Variationally Computed IR Line List for the Methyl Radical CH_3

Ahmad Y. Adam, *University of Wuppertal, Germany*

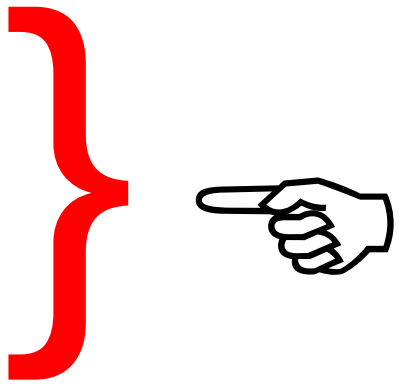
Andrey Yachmenev, *Center for Free-Electron Laser Science and Hamburg Center for Ultrafast Imaging, Hamburg, Germany*

Sergey N. Yurchenko, *University College London, UK*

Per Jensen, *University of Wuppertal, Germany*

CH_3 radical:

- Hydrocarbon combustion processes
- Atmospheric chemistry
- Chemistry of semiconductor production
- Chemical vapor deposition of diamond
- Intermediary in many chemical processes of current industrial and environmental interest
- Exoplanetary atmospheres
- Atmospheres of Saturn and Neptune
- Interstellar medium



Line list for CH_3:

- *Goal: Catalogue of predicted transitions (wavenumbers & intensities)*

- RCCSD(T)-F12b /cc-pVQZ-F12 *ab initio* calculation; MOLPRO
- Equilibrium geometry planar; empirical adjustment of equilibrium C-H bond length
- Simulation of rotation-vibration spectrum with the program TROVE; line list expected to be accurate to T = 1500 K.

Potential energy expansion:

$$
\begin{aligned}
V(\xi_1,\xi_2,\xi_3,\xi_{4a},\xi_{4b};\sin\bar{\rho}) &= V_{\mathrm{e}} + V_0(\sin\bar{\rho}) + \sum_j F_j(\sin\bar{\rho})\,\xi_j \\
&+ \sum_{j\leqslant k} F_{jk}(\sin\bar{\rho})\,\xi_j\,\xi_k + \sum_{j\leqslant k\leqslant l} F_{jkl}(\sin\bar{\rho})\,\xi_j\,\xi_k\,\xi_l \\
&+ \sum_{j\leqslant k\leqslant l\leqslant m} F_{jklm}(\sin\bar{\rho})\,\xi_j\,\xi_k\,\xi_l\,\xi_m + \ldots;
\end{aligned}
$$

in

$$\xi_k = 1 - \exp\left[-a(r_k - r_{\mathrm{e}})\right], \quad k = 1,2,3,$$

$$(\xi_{4a},\xi_{4b}) = \left(\frac{1}{\sqrt{6}}[2\,\alpha_1 - \alpha_2 - \alpha_3], \frac{1}{\sqrt{2}}[\alpha_2 - \alpha_3]\right)$$

$$\sin\bar{\rho} = \frac{2}{\sqrt{3}}\sin[(\alpha_1+\alpha_2+\alpha_3)/6]$$

Dipole moment expansion:

(Symmetrized Molecular Bond (SMB) expansion)

Dipole moment expanded in terms of unit vectors $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$, $\mathbf{e}_N$

$$\mathbf{e}_k = \frac{\mathbf{r}_k - \mathbf{r}_4}{|\mathbf{r}_k - \mathbf{r}_4|}$$

