Nonresonant Raman spectra of the methyl radical $^{12}CH_3$ simulated in variational calculations

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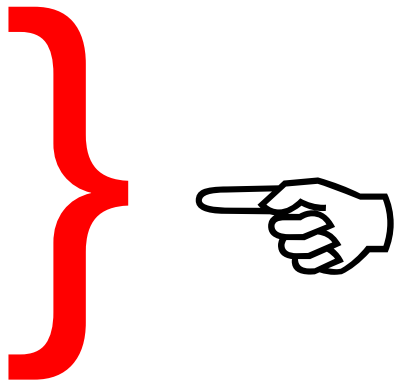
CH_3 radical:

- 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



Raman spectra (here for CH_3):

- RCCSD(T)-F12b /cc-pVQZ-F12 *ab initio* calculation of potential energy and polarizability surfaces; MOLPRO
- Equilibrium geometry planar; empirical adjustment of equilibrium C-H bond length
- Simulation of *nonresonant* Raman spectrum with the program TROVE.

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

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

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

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

Polarizability tensor expansion:

(Symmetrized Molecular Bond (SMB) expansion)

Dipole moment expanded in terms of unit vectors $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$, $\mathbf{e}_4$

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

$$\mathbf{e}_4 = \mathbf{q}_\mathrm{N}/|\mathbf{q}_\mathrm{N}|$$

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

$$\begin{aligned}
\bar{\alpha}^{(1)}_{A'_1} &= \frac{1}{\sqrt{3}}(\bar{\alpha}_{11} + \bar{\alpha}_{22} + \bar{\alpha}_{33}),\\
\bar{\alpha}^{(2a)}_{E'_a} &= \frac{1}{\sqrt{6}}(\bar{\alpha}_{12} - \bar{\alpha}_{13} - \bar{\alpha}_{23}),\\
\bar{\alpha}^{(2b)}_{E'_b} &= \frac{1}{\sqrt{2}}(\bar{\alpha}_{13} - \bar{\alpha}_{23}),\\
\bar{\alpha}^{(3)}_{A'_1} &= \bar{\alpha}_{44},\\
\bar{\alpha}^{(4a)}_{E''_a} &= \frac{1}{\sqrt{6}}(2\bar{\alpha}_{14} - \bar{\alpha}_{24} - \bar{\alpha}_{34}),\\
\bar{\alpha}^{(4b)}_{E''_b} &= \frac{1}{\sqrt{2}}(\bar{\alpha}_{24} - \bar{\alpha}_{34}),
\end{aligned}$$

where

$$\bar{\alpha}_{ij} = \mathbf{e}_i \cdot \left(\bar{\alpha}\,\mathbf{e}_j^{\mathrm{T}}\right), \quad i, j = 1, 2, 3, 4$$

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

Raman intensities I:

Raman scattering cross section

$$\left[\frac{d\sigma_k}{d\Omega}(\nu_0)\right]_{\text{Stokes}} = \left(\frac{\pi}{\epsilon_0}\right)^2 \times (\nu_0 - \nu_k)^4 \times \frac{\exp(-E''/kT)}{Q_v} \times \sum_{FF'} |\langle \Phi'_{\text{rv}} | \bar{\alpha}_{FF'} | \Phi''_{\text{rv}} \rangle|^2.$$

Raman transition probability („line strength“)

$$\mathcal{R}(f \leftarrow i) = g_{\text{ns}} \sum_{m',m''} \sum_{F=X,Y,Z} \sum_{F'=X,Y,Z} |\langle \Phi'_{\text{rv}} | \bar{\alpha}_{FF'} | \Phi''_{\text{rv}} \rangle|^2.$$

Raman intensities II:

Isotropic/anisotropic Raman scattering:

$\mathscr{R}_0$ (f ← i) and $\mathscr{R}_2$ (f ← i) contributions to „line strength“

Cross sections for perpendicular Raman scattering assuming the laser light is polarized in the *Y* direction and the exciting laser beam is propagating in the X direction.

$$\left[\frac{d\sigma_k}{d\Omega}(\nu_0)\right]_{\text{Stokes}} = \left(\frac{\pi}{\epsilon_0}\right)^2 \times (\nu_0 - \nu_k)^4 \times \frac{\exp(-E''/kT)}{Q_v}$$
$$\times \frac{1}{30}\Big(10\,\mathcal{R}_0(f \leftarrow i) + 7\,\mathcal{R}_2(f \leftarrow i)\Big).$$

