

Variational Calculation of a $T = 1500$ K Line List for the Methyl Radical CH_3 , and Simulation of the Raman Spectrum

Andrey Yachmenev,^a Sergey N. Yurchenko,^b Ahmad Y. Adam,^c Per Jensen^c

^aCenter for Free-Electron Laser Science (CFEL), Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany; ^bDepartment of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK; ^cSchool of Mathematics and Natural Sciences, University of Wuppertal, Germany

Line list / Simulated absorption spectra

We present the first variational calculation of a high-temperature *ab initio* line list for the CH_3 radical. It is based on a high level *ab initio* potential energy surface and dipole moment surface of CH_3 in the ground electronic state. The ro-vibrational energy levels and Einstein A coefficients were calculated using the general-molecule variational approach implemented in the computer program TROVE [1, 2]. Vibrational energies and vibrational intensities are found to be in very good agreement with the available experimental data.

Potential energy surface/electronic properties: RCCSD(T)-F12b /cc-pVQZ-F12 *ab initio* calculation with MOLPRO. Equilibrium geometry planar; empirical adjustment of equilibrium C-H bond length.

For more information, see Ref. [3].

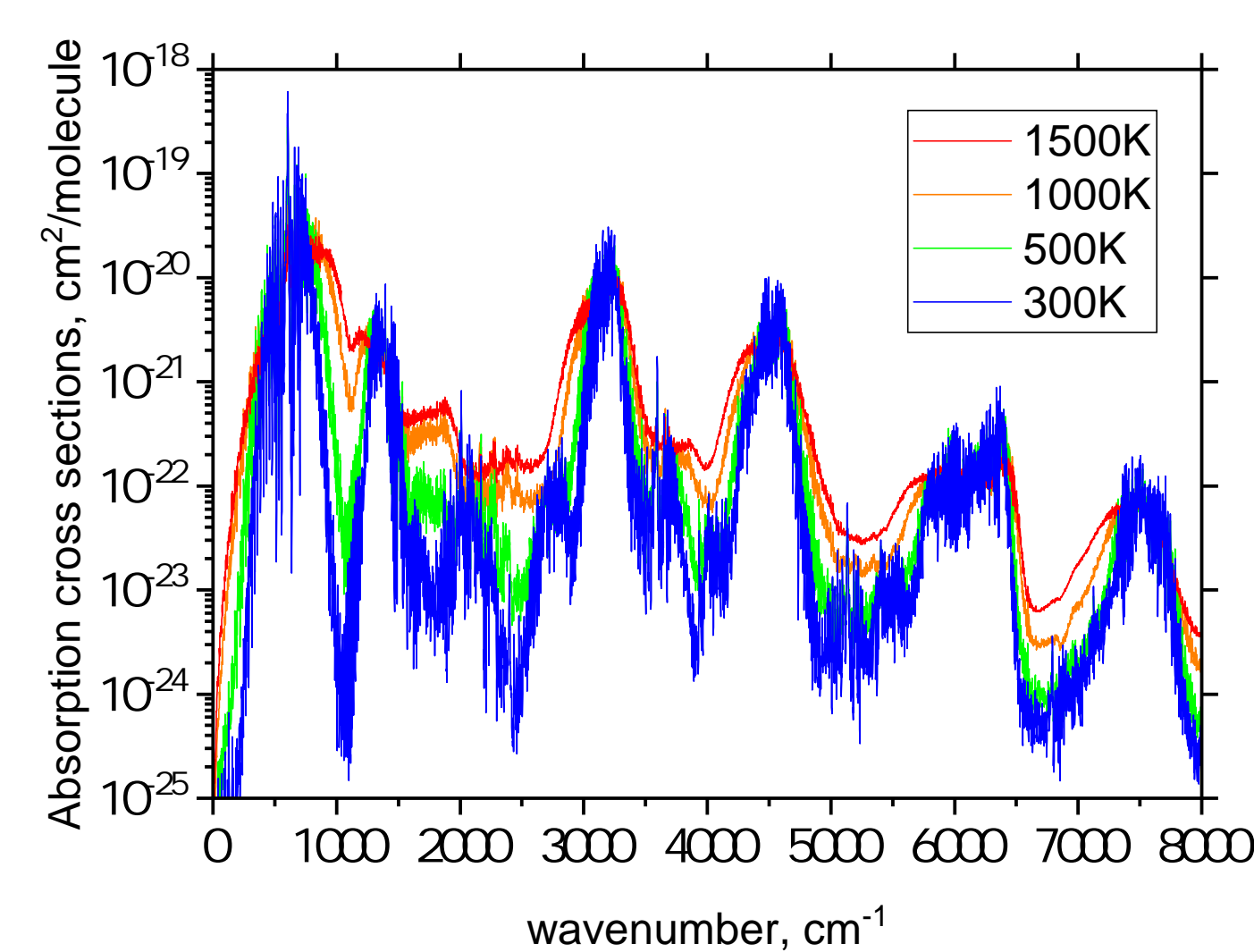


Figure 1: An overview of the absorption spectrum (cross sections) of CH_3 at different temperatures $T = 300, 500, 1000$ and 1500 K generated using our line list and the Gaussian line profile with the full-width-at-half-maximum of 1 cm^{-1} .