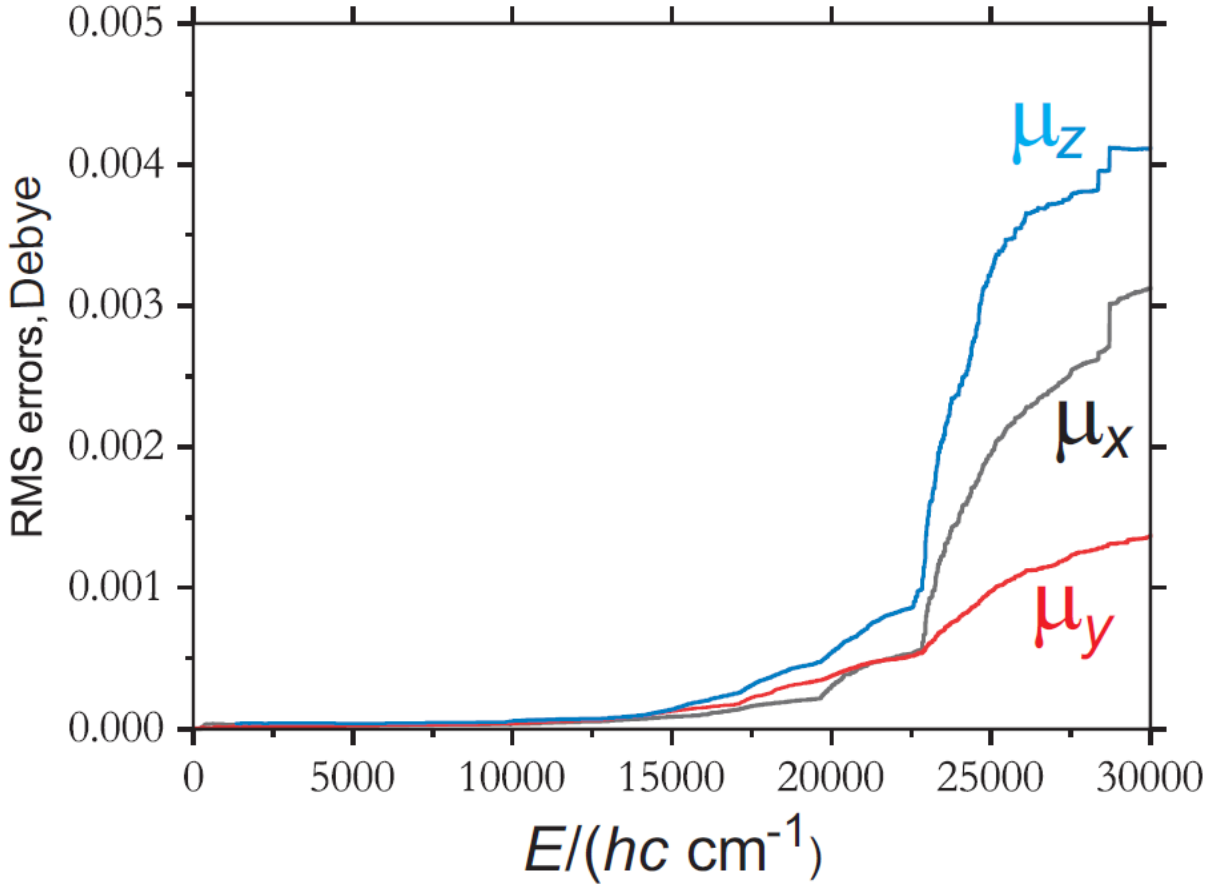
$$\mathbf{e}_N = \mathbf{q}_N/|\mathbf{q}_N|$$

$$\mathbf{q}_N = (\mathbf{e}_1 \times \mathbf{e}_2) + (\mathbf{e}_2 \times \mathbf{e}_3) + (\mathbf{e}_3 \times \mathbf{e}_1).$$

