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

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Overview

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

Introduction

Simulated spectrum of CH_3 radical with hyperfine coupling constant a

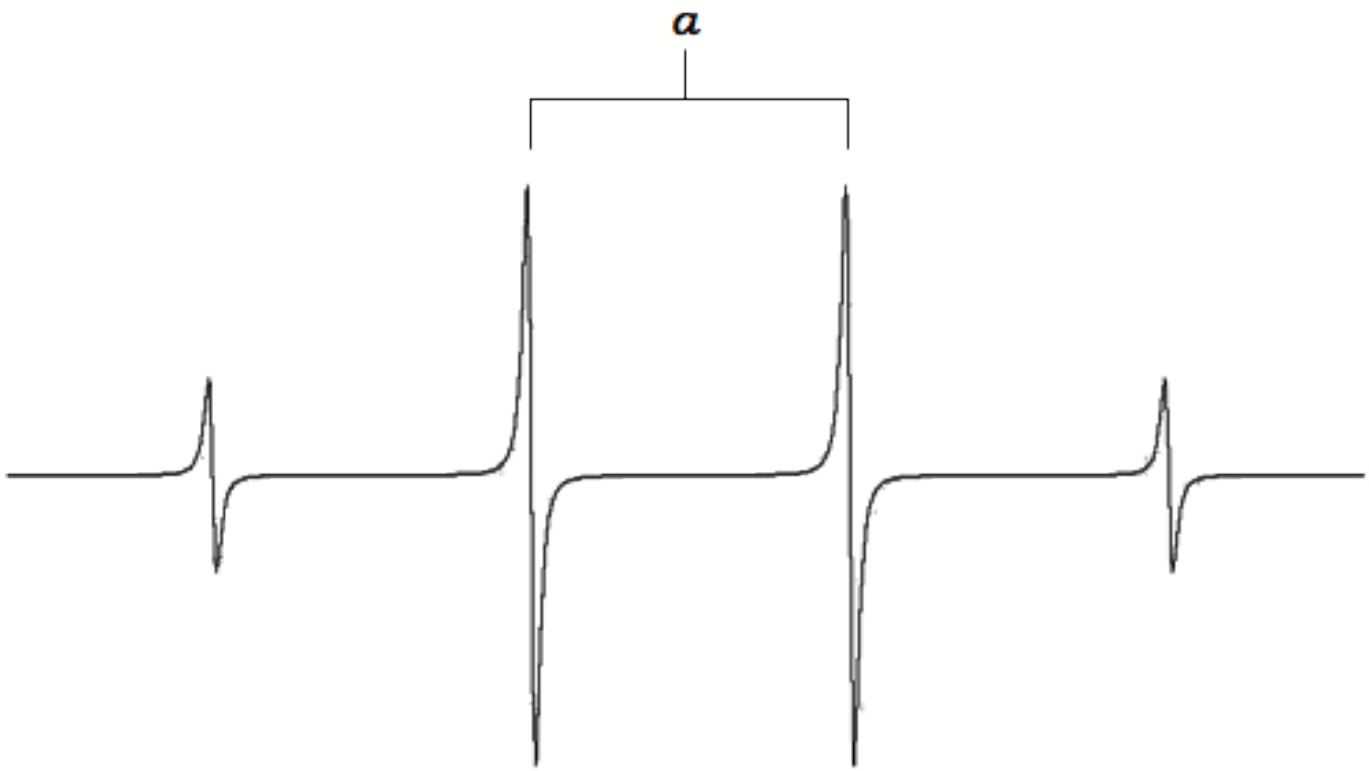

Figure : Bovet, C.; Barron, A. EPR Spectroscopy: An Overview, OpenStax-CNX Web site. http//cnx.org/content/m22370/1.3/, May 23, 2009

