Theoretical Spectroscopy of the Methyl Radical

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The Methyl Radical: Applications

- Hydrocarbon combustion processes
- Atmospheric chemistry
- Chemistry of semiconductor
- Chemical vapor deposition of diamond
- Many chemical processes of industrial and environmental interest.

The Methyl Radical: Structure



wps.prenhall.com

The Hyperfine Coupling Constant (HFCC)



Encyclopedia of Radicals in Chemistry, Biology and Materials, 2012 John Wiley & Sons, Ltd.

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ROVE meeting, Hamburg (DESY), 2017

How to compute the isotropic HFCC?

$$A_{iso}^{(N)} = \frac{2}{3}\mu_0\mu_N g_N \rho(N)$$

 $A_{iso}^{(N)}$: isotropic hyperfine couling constant. μ_0 : vacuum permeability μ_N : nuclear magneton g_N : nuclear g-factor $\rho(N)$: spin density at nucleus N

Electronic Structure Calculations: RHF, ROHF, and UHF



Electronic Structure Calculations: aug-cc-pVTZ-J





pubs.acs.org/JCTC

Optimized Basis Sets for Calculation of Electron Paramagnetic Resonance Hyperfine Coupling Constants: aug-cc-pVTZ-J for the 3d Atoms Sc–Zn

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Supporting Information

Electronic Structure Calculations: aug-cc-pVTZ-J

C:aug-cc-pVTZ EMSL BASIS SET LIBRARY 4 3 0 1 2 3 4 3 2 5 11 6 3 2 8236.0000000 1235.0000000 280.8000000 79.2700000 25,5900000 8.9970000 3.3190000 0.9059000 0.3643000 0.1285000 0.0440200

C:aug-cc-pVTZ-J EMSL BASIS SET LIBRARY

EMSL BASIS SET LIBRARY

4				
0	1	2	3	
9	5	3	1	
21	8	3	1	

16289729.0000	2442668.00000	366281.000000	54924.0000000	8236.0000000
1235.0000000	280.800000	79.2700000	25.5900000	8.9970000
3.3190000	0.9059000	0.3643000	79.2700000	25.5900000
8.9970000	3.3190000	0.9059000	0.3643000	0.1285000
0.0440200				

Electronic Structure Calculations: carbon HFCC in ¹³CH₃

method/basis*	A ^{iso} _{eql} (G)
P(CI)/DZ	22.2
QCISD(T)/TZVP	27.8
MCSCF/cc-pVTZus2st	27.7
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CCSD(T)/aug-cc-pVTZ-J	25.8**

*J. Chem. Phys. 138, 054310 (2013)

**our work

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Experiment	38.3

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**our work

How do we determine the (molecular) observable by theory?

How do we determine the (molecular) observable by theory?

$\mathsf{H}_{tot} \Psi_{tot}(\mathsf{r},\mathsf{R}) = \mathsf{E}_{tot} \Psi_{tot}(\mathsf{r},\mathsf{R})$

The molecular Hamiltonian $= T_N + T_e + V_{eN} + V_{ee} + V_{NN}$ The molecular wave function Eigenvalues (Energies)

We solve the Schrödinger equation! Too complicated to be solved Simplification of the Schrödinger Equation

$$\Psi(\mathsf{r},\mathsf{R}) \;= \psi_{m{R}}(\mathsf{r})\;\psi(\mathsf{R})$$

The Electronic Wave Function - $[T_e + V_{eN} + V_{ee}] \psi_R(r) = E_e(R) \psi_R(r)$ The Nuclear Wave Function - $[T_N + E_e(R) + V_{NN}] \psi(R) = E \psi(R)$

Born–Oppenheimer approximation We solve two equations

The Nuclear Wave Function: TROVE algorithm



International Journal of Quantum Chemistry 2016 (Tennyson and Yurchenko)

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Ro-Vibrational Averaging: TROVE

$$\langle A_{iso} \rangle_i = \langle \phi_{\rm rv}^{(i)} | A_{iso} | \phi_{\rm rv}^{(i)} \rangle$$

 $\langle A_{iso} \rangle_i$ is an expectation value of the operator A_{iso} in a rovibrational state i

$$\langle A_{iso} \rangle_T = \frac{1}{Q} \sum_i g_i \exp\left(-\frac{E_{rv}^{(i)}}{kT}\right) \langle A_{iso} \rangle_i$$

where g_i is the degeneracy of the *i*th state with the energy $E_{rv}^{(i)}$ relative to the ground state energy, k is the Boltzmann constant, Q is the internal partition function defined as

$$Q = \sum_{i} g_{i} \exp\left(-rac{E_{\mathrm{rv}}^{(i)}}{kT}
ight)$$

*J. Chem. Phys. 132, 114305 (2010)