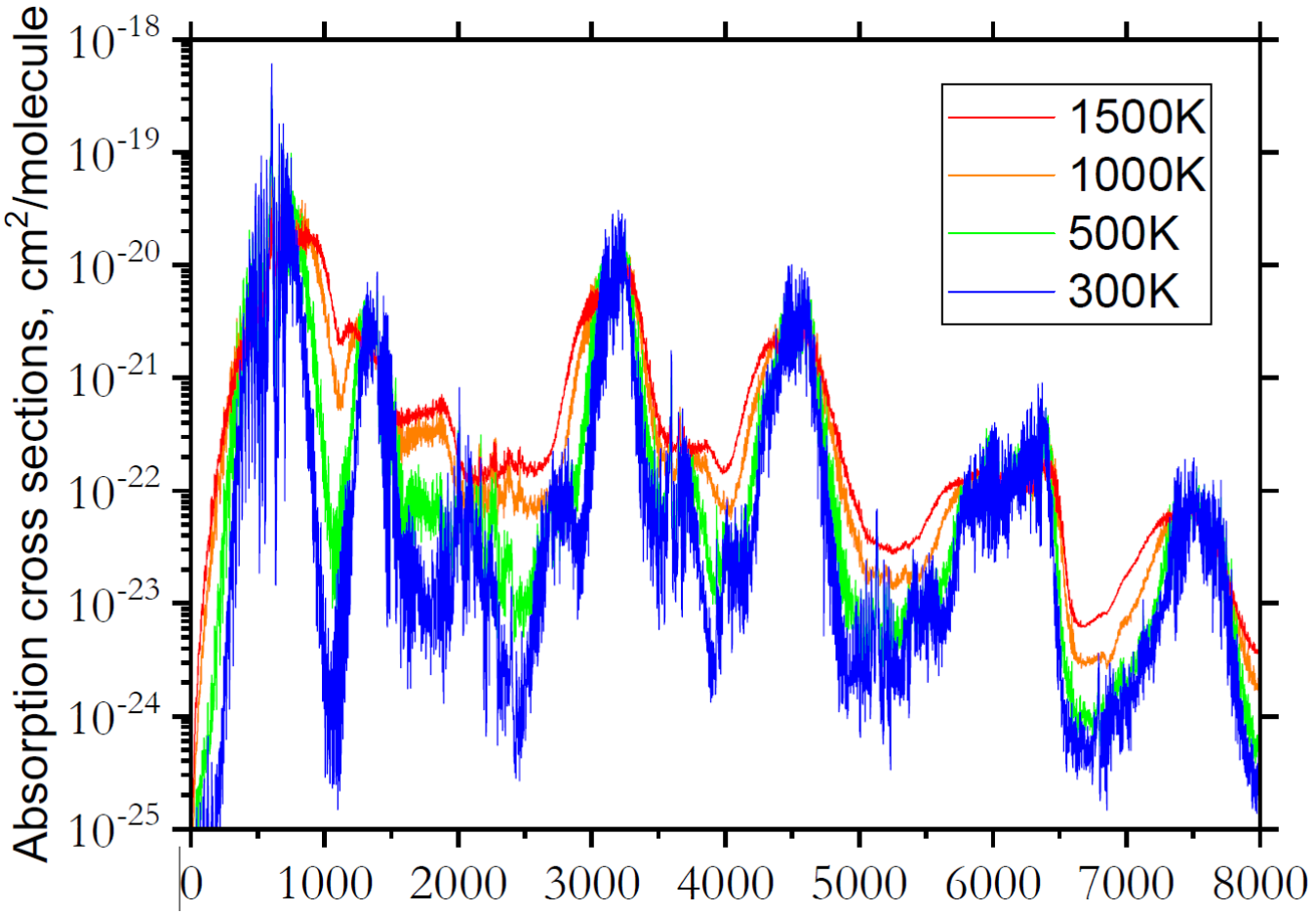
$$\begin{aligned}
\bar{\mu}^{\mathrm{SMB}}_{A''_2} &= (\bar{\boldsymbol{\mu}} \cdot \mathbf{e}_N) \\
\bar{\mu}^{\mathrm{SMB}}_{E'_a} &= \frac{1}{\sqrt{6}} \left[2\,(\bar{\boldsymbol{\mu}} \cdot \mathbf{e}_1) - (\bar{\boldsymbol{\mu}} \cdot \mathbf{e}_2) - (\bar{\boldsymbol{\mu}} \cdot \mathbf{e}_3)\right] \\
\bar{\mu}^{\mathrm{SMB}}_{E'_b} &= \frac{1}{\sqrt{2}} \left[(\bar{\boldsymbol{\mu}} \cdot \mathbf{e}_2) - (\bar{\boldsymbol{\mu}} \cdot \mathbf{e}_3)\right],
\end{aligned}$$

