

ExoMol line lists – LVII. High accuracy ro-vibrational line list for methane (CH₄)

Sergei N. Yurchenko ^{*}, Alec Owens , Kyriaki Kefala and Jonathan Tennyson ^{*}

Department of Physics and Astronomy, University College London, Gower Street, WC1E 6BT London, UK

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ABSTRACT

The MM ro-vibrational line list for methane (¹²CH₄) is presented; MM covers wavelengths $\lambda > 0.83 \mu\text{m}$ (wavenumbers up to 12 000 cm⁻¹) and contains over 50 billion transitions between 9155 208 states with total angular momentum $J \leq 60$. MM was generated through solution of the nuclear motion Schrödinger equation using variational program TROVE for an empirically derived potential energy surface (PES) and a new high-level *ab initio* dipole moment surface. The PES was constructed by fitting the ro-vibrational energies of CH₄ to a set of highly accurate, experimentally derived energies. Molecular states are classified using the $T_d(M)$ symmetry group and are fully assigned with rotation and vibration quantum numbers. The MM line list is adapted to high-resolution applications by replacing the calculated ro-vibrational energies with the experimentally derived values where available, namely for 23 208 states with $J \leq 27$ below 9986 cm⁻¹. Doing so leads to over 1 000 000 experimentally derived CH₄ lines compared to approximately 330 000 lines of ¹²CH₄ in the HITRAN data base. The MM line list is shown to be more complete than the recent HITEMP methane line list. Methane spectra computed using MM across a broad range of temperatures and wavenumbers show excellent agreement with experiment. The MM line list supersedes the previous ExoMol methane line lists 10to10 and 30to10 both in terms of accuracy and coverage. Together with the pre-computed ExoMolOP molecular atmospheric opacity tables, it is now the recommended CH₄ data set in the ExoMol data base (www.exomol.com).

Key words: molecular data – exoplanets – stars: atmospheres – stars: low-mass.

1 INTRODUCTION

Methane was detected in the exoplanet HD189733b by Swain, Vasisht & Tinetti (2008). Since then, there were many more tentative detections of CH₄ in hot exoplanetary atmospheres using both the low and high resolution methods [see Beaulieu et al. (2011) and references therein]. Although methane is expected to have significant presence in H₂-rich atmospheres at temperatures below ~ 600 K (Burrows & Sharp 1999; Lodders & Fegley 2002), there were no robust detection of CH₄ at these temperatures, see, e.g. Stevenson et al. (2010), Knutson et al. (2014), Benneke et al. (2019a, b), and Blain, Charnay & Bézard (2021). Very recently, methane was detected in the *JWST* spectra of K2-18b at $\sim 5\sigma$ confidence by Madhusudhan et al. (2023), thus resolving the problem of the lack of CH₄ in the atmospheres of low temperature exoplanets (Madhusudhan & Seager 2011).

Methane is one of the dominant constituents of atmospheres of brown dwarfs (Bochanski et al. 2011; Canty et al. 2015). The quality of the line lists have been shown to play a critical role for the atmospheric retrievals of these objects, both in terms of the completeness (Yurchenko et al. 2014) and accuracy (Hood et al. 2023). *JWST* now provides an ideal platform for the spectroscopy of CH₄ in even cooler objects, Y dwarfs (Lacy & Burrows 2023).

The first ExoMol line list for methane, 10to10 (Yurchenko & Tennyson 2014; Yurchenko et al. 2014), containing almost 10 billion transitions, was developed back in 2014 to meet the huge demand for methane spectroscopic data in the exoplanetary and cool star research. 10to10 revolutionized atmospheric retrievals, demonstrating the considerable importance of hot transitions at elevated temperatures (Yurchenko et al. 2014). Many exoplanetary atmospheric studies have utilized the 10to10 line list (Tennyson & Yurchenko 2021), such as for example, the discovery of carbon and nitrogen bearing species in the hot Jupiter exoplanet HD 209458 b (Giacobbe et al. 2021). Although 10to10 filled the gaps in methane high-temperature absorption by providing the necessary completeness, it was shown to be not sufficiently accurate in the near-infrared (NIR), especially for high-resolution spectroscopic applications of brown dwarfs and exoplanets (Hood et al. 2023). The higher resolution Doppler spectroscopy technique (Snellen 2014; Birkby 2018) is now an integral part of modern exoplanetary atmospheric studies (Brogi & Line 2019; Brogi & Birkby 2021) and is providing definitive detections of molecules based on high-resolution laboratory spectroscopic data (Brogi et al. 2012).

The 10to10 line list was based on an empirically-refined potential energy surface (PES) constructed through fitting to high-resolution experimental data available from the spectroscopic literature at that time. Since then, a large number of high-quality laboratory methane data has been made available [see a comprehensive review of the experimental literature on the methane experimental spectroscopy in Kefala et al. (2024)]. The line list production in the ExoMol

* E-mail: s.yurchenko@ucl.ac.uk (SNY); j.tennyson@ucl.ac.uk (JT)

data base has also seen significant developments, most notably towards the high-resolution applications, see for e.g. Bowesman et al. (2021). The current ExoMol line list production relies on the extraction of all meaningful experimental ro-vibrational line positions from the literature and subsequent processing of them through the MARVEL (Measured Active Rotational Vibrational Energy Levels) algorithm (Császár et al. 2007; Furtenbacher, Császár & Tennyson 2007; Furtenbacher & Császár 2012; Tóbiás et al. 2019; Tennyson et al. 2024). MARVEL produces a consistent data set of highly accurate empirical-quality energy levels which serves two purposes: (i) to refine the PES for the improvement of the accuracy of the predicted line positions, and (ii) to replace the computed line list energy levels with the more accurate MARVEL values. The latter process is known as a ‘MARVELization’ procedure. In this work, we use a newly established MARVEL data set of $^{12}\text{CH}_4$ energy levels compiled from the most up-to-date experimental spectroscopic data (Kefala et al. 2024). Our MARVEL data set of CH_4 contains 23 264 states determined from 82 173 transition frequencies from 96 experimental sources. It is the most comprehensive experimentally derived set of CH_4 energies that we know of and it is central to the production of the MM line list. Using the variational code TROVE (Yurchenko, Thiel & Jensen 2007), we have computed 50 395 644 806 lines, covering 9155 208 ro-vibrational states for $J \leq 60$, with transitions in the wavenumber range 0–12 000 cm^{-1} for upper state energies up to $E' = 18\,000 \text{ cm}^{-1}$ and lower state energies $E'' = 10\,000 \text{ cm}^{-1}$. The calculated CH_4 energies have been MARVELized using values from Kefala et al. (2024) and will be continually improved upon as new experimental data is published. The MM line list is recommended to replace the outdated 10to10 and 30to10 ExoMol line lists.