Bond distance

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

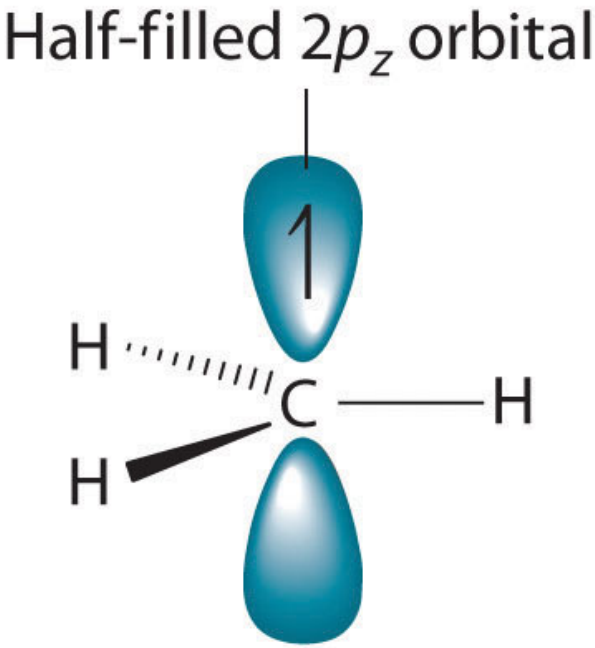

Figure : from Principles of General Chemistry (v.1.0 M) by Bruce A. Averill

Method/Basis Set	$\mathbf{A}_{eql}^{iso}$**,G**
UB3LYP/ERP-III	28.2
CISD/DZ	25.7
CCSD(T)/Chipman	28.5
B3LYP/Huz-IVu4s	30.1
UB3LYP/EPR-III	28.6
UB2PLYP/EPR-III	30.0
OO-RI-MP2/EPR-III	30.0
OO-SCS-RI-MP2/EPR-III	22.0
CCSD(T)/EPR-III	24.7

Table : ^{13}C isotropic HFCC in CH_3 (*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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CCSD(T)/EPR-III	24.7
Experiment	38.3

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Nuclear Motion
Thermal Averaging

Theory

- $< P >_T = \frac{1}{Q} \sum_i g_i exp(-\frac{E_{rv}^{(i)}}{kT}) < P >_i$
- $Q = \sum_i g_i exp(-\frac{E_{rv}^{(i)}}{kT})$
- $< P >_i = < \Phi_{rv}^{(i)} | P | \Phi_{rv}^{(i)} >$

where ..

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

Nuclear Motion
Thermal Averaging

Theory

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where ..

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T = absolute temperature
Q = partition function
g_i = degeneracy

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

Nuclear Motion
Thermal Averaging – more details

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

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

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- 2625 unique symmetry points near equilibrium geometry
- UHF-CCSD(T)/aug-cc-pVTZ for Potential Energy Surface
- UHF-CCSD(T)/EPR-III for HFCC surface
- Least squares fitting

Method/Basis Set	$\mathbf{A}^{iso}_{eql}$ (G)	$\mathbf{A}^{iso}_{vib}$ (G)	$\Delta\ \mathbf{A}^{iso}_{vib}$ (G)	**Temp.** (K)
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_3 (*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

Nuclear Motion
Effect of Temperature

Method/Basis Set	$\mathbf{A}^{iso}_{eql}$ (G)	$\mathbf{A}^{iso}_{vib}$ (G)	$\Delta\ \mathbf{A}^{iso}_{vib}$ (G)	**Temp.** (K)
B3LYP/Huz-IIIsu3	29.9	42.2	12.3 (41%)	0
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CCSD(T)/EPR-III	24.7	36.51	11.8 (48%)	96
Experiment	–	38.3	–	96
CCSD(T)/EPR-III	24.7	37.53	12.8 (52%)	300

Table : ^{13}C isotropic HFCC in CH_3 (*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

Summary and Conclusions

- Vibrational effects cannot be ignored in the case of ^{13}C isotropic HFCC for CH_3
- 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

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DFG Deutsche Forschungsgemeinschaft