$$\begin{aligned}
\bar{\mu}^{\mathrm{SMB}}_{\Gamma}(\chi_1, \chi_2, \chi_3, \chi_{4a}, \chi_{4b}; \rho) =& \mu^{\Gamma}_0(\sin\bar{\rho}) + \sum_i \mu^{\Gamma}_i(\sin\bar{\rho})\chi_i + \sum_{i\le j} \mu^{\Gamma}_{ij}(\sin\bar{\rho})\chi_i\chi_j \\
&+ \sum_{i\le j\le k} \mu^{\Gamma}_{ijk}(\sin\bar{\rho})\chi_i\chi_j\chi_k + \sum_{i\le j\le k\le l} \mu^{\Gamma}_{ijkl}(\sin\bar{\rho})\chi_i\chi_j\chi_k\chi_l,
\end{aligned}$$

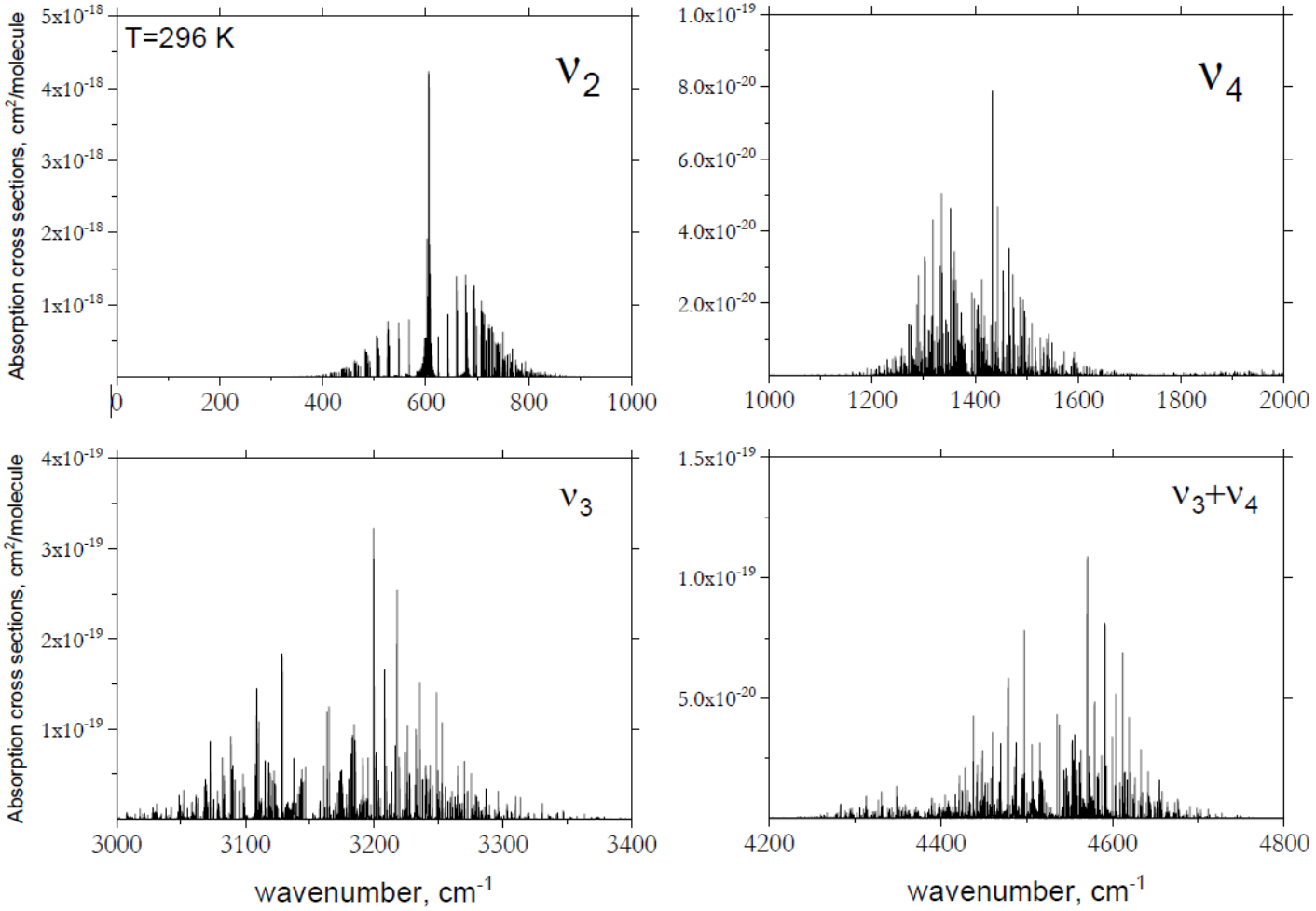
Dipole moment fitting:



Simulated spectra for CH_3:



Simulated spectra for CH_3:



Vibrational term values for CH_3:

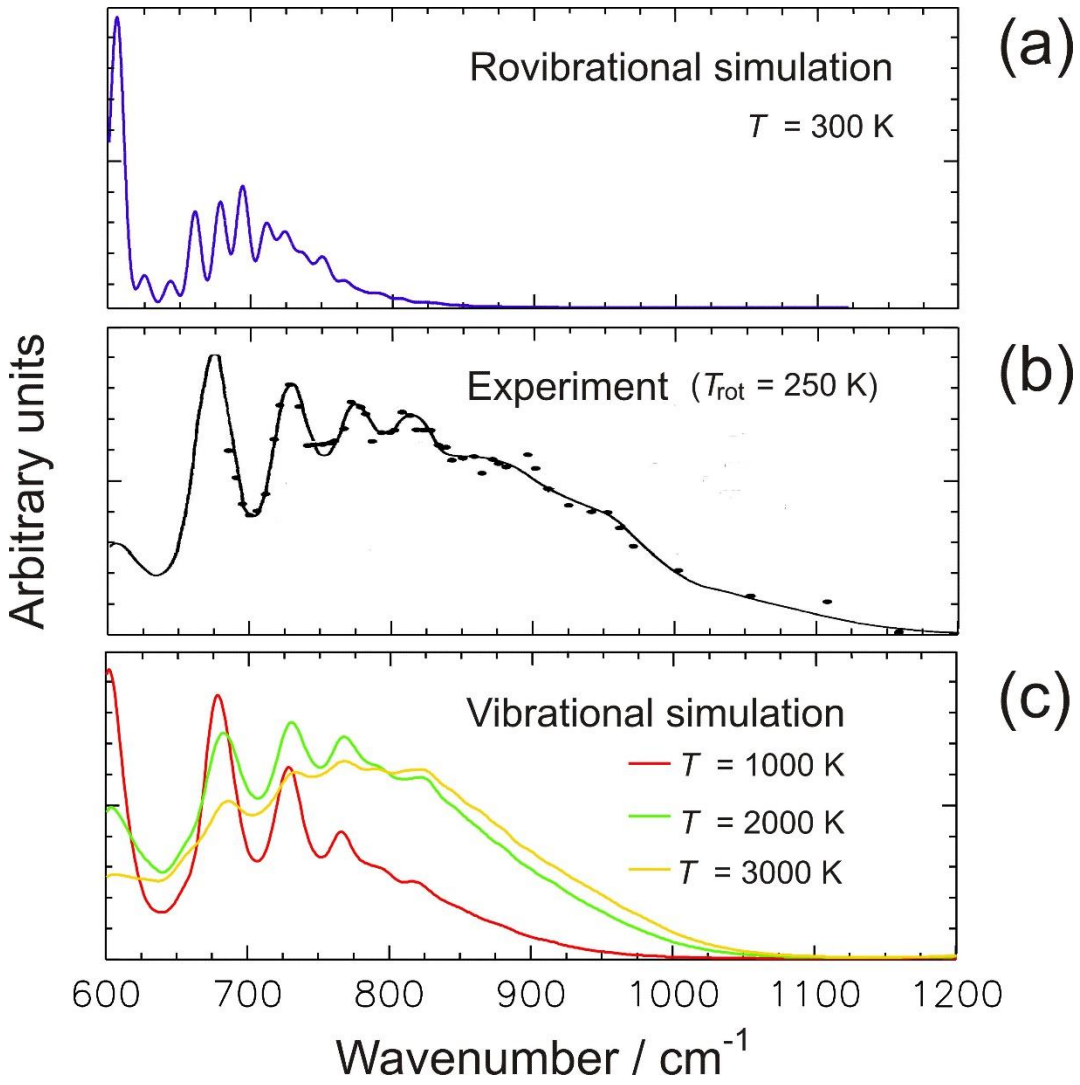
Γ	State	Ref.	Obs.[a]	$P_{max} = 24$[b]	$P_{max} = 32$[c]
A_1'	$2\nu_2$	61	1288.1	1279.77	1281.24
	$2\nu_4$			2737.63	2739.64
	$4\nu_2$			2773.65	2776.86
	ν_1	13	3004.42	3002.71	3002.76
	$3\nu_4^3$			4118.59	4120.58
	$\nu_1 + 2\nu_2$			4258.97	4260.53
	$6\nu_2$			4391.99	4397.00
	$\nu_3^1 + \nu_4^1$			4537.94	4538.93
	$4\nu_4$			5371.39	5364.56
	$2\nu_2 + 3\nu_4^3$			5475.84	5480.07
	$4\nu_2 + 2\nu_4$			5601.91	5607.20
E'	ν_4^1	62	1397.0	1385.99	1387.26
	$2\nu_2 + \nu_4^1$			2688.80	2691.61
	$2\nu_4^2$			2759.77	2762.05
	ν_3^1	58	3160.8	3158.88	3158.83
	$3\nu_4^1$			4074.69	4075.46
	$2\nu_2 + 2\nu_4^2$			4087.92	4091.72