The importance of methane has led to the construction of many line lists (Borysov et al. 2003; Hargreaves et al. 2012; Yurchenko & Tennyson 2014; Nikitin et al. 2014; Hargreaves et al. 2015; Rey, Nikitin & Tyuterev 2017; Makhnev et al. 2018; Hargreaves et al. 2020). Here we concentrate on those complete enough to be reliable at higher temperatures. The TheoReTS data base (Rey et al. 2016) contains the CH_4 line list of Rey, Nikitin & Tyuterev (2014, 2017) which has been shown to be accurate for a large range of temperatures (Wong et al. 2019), and to outperform the 10to10 line list in the accuracy of line positions, particularly at higher frequencies. The TheoReTS CH_4 line list has been very useful in the analysis of laboratory data (Rodina et al. 2019; Nikitin et al. 2020) and facilitated a series of methane data releases in the past few years, see e.g. Kefala et al. (2024). The line list of Rey, Nikitin & Tyuterev (2014, 2017) forms the basis of the HITEMP CH_4 line list (Hargreaves et al. 2020), a hot synthetic line list applicable for temperatures up to 2000 K. This line list has been adopted by numerous exoplanetary groups, especially those specializing in high-resolution retrievals, see e.g. Gandhi et al. (2020). The TheoReTS line list also utilized an empirically constructed PES of CH_4 and was continuously improved by replacing the calculated ro-vibrational line positions with experimental values.

2 POTENTIAL ENERGY SURFACE

A new empirical PES of CH_4 was constructed for the present work. We started from the highly accurate *ab initio* PES of methane by Owens et al. (2016), which is given analytically as an expansion in terms of 1D coordinates. Morse oscillator functions describe the stretch coordinates,

$$\xi_i = 1 - \exp(-a(r_i - r_{\text{ref}})); \quad i = 1, 2, 3, 4 \quad (1)$$

while symmetrized combinations of inter-bond angles are used for the angular terms,

$$\xi_5 = \frac{1}{\sqrt{12}} (2\alpha_{12} - \alpha_{13} - \alpha_{14} - \alpha_{23} - \alpha_{24} + 2\alpha_{34}), \quad (2)$$

$$\xi_6 = \frac{1}{2} (\alpha_{13} - \alpha_{14} - \alpha_{23} + \alpha_{24}), \quad (3)$$

$$\xi_7 = \frac{1}{\sqrt{2}} (\alpha_{24} - \alpha_{13}), \quad (4)$$

$$\xi_8 = \frac{1}{\sqrt{2}} (\alpha_{23} - \alpha_{14}), \quad (5)$$

$$\xi_9 = \frac{1}{\sqrt{2}} (\alpha_{34} - \alpha_{12}). \quad (6)$$

Here r_1, r_2, r_3, r_4 are the C–H bond lengths and $\alpha_{12}, \alpha_{13}, \alpha_{14}, \alpha_{23}$, and α_{24} are the five $\angle(\text{H}_j\text{--C--H}_k)$ inter-bond angles where j and k label the respective hydrogen atoms; a and r_{ref} are the Morse and reference equilibrium structural parameter, respectively.

The coordinate transformation from the six bending coordinates α_{ij} to the five independent coordinates $\xi_5, \xi_6, \xi_7, \xi_8$, and ξ_9 defined by equations (2)–(6) has to be complemented by the redundancy condition (Halonen 1997),

$$\begin{vmatrix} 1 & \cos \alpha_{12} & \cos \alpha_{13} & \cos \alpha_{14} \\ \cos \alpha_{12} & 1 & \cos \alpha_{23} & \cos \alpha_{24} \\ \cos \alpha_{13} & \cos \alpha_{23} & 1 & \cos \alpha_{34} \\ \cos \alpha_{14} & \cos \alpha_{24} & \cos \alpha_{34} & 1 \end{vmatrix} = 0. \quad (7)$$

The potential energy function was represented by a symmetry adapted expansion

$$V(\xi_1, \xi_2, \xi_3, \xi_4, \xi_5, \xi_6, \xi_7, \xi_8, \xi_9) = \sum_{ijk\dots} f_{ijk\dots} V_{ijk\dots}, \quad (8)$$

where $V_{ijk\dots}$ are symmetrized combinations of different permutations of the coordinates ξ_i that transform according to the A_1 representation of the $T_d(M)$ molecular symmetry group (Bunker & Jensen 1998),

$$V_{ijk\dots} = \{\xi_1^i \xi_2^j \xi_3^k \xi_4^l \xi_5^m \xi_6^n \xi_7^p \xi_8^q \xi_9^r\}^{T_d}. \quad (9)$$

The *ab initio* PES of CH_4 (Owens et al. 2016) was then refined by fitting the expansion parameters $f_{ijk\dots}$ in equation (9) to the MARVEL energies of CH_4 (Kefala et al. 2024) using the simultaneous fitting procedure by Yurchenko et al. (2003) as implemented in TROVE (Yurchenko, Thiel & Jensen 2007); see also Yurchenko et al. (2011) and Yurchenko (2023). In this procedure, the newly determined PES is constrained to the original *ab initio* PES to ensure the refinement does not produce nonphysical deformations of the surface. Full details of the variational calculations are given below in Section 4.

Only the $J = 0, 1, 2, 3, 4, 5$, and 8 energies were used in the fitting and only 77 potential parameters were refined. The quality of the refinement is illustrated in Fig. 1, where the theoretical ro-vibrational energies of CH_4 computed with the refined PES are compared to the experimentally derived MARVEL energies of CH_4 . All 23 292 MARVEL energies from Kefala et al. (2024) covering rotational excitations up to $J = 27$ are reproduced with an rms error of 0.14 cm^{-1} . If we exclude MARVEL energies that only have one transition supporting them as possible outliers, i.e. no combination differences, the rms error for the resulting 16 894 values reduces to 0.11 cm^{-1} .