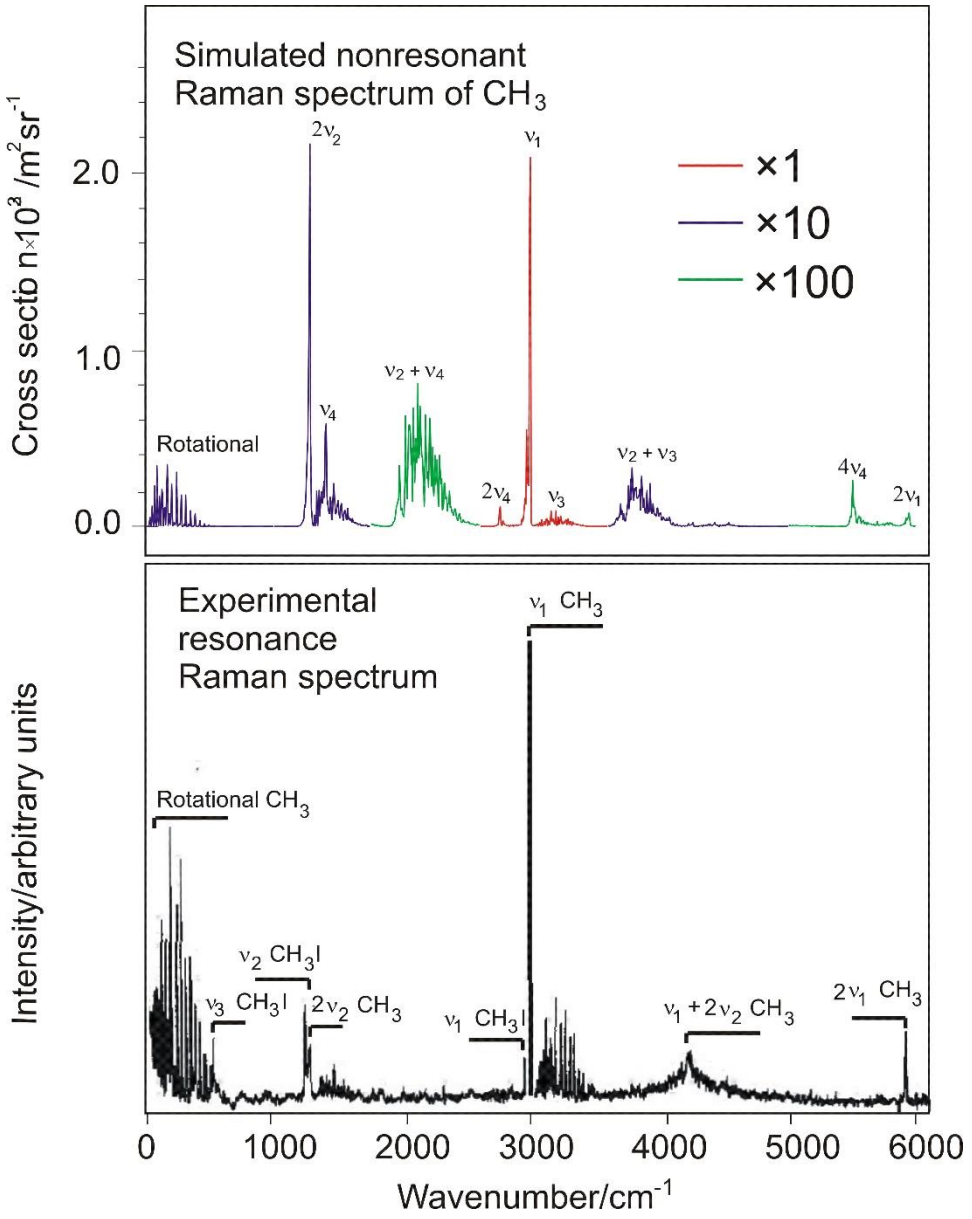
Vibrational term values for $^{12}CH_3$:

Table 1: Comparison of experimental and theoretical term values (cm^{-1}) for selected $^{12}CH_3$ levels.

State	Γ^a	Obs.^{b}	Ref.^{c}	Calc.^{d}
ν_1	A_1'	3004.42	[27]	3002.76
ν_2	A_2''	606.45	[57]	602.43
$2\nu_2$	A_1'	1288.1	[57]	1281.24
ν_3	E'	3160.8	[58]	3158.83
ν_4	E'	1397.0	[59]	1387.26

Comparison between simulated nonresonant Raman spectrum and experimental resonance Raman spectrum of CH_3.