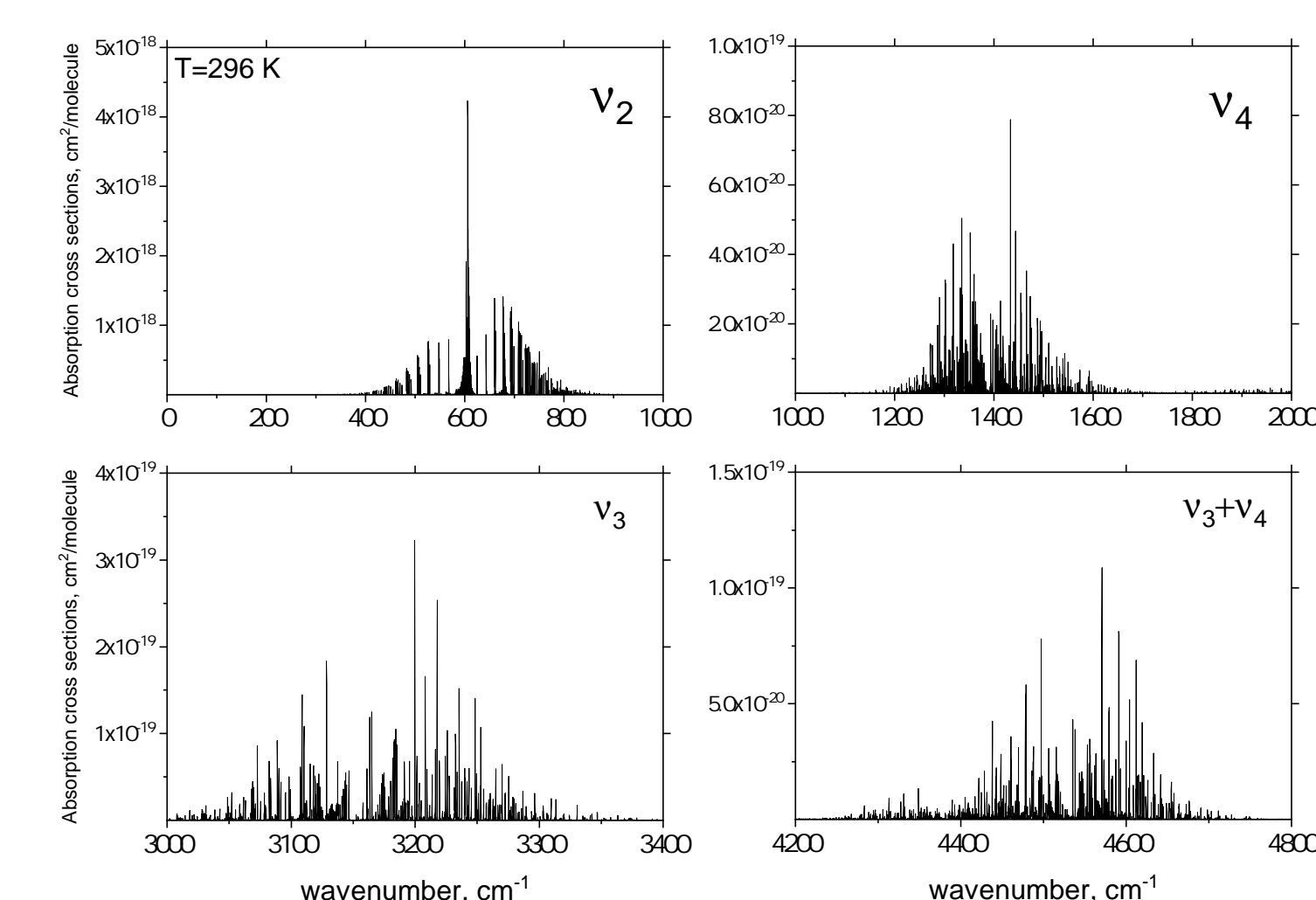


Figure 2: A selection of the strongest absorption bands of CH_3 at $T = 296$ K generated using the line list. A Gaussian line profile with the half-width-at-half-maximum of 0.08 cm^{-1} was used in production of the cross sections shown.

Comparison of experimental and theoretical term values (cm^{-1}) for selected $^{12}\text{CH}_3$ levels.

State	Γ^a	Obs. ^b	Ref. ^c	Calc. ^d
ν_1	A_1'	3004.42	[4]	3002.76
ν_2	A_2''	606.45	[5]	602.43
$2\nu_2$	A_1'	1288.1	[5]	1281.24
ν_3	E'	3160.8	[6]	3158.83
ν_4	E'	1397.0	[7]	1387.26

^a $D_{3h}(M)$ symmetry of the vibrational state.

^b Experimental term value.

^c Reference for experimental term value.

^d Variationally computed value from Ref. [3]; TROVE calculation with basis set $P_{\text{max}} = 32$ [3].

