

Theoretical Spectroscopy

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Plan

- Ground-state properties
 - Geometries
 - Vibrational spectroscopy
 - Electron spectroscopy: excited states
 - Transition metal complexes
- Energy scales
- rotational energies: $1-10 \text{ cm}^{-1}$ ($0.1 \dots 1 \text{ meV}$)
 - vibrational energies: $200 - 3500 \text{ cm}^{-1}$
 - electronic excitations $5000 \text{ cm}^{-1} - 50000 \text{ cm}^{-1}$ ($1-10 \text{ eV}$)
 - ionization: $> 10 \text{ eV}$

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Geometries

Some initial considerations:

- Experimentalists: rotationally/vibrationally averaged structures neutron scattering: short-time perturbation, momentary picture
- vibrations within 0.1 pm (zero-point motion), 0.5 deg.
- Optimization: gradients, Hessians ? 3N-6 coordinates to optimize.
- One step per coordinate (empirical)
- Work in internal coordinates to decouple oscillators
- Avoid multiple minima
- Exploit whole potential surfaces for reaction mechanisms
- Search for transition points (saddle points)
- Calculation of vibrational frequencies: all real frequencies

$$\omega = \sqrt{\frac{k}{\mu}} \quad k \sim \frac{\partial^2 E}{\partial N_\alpha \partial N_\beta}$$

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Vibrational spectroscopy

Double-harmonic approximation:

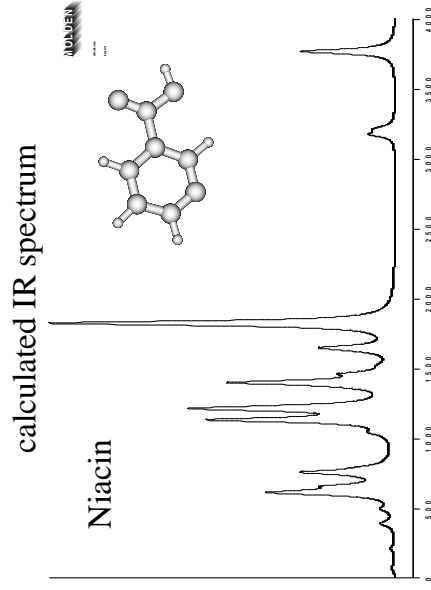
1. Potential around the equilibrium as (3N-6) coupled harmonic oscillators
 - Needed: 2nd derivatives (3-5 points per degree of freedom) Or: 2 gradients at $\pm \delta x$
 - 10 atoms: 26 coordinates (frequencies) \rightarrow 150 energy calculations. Full Hessian: several 100 individual points
 - Anharmonic constants ? Comparison to model potentials (Morse, Buckingham)
 - How are comparisons with experiment possible? Harmonic experimental spectra? Doppler shifts ?
 - Molecular symmetry!
2. Derivatives of dipole moments for calculating intensities:

$$I = \frac{\partial \vec{\mu}}{\partial N_\alpha}$$

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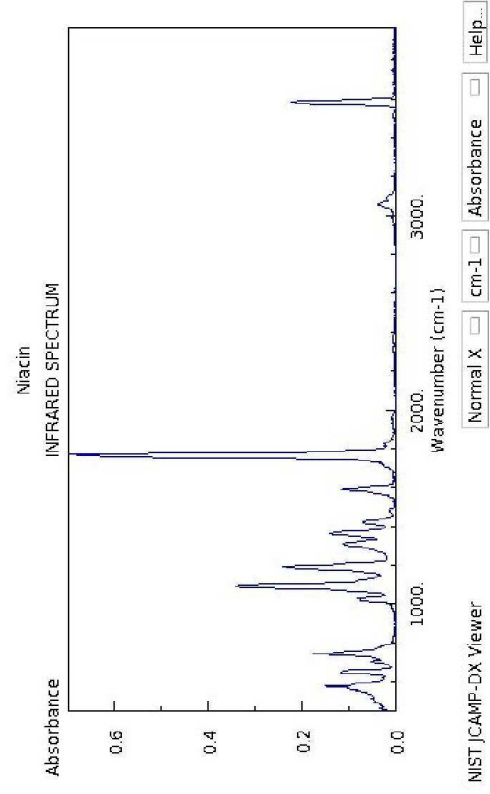
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Example