Γ	State	Ref.	Obs.[a]	$P_{max} = 24$[b]	$P_{max} = 32$[c]
A_2''	ν_2	13	606.453	602.43	602.43
	$3\nu_2$			2010.09	2010.09
	$\nu_2 + 2\nu_4^0$			3372.27	3371.59
	$5\nu_2$			3569.96	3569.95
	$\nu_1 + \nu_2$			3596.35	3596.30
	$3\nu_4^3$			4768.70	4767.06
	$\nu_2 + 2\nu_4^0$			4823.32	4822.79
	$\nu_1 + 3\nu_2$			4981.58	4981.52
E''	$\nu_2 + \nu_4^1$			2000.24	2002.22
	$\nu_2 + 2\nu_4^2$			3388.24	3391.11
	$3\nu_2 + \nu_4^1$			3426.45	3430.06
	$\nu_2 + \nu_3^1$			3736.40	3736.97
	$\nu_2 + 3\nu_4^1$			4726.62	4728.62
	$3\nu_2 + 2\nu_4^2$			4835.22	4839.85
	$\nu_1 + \nu_2 + \nu_4^1$			4980.92	4983.16

Comparison between experimental emission spectrum and simulations for CH_3.

CH_3 radicals produced by dissociation of CH_3I

Contributions from υ_2 and hot bands only in vibrational simulations



Experimental spectrum reproduced from Hermann, H. W.; Leone, S. R. The Journal of Chemical Physics 1982, 76, 4759-4765, with the permission of AIP Publishing.

Thank you for your attention!

A. Y. Adam, A. Yachmenev, S. N. Yurchenko, and Per Jensen: A variationally computed IR line list for the methyl radical CH_3, *J. Phys. Chem. A* **123**, 4755-4763 (2019). **DOI:** *10.1021/acs.jpca.9b02919*