3 DIPOLE MOMENT SURFACE

The electric dipole moment surfaces (DMSs) of CH_4 representing its μ_x, μ_y , and μ_z dipole moment components were computed *ab*

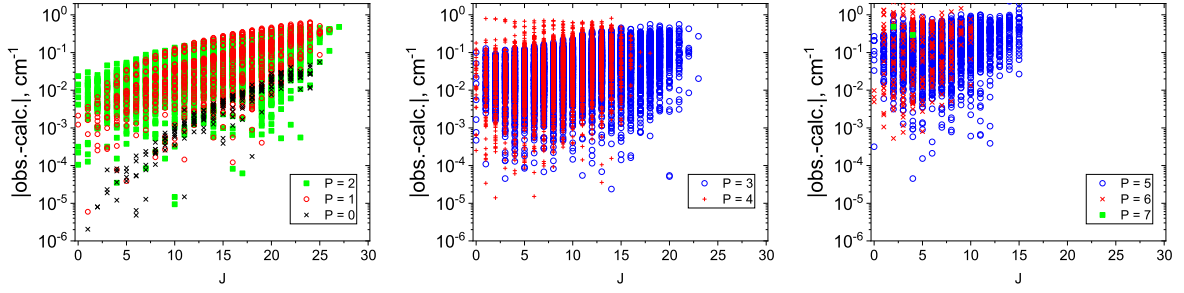


Figure 1. Residual fitting errors of the calculated (TROVE) energy term values (cm^{-1}) of CH₄ as obs.-calc. differences from the experimentally derived (MARVEL) values as function of J for different polyad numbers P .

initio as first-derivatives of the electronic energy with respect to an external electric field. To this end, the central finite difference scheme was used with an external electric field of ± 0.005 a.u. along each x , y , and z Cartesian coordinate axes. Calculations were done at the CCSD(T)/aug-cc-pVQZ level of theory in the frozen core approximation using the quantum chemistry package MOLPRO (Werner et al. 2015). We used the same 9D grid of 97 721 nuclear geometries covering energies up to $hc \times 50\,000$ cm^{-1} that was used to calculate the *ab initio* PES of Owens et al. (2016).

To construct the DMSs of CH₄ analytically, we followed the procedure of Yurchenko et al. (2013) and Owens et al. (2017) based on the symmetrized molecular bond representation of DMSs of XY₄-type molecules. In this representation, the molecular dipole moment vector is projected onto the symmetrically independent reference vectors \mathbf{n}_i ($i = 1, 2, 3$) given by

$$\mathbf{n}_1 = \frac{1}{2}(\mathbf{e}_1 - \mathbf{e}_2 + \mathbf{e}_3 - \mathbf{e}_4), \quad (10)$$

$$\mathbf{n}_2 = \frac{1}{2}(\mathbf{e}_1 - \mathbf{e}_2 - \mathbf{e}_3 + \mathbf{e}_4), \quad (11)$$

$$\mathbf{n}_3 = \frac{1}{2}(\mathbf{e}_1 + \mathbf{e}_2 - \mathbf{e}_3 - \mathbf{e}_4), \quad (12)$$

where the unit vectors along the four C–H bonds are

$$\mathbf{e}_i = \frac{\mathbf{r}_i - \mathbf{r}_0}{|\mathbf{r}_i - \mathbf{r}_0|}; \quad i = 1, 2, 3, 4. \quad (13)$$

Here, \mathbf{r}_0 is the position vector of the C nucleus and \mathbf{r}_i is the position of the respective H_{*i*} atom. The three reference vectors \mathbf{n}_i span the F_2 irreducible representation in \mathcal{T}_d .

The *ab initio* dipole moment vector $\boldsymbol{\mu}$ is given by

$$\boldsymbol{\mu} = \mu_x \mathbf{n}_1 + \mu_y \mathbf{n}_2 + \mu_z \mathbf{n}_3, \quad (14)$$

where μ_α ($\alpha = x, y, z$) are the DMSs (also of F_2 symmetry) taking the form,

$$\mu_\alpha(\xi_1, \xi_2, \xi_3, \xi_4, \xi_5, \xi_6, \xi_7, \xi_8, \xi_9) = \sum_{ijk\dots} F_{ijk\dots}^{(\alpha)} \mu_{\alpha,ijk\dots}^{F_2}. \quad (15)$$

The expansion terms $\mu_{\alpha,ijk\dots}^{F_2}$ are constructed as symmetrized F_2 symmetry combinations of different permutations of the coordinates ξ_i ,

$$\mu_{\alpha,ijk\dots}^{F_2} = \{\xi_1^i \xi_2^j \xi_3^k \xi_4^l \xi_5^m \xi_6^n \xi_7^p \xi_8^q \xi_9^r\}^{F_{2\alpha}}, \quad (16)$$

where we use,

$$\xi_i = (r_i - r^{\text{ref}}) \exp(-\beta(r_i - r^{\text{ref}})^2); \quad i = 1, 2, 3, 4, \quad (17)$$

for the stretches and the angular coordinates as in equations (2)–(6). The four stretching coordinates span the $F_{2\alpha}$ representation of the

$\mathcal{T}_d(M)$ symmetry group. A sixth order expansion was employed. The expansion coefficients $F_{ijk\dots}^{(\alpha)}$ $\alpha = x, y, z$ were determined simultaneously through a least squares fitting to the *ab initio* data. A total of 265 parameters were used (including the reference parameter $r^{\text{ref}} = 1.256$ Å) and reproduced the *ab initio* data with a root-mean-square (rms) error of 0.0049 Debye. All parameters defining the PES and DMSs of CH₄ are provided as a supplementary material along with Fortran 95 routines to construct the corresponding analytic representations. We also provide an input file for the TROVE program, which contains both the parameters and the subroutines, respectively.

4 VARIATIONAL CALCULATIONS

To calculate the ro-vibrational spectrum (or line list) of CH₄ we solve the Schrödinger equation for the motion of the C and H nuclei using the variational program TROVE (Yurchenko, Thiel & Jensen 2007). TROVE is an open-access¹ nuclear motion code for arbitrary medium size polyatomic molecules. It can provide a complete solution for modern spectroscopic high-resolution applications, including the refinement of the PES by fitting to experimental ro-vibrational energies, and computing extensive molecular line lists (Tennyson & Yurchenko 2017). The calculation setup is very similar to that employed in Yurchenko & Tennyson (2014), but here we utilize a more accurate kinetic energy operator (KEO) and PES, and a larger ro-vibrational basis set.

4.1 KEO

The KEO was represented in an Eckart frame, see e.g. Yurchenko (2023), as a sixth-order expansion in terms of nine curvilinear coordinates given by

$$\xi_i = r_i - r_e, \quad i = 1, 2, 3, 4, \quad (18)$$

and ξ_j , $j = 5, 6, 7, 8, 9$ as in equations (2)–(6). Here, r_e is the equilibrium value of the bond length C–H_{*i*}. The expansion was performed using the automatic differentiation method implemented in TROVE (Yachmenev & Yurchenko 2015). Our previous CH₄ line list 10to10 was computed using a similar KEO expansion but in terms of linearized coordinates, which possessed slower convergence (Yachmenev & Yurchenko 2015).