Calculation B3LYP

Example



Experimental spectrum

Electronic spectroscopy

Several states to consider, all composed of

$$\Psi = \Psi_{\text{vib}} \Psi_{\text{elec}} \Psi_{\text{spin}}$$

Transition probability is

$$\begin{aligned} M_{12} &= \langle \Psi_1 | \hat{\mu} | \Psi_2 \rangle \\ &= \langle \Psi_{\text{vib},1} | \Psi_{\text{vib},2} \rangle \langle \Psi_{\text{elec},1} | \hat{\mu} | \Psi_{\text{elec},2} \rangle \langle \Psi_{\text{spin},1} | \Psi_{\text{spin},2} \rangle \end{aligned}$$

- $|\langle \Psi_{\text{vib},1} | \Psi_{\text{vib},2} \rangle|^2$ Franck-Condon factor (0.1 ... 1)
- $\langle \Psi_{\text{spin},1} | \Psi_{\text{spin},2} \rangle$ spin selection rules $\Delta S = 0$
- $\langle \Psi_{\text{elec},1} | \hat{\mu} | \Psi_{\text{elec},2} \rangle$ dipole transition moment, orbital selection
- Molecular extinction coefficient ϵ (in cm^2/mol)

10^{-5} to 1

spin forbidden

1 to 10^3 spin allowed, but orbital forbidden

10^3 to 10^5 totally allowed

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General considerations

State specific versus state-averaged

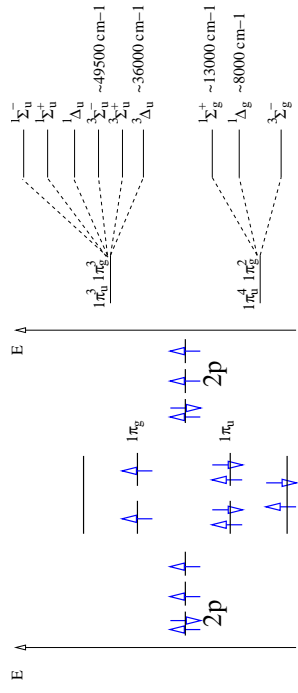
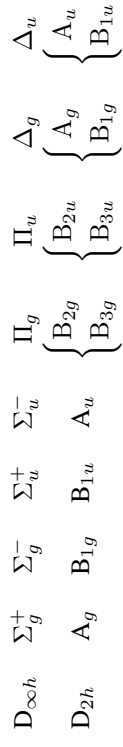
- State-averaged calculation: same orbitals for different spectroscopic states.
 - Systematic errors common on all states
 - Differences between states coherently calculated
 - Wavefunction can not relax during a transition (10^{-15} s)
- State specific: each state (symmetry) treated via a separate calculation
 - Ground state of each symmetry
 - Perturbation theory, Coupled-Cluster
 - Dressing of CI matrices

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Example O₂

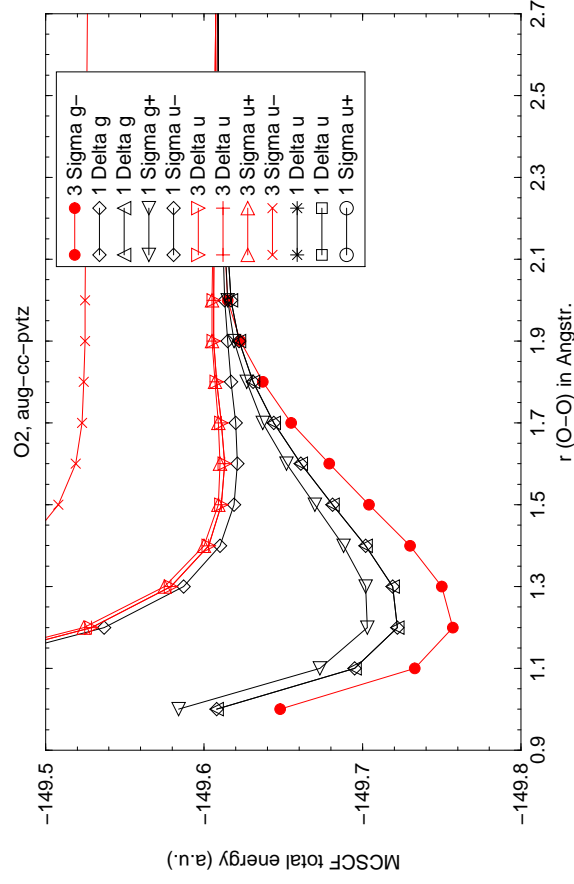
Linear diatomic molecule, point group D_{∞h}. Calculation in D_{2h}.
Correspondance:



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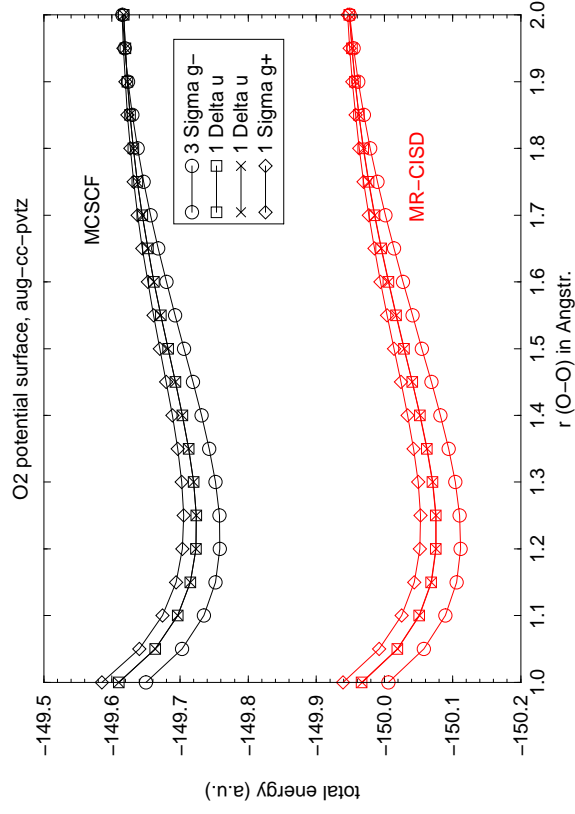
Example O₂



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Example O₂



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Example O₂

method	symm.	state to ${}^3\Sigma_g^+$	state ave.	state sp.
MCSCF	B_{1g}	${}^1\Delta_g$	-7778.29	-7840.77
MCSCF	A_g	${}^1\Delta_g$	-7778.29	-7840.77
MCSCF	A_g	${}^1\Sigma_g^+$	-12129.20	-12154.80
MRCI	B_{1g}	${}^1\Delta_g$	-7983.99	-8053.04
MRCI	A_g	${}^1\Delta_g$	-7873.34	-7942.93
MRCI	A_g	${}^1\Sigma_g^+$	-13138.70	-13036.70

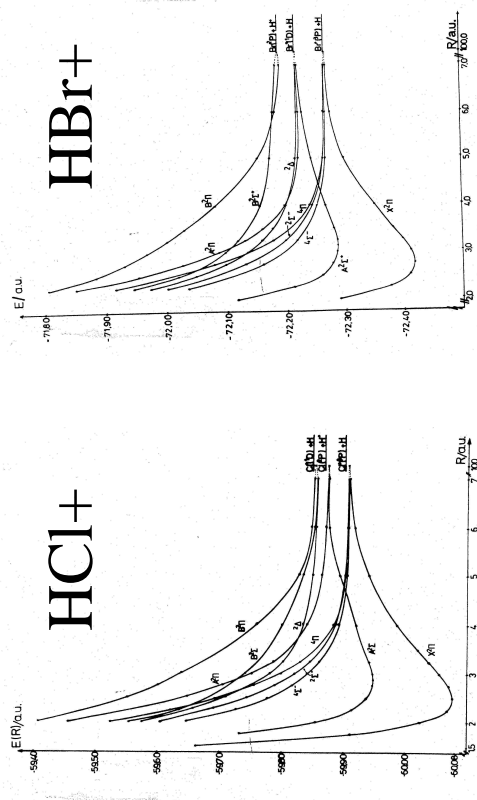
Reproduction of the two observed weak bands of O₂: 7918.1 cm⁻¹, 13195.1 cm⁻¹