Ro-vibrational Averaging: Computational Details

- PES
- 22640 symmetry-unique molecular geometries
- RCCSD(T)/cc-pVQZ-F12
- molpro package (https://www.molpro.net/)
- HFCC surface
- 19959 symmetry-unique molecular geometries
- UHF-CCSD(T)/aug-cc-pVTZ-J
- CFOUR package (http://www.cfour.de/)
- Analytical repesentation was obtained in a least-squares fitting procedure

Calculated Vibrational energies for ¹²CH₃

- electronic ground state -

Irrep	Calculated*	Experiment	$v_1 \ v_2 \ v_3^{\ell_3} \ v_4^{\ell_4}$
A_1^{\prime}	0	_	0 0 0 0 0 0
$A_2^{\prime\prime}$	601.1	606.5	$0 \ 1 \ 0^0 \ 0^0$
$A_{1}^{'}$	1278.3	1288.1	0 2 0 ⁰ 0 ⁰
Ē	1389.0	1397.0	$0 \ 0 \ 0^0 \ 1^1$
Е″	2001.8	_	$0\ 1\ 0^0\ 1^1$
$A_{2}^{''}$	2006.0	2019.2	0 3 0 ⁰ 0 ⁰
Ē	2688.8	_	$0 \ 2 \ 0^0 \ 1^1$
A_{1}^{\prime}	2752.4	_	0 0 0 ⁰ 2 ⁰
Ē	2770.9	_	$0 \ 0 \ 0^0 \ 2^2$
$A_{1}^{'}$	2771.8	_	0 4 0 ⁰ 0 ⁰
$A_1^{\overline{i}}$	3003.4	3004.4	$1 \ 0 \ 0^0 \ 0^0$
E	3159.5	3160.8	$0 \ 0 \ 1^1 \ 0^0$

*relative to the zero-point energy of 6466.9 cm $^{-1}$

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Calculated Vibrational Energies for $^{13}\text{CH}_3$ and $^{13}\text{CD}_3$ - electronic ground state -

Irrep	¹³ CH ₃ *	¹³ CD ₃ **	$v_1 \ v_2 \ v_3^{\ell_3} \ v_4^{\ell_4}$
$A_{1}^{'}$	0	0	0 0 0 0 0 0
$A_2^{\prime\prime}$	596.1	447.4	$0 \ 1 \ 0^0 \ 0^0$
$A_{1}^{'}$	1267.7	944.6	$0 \ 2 \ 0^0 \ 0^0$
E	1384.1	1022.8	$0 \ 0 \ 0^0 \ 1^1$
$E^{''}$	1992.1	1475.7	$0\ 1\ 0^0\ 1^1$
$A_2^{\prime\prime}$	1989.2	1476.4	0 3 0 ⁰ 0 ⁰
Ē	2673.7	1977.6	$0 \ 2 \ 0^0 \ 1^1$
A_1^{\prime}	2742.4	2022.6	0 0 0 ⁰ 2 ⁰
Ē	2761.1	2039.5	$0 \ 0 \ 0^0 \ 2^2$
$A_1^{'}$	2749.6	2034.9	0 4 0 ⁰ 0 ⁰
$A_1^{\overline{\prime}}$	3002.6	2154.1	$1 \ 0 \ 0^0 \ 0^0$
Ē	3147.3	2362.0	$0 \ 0 \ 1^1 \ 0^0$

*relative to the zero-point energy of 6446.9 cm⁻¹; **relative to the zero-point energy of 4742.1 cm⁻¹

method/basis	$\mathbf{A}_{eql}^{iso}(\mathbf{G})$	A ^{iso} vib(G)	[A ^{iso} _{vib} - A ^{iso} _{eql}](G)
P(CI)/DZ	22.2		
QCISD(T)/TZVP	27.8		
MCSCF/cc-pVTZus2st	27.7		
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P(CI)/DZ	22.2	35.1	
QCISD(T)/TZVP	27.8	37.7	
MCSCF/cc-p $VTZus2st$	27.7	37.3	
B3LYP/Huz-IIIsu3	29.9	42.2	
CCSD(T)/aug-cc-pVTZ-J	25.8	37.1	
Experiment*		38.3	

method/basis	$A_{eql}^{iso}(G)$	A ^{iso} vib(G)	[A ^{iso} _{vib} - A ^{iso} _{eql}](G)
P(CI)/DZ	22.2	35.1	12.9 (58%)
QCISD(T)/TZVP	27.8	37.7	9.9 (36%)
MCSCF/cc-pVTZus2st	27.7	37.3	9.6 (35%)
B3LYP/Huz-IIIsu3	29.9	42.2	12.3 (41%)
CCSD(T)/aug-cc-pVTZ-J	25.8	37.1	11.3 (44%)
Experiment*		38.3	

moue.		lucs
Level	$T_{ m vib}(m cm^{-1})$	$\langle A_{^{13}\mathrm{C}}^{\mathrm{iso}} angle (G)$
	umbrella motion	
<i>v</i> ₂		
1	596.1	52.8
2	1267.7	64.5
3	1989.2	74.6
4	2749.6	76.0
5	3536.3	90.5
6	4353.7	98.5
7	5188.7	105.9
8	6042.1	112.6
	stretching motion	
v_1		
1	3002.6	39.0
2	5960.1	41.4

out-of-plane mode: Expectation Values

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Umbrella Motion Contribution to HFCC