4.2 Basis set

The vibrational basis wavefunctions were constructed using a multi-step contraction scheme detailed below, based on the the following

¹ github.com/exomol

polyad condition applied at each step

$$P = 2(v_1 + v_2 + v_3 + v_4) + v_5 + v_6 + v_7 + v_8 + v_9 \leq 14, \quad (19)$$

where v_i is a vibrational quantum number associated with a 1D primitive basis function $\phi_{v_i}(\xi_i)$ ($i = 1, 2, 3, \dots, 9$). In the conventional normal mode representation this condition corresponds to

$$P = 2(n_1 + n_3) + n_2 + n_4, \quad (20)$$

where n_1, n_2, n_3 , and n_4 are the standard normal mode quantum numbers used for methane (Albert et al. 2009). This is a significant improvement in the accuracy comparing to the 10to10 model, where a $P = 10$ basis set was used.

At contraction step 1, nine sets of 1D primitive basis function $\phi_{v_i}(\xi_i)$ ($i = 1, 2, 3, \dots, 9$) are generated using the Numerov-Cooley (Cooley 1961; Noumerov 1924) method by solving the 1D Schrödinger equations for 1D Hamiltonian operators obtained by freezing all but one vibrational coordinate in the 9D Hamiltonian operator ($J = 0$) at their equilibrium values.

At step 2, the 9D coordinate space is divided into the three reduced sub-spaces, (i) $\{\xi_1, \xi_2, \xi_3, \xi_4\}$, (ii) ξ_5, ξ_6 , and (iii) ξ_7, ξ_8, ξ_9 as dictated by \mathcal{T}_d symmetry; each of the sub-spaces is symmetrically independent and can be processed separately. For each of these sub-spaces, three reduced Hamiltonian operators were constructed as follows:

$$\hat{H}^{(1)}(\xi_1, \xi_2, \xi_3, \xi_4) = \langle 0_5, 0_6, 0_7 | \langle 0_8, 0_9 | \hat{H} | 0_8, 0_9 \rangle | 0_5, 0_6, 0_7 \rangle, \quad (21)$$

$$\hat{H}^{(2)}(\xi_5, \xi_6) = \langle 0_1 | \langle 0_2 | \langle 0_3 | \langle 0_4 | \langle 0_7, 0_8, 0_9 | \hat{H} | 0_7, 0_8, 0_9 \rangle | 0_4 \rangle | 0_3 \rangle | 0_2 \rangle | 0_1 \rangle, \quad (22)$$

$$\hat{H}^{(3)}(\xi_7, \xi_8, \xi_9) = \langle 0_1 | \langle 0_2 | \langle 0_3 | \langle 0_4 | \langle 0_5, 0_6 | \hat{H} | 0_5, 0_6 \rangle | 0_4 \rangle | 0_3 \rangle | 0_2 \rangle | 0_1 \rangle, \quad (23)$$

where $|0\rangle_k$ are ground state vibrational basis functions $\phi_0(\xi_k)$ ($k = 1, \dots, 9$). These yield the following three eigenvalue problems,

$$\hat{H}^{(i)}(\xi^{(i)}) \Phi_{\lambda_i}^{(i)}(\xi^{(i)}) = E_{\lambda_i} \Phi_{\lambda_i}^{(i)}(\xi^{(i)}). \quad (24)$$

Because of the property of the Hamiltonian operator to commute with the symmetry operations of the group in question, see Yurchenko (2023), such as $\mathcal{T}_d(\mathbf{M})$, all eigenvectors of equation (24) are expected to transform according to some irreducible representations $\Gamma \in \mathcal{T}_d(\mathbf{M})$. TROVE uses standard irreducible representation techniques together with a symmetry sampling method (Yurchenko, Yachmenev & Ovsyannikov 2017) to classify these eigenfunctions according to the group symmetry.

The three sets of eigenfunctions $\Phi_{\lambda_1}^{(i)}(\xi_1, \xi_2, \xi_3, \xi_4)$, $\Phi_{\lambda_2}^{(ii)}(\xi_5, \xi_6)$ and $\Phi_{\lambda_3}^{(iii)}(\xi_7, \xi_8, \xi_9)$ resulting from these solutions were symmetrized and assigned local mode quantum numbers (i) v_1, v_2, v_3, v_4 , (ii) v_5, v_6 , and (iii) v_7, v_8, v_9 and vibrational symmetry Γ_{vib} . The final 9D vibrational basis functions $\Phi_{\lambda_1, \lambda_2, \lambda_3}^{\Gamma_a}$ were then formed as symmetry adapted combinations of products $\Phi_{\lambda_1}^{(1)}$, $\Phi_{\lambda_2}^{(2)}$, and $\Phi_{\lambda_3}^{(3)}$,

$$\Phi_{\lambda_1, \lambda_2, \lambda_3}^{\Gamma_a} = \left\{ \Phi_{\lambda_1}^{(1)} \times \Phi_{\lambda_2}^{(2)} \times \Phi_{\lambda_3}^{(3)} \right\}^{\Gamma_a},$$

where Γ_a is an irreducible representation of $\mathcal{T}_d(\mathbf{M})$,

$$\Gamma_a = \{A_1, A_2, E_a, E_b, F_{1x}, F_{1y}, F_{1z}, F_{2x}, F_{2y}, F_{2z}\}.$$

The pure vibrational ($J = 0$) 9D Schrödinger equations were solved on this contracted symmetry adapted basis set Φ_{λ}^{Γ}

$$\hat{H} \Phi_{\lambda}^{J=0, \Gamma} = E_{\lambda}^{J=0, \Gamma} \Phi_{\lambda}^{J=0, \Gamma}.$$

At step 3, the $J = 0$ eigenfunctions $\Phi_{\lambda}^{J=0, \Gamma}$ were turned into a vibrational basis set. To this end, all vibrational matrix elements of

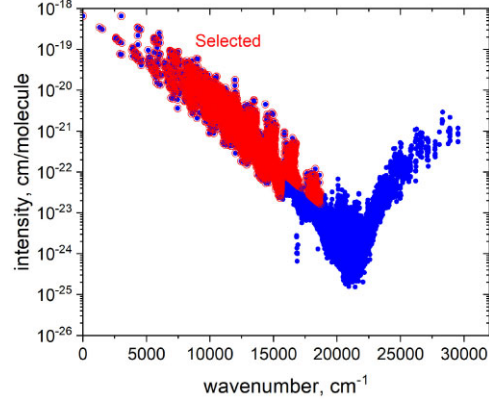


Figure 2. Intensity pruning: Blue filled circles are pure vibrational intensities (cm per molecule) at $T = 3000$ K as a function of the upper state energy term values. Red open circles indicate states selected for the final vibrational basis set in ro-vibrational calculations.

the Hamiltonian as well as of the DMSs, originally computed in the primitive basis set, were transformed to the $J = 0$ representation. In order to reduce the otherwise impractically large $J = 0$ basis set even more, it is further truncated using the intensity basis set pruning (IBSP) introduced by Owens et al. (2017); see also Mant et al. (2018) who it applied it to C_2H_4 calculations. The idea of IBSP is to remove specific vibrational functions of states with only a marginal contribution to the absorption opacity (smaller than some intensity threshold I_{max}).

