# COUPLED CLUSTER INVESTIGATIONS OF HEAVIEST ELEMENTS

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## Research:

Using state of the art methods from computational chemistry to perform high accuracy calculations of atomic and molecular properties in the context of fundamental problems in physics:

> Search for new physics with low-energy precision measurements

Violation of fundamental symmetries in atoms and in molecules

 $\geq$  Search for variation of fundamental constants

> Highly accurate calculations of spectra and properties of heavy and superheavy atoms and highly charged ions

## Most work done in collaboration with experimental groups







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# MOTIVATION

# Why investigate heavy, unstable, and artificial elements?

- (Exotic) nuclear and electronic structure and properties
- Information about new elements, assignment in Periodic Table
- Behaviour and trends in lower part of the Periodic Table
- Benchmarks for atomic theory (e.g. contribution of QED effects)









# Why investigate heavy, unstable, and artificial elements?

- Access to nuclear properties (moments, charge radii)
- Tests of nuclear theories



https://journals.aps.org/prl/abstract/10.1103/PhysRevLett.122.192502



https://www.nature.com/articles/s41567-020-0868-y

# Why investigate heavy, unstable, and artificial elements?

- Promising systems to search for physics beyond the Standard Model (e.g. violation of fundamental symmetries)
- Heavy systems, effects scale as Z<sup>2-5</sup>
- Possible strong further enhancements due to the nuclear structure
- Versatile: sensitive to eEDM, hadronic EDMs, nuclear anapole moments, nuclear magnetic quadrupole moments, etc.



Search for new physics with atoms and molecules

M. S. Safronova, D. Budker, D. DeMille, Derek F. Jackson Kimball, A. Derevianko, and Charles W. Clark Rev. Mod. Phys. **90**, 025008 – Published 29 June 2018 https://phys.org/news/2021-03radioactive-molecules-mysteryantimatter.html

# **Challenging experiments!**

- Dealing with small amounts of unstable, short lived elements
- Combined with the challenge of achieving unprecedented sensitivity needed to detect the tiny effects of new physics
- Alongside specially developed experimental techniques, theoretical studies become crucial

## How can (atomic and molecular) theory be of use?

- (Important to remember: for us the practical considerations do not play a role!)
- Parameters for planning the experiments (predictions of transition energies, lasercooling schemes, etc.)
- Parameters for the interpretation of the results (HFS parameters for extraction of nuclear properties, coupling parameters for new physics phenomena, etc.)
- Investigations where experiment is not yet possible

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Thus we need:

- Reliable predictions based on high accuracy calculations
- Possibility of assigning uncertainties

**Choice of computational method becomes important** 

# COMPUTATIONAL METHODS



Figure courtesy of P. Schwerdtfeger

## What do we need?

- Atomic and molecular parameters needed in experiments
  - Heavy (radioactive) systems, hence relativistic methods
- Coupling parameters describing the effect of P(T)-violating phenomena (or variation of constants) on electronic structure
  - Relativistic in nature, hence relativistic methods
- High accuracy
  - State-of-the-art treatment of correlation, large basis sets
- Uncertainty estimates
  - Robust, transparent methods

#### **Relativistic coupled cluster**

- **CCSD(T)** single reference coupled cluster
- **FSCC** multireference Fock space coupled cluster

Open shell systems, excited states, bond dissociation (good example: ThO  ${}^{3}\Delta_{1}$  or any atomic spectrum)

• Large, converged Dyall's basis sets

(K.G. Dyall, Theor. Chem Acc. 2002, 2004, 2006, 2007, 2009, 2011, 2012, etc.)

### **Relativistic coupled cluster**



#### What can we calculate?

- Atomic properties: energies, IPs, EAs, spectra, hyperfine structure parameters, polarisabilities
- Molecular properties: geometries, spectroscopic constants, electronic structure, Franck-Condon Factors (FCFs), transition strengths
- Specific properties:
  - W<sub>d</sub>,W<sub>s</sub> (eEDM experiments)
  - W<sub>A</sub> (NSD-PV, nuclear anapole moments)
  - W<sub>M</sub> (nuclear magnetic quadrupole moments)
  - Sensitivity to variation of  $\alpha$

• ...

