

Theoretical Infrared Intensities of the Methyl Radical

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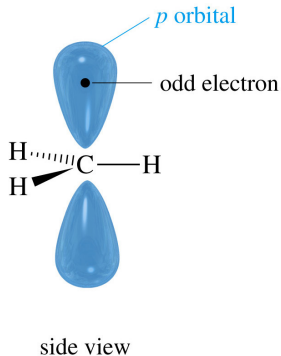
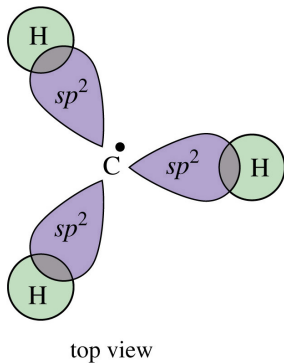
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Overview

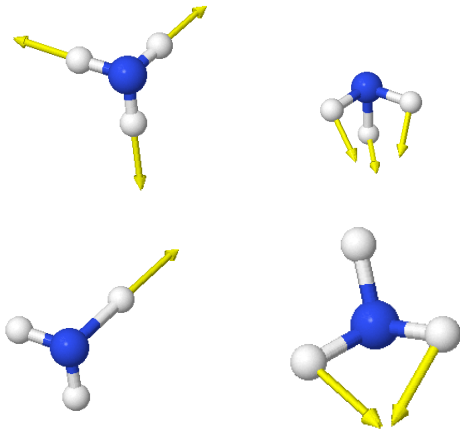
- 1 Introduction
- 2 Nuclear Motion Calculations
- 3 Infrared Intensities
- 4 Summary and Conclusions

The Methyl Radical: Structure



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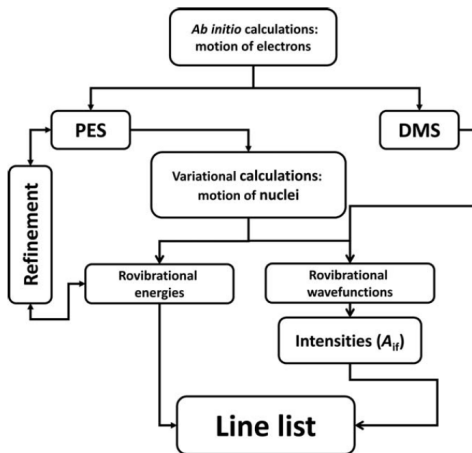
The Methyl Radical: Vibrational Modes



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.

First-principles calculation of the rotation-vibration spectrum



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

$$\begin{aligned}
 V(\xi_k; \sin \bar{\rho}) &= V_e + V_0(\sin \bar{\rho}) + \sum_j F_j(\sin \bar{\rho}) \xi_j \\
 &+ \sum_{j \leq k} F_{jk}(\sin \bar{\rho}) \xi_j \xi_k \\
 &+ \sum_{j \leq k \leq l} F_{jkl}(\sin \bar{\rho}) \xi_j \xi_k \xi_l \\
 &+ \sum_{j \leq k \leq l \leq m} F_{jklm}(\sin \bar{\rho}) \xi_j \xi_k \xi_l \xi_m + \dots
 \end{aligned}$$

The Potential Energy Surface: fitting

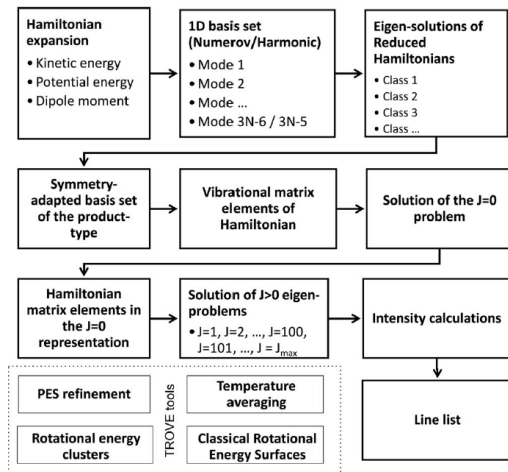
$$\xi_k = (r_k - r_e) \exp(-(r_k - r_e)^2), \quad k = 1, 2, 3,$$

$$\xi_4 = (2\alpha_1 - \alpha_2 - \alpha_3)/\sqrt{6},$$

$$\xi_5 = (\alpha_2 - \alpha_3)/\sqrt{2},$$

$$\xi_6 = 1 - 2/\sqrt{3} \sin([\alpha_1 + \alpha_2 + \alpha_3]/6),$$

TROVE algorithm



Rotation-Vibration Energies: Compare to Experiment

Compare to Experiment

Calculated Vibrational energies for $^{12}\text{CH}_3$

- electronic ground state -

Irrep	Calculated*	Experiment	v_1	v_2	$v_3^{\ell_3}$	$v_4^{\ell_4}$
A_1'	0	–	0	0	0^0	0^0
A_2''	601.1	606.5	0	1	0^0	0^0
A_1'	1278.3	1288.1	0	2	0^0	0^0
E'	1389.0	1397.0	0	0	0^0	1^1
E''	2001.8	–	0	1	0^0	1^1
A_2''	2006.0	2019.2	0	3	0^0	0^0
E'	2688.8	–	0	2	0^0	1^1
A_1'	2752.4	–	0	0	0^0	2^0
E'	2770.9	–	0	0	0^0	2^2
A_1'	2771.8	–	0	4	0^0	0^0
A_1'	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}

Calculated Vibrational Energies for $^{12}\text{CH}_3$

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Intensities: Line strength (S), Einstein coefficient (A), and Intensity (I)

$$S(f \leftarrow i) = \sum_{\lambda', \lambda} \sum_{A=X,Y,Z} |\langle \Psi_{\lambda'}^f | \bar{\mu}_A | \Psi_{\lambda}^i \rangle|^2$$

$$A_{if} = \frac{8\pi^4 \tilde{\nu}_{if}^3}{3h} (2J_i + 1) \sum_{A=X,Y,Z} |\langle \Psi^f | \bar{\mu}_A | \Psi^i \rangle|^2$$

$$I(f \leftarrow i) = \frac{A_{if}}{8\pi c} g_{ns} (2J_f + 1) \frac{\exp\left(-\frac{E_i}{kT}\right)}{Q(T) \tilde{\nu}_{if}^2} \left[1 - \exp\left(\frac{-c_2 \tilde{\nu}_{if}}{T}\right) \right]$$

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

- vibrational ground state -

States		Term Values (cm^{-1})		
J	K	Obs.	Obs-Cal (I)	Obs-Cal (II)
			$r_e = 1.07736$	$r_e = 1.07629$
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

*J. Phys. Chem. A. 112, 6285 (2008)

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 show good agreement with the experiment.

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