The vibrational absorption band intensities were computed between all $J = 0$ states of CH_4 . These intensities (cm per molecule) are shown in Fig. 2, where we used a high $T = 3000$ K as a reference value describing highest excitation. The intensities at $\tilde{E} > 22000$ cm^{-1} appear to grow in a nonphysical manner, indicating some numerical issues in the TROVE calculations for very high excitations. Before this effect kicks in, the intensities of the high overtone transitions reduce exponentially by four orders of magnitude down to 10^{-22} cm per molecule at $T = 3000$ K. The corresponding upper energies above some wavenumber threshold (chosen to be hc 18700 cm^{-1}) are therefore omitted from the final vibrational basis set as not very significant spectroscopically.

We also removed certain states with weaker band intensities above hc 15600 cm^{-1} shown in Fig. 2, using an empirical threshold of $I_{\text{vib}} < 1.2 \times 10^{-18} \exp(-0.0006 \cdot \tilde{E}'/\text{cm})$, where the coefficients were selected to reduce the basis set to a manageable size for the high-performance computing facilities available to us (see below). The final pruned vibrational ($J = 0$) basis set consisted of 28758 functions: 1336 of A_1 , 1025 of A_2 , 2439×2 of E , 3419×3 of F_1 , and 3754×3 of F_2 symmetry.

At step 4, the $J = 0$ eigenfunctions were used to construct the ro-vibrational basis functions,

$$\Phi_{i_{\text{vib}}, n}^{J, \Gamma} = \left\{ \Phi_{i_{\text{vib}}}^{(J=0), \Gamma_{\text{vib}}} \times |J, \Gamma_{\text{rot}}, n\rangle \right\}^{\Gamma}, \quad (25)$$

to solve the ro-vibrational eigen-problem for $J \geq 0$, in the so-called $J = 0$ representation. In equation (25), Γ , Γ_{vib} , and Γ_{rot} are the total, vibrational, and rotational symmetries in $\mathcal{T}_d(\mathbf{M})$, respectively, i_{vib} is a TROVE vibrational index to count the $\Phi_{i_{\text{vib}}}^{J=0, \Gamma_{\text{vib}}}$ functions regardless of their symmetry, n is a rotational counting number, see Section 4.3. For further details of the TROVE symmetry-adaptation and contraction procedure, see Yurchenko, Yachmenev & Ovsyannikov (2017).

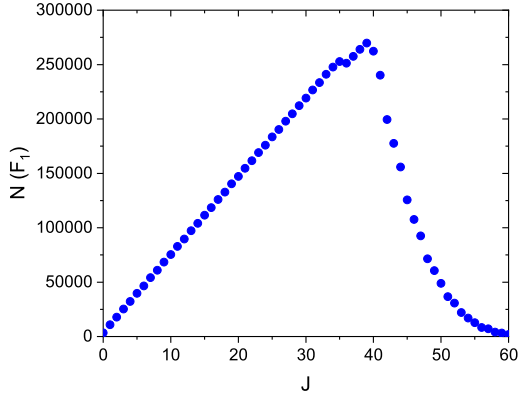


Figure 3. The dimension of the F_1 Hamiltonian matrices as a function of J .

The ro-vibrational basis, and hence the corresponding Hamiltonian matrices, were further pruned by applying an energy threshold as follows:

$$\tilde{E}_{v,J}^{\text{approx}} = \tilde{E}_v^{(J=0),\Gamma_{\text{vib}}} + \tilde{E}_n^{(v=0),\Gamma_{\text{rot}}} < 25\,000 \text{ cm}^{-1},$$

where $\tilde{E}_v^{(J=0),\Gamma_{\text{vib}}}$ is a $J = 0$ eigenvalue and

$$\tilde{E}_n^{(v=0),\Gamma_{\text{rot}}} = BJ(J+1)$$

is a rigid rotor energy estimate. The sizes of the matrices $N_{F_1}(J)$ for $\Gamma = F_1$ as a function of J are illustrated in Fig. 3. The dimensions of the other matrices are approximately related to $N_{F_1}(J)$ as

$$N_{F_1}(J) \approx N_{F_2}(J) \approx 3N_{A_1}(J) \approx 3N_{A_2}(J) \approx \frac{3}{2}N_E(J).$$

In $\mathcal{T}_d(\text{M})$, the ro-vibrational basis set consists of ten irreducible representations $A_1, A_2, E_a, E_b, F_{1x}, F_{1y}, F_{1z}, F_{2x}, F_{2y}, F_{2z}$, where only A_1, A_2, E_a, F_{1x} , and F_{2x} need to be processed to provide unique solutions. For each J , five ro-vibrational Hamiltonian matrices were constructed and diagonalized using the eigensolver DSYEV from LAPACK (Anderson et al. 1999) as implemented in Intel’s MKL libraries.

4.3 Rotational basis set and symmetrization

The rotational basis $|J, \Gamma_{\text{rot}}, n\rangle$ used for the spherical top CH₄ in equation (25) are not the standard Wang combinations. The latter cannot form symmetry adapted combinations that transform irreducibly according to $\mathcal{T}_d(\text{M})$. This is because some of the equivalent rotations of the group cannot be related to the standard rotational operations associated with the molecular frame axes R_x, R_y , or R_z . This is discussed in detail by Bunker & Jensen (1998), Alvarez-Bajo et al. (2011), and Yurchenko (2023).

In this work, the irreducible representations Γ were defined using the standard irreducible technique, see e.g. Bunker & Jensen (1998), where the reducible representations are constructed by applying the equivalent rotations $R(\alpha, \beta, \gamma)$ of $\mathcal{T}_d(\text{M})$ to the rigid rotor wavefunctions $|J, k, m\rangle$ as given by

$$R(\alpha, \beta, \gamma)|J, k, m\rangle = \sum_{k'=-J}^J D_{k',k}^{(J)*}(\alpha, \beta, \gamma)|J, k', m\rangle. \quad (26)$$

Here, α, β , and γ are the Euler angles, k and m are the projections of the rotational angular momentum on the molecular fixed z and laboratory fixed Z axes, respectively, and $D_{k',k}^{(J)*}(\alpha, \beta, \gamma)$ are the Wigner D functions. The angles of the equivalent rotation operations

$R(\alpha, \beta, \gamma)$ of $\mathcal{T}_d(\text{M})$ were taken from Alvarez-Bajo et al. (2011), see their table 4.

The symmetry adapted rotational basis functions were then constructed as linear combinations of $|J, k, m\rangle$ involving a range of k values

$$|J, \Gamma_{\text{rot}}, n\rangle = \sum_{k=-J}^J T_{n,k}^{(J,\Gamma_{\text{rot}})}|J, k, m\rangle, \quad (27)$$

where n is simply a counting number for a given J and Γ_{rot} and the rotational quantum number k can no longer be used for classification as a rotational label and m is omitted in the left hand side. The procedure has been established by Yurchenko, Yachmenev & Ovsyannikov (2017) and given in detail by Yurchenko (2023).