Thermal contribution to carbon-13 lsotropic HFCC(G)

Temp.(K)	$^{13}CH_3$	¹³ CD ₃
0	37.068	34.239
96	37.092	34.275
300	38.076	35.917

*ESR experiment at 96K

Summary and Conclusions

- Molecular properties reported in the literature are often purely electronic.
- The case of methyl radical highlights the importance of vibrational corrections to carbon HFCC.
- use UHF to account for spin polarization
- use basis sets with tight functions to ensure proper nuclear-cusp behaviour for $\psi_{elec.}.$
- The vibrational corrections can be dominated by the contribution of a single vibrational mode (out-of-plane motion).
- For ESR experiment at 96K, temperature effects are small.

Infrared Intensities



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First-principles calculation of the rotation-vibration spectrum



International Journal of Quantum Chemistry 2016 (Tennyson and Yurchenko)

The Potential Energy Surface: ab initio calculations

- Open-shell
- Coupled-cluster calculations
- $\bullet \sim$ 20,000 symmetry-unique molecular geometries
- Analytical repesentation was obtained in a least-squares fitting procedure
- molpro package (https://www.molpro.net/)

The Potential Energy Surface: fitting

We have fitted the calculated points to the totally symmetric sixth-order power series expansion in terms of six variables

$$V(\xi_k;\sin\overline{\rho}) = V_e + V_0(\sin\overline{\rho}) + \sum_j F_j(\sin\overline{\rho})\xi_j$$
$$+ \sum_{j \le k} F_{jk}(\sin\overline{\rho})\xi_j\xi_k$$
$$+ \sum_{j \le k \le l} F_{jkl}(\sin\overline{\rho})\xi_j\xi_k\xi_l$$
$$+ \sum_{j \le k \le l \le m} F_{jklm}(\sin\overline{\rho})\xi_j\xi_k\xi_l\xi_m + \cdot$$

The Potential Energy Surface: fitting

$$\xi_{k} = (r_{k} - r_{e}) \exp\left(-(r_{k} - r_{e})^{2}\right), \quad k = 1, 2, 3,$$

$$\xi_{4} = (2\alpha_{1} - \alpha_{2} - \alpha_{3})/\sqrt{6},$$

$$\xi_{5} = (\alpha_{2} - \alpha_{3})/\sqrt{2},$$

$$\xi_{6} = 1 - 2/\sqrt{3} \sin([\alpha_{1} + \alpha_{2} + \alpha_{3}]/6),$$

Rotation-Vibration Energies:Compare to Experiment

Compare to Experiment

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Theoretical Rotational Term Values for $^{12}\text{CH}_3$

- vibrational ground state -

States		Term Values (cm $^{-1}$)		
J	Κ	Obs.	Obs-Cal (I)	Obs-Cal (II)
			r _e = <mark>1.07736</mark>	$r_e = 1.07629$
1	1	14.3189	0.032377	0.004027
2	0	57.4396	0.112005	-0.002023
2	2	38.1186	0.092340	0.017004
2	1	52.6112	0.106875	0.002511
3	2	95.5353	0.203902	0.014649
3	3	71.3965	0.179934	0.038989
3	1	110.0032	0.219365	0.001200
4	0	191.2473	0.375024	-0.004034
4	4	114.1491	0.295456	0.070301
4	2	172.0038	0.353500	0.012772
4	3	147.9203	0.327970	0.035289

Vibrational Band Centers (cm⁻¹) of the ν_2 mode

vibrational band	Calc.	Exp.
1-0	601.1	606.4
2–1	677.2	681.6
3–2	727.7	731.0
4–3	765.8	772
5–4	792.7	811

Vibrational Transition Moments μ_{fi} (D)

state	Calc.	Exp.
ν_2	0.2039	0.215
$2\nu_2$	0.2567	0.316
ν_3	0.0283	0.029

Summary and Conclusions

- Methyl radical is important to many chemical processes of industrial and environmental interest
- The development and application of theoretical quantitative spectroscopic probes of methyl radicals can benefit several fields of research.
- We have produced spectra of CH₃ in the infrared region with variational nuclear motion calculations
- The computed vibrational transition moments were compared to the available data
- Detailed comparison with the observed spectrum of the CH₃ (ν_2) umbrella mode shows a good agreement with experiment.

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Thank You