CH_3 radicals produced by dissociation of CH_3I



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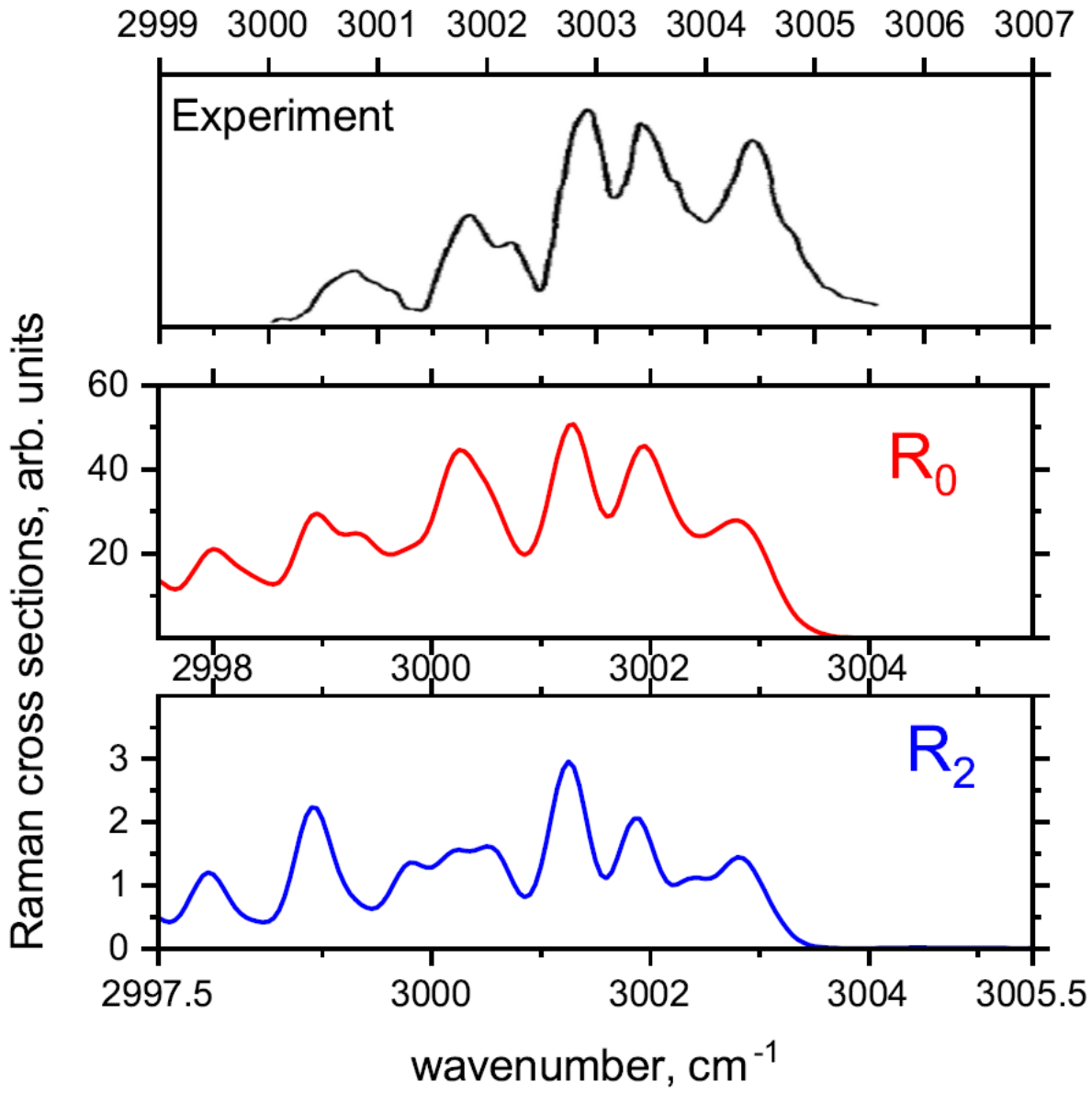
Comparison between simulated nonresonant Raman spectrum and experimental CARS spectrum of the CH_3 υ_1 Q branch.



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Thank you for your attention!

A. Y. Adam, Per Jensen, A. Yachmenev, and S. N. Yurchenko: Non-resonant Raman spectra of the methyl radical $^{12}CH_3$ simulated in variational calculations, *J. Mol. Spectrosc., in press*.