4.4 Vibrational band centre correction

The $J = 0$ contraction scheme allows one to introduce an additional, post-fitting systematic correction to the vibrational energies (‘band centres’) following the empirical basis set correction (EBSC) approach from Yurchenko et al. (2009). This is done by replacing the diagonal matrix elements of the vibrational Hamiltonian operator \hat{H}_{vib} with the empirically-derived values for the vibrational energies $\tilde{E}_v^{(J=0),\Gamma_{\text{vib}}}$, where available. Indeed, \hat{H}_{vib} is diagonal on the $J = 0$ basis set and such a simple empirical shift is propagated to all the ro-vibrational Hamiltonian matrices with $J > 0$ and hence to the corresponding ro-vibrational energy levels obtained.

Empirical corrections were applied to 198 $J = 0$ energy levels as the best averaged estimate relative to the MARVEL energies below $J = 8$. The typical shifts were within 0.1 cm^{-1} , with the largest being 0.78 cm^{-1} and the rms difference being 0.48 cm^{-1} . The full set of calculated $J = 0$ energies with the empirical corrections is provided as supplementary material.

5 THE MM LINE LIST

The ro-vibrational Einstein A coefficients of CH₄ were computed with TROVE using the ro-vibrational eigen-functions and *ab initio* electric DMS for all transitions between 0 and $12\,000 \text{ cm}^{-1}$, covering states up to $J = 60$, lower state energies below $hc \times 12\,000 \text{ cm}^{-1}$, and upper state energies below $hc \times 18\,000 \text{ cm}^{-1}$. The Einstein A coefficients and energy levels form the new line list for CH₄, called MM (MARVELous Methane), comprising of 50 395 644 806 lines and covering 9155 208 ro-vibrational states. The ExoMol line list format assumes a States file (.states), containing the state ID, energy term values (cm^{-1}), total state degeneracies, state uncertainties, lifetimes, quantum numbers, and labels etc, and Transition files (.trans), containing the upper/lower state IDs and Einstein coefficients (s^{-1}). The MM transitions are sorted and divided into 1200 files in 100 cm^{-1} windows. Extracts from the States and Transition files are given in Tables 1 and 2, respectively.

5.1 Quantum numbers and labels

In order to help future users of our data, a variety of methane quantum numbers and labels are provided as part of the MM States file, see Table 1. Most importantly, the ro-vibrational states of CH₄ are classified by the rigorous quantum numbers: the total angular momentum J and the total symmetry Γ_{tot} , either A_1, A_2, E, F_1 , or F_2 in the molecular symmetry group $\mathcal{T}_d(\text{M})$ (Bunker & Jensen 2004). As non-rigorous quantum numbers, we provide ‘experimental’ (MARVEL),

Table 1. Extract from the .states file of the CH₄ MM line list.