- CCSD(T), FSCC (applicable to different systems/states)
- Expected accuracy: ~10 meV for energies, single % for properties
- Systematic investigation of effect of computational parameters and uncertainty evaluation

# APPLICATIONS

- Electron affinity of At: benchmark accuracy and uncertainty evaluation
- SHE: Nh and Og

# ELECTRON AFFINITY OF AT

- Measurement at ISOLDE by laser-photodetachment spectroscopy
- Knowledge of EA important for targeted alpha cancer therapy
- Calculations <u>before</u> the experiment





#### Accuracy: ~I0s of meV



(eV)	EA	l I	At
"Golden Standard"	DC-CCSD(T), d-aug-ae4z	3.010	2.372
	Exp.	3.059038(10)	

#### Accuracy: ~I0s of meV

#### Can we do better?





(eV)	EA	l I	At
"Golden Standard"	DC-CCSD(T), d-aug-ae4z	3.010	2.372
Extrapolated to CBSL	DC-CCSD(T)	3.040	2.402
	Exp.	3.059038(10)	



t; abc abco iikl

(eV)	EA	l l	At
"Golden Standard"	DC-CCSD(T), d-aug- ae4z	3.010	2.372
Extrapolated to CBSL	DC-CCSD(T)	3.040	2.402
Higher order	+∆T	0.004	0.003
correlation effects*	+(Q)	0.004	0.004
	Exp.	3.059038(10)	

\*mrcc program, M. Kallay



 $H_{\rm DC} = \sum_{i} h_{\rm D}(i) + \sum_{i < j} (1/r_{ij})$  $h_{\rm D}(i) = c \boldsymbol{\alpha}_i \cdot \mathbf{p}_i + c^2 \beta_i + V^n(i)$ 

**Reaching meV accuracy** 

Breit correction:  $B_{ij} = -\frac{1}{2r_{ij}} [\alpha_i \cdot \alpha_j + \frac{(\alpha_i \cdot r_{ij})(\alpha_j \cdot r_{ij})}{r_{ij}^2}]$ Lamb shift:  $(a) \qquad (b)$ 

(eV)	EA	l I	At
"Golden Standard"	DC-CCSD(T), d-aug- ae4z	3.010	2.372
Extrapolated to CBSL	DC-CCSD(T)	3.040	2.402
Higher order	+∆T	0.004	0.003
correlation effects	+∆(Q)	0.004	0.004
Relativity	+Breit*	0.003	0.003
	+QED (VP+SE)**	0.003	0.003
	Final		
	Exp.	3.059038(10)	

\* Tel Aviv atomic program

\*\* Model Lamb shift operator (MLSO) of Shabaev (Comput. Phys. Commun. 189, 175 (2015))

(eV)	EA	l I	At
"Golden Standard"	DC-CCSD(T), d-aug- ae4z	3.010	2.372
Extrapolated to CBSL	DC-CCSD(T)	3.040	2.402
Higher order	+∆T	0.004	0.003
correlation effects	+∆(Q)	0.004	0.004
Relativity	+Breit	0.003	0.003
	+QED (VP+SE)*	0.003	0.003
	Final	3.055	2.414
	Exp.	3.059038(10)	

\*Model Lamb shift operator (MLSO) of Shabaev (Comput. Phys. Commun. 189, 175 (2015))

## **Uncertainty evaluation**



#### **Uncertainty evaluation**

Higher order QED effects: smaller than vacuum polarization+self energy contributions

Higher excitations (full quadruples and higher): smaller than (Q) Basis set: half the difference between CBSL and d-aug-ae4z basis results

Source of uncertainty	I	At
Higher order QED	0.003	0.003
Higher excitations	0.004	0.004
Basis set	0.014	0.015
Total (eV)	0.015	0.016

(eV)	EA	l l	At
"Golden Standard"	DC-CCSD(T), d-aug- ae4z	3.040	2.402
Extrapolated to CBSL	DC-CCSD(T)	3.040	2.402
Higher order	+∆T	0.004	0.003
correlation effects	+∆(Q)	0.004	0.004
Relativity	+Breit	0.003	0.003
	+QED (VP+SE)*	0.003	0.003
	Final	3.055(15)	2.414(16)
	Exp.	3.059038(10)	



(eV)	EA	l I	At
"Golden Standard"	DC-CCSD(T), d-aug- ae4z	3.040	2.402
Extrapolated to CBSL	DC-CCSD(T)	3.040	2.402
Higher order	+∆T	0.004	0.003
correlation effects	+∆(Q)	0.004	0.004
Relativity	+Breit	0.003	0.003
	+QED (VP+SE)*	0.003	0.003
	Final	3.055(15)	2.414(16)
	Exp.	3.059038(10)	2.41579(5)



Lowest for halogens, highest among the rest of the PT



# ATOMIC PROPERTIES OF NH (Z=113)



- Accurate predictions of IP and EA
- Similar calculations for the lighter homologues as a test



Figure 1. Contributions of the different sources of uncertainty; HOC stands for higher order correlation.

- Accurate predictions of IP and EA
- Similar calculations for the lighter homologues as a test
- Uncertainty estimates



Figure 2. Calculated IPs and EAs with error bars of In, Tl and Nh (black squares), compared with experimental values for In and Tl (red crosses).

- Accurate predictions of IP and EA
- Similar calculations for the lighter homologues as a test
- Uncertainty estimates
- Relativistic effects: higher IP and EA than in lighter homologues!

	In	ТІ	Nh
	IP		
DC(B)-CCSDTQ+QED	5.801(22)	6.135(32)	7.569(48)
Exp.	5.78636 (1)	6.10818(2)	
	EA		
DC(B)-CCSDTQ+QED	0.375(18)	0.311(12)	0.776(30)
Exp.	0.3839(60)	0.32005(19)	

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Figure 2. Calculated IPs and EAs with error bars of In, Tl and Nh (black squares), compared with experimental values for In and Tl (red crosses).

	In	ті	Nh				
	IP			0.9	- present ⊢-•-		
DC(B)-CCSDTQ+QED	5.801(22)	6.135(32)	7.569(48)		experiment X		Ţ
Exp.	5.78636 (I)	6.10818(2)		0.7	2		T
	EA			EA (e)			
DC(B)-CCSDTQ+QED	J. Phys. B: At. Mol. Opt. Ph	ıys. <b>55</b> (2022) 155003 (7pp)		https://doi.org/10.108	38/1361-6455/ac761f		
Exp.	Relativi	istic coup	led cluster o	alculation	S	¥	
	of the e	electron af	finity and io	nization			
Accurate predictions o	potentia	al of Nh(1	13)				Ŧ
Similar calculations for	Yangyang Guo <sup>1</sup>	, Anastasia Borsch	evsky <sup>1</sup> , Ephraim Eliav <sup>2</sup>				
• Similar calculations for	and Lukáš F Pa	šteka <sup>3,*</sup> ©		-	-		
<ul> <li>Uncertainty estimates</li> </ul>				1 A	A	¥	
Relativistic effects: higher	er IP and EA th	han in lighter h	omologues!		R		
						81(TI)	113(Nb)
				Yangyang Guo	o 👘	Z	110(.11)

Figure 2. Calculated IPs and EAs with error bars of In, Tl and Nh (black squares), compared with experimental values for In and Tl (red crosses).

Ionization potentials and electron affinities of Rg, Cn, Nh, and Fl superheavy elements M. Y. Kaygorodov, D. P. Usov, E. Eliav, Y. S. Kozhedub, A. V. Malyshev, A. V. Oleynichenko, V. M. Shabaev, L. V. Skripnikov, A. V. Titov, I. I. Tupitsyn, and A. V. Zaitsevskii

Phys. Rev. A 105, 062805 – Published 8 June 2022

# ATOMIC PROPERTIES OF OG (Z=118)



- Accurate predictions of IP and EA
- Similar calculations for the lighter homologue as a test



- Accurate predictions of IP and EA
- Similar calculations for the lighter homologues as a test
- New basis set extrapolation scheme (diffuse functions)

Dania ant	R	ln		Og		
Dasis set	IP <sub>1</sub>	$IP_2$	IP <sub>1</sub>	$IP_2$	EA	
cv3z	10.465	18.683	8.627	15.922	-2.994	
cv4z	10.629	18.857	8.755	16.079	-2.092	
ae4z	10.624	18.854	8.756	16.084	-2.085	
(1-aug)-cv4z	10.659	18.877	8.791	16.092	-0.223	
(1-aug)-ae4z	10.655	18.875	8.791	16.097	-0.221	
(2-aug)-cv4z	10.659	18.877	8.791	16.092	0.040	
(3-aug)-cv4z	10.659	18.877	8.791	16.092	0.069	
(3-aug)-CBS-cvNz	10.772	19.001	8.882	16.197	0.078	
$\infty$ -CBS-cvNz	10.772	19.001	8.882	16.197	0.082	

- Accurate predictions of IP and EA
- Similar calculations for the lighter homologues as a test
- New basis set extrapolation scheme (diffuse functions)
- Og confirmed as having a positive EA (in agreement with other recent works, 0.096 eV<sup>1</sup> and 0.076(4)<sup>2</sup> )

Courses	R	n		Og	
Sources	$IP_1$	$IP_2$	$IP_1$	$IP_2$	EA
$\Delta(T)$	68.0	72.1	103.1	95.2	15.9
$\Delta T$	-15.1	-8.0	-5.7	-17.3	-2.8
$\Delta Q$	2.7	0.8	4.0	2.8	4.7
Breit	-1.7	-9.0	1.4	-1.8	-0.3
QED	3.1	5.3	6.5	14.0	-3.0

Lackenby, B. G. C., Dzuba, V. A. & Flambaum, V. V. Atomic structure calculations of superheavy noble element oganesson (Z = 118). *Phys. Rev. A* **98**, 042512 (2018).

#### Electron affinity of oganesson

M. Y. Kaygorodov, L. V. Skripnikov, I. I. Tupitsyn, E. Eliav, Y. S. Kozhedub, A. V. Malyshev, A. V. Oleynichenko, V. M. Shabaev, A. V. Titov, and A. V. Zaitsevskii Phys. Rev. A **104**, 012819 – Published 30 July 2021

Category	Eman annas	F	łn	Og		
	Error source	IP <sub>1</sub>	$IP_2$	$IP_1$	$IP_2$	EA
Basis set	core corr. functions	-4.4	-1.6	0.3	4.5	1.9
	CBS	57.1	65.2	43.2	48.9	3.2
	augmentation	0.0	0.0	0.0	0.0	1.8
Correlation	virtual cutoff	-0.1	0.0	-0.1	-0.1	0.2
	higher excitations	2.0	0.9	3.1	4.3	2.4
Relativity	QED	3.1	5.3	6.5	14.0	-3.0
Total		57.4	65.4	43.8	51.3	5.7

- Accurate predictions of IP and EA
- Similar calculations for the lighter homologues as a test
- New basis set extrapolation scheme (diffuse functions)
- Og confirmed as having a positive EA
- Uncertainty estimates

	IPI	IP2	EA					
Rn								
DC(B)-CCSDT(Q)+QED	10.761(57)	18.990(65)	-					
Exp.	10.7485	21.4(19)						
Og								
DC(B)-CCSDT(Q)+QED	8.888(44)	16.195(51)	0.080(6)					

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- Uncertainty estimates
- Prediction for the IP2 of Rn

		IP		IP2	EA				
			Rn						
ASD NIST Aton Rn II 3 Le z = 86, At iso	Lines Le nic Spece evels For electronic	INFORMATION VELS SPECTRA A	GROUND STATES & ONIZATION ENERGIES E Levels D	BibliogRaphy Help	•	Example of how to r Kramida, A., Ralchen Spectra Database (ve October 21]. National https://doi.org/10.184	eference these results: ko, Yu., Reader, J., and Ni r. 5.10), [Online]. Availabl Institute of Standards and 34/T4W30F	ST ASD Team (2022). <i>NIST A</i> e: https://physics.nist.gov/asd I Technology, Gaithersburg, Mi <u>BibTex Citatio</u>	tomic 2022, D. DOI: <u>n</u> (new window)
Data on Landé fac Some data for neutral a Primary data s <u>Moor</u>	tors and level of a singly-charged in ource Que e 1958	compositions are not av ons are available in the <u>Handbo</u> ry NIST Bibliographi <u>Literature</u>	vailable for this ion tok of Basic Atomic Spec C Database for I on Rn II Energy Leve	in ASD troscopic Data Rn II (new window)	<ul> <li>NIST Energy Levels and Wavele</li> <li>physics.nist.gov/cgi-</li> <li>NIST Energy Levels</li> <li>Ionization Potentials</li> <li>X-X Guo L E</li> </ul>	ngths Reference for R bin/ASBib1/get_AS and Waveleng and Electron A Pašteka E Eliav	n II - Google Chrome Bib_ref.cgi?db=el&db_ ths Bibliographic 1 ffinity of Oganesso and A. Borscheysky	_id=22090&comment_cod <b>Reference # 22090</b> n with Relativistic Cou	e=&element=Rn&spectr_
Configuration	Term         J <sup>2</sup> P° <sup>3</sup> / <sub>2</sub> <sup>1</sup> / <sub>2</sub>	Level (cm <sup>-1</sup> ) 0.0 30 895.1	(cm <sup>-1</sup> )	L3466 L16068	Adv. Quantum C DOI:10.1016/bs. Get all bibliography on	hem. <b>83</b> , 107–123 aiq.2021.05.007 <u>Rn II energy leve</u>	(2021)		
Rn III (6p <sup>4</sup> <sup>3</sup> P <sub>2</sub> )	Limit	(153 160) you need, please <u>i</u>	nform the ASD	L22090 <u>Team</u> .					



# CONCLUSIONS

- State of the art high accuracy computational approach
- Versatile method: many possible applications
- Reliable predictions, uncertainty estimates possible
- Close collaborations with experimental groups (where possible)
- > Uncertainties often limited by basis set: development of 5 $\xi$  basis sets in collaboration with Ken Dyall
- > Expanding FSCC applicability (Mass shifts, more complex systems)





Ephraim Eliav

Ken Dyall, <u>Schrödinger Inc.</u>





Lukas Pasteka



# RELATIVISTIC COUPLED CLUSTER

- Based on the 4c Dirac Hamiltonian
- Exponential wave operator:

$$\Psi = \exp(S)\Psi_0 = \left(1 + S + \frac{S^2}{2!} + \cdots\right)\Psi_0$$

• S is the excitation operator:

$$S = S_1 + S_2 + \dots + S_N; \ S_1 = \sum_{ia} s_i^a a_a^{\dagger} a_i; \ S_2 = \sum_{ijab} s_{ij}^{ab} a_a^{\dagger} a_b^{\dagger} a_j a_i$$

• CC energy equations:

$$\langle \Phi_0 | (H - E_{\text{CCSD}}) \exp(S_1 + S_2) | \Phi_0 \rangle = 0$$

• Accurate, all-order in PT, size-extensive, and size-consistent

## Complete basis set limit extrapolation





V.Vasilyev, http://sf.anu.edu.au/~vvv900/cbs

Why look for physics beyond the Standard Model (SM)?

- The SM is currently the best fitting physical description of the world around us.
- So far successfully explained the majority of observed natural phenomena and has strong predictive power (Higgs boson, top quark, tau neutrino)
- But... it is incomplete



Why look for physics beyond the Standard Model (SM)?

- Extensions to the SM attempt to fill these knowledge gaps.
  - Grand Unified Theories, String Theory, SUSY, ...
- These extensions predict new physical phenomena beyond the SM.
  - Variation of fundamental constants (VFC)
  - Violation of fundamental symmetries (CP, P, T)
- (non) discovery of these phenomena allows to discriminate between extensions or new theories.

#### Why look for physics beyond the SM with atoms and molecules?

- Accelerator research (LHCb, T2K, etc.)
- Table-top experiments



A panoramic picture of the four meter long traveling-wave decelerator that has been built in Groningen. It is in use for decelerating packets of the heavy diatomic molecule SrF, which is a prototypical system for the investigation of broken symmetries.



Why look for physics beyond the SM with atoms and molecules?

- Table-top experiments: promising alternative to high energy research
  - Versatile, sensitive to different phenomena
    - Parity violation
    - EDMs (electron, hadronic)
    - Variation of fundamental constants
    - Dark matter
    - •
  - Various enhancement effects  $\rightarrow$  high sensitivity
  - Small scale
  - (Relatively) inexpensive

Search for new physics with atoms and molecules

M. S. Safronova, D. Budker, D. DeMille, Derek F. Jackson Kimball, A. Derevianko, and Charles W. Clark Rev. Mod. Phys. **90**, 025008 – Published 29 June 2018



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# PARITY VIOLATION IN CHIRAL MOLECULES

• Is there a difference in the properties of the right- and the left handed enantiomers?



- PV is firmly established in nuclear and atomic physics
- In chiral molecules, the weak neutral current between the electrons and the nuclei is predicted to result in a tiny energy difference between the enantiomers.
- If detected, this could help explain the origins of <u>biohomochirality</u>

• Is there a difference in the properties of the rightand the left handed enantiomers?



- So far, no detection!
- The search continues: in electronic transitions, NMR spectroscopy, and in **vibrational spectroscopy**

• Search for parity violation in vibrational spectroscopy.



- Measure  $hv_L hv_R$
- Measurements performed at Laboratoire de Physique des Lasers (LPL), on the C-F stretch vibration in CHFCIBr

- Search for parity violation in vibrational spectroscopy.
- Measure  $hv_{s}-hv_{R}$
- Measurements performed at Laboratoirede Physique des Lasers (LPL), on the C-F stretch vibration in CHFCIBr
- Upper limit of 10<sup>-13</sup>
- Theoretical estimates of the effect  $\sim 10^{-17}$

(Phys. Rev. Lett. **84**, 3807 (2000); Phys. Rev. A **71**, 012103 (2005); Phys. Rev. A **103**, 042819 (2021); Phys. Rev. Lett. **125**, 123004 (2020)

Progress toward the first observation of parity violation in chiral molecules by high-resolution laser spectroscopy<sup>†</sup>

Benoît Darquié 🕵 Clara Stoeffler, Alexander Shelkovnikov, Christophe Daussy, Anne Amy-Klein, Christian Chardonnet, Samia Zrig, Laure Guy, Jeanne Crassous 🕿 ... See all authors 🗸

First published: 13 September 2010 | https://doi.org/10.1002/chir.20911 | Citations: 95

18 C. Daussy, T. Marrel, A. Amy-Klein, C. Nguyen, C. J. Bordé and C. Chardonnet, *Physical Review Letters*, 1999, 83, 1554.





- Search for parity violation in vibrational spectroscopy.
- Better candidate molecule needed!
- Shopping list:
  - Stable, commercially available
  - Can be separated into pure enantiomers
  - Can be brought into the gas phase
  - Should contain heavy elements (absolute PV energy predicted to scale as Z<sup>5</sup>)
  - Should have strong vibrational transitions in the range of the lasers (4-15  $\mu m)$
- Relative effects of the order 10<sup>-15</sup> can now be detected at LPL

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Fig. 1 Chemical structure of  $\Delta$ -Ru(acac)<sub>3</sub>

a) Propeller-like chirality



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- Relative effects of the order 10<sup>-15</sup>?
- Relativistic calculations, DFT method



Fig. 1 Chemical structure of  $\Delta$ -Ru(acac)<sub>3</sub>

mode no.	$v(cm^{-1})$	IR int.(KM/mol)	$\Delta v_{PV}$ (mHz)	$ \Delta v_{PV}/v $
17	182.0	0.009	-448.7	7.22E-14
19	200.8	1.718	-297.9	4.57E-14
20	222.9	0.065	279.2	3.80E-14
29	327.2	7.884	325.3	3.40E-14
52	952.6	9.564	-30.4	1.04E-15
53	953.7	1.793	-33.0	1.13E-15
100	1586.0	453.5	-83.0	1.70E-15
102	1612.3	44.22	-110.9	2.25E-15



Fig. 3 Plot of all calculated relative parity violating frequency shifts  $(\Delta v_{PV}/v)$  of several vibrational transitions in Ru(acac)<sub>3</sub> as a function of the indicator (sum of moduli of Ru-O displacement, see text). The larger dots highlighted in blue correspond to the modes shown in Table 1, and

- Search for parity violation in vibrational spectroscopy.
- Better candidate molecule needed!
- Relative effects of the order 10<sup>-15</sup>? Yes!
- Relativistic calculations, DFT method

mode no.	$v(cm^{-1})$	IR int.(KM/mol)	$\Delta v_{PV}$ (mHz)	$ \Delta v_{PV}/v $
17	182.0	0.009	-448.7	7.22E-14
19	200.8	1.718	-297.9	4.57E-14
20	222.9	0.065	279.2	3.80E-14
29	327.2	7.884	325.3	3.40E-14
52	952.6	9.564	-30.4	1.04E-15
53	953.7	1.793	-33.0	1.13E-15
100	1586.0	453.5	-83.0	1.70E-15
102	1612.3	44.22	-110.9	2.25E-15







Fig. 3 Plot of all calculated relative parity violating frequency shifts  $(\Delta v_{PV}/v)$  of several vibrational transitions in Ru(acac)<sub>3</sub> as a function of the indicator (sum of moduli of Ru-O displacement, see text). The larger dots highlighted in blue correspond to the modes shown in Table 1, and

- Search for parity violation in vibrational spectroscopy.
- Better candidate molecule needed!
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- Even better: Os(acac)<sub>3.</sub> effects of 10<sup>-13</sup>
- Scaling better than Z<sup>5</sup> predicted for total PV energies
- Practical challenges to be solved

mode Os	corresp. mode Ru	overlap	$v_{PV}(Os)$ (Hz)	$v_{PV}(Os)/v_{PV}(Ru)$	$v (cm^{-1})$	IR int.(KM/mol)	$ \Delta v/v $
16	17	0.996	-9.72	21.7	191.4	0.091	1.51E-12
19	19	0.961	-9.59	32.2	210.9	2.356	1.44E-12
20	20	0.948	4.30	15.4	224.2	0.013	5.86E-13
29	29	0.838	3.09	9.5	307.6	2.392	3.39E-13
52	52	0.830	-1.47	48.4	952.2	0.464	5.00E-14
53	53	0.831	-1.32	40.1	954.0	1.272	4.48E-14
100	100	0.955	-1.04	12.7	1562.5	245.6	2.16E-14
102	102	0.985	-0.31	3.6	1589.2	102.2	6.29E-15

Table 2 The PV shift of vibrational modes in  $Os(acac)_3$  and a comparison to  $Ru(acac)_3$ . Modes in the two compounds were matched to each other according to their overlap as defined in section 3.





- Search for parity violation in vibrational spectroscopy.
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- Relative effects of the order 10<sup>-15</sup>? Yes!
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- Even better: Os(acac)<sub>3</sub>, effects of 10<sup>-13</sup>
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