 6 .

6. Acknowledgement

This work is supported by the “Joint Usage/Research Center for Interdisciplinary Large-scale Information Infrastructures (JHPCN)”. All calculations have been done using the supercomputer system SQUID at the Cybermedia Center, Osaka University, and AOBA-B at the Cyberscience Center, Tohoku University.

7. References

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3. A. Santria, N. Ishikawa, *Inorg. Chem.*, 2020, **59**, 14326-14336.
4. F. Branzoli, P. Carretta, M. Filibian, G. Zoppellaro, M. J. Graf, J. R. GalanMascaros, O. Fuhr, S. Brink, M. Ruben, *J. Am. Chem. Soc.* 2009, **131**, 4387-4396