<i>i</i>	\tilde{E} (cm ⁻¹)	<i>g_i</i>	<i>J</i>	unc	$\bar{\tau}$	Γ_{tot}	<i>P</i>	<i>n</i>	<i>n</i> ₁	<i>n</i> ₂	<i>n</i> ₃	<i>n</i> ₄	<i>n</i> ₅	<i>n</i> ₆	<i>n</i> ₇	<i>n</i> ₈	<i>n</i> ₉	<i>n</i> ₁₀	<i>n</i> ₁₁	<i>n</i> ₁₂	<i>n</i> ₁₃	<i>n</i> ₁₄	<i>n</i> ₁₅	<i>n</i> ₁₆	<i>n</i> ₁₇	<i>n</i> ₁₈	<i>n</i> ₁₉	<i>n</i> ₂₀	<i>n</i> ₂₁	<i>n</i> ₂₂	<i>n</i> ₂₃	<i>n</i> ₂₄	<i>n</i> ₂₅	<i>n</i> ₂₆	<i>n</i> ₂₇	<i>n</i> ₂₈	<i>n</i> ₂₉	<i>n</i> ₃₀	<i>n</i> ₃₁	<i>n</i> ₃₂	<i>n</i> ₃₃	<i>n</i> ₃₄	<i>n</i> ₃₅	<i>n</i> ₃₆	<i>n</i> ₃₇	<i>n</i> ₃₈	<i>n</i> ₃₉	<i>n</i> ₄₀	<i>n</i> ₄₁	<i>n</i> ₄₂	<i>n</i> ₄₃	<i>n</i> ₄₄	<i>n</i> ₄₅	<i>n</i> ₄₆	<i>n</i> ₄₇	<i>n</i> ₄₈	<i>n</i> ₄₉	<i>n</i> ₅₀	<i>n</i> ₅₁	<i>n</i> ₅₂	<i>n</i> ₅₃	<i>n</i> ₅₄	<i>n</i> ₅₅	<i>n</i> ₅₆	<i>n</i> ₅₇	<i>n</i> ₅₈	<i>n</i> ₅₉	<i>n</i> ₆₀	<i>n</i> ₆₁	<i>n</i> ₆₂	<i>n</i> ₆₃	<i>n</i> ₆₄	<i>n</i> ₆₅	<i>n</i> ₆₆	<i>n</i> ₆₇	<i>n</i> ₆₈	<i>n</i> ₆₉	<i>n</i> ₇₀	<i>n</i> ₇₁	<i>n</i> ₇₂	<i>n</i> ₇₃	<i>n</i> ₇₄	<i>n</i> ₇₅	<i>n</i> ₇₆	<i>n</i> ₇₇	<i>n</i> ₇₈	<i>n</i> ₇₉	<i>n</i> ₈₀	<i>n</i> ₈₁	<i>n</i> ₈₂	<i>n</i> ₈₃	<i>n</i> ₈₄	<i>n</i> ₈₅	<i>n</i> ₈₆	<i>n</i> ₈₇	<i>n</i> ₈₈	<i>n</i> ₈₉	<i>n</i> ₉₀	<i>n</i> ₉₁	<i>n</i> ₉₂	<i>n</i> ₉₃	<i>n</i> ₉₄	<i>n</i> ₉₅	<i>n</i> ₉₆	<i>n</i> ₉₇	<i>n</i> ₉₈	<i>n</i> ₉₉	<i>n</i> ₁₀₀	<i>n</i> ₁₀₁	<i>n</i> ₁₀₂	<i>n</i> ₁₀₃	<i>n</i> ₁₀₄	<i>n</i> ₁₀₅	<i>n</i> ₁₀₆	<i>n</i> ₁₀₇	<i>n</i> ₁₀₈	<i>n</i> ₁₀₉	<i>n</i> ₁₁₀	<i>n</i> ₁₁₁	<i>n</i> ₁₁₂	<i>n</i> ₁₁₃	<i>n</i> ₁₁₄	<i>n</i> ₁₁₅	<i>n</i> ₁₁₆	<i>n</i> ₁₁₇	<i>n</i> ₁₁₈	<i>n</i> ₁₁₉	<i>n</i> ₁₂₀	<i>n</i> ₁₂₁	<i>n</i> ₁₂₂	<i>n</i> ₁₂₃	<i>n</i> ₁₂₄	<i>n</i> ₁₂₅	<i>n</i> ₁₂₆	<i>n</i> ₁₂₇	<i>n</i> ₁₂₈	<i>n</i> ₁₂₉	<i>n</i> ₁₃₀	<i>n</i> ₁₃₁	<i>n</i> ₁₃₂	<i>n</i> ₁₃₃	<i>n</i> ₁₃₄	<i>n</i> ₁₃₅	<i>n</i> ₁₃₆	<i>n</i> ₁₃₇	<i>n</i> ₁₃₈	<i>n</i> ₁₃₉	<i>n</i> ₁₄₀	<i>n</i> ₁₄₁	<i>n</i> ₁₄₂	<i>n</i> ₁₄₃	<i>n</i> ₁₄₄	<i>n</i> ₁₄₅	<i>n</i> ₁₄₆	<i>n</i> ₁₄₇	<i>n</i> ₁₄₈	<i>n</i> ₁₄₉	<i>n</i> ₁₅₀	<i>n</i> ₁₅₁	<i>n</i> ₁₅₂	<i>n</i> ₁₅₃	<i>n</i> ₁₅₄	<i>n</i> ₁₅₅	<i>n</i> ₁₅₆	<i>n</i> ₁₅₇	<i>n</i> ₁₅₈	<i>n</i> ₁₅₉	<i>n</i> ₁₆₀	<i>n</i> ₁₆₁	<i>n</i> ₁₆₂	<i>n</i> ₁₆₃	<i>n</i> ₁₆₄	<i>n</i> ₁₆₅	<i>n</i> ₁₆₆	<i>n</i> ₁₆₇	<i>n</i> ₁₆₈	<i>n</i> ₁₆₉	<i>n</i> ₁₇₀	<i>n</i> ₁₇₁	<i>n</i> ₁₇₂	<i>n</i> ₁₇₃	<i>n</i> ₁₇₄	<i>n</i> ₁₇₅	<i>n</i> ₁₇₆	<i>n</i> ₁₇₇	<i>n</i> ₁₇₈	<i>n</i> ₁₇₉	<i>n</i> ₁₈₀	<i>n</i> ₁₈₁	<i>n</i> ₁₈₂	<i>n</i> ₁₈₃	<i>n</i> ₁₈₄	<i>n</i> ₁₈₅	<i>n</i> ₁₈₆	<i>n</i> ₁₈₇	<i>n</i> ₁₈₈	<i>n</i> ₁₈₉	<i>n</i> ₁₉₀	<i>n</i> ₁₉₁	<i>n</i> ₁₉₂	<i>n</i> ₁₉₃	<i>n</i> ₁₉₄	<i>n</i> ₁₉₅	<i>n</i> ₁₉₆	<i>n</i> ₁₉₇	<i>n</i> ₁₉₈	<i>n</i> ₁₉₉	<i>n</i> ₂₀₀	<i>n</i> ₂₀₁	<i>n</i> ₂₀₂	<i>n</i> ₂₀₃	<i>n</i> ₂₀₄	<i>n</i> ₂₀₅	<i>n</i> ₂₀₆	<i>n</i> ₂₀₇	<i>n</i> ₂₀₈	<i>n</i> ₂₀₉	<i>n</i> ₂₁₀	<i>n</i> ₂₁₁	<i>n</i> ₂₁₂	<i>n</i> ₂₁₃	<i>n</i> ₂₁₄	<i>n</i> ₂₁₅	<i>n</i> ₂₁₆	<i>n</i> ₂₁₇	<i>n</i> ₂₁₈	<i>n</i> ₂₁₉	<i>n</i> ₂₂₀	<i>n</i> ₂₂₁	<i>n</i> ₂₂₂	<i>n</i> ₂₂₃	<i>n</i> ₂₂₄	<i>n</i> ₂₂₅	<i>n</i> ₂₂₆	<i>n</i> ₂₂₇	<i>n</i> ₂₂₈	<i>n</i> ₂₂₉	<i>n</i> ₂₃₀	<i>n</i> ₂₃₁	<i>n</i> ₂₃₂	<i>n</i> ₂₃₃	<i>n</i> ₂₃₄	<i>n</i> ₂₃₅	<i>n</i> ₂₃₆	