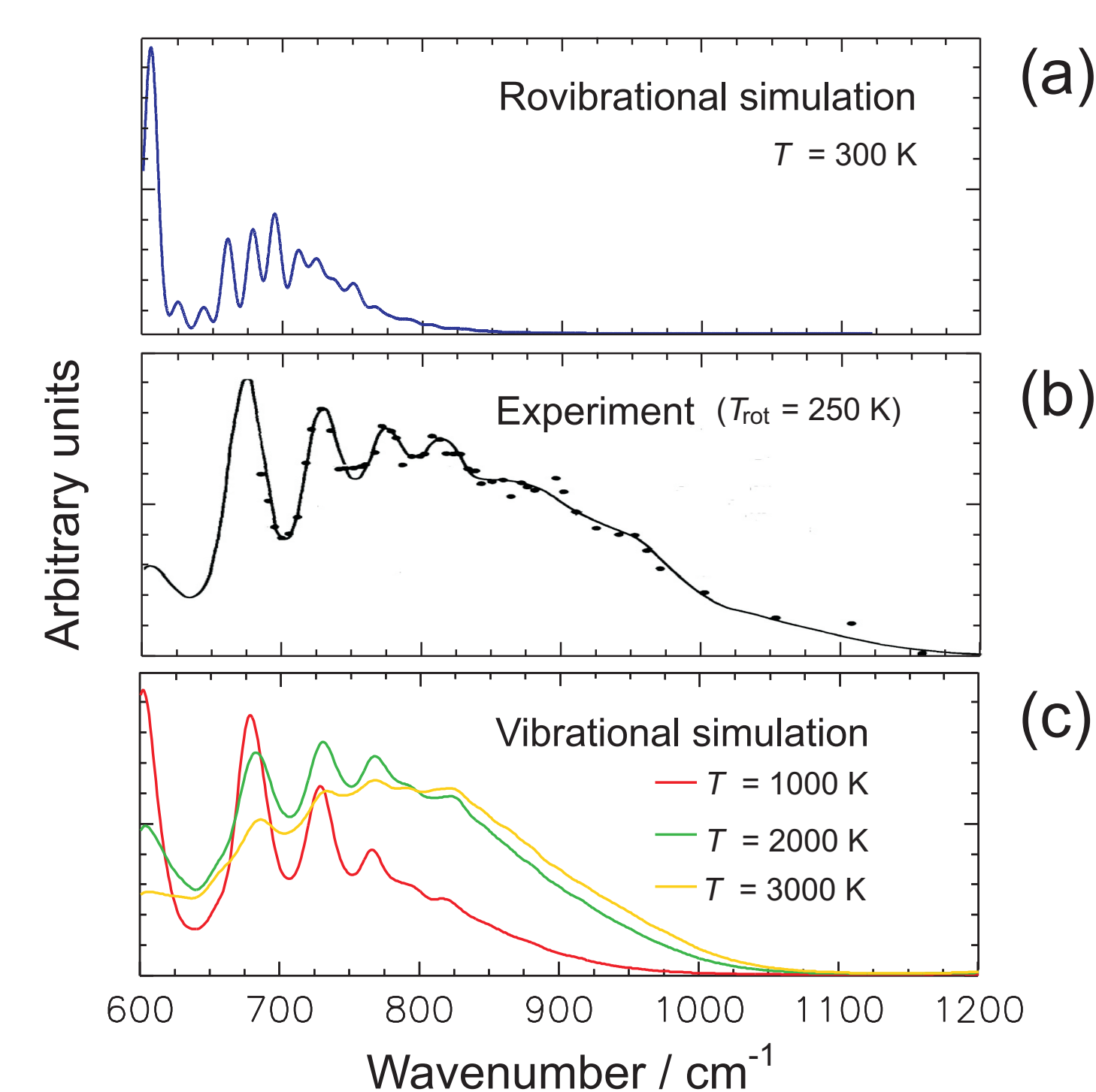


Figure 3: Emission spectra of CH_3 . (a) Rovibrational simulation at $T = 300$ K thermal equilibrium. (b) CH_3 (ν_2) out-of-plane bending mode emission spectrum (dots) obtained [8] after dissociation of $\text{CH}_3\text{I} \rightarrow \text{CH}_3(\nu_2) + \text{I}^*$. The continuous curve is the best fit [8] involving the hot bands $(\nu_2 + 1)\nu_2 \leftarrow \nu_2\nu_2$ with $\nu_2 \leq 9$. The spectrometer slit function has a FWHM of 33 cm^{-1} ; 19 cm^{-1} bandwidth ascribed to the breadth of the $\Delta K = 0$ manifold of transitions with varying J values. (c) Vibrational simulations at $T = 1000, 2000,$ and 3000 K, respectively of the vibrational transitions $(\nu_2 + 1)\nu_2 \leftarrow \nu_2\nu_2$ with $\nu_2 \leq 9$.

Simulated Raman spectra

We have extended the applicability of TROVE towards simulations of Raman spectra and carried out a first-principles variational simulation of the non-resonant Raman spectrum for methyl radical ($^{12}\text{CH}_3$) in the electronic ground state. Calculations are based on the high-level *ab initio* potential energy surface used also for the line-list computations, and polarizability tensor surfaces newly calculated by *ab initio* methods. The simulations for CH_3 are found to be in good agreement with the available experimental data. For more information, see Ref. [9].

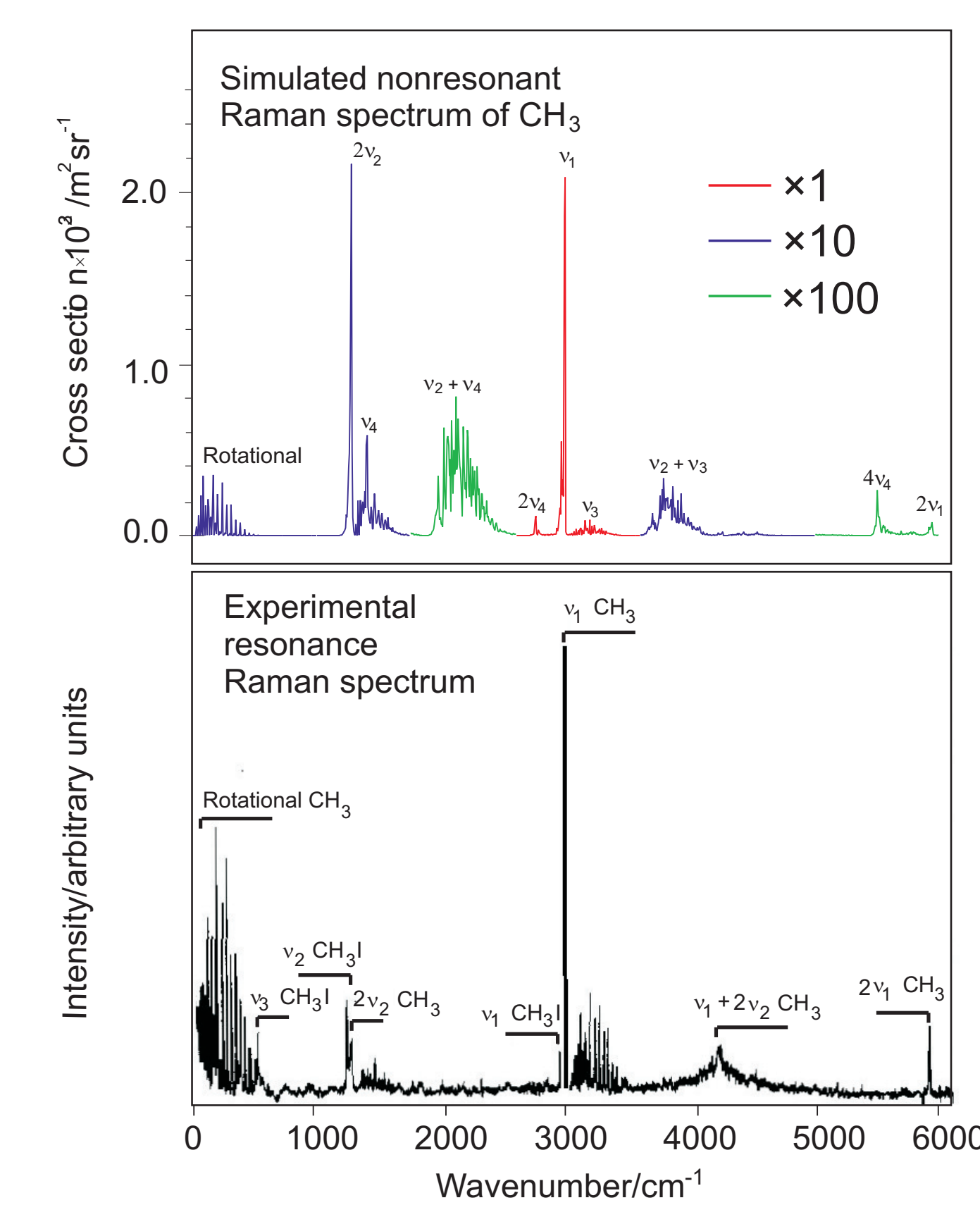


Figure 4: A comparison between the simulated nonresonant (at $T = 300$ K) and an observed resonance Raman spectrum of CH_3 . The experimental resonance Raman spectrum contains transitions of CH_3 and CH_3I [10].

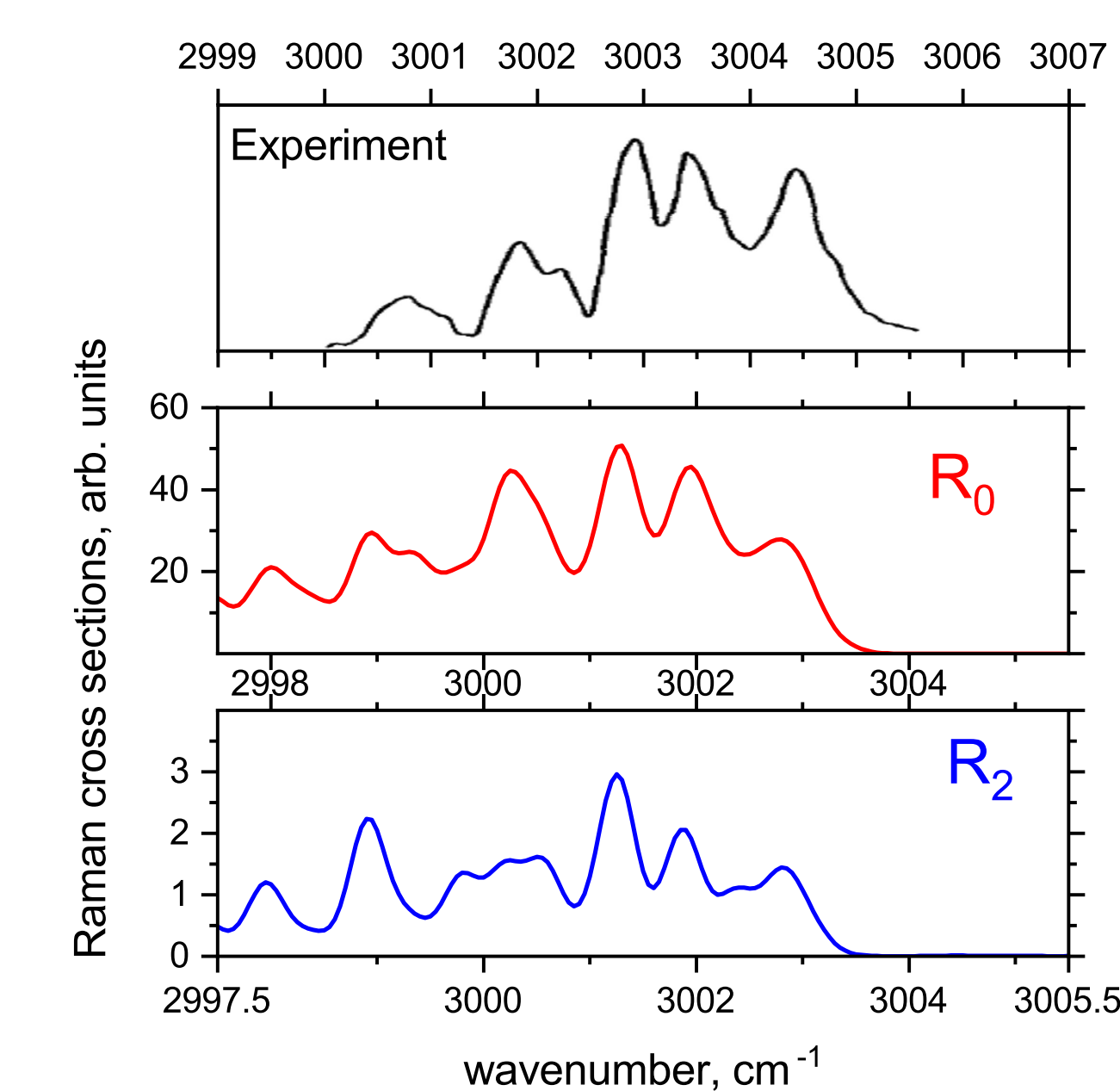


Figure 5: A comparison between the simulated nonresonant Raman spectrum (at $T = 300$ K) and an observed CARS spectrum of the ν_1 band Q branch of CH_3 (top display) [11]. Individual contributions from \mathcal{R}_0 and \mathcal{R}_2 ; Placzek coefficients of $10/30$ and $7/10$. The simulated spectra were convolved with a Gaussian line profile with a half-width-at-half-maximum of 0.2 cm^{-1} . Note that the theoretical spectra are shifted by about 1.5 cm^{-1} relative to the experimental CARS spectrum to account for the obs-calc difference for the ν_1 band center.

References

- [1] S. N. Yurchenko, W. Thiel, P. Jensen, Theoretical ROVibrational Energies (TROVE): A robust numerical approach to the calculation of rovibrational energies for polyatomic molecules, *J. Mol. Spectrosc.* 245 (2007) 126–140.
- [2] A. Yachmenev, S. N. Yurchenko, Automatic differentiation method for numerical construction of the rotational-vibrational Hamiltonian as a power series in the curvilinear internal coordinates using the Eckart frame, *J. Chem. Phys.* 143 (2015) 014105/1–16.
- [3] A. Y. Adam, A. Yachmenev, S. N. Yurchenko, P. Jensen, Variationally computed ir line list for the methyl radical CH_3 , *The Journal of Physical Chemistry A* 123 (22) (2019) 4755–4763.
- [4] N. E. Triggs, M. Zahedi, J. W. Nibler, P. DeBarber, J. J. Valentini, High Resolution Study of the ν_1 Vibration of CH_3 by Coherent Raman Photofragment Spectroscopy, *J. Chem. Phys.* 96 (1992) 1822–1831.
- [5] C. Yamada, E. Hirota, K. Kawaguchi, Diode Laser Study of the ν_2 Band of the Methyl Radical, *J. Chem. Phys.* 75 (1981) 5256–5264.
- [6] S. Davis, D. T. Anderson, G. Duxbury, D. J. Nesbitt, Jet-Cooled Molecular Radicals in Slit Supersonic Discharges: Sub-Doppler Infrared Studies of Methyl Radical, *J. Chem. Phys.* 107 (1997) 5661–5675.
- [7] M. E. Jacox, *Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules*, Supplement B, Vol. 1, American Chemical Society, New York, 2005.
- [8] H. W. Hermann, S. R. Leone, Photofragment Infrared Emission Spectroscopy: Vibrational Progression and Potential Parameters of the $\text{CH}_3(\nu_2)$ “Umbrella” Mode, *J. Chem. Phys.* 76 (1982) 4759–4765.
- [9] A. Y. Adam, P. Jensen, A. Yachmenev, S. N. Yurchenko, Nonresonant Raman spectra of the methyl radical $^{12}\text{CH}_3$ simulated in variational calculations, *Journal of Molecular Spectroscopy* 362 (2019) 77–83.
- [10] P. B. Kelly, S. G. Westre, Resonance Raman Spectroscopy of the Methyl Radical, *Chem. Phys. Lett.* 151 (1988) 253–257.
- [11] P. L. Holt, K. E. McCurdy, R. B. Weisman, J. S. Adams, P. S. Engel, Transient CARS Spectroscopy of the ν_1 Band of Methyl Radical, *J. Chem. Phys.* 81 (1984) 3349–3350.

Acknowledgements

A.Y. acknowledges support from DESY (HGF IVF) and from the Cluster of Excellence “The Hamburg Centre for Ultrafast Imaging” of the Deutsche Forschungsgemeinschaft (DFG) - EXC 1074 - project ID 194651731. S.Y. is grateful for support from the UK Science and Technology Research Council (STFC) ST/R000476/1. This work made extensive use of UCL’s Legion high performance (HPC) computing facilities as well as of HPC provided by DiRAC supported by STFC and BIS. It was further supported in part by grant JE 144/25-1 from the DFG.