- Spin changes from triplet to singlet (spin forbidden)
- Direct product of electronic function and dipole moment does not contain a totally symmetric component: orbital forbidden as well
- Observation with $\epsilon \approx 10^{-4}$: violation of the selection rules

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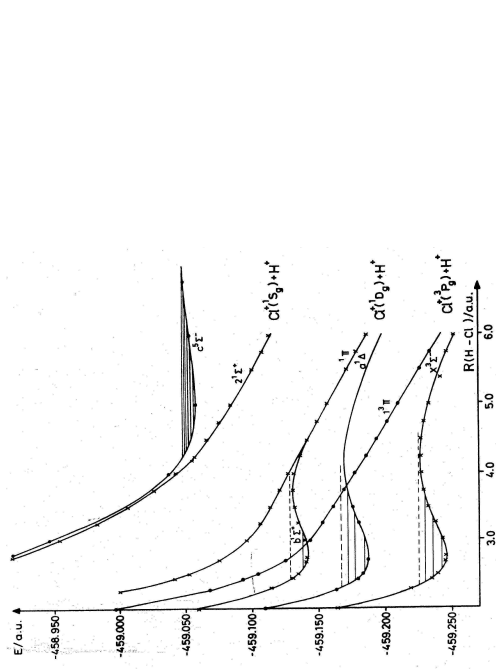
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Other Examples



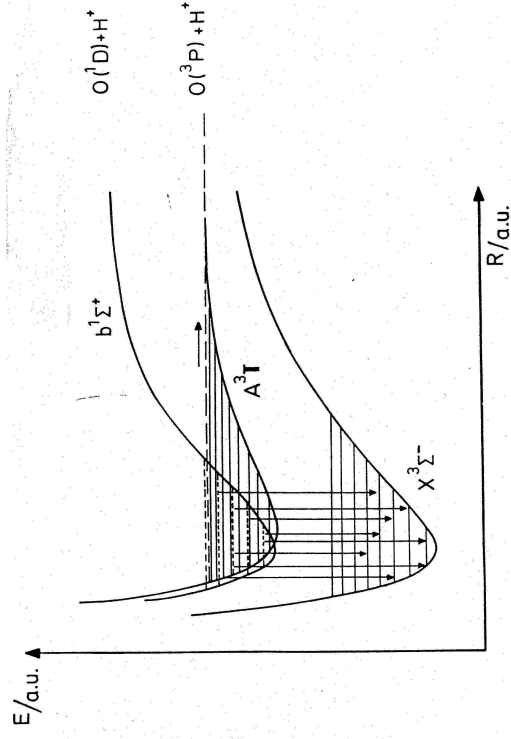
B.A.Heß, C.M.Marian, S.D.Peyerimhoff, In: D.R.Yarkony, Editor, Modern Electronic Structure Theory, World Scientific, (1995) 152-278

Other Examples



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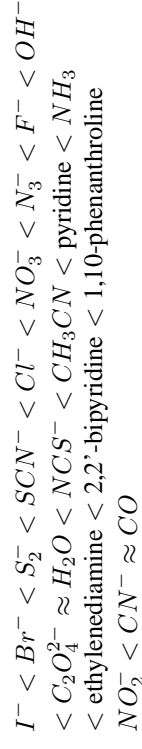
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1-center transition metal complexes

Ligand field theory: splitting depends on coordination geometry and ligands

- $d-d$ Transitions
- Charge-transfer transitions
- Jahn-Teller distortions

Spectrochemical series:



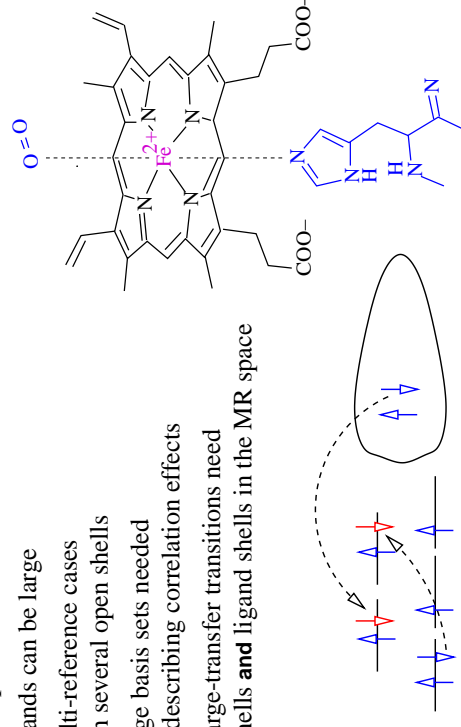
- Small Δ_0 values: high-spin complexes
- Large Δ_0 values: low-spin complexes

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1-center transition metal complexes

The central problem:

- Ligands can be large
- Multi-reference cases with several open shells
- Large basis sets needed for describing correlation effects
- Charge-transfer transitions need d shells **and** ligand shells in the MR space



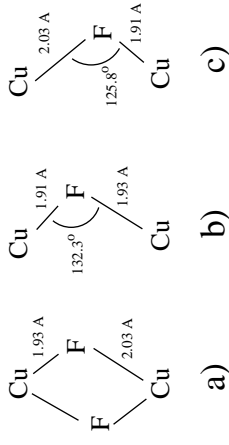
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Multi-center transition metal complexes

- Coupling between spins of individual centers weak
- Direct coupling: Hund's rule, ferromagnetic
- Indirect coupling: anti-ferromagnetic.
- Model Hamiltonian: Heisenberg $\hat{H}_{\text{Heisenberg}} = -J \hat{S}_i \hat{S}_j$
- Ising model hamiltonian $\hat{H}_{\text{Ising}} = -J \hat{S}_{z,i} \hat{S}_{z,j}$

Cu-Cu in a crystal CuF₂: triplet or (open shell) singlet ?



Experimental estimate: AFM, Néel temperature 69 K $\rightarrow J \approx -120$ K
1 a.u. = 315773.21 K

Multi-center transition metal complexes

- Difference-dedicated CI (DDCI):
 - Calculate only the contributions passing through the active space
 - DDCI2: replace up to two holes or 2 particles of the MCSCF space
 - DDCI3: replace up to 3 indices of the MCSCF determinants
 - Diagonalize \hat{H} in the resulting CI space.
 - Much smaller than the full CISD space on the CAS, as no completely external excitations included.
- In the present case: 2 electrons in 2 orbitals
 - WFs $|\phi_1 \bar{\phi}_2\rangle \pm |\bar{\phi}_1 \phi_2\rangle$
 - Add the ionic WFs to the MCSCF space: $|\phi_1 \bar{\phi}_1\rangle$ and $|\phi_2 \bar{\phi}_2\rangle$
 - Singlet and triplet state-averaged MCSCF

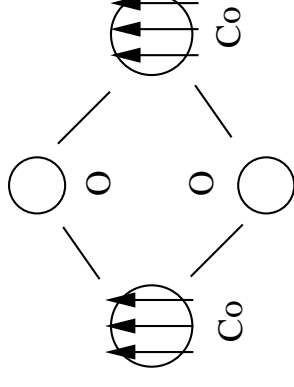
Results:

method	J_1	J_2	J_3
MCSCF	0.63	-26.32	0.93
DDCI2	1.02	-67.58	1.15
DDCI3	2.41	-132.80	3.49

Example Co_2O_2

Co_2O_2 : what is the ground state ?