<i>n</i> ₂₃₇	<i>n</i> ₂₃₈	<i>n</i> ₂₃₉	<i>n</i> ₂₄₀	<i>n</i> ₂₄₁	<i>n</i> ₂₄₂	<i>n</i> ₂₄₃	<i>n</i> ₂₄₄	<i>n</i> ₂₄₅	<i>n</i> ₂₄₆	<i>n</i> ₂₄₇	<i>n</i> ₂₄₈	<i>n</i> ₂₄₉	<i>n</i> ₂₅₀	<i>n</i> ₂₅₁	<i>n</i> ₂₅₂	<i>n</i> ₂₅₃	<i>n</i> ₂₅₄	<i>n</i> ₂₅₅	<i>n</i> ₂₅₆	<i>n</i> ₂₅₇	<i>n</i> ₂₅₈	<i>n</i> ₂₅₉	<i>n</i> ₂₆₀	<i>n</i> ₂₆₁	<i>n</i> ₂₆₂	<i>n</i> ₂₆₃	<i>n</i> ₂₆₄	<i>n</i> ₂₆₅	<i>n</i> ₂₆₆	<i>n</i> ₂₆₇	<i>n</i> ₂₆₈	<i>n</i> ₂₆₉	<i>n</i> ₂₇₀	<i>n</i> ₂₇₁	<i>n</i> ₂₇₂	<i>n</i> ₂₇₃	<i>n</i> ₂₇₄	<i>n</i> ₂₇₅	<i>n</i> ₂₇₆	<i>n</i> ₂₇₇	<i>n</i> ₂₇₈	<i>n</i> ₂₇₉	<i>n</i> ₂₈₀	<i>n</i> ₂₈₁	<i>n</i> ₂₈₂	<i>n</i> ₂₈₃	<i>n</i> ₂₈₄	<i>n</i> ₂₈₅	<i>n</i> ₂₈₆	<i>n</i> ₂₈₇	<i>n</i> ₂₈₈	<i>n</i> ₂₈₉	<i>n</i> ₂₉₀	<i>n</i> ₂₉₁	<i>n</i> ₂₉₂	<i>n</i> ₂₉₃	<i>n</i> ₂₉₄	<i>n</i> ₂₉₅	<i>n</i> ₂₉₆	<i>n</i> ₂₉₇	<i>n</i> ₂₉₈	<i>n</i> ₂₉₉	<i>n</i> ₃₀₀	<i>n</i> ₃₀₁	<i>n</i> ₃₀₂	<i>n</i> ₃₀₃	<i>n</i> ₃₀₄	<i>n</i> ₃₀₅	<i>n</i> ₃₀₆	<i>n</i> ₃₀₇	<i>n</i> ₃₀₈	<i>n</i> ₃₀₉	<i>n</i> ₃₁₀	<i>n</i> ₃₁₁	<i>n</i> ₃₁₂	<i>n</i> ₃₁₃	<i>n</i> ₃₁₄	<i>n</i> ₃₁₅	<i>n</i> ₃₁₆	<i>n</i> ₃₁₇	<i>n</i> ₃₁₈	<i>n</i> ₃₁₉	<i>n</i> ₃₂₀	<i>n</i> ₃₂₁	<i>n</i> ₃₂₂	<i>n</i> ₃₂₃	<i>n</i> ₃₂₄	<i>n</i> ₃₂₅	<i>n</i> ₃₂₆	<i>n</i> ₃₂₇	<i>n</i> ₃₂₈	<i>n</i> ₃₂₉	<i>n</i> ₃₃₀	<i>n</i> ₃₃₁	<i>n</i> ₃₃₂	<i>n</i> ₃₃₃	<i>n</i> ₃₃₄	<i>n</i> ₃₃₅	<i>n</i> ₃₃₆	<i>n</i> ₃₃₇	<i>n</i> ₃₃₈	<i>n</i> ₃₃₉	<i>n</i> ₃₄₀	<i>n</i> ₃₄₁	<i>n</i> ₃₄₂	<i>n</i> ₃₄₃	<i>n</i> ₃₄₄	<i>n</i> ₃₄₅	<i>n</i> ₃₄₆	<i>n</i> ₃₄₇	<i>n</i> ₃₄₈	<i>n</i> ₃₄₉	<i>n</i> ₃₅₀	<i>n</i> ₃₅₁	<i>n</i> ₃₅₂	<i>n</i> ₃₅₃	<i>n</i> ₃₅₄	<i>n</i> ₃₅₅	<i>n</i> ₃₅₆	<i>n</i> ₃₅₇	<i>n</i> ₃₅₈	<i>n</i> ₃₅₉	<i>n</i> ₃₆₀	<i>n</i> ₃₆₁	<i>n</i> ₃₆₂	<i>n</i> ₃₆₃	<i>n</i> ₃₆₄	<i>n</i> ₃₆₅	<i>n</i> ₃₆₆	<i>n</i> ₃₆₇	<i>n</i> ₃₆₈	<i>n</i> ₃₆₉	<i>n</i> ₃₇₀	<i>n</i> ₃₇₁	<i>n</i> ₃₇₂	<i>n</i> ₃₇₃	<i>n</i> ₃₇₄	<i>n</i> ₃₇₅	<i>n</i> ₃₇₆	<i>n</i> ₃₇₇	<i>n</i> ₃₇₈	<i>n</i> ₃₇₉	<i>n</i> ₃₈₀	<i>n</i> ₃₈₁	<i>n</i> ₃₈₂	<i>n</i> ₃₈₃	<i>n</i> ₃₈₄	<i>n</i> ₃₈₅	<i>n</i> ₃₈₆	<i>n</i> ₃₈₇	<i>n</i> ₃₈₈	<i>n</i> ₃₈₉	<i>n</i> ₃₉₀	<i>n</i> ₃₉₁	<i>n</i> ₃₉₂	<i>n</i> ₃₉₃	<i>n</i> ₃₉₄	<i>n</i> ₃₉₅	<i>n</i> ₃₉₆	<i>n</i> ₃₉₇	<i>n</i> ₃₉₈	<i>n</i> ₃₉₉	<i>n</i> ₄₀₀	<i>n</i> ₄₀₁	<i>n</i> ₄₀₂	<i>n</i> ₄₀₃	<i>n</i> ₄₀₄	<i>n</i> ₄₀₅	<i>n</i> ₄₀₆	<i>n</i> ₄₀₇	<i>n</i> ₄₀₈	<i>n</i> ₄₀₉	<i>n</i> ₄₁₀	<i>n</i> ₄₁₁	<i>n</i> ₄₁₂	<i>n</i> ₄₁₃	<i>n</i> ₄₁₄	<i>n</i> ₄₁₅	<i>n</i> ₄₁₆	<i>n</i> ₄₁₇	<i>n</i> ₄₁₈	<i>n</i> ₄₁₉	<i>n</i> ₄₂₀	<i>n</i> ₄₂₁	<i>n</i> ₄₂₂	<i>n</i> ₄₂₃	<i>n</i> ₄₂₄	<i>n</i> ₄₂₅	<i>n</i> ₄₂₆	<i>n</i> ₄₂₇	<i>n</i> ₄₂₈	<i>n</i> ₄₂₉	<i>n</i> ₄₃₀	<i>n</i> ₄₃₁	<i>n</i> ₄₃₂	<i>n</i> ₄₃₃	<i>n</i> ₄₃₄	<i>n</i> ₄₃₅	<i>n</i> ₄₃₆	<i>n</i> ₄₃₇	<i>n</i> ₄₃₈	<i>n</i> ₄₃₉	<i>n</i> ₄₄₀	<i>n</i> ₄₄₁	<i>n</i> ₄₄₂	<i>n</i> ₄₄₃	<i>n</i> ₄₄₄	<i>n</i> ₄₄₅	<i>n</i> ₄₄₆	<i>n</i> ₄₄₇	<i>n</i> ₄₄₈	<i>n</i> ₄₄₉	<i>n</i> ₄₅₀	<i>n</i> ₄₅₁	<i>n</i> ₄₅₂	<i>n</i> ₄₅₃	<i>n</i> ₄₅₄	<i>n</i> ₄₅₅	<i>n</i> ₄₅₆	<i>n</i> ₄₅₇	<i>n</i> ₄₅₈	<i>n</i> ₄₅₉	<i>n</i> ₄₆₀	<i>n</i> ₄₆₁	<i>n</i> ₄₆₂	<i>n</i> ₄₆₃	<i>n</i> ₄₆₄	<i>n</i> ₄₆₅	<i>n</i> ₄₆₆	<i>n</i> ₄₆₇	<i>n</i> ₄₆₈	<i>n</i> ₄₆₉	<i>n</i> ₄₇₀	<