### Theoretical Spectroscopy

Ahmad Adam Per Jensen<sup>1</sup>, Andrey Yachmenev<sup>2</sup>, and Sergei Yurchenko<sup>2</sup>

#### Introduction

Electronic Structure Calculations Equilibrium Geometry Theoretical Models and HFCC

Comparison to Experiment

Nuclear Motion

I heory Potential Energy Surface HFCC surface Vibrational Contribution to HFCC

## Vibrational Averaging of the Isotropic Hyperfine Coupling Constants for the Methyl Radical

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June 19, 2014

### Overview

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# Introduction ESR Spectroscopy

### Theoretical Spectroscopy

Ahmad Adam<sup>1</sup> Per Jensen<sup>1</sup>, Andrey Yachmenev<sup>2</sup>, and Sergei Yurchenko<sup>2</sup>

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Effect of

- structure of radicals
- detection of radicals
- chemical kinetics
- chemistry, biology, and medicine

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### Introduction

Simulated spectrum of CH<sub>3</sub> radical with hyperfine coupling constant a



Figure : Bovet, C.; Barron, A. EPR Spectroscopy: An Overview, OpenStax-CNX Web site. http//cnx.org/content/m22370/1.3/, May 23, 2009

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# Electronic Structure Calculations Equilibrium Geometry

### Theoretical Spectroscopy

<u>Ahmad Adam<sup>1</sup></u> Per Jensen<sup>1</sup>, Andrey Yachmenev<sup>2</sup>, and Sergei Yurchenko<sup>2</sup>

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### Bond distance

- CCSD(T)/aVTZ = 1.0762 Å
- CCSD(T)/aQTZ = 1.0759 Å
  - Experiment = 1.079 Å



Figure : from Principles of General Chemistry (v.1.0 M) by Bruce A. Averill

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## Electronic Structure Calculations Theoretical Models and HFCC

Theoretical pectroscopy	Method/Basis Set	A <sup>iso</sup> <sub>eql</sub> ,G
<u>lad Adam<sup>1</sup>,</u> Jensen <sup>1</sup> ,	UB3LYP/ERP-III	28.2
ndrey menev <sup>2</sup> ,	CISD/DZ	25.7
Sergei chenko <sup>2</sup>	CCSD(T)/Chipman	28.5
duction	B3LYP/Huz-IVu4s	30.1
onic	UB3LYP/EPR-III	28.6
ure	UB2PLYP/EPR-III	30.0
ium rv	00-RI-MP2/EPR-III	30.0
tical s and	00-SCS-RI-MP2/EPR-III	22.0
arison to iment	CCSD(T)/EPR-III	24.7
r		
on rv		

Table :  ${}^{13}$ C isotropic HFCC in CH<sub>3</sub> (*Table data from Chen X, Rinkevicius Z, Ruud K, Ågren H., J. Chem. Phys. 2013, 138, 054310. See this paper for original references.*)

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# Electronic Structure Calculations Comparison to Experiment

Theoretical Spectroscopy		Method/Basis Set	A <sup>iso</sup> ,G			
hmad Adam <sup>1</sup> ,						
Per Jensen <sup>1</sup> ,		UB3LYP/ERP-III	28.2			
Yachmenev <sup>2</sup> ,		CISD/DZ	25.7			
and Sergei Yurchenko <sup>2</sup>		CCSD(T)/Chipman	28.5			
ntroduction		B3LYP/Huz-IVu4s	30.1			
lectronic		UB3LYP/EPR-III	28.6			
tructure			30.0			
Calculations			50.0			
Equilibrium Geometry		OO-RI-MP2/EPR-III	30.0			
Theoretical Models and		OO-SCS-RI-MP2/EPR-III	22.0			
Comparison to Experiment		CCSD(T)/EPR-III	24.7			
luclear		Experiment	38.3			
lotion						

Table :  ${}^{13}C$  isotropic HFCC in CH<sub>3</sub> (*Table data from Chen X, Rinkevicius Z, Ruud K, Ågren H., J. Chem. Phys. 2013, 138, 054310. See this paper for original references.*)

# Nuclear Motion Thermal Averaging

Theoretical Spectroscopy

Ahmad Adam Per Jensen<sup>1</sup>, Andrey Yachmenev<sup>2</sup>, and Sergei Yurchenko<sup>2</sup>

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### Theory

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### where ..

- P = operator
- T = absolute temperature
- Q = partition function
- $g_i = degeneracy$

# Nuclear Motion Thermal Averaging

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### where ..

- P = operator
- T = absolute temperature
- Q = partition function
- $g_i = degeneracy$

$$E_{rv}^{(i)} = eigenvalues$$
  
 $\Phi_{rv}^{(i)} = eigenvectors$ 

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# Nuclear Motion Thermal Averaging – more details

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Journal of Molecular Spectroscopy 245 (2007) 126-140

www.elsevier.com/locate/jms

### Theoretical ROVibrational Energies (TROVE): A robust numerical approach to the calculation of rovibrational energies for polyatomic molecules

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> Received 18 May 2007; in revised form 12 July 2007 Available online 17 August 2007

THE JOURNAL OF CHEMICAL PHYSICS 132, 114305 (2010)

# Thermal averaging of the indirect nuclear spin-spin coupling constants of ammonia: The importance of the large amplitude inversion mode

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### Theoretical Spectroscopy

Ahmad Adam Per Jensen<sup>1</sup>, Andrey Yachmenev<sup>2</sup>, and Sergei Yurchenko<sup>2</sup>

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# Nuclear Motion Potential Energy and HFCC Surfaces

### Theoretical Spectroscopy

Ahmad Adam<sup>1</sup> Per Jensen<sup>1</sup>, Andrey Yachmenev<sup>2</sup>, and Sergei Yurchenko<sup>2</sup>

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- Electronic Structure Calculations Equilibrium Geometry Theoretical Models and
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- Theory

#### Potential Energy Surface

- HFCC surface
- Vibrational Contribution to HFCC
- Effect of

- 2625 unique symmetry points near equilibrium geometry
  - UHF-CCSD(T)/aug-cc-pVTZ for Potential Energy Surface

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- UHF-CCSD(T)/EPR-III for HFCC surface
- Least squares fitting

# Nuclear Motion Vibrational Contribution to HFCC

The	oretical	
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Ahmad Adam <sup>1</sup>
and Sergei

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Effect of

Method/Basis Set	$\mathbf{A}_{eql}^{iso}$ (G)	A <sup>iso</sup> vib (G)	$\Delta \mathbf{A}_{vib}^{iso}$ (G)	<b>Тетр.</b> (К)
B3LYP/Huz-IIIsu3	29.9	42.2	12.3 (41%)	0
P(CI)/DZ	22.2	35.1	12.9 (58%)	96
MCSCF/cc-pVTZus2st	27.7	37.3	9.6 (35%)	0
CCSD(T)/EPR-III	24.7	36.49	11.8 (48%)	0
CCSD(T)/EPR-III	24.7	36.51	11.8 (48%)	96
Experiment	_	38.3	-	96

Table :  ${}^{13}C$  isotropic HFCC in CH<sub>3</sub> (*Table data from Chen X, Rinkevicius Z, Ruud K, Ågren H., J. Chem. Phys. 2013, 138, 054310. See this paper for original references.*) Our work is in blue color

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# Nuclear Motion Effect of Temperature

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HFCC

Method/Basis Set	$\begin{array}{c} \mathbf{A}_{eql}^{iso} \\ (G) \end{array}$	$\begin{array}{c} \mathbf{A}_{vib}^{iso} \\ (G) \end{array}$	$\Delta \mathbf{A}_{vib}^{iso}$ (G)	<b>Тетр.</b> (К)
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Experiment	_	38.3	-	96
CCSD(T)/EPR-III	24.7	37.53	12.8 (52%)	300

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## Summary and Conclusions

### Theoretical Spectroscopy

Ahmad Adam<sup>1</sup> Per Jensen<sup>1</sup>, Andrey Yachmenev<sup>2</sup>, and Sergei Yurchenko<sup>2</sup>

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- Vibrational effects cannot be ignored in the case of <sup>13</sup>C isotropic HFCC for CH<sub>3</sub>
  - Compared to other averaging methods, our averaging included the rotational motion and coupling between vibrational modes
  - With temperature effects, the ro-vibrational contribution will exceed the electronic contribution

### Acknowledgment

### Theoretical Spectroscopy

Ahmad Adam<sup>1</sup> Per Jensen<sup>1</sup>, Andrey Yachmenev<sup>2</sup>, and Sergei Yurchenko<sup>2</sup>

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Effect of



### Thanks to ..

- Andrey Yachmenev (UCL) for many helpful discussions
- Sergei Yurchenko (UCL) and Per Jensen (BUW)
- Financial support by DFG Deutsche
  - Forschungsgemeinschaft



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