- Vibrational spectrum: D_{2h}
- Assuming Co^{2+} and O^{2-}
- 6 unpaired d electrons
- Anything between Singlet and Septet



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Example Co_2O_2

DFT broken-symmetry calculation:

- Geometry optimization
- Analysis of vibrational frequencies
- Only S_z fixed in advance (α and β given on each Co center)
- S^2 through analysis of the converged wavefunction

S_z	$S(S+1)$ expected	$S(S+1)$ found
0	0	2.254
1	2	3.215
2	6	6.123
3	12	12.026

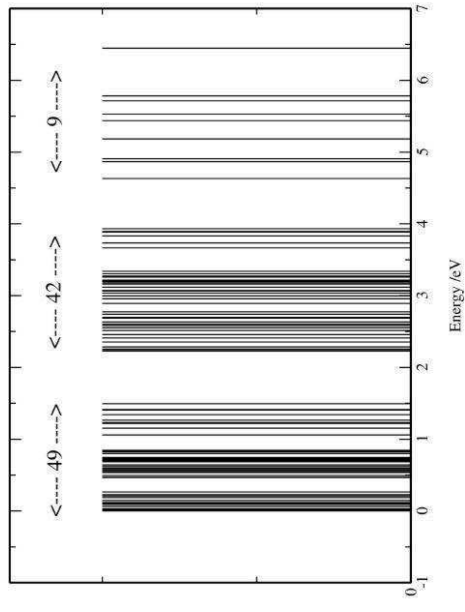
TPSS functional(J.Tao, J.P.Perdew, V.N.Staroverov, G.E.Scuseria, Phys.Rev.Lett., 91 (2003) 146401)

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Example Co_2O_2

Co₂O₂, septet states



Example Co_2O_2

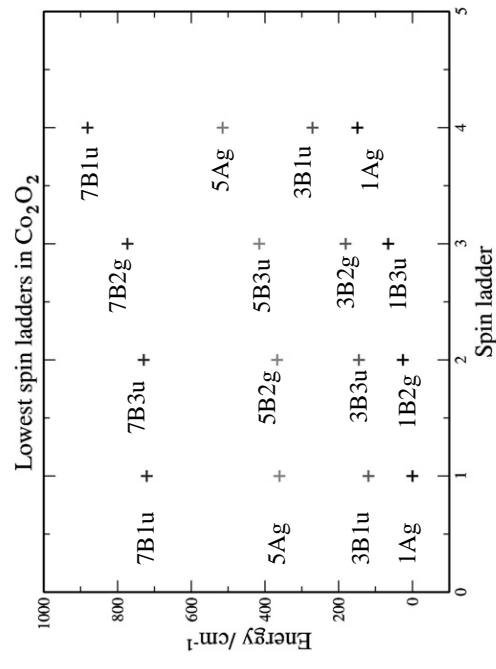


Fig. 2. CAS-CI results for the four lowest spin ladders in Co_2O_2 .

Example Co_2O_2

Ab-initio:

- Co^{2+} cation: $3d^7 4s^0$ configuration
- ground state 4F , first excited state 4P at 2.0 eV

$$\binom{{}^4F(7 \text{ states})}{{}^4P(3 \text{ states})} \times \binom{{}^4F(7 \text{ states})}{{}^4P(3 \text{ states})} = 100 \text{ states } (49 + 42 + 9)$$

- 14 electrons in 10 orbitals, septet states for obtaining orbitals
- 4 lowest states ${}^7B_{1u}$, ${}^7B_{3u}$, ${}^7B_{2g}$, and 7A_u , within small energy window.
- All but ${}^7B_{1u}$ genuine multi-determinant states
- ${}^7B_{1u}$: $(d_{x^2})^2 (d_{xy})^2 (d_{xz})^1 (d_{yz})^1 (d_{yz})^1$ occupation
- Septet orbitals \rightarrow no charge-transfer states $d^7 d^7 \rightarrow d^6 d^8, d^8 d^6$
- Including quintet, triplet and singlet states: spin ladders

Coupling constants: -60.8 cm^{-1} , -57.9 cm^{-1} , -58.9 cm^{-1} , -61.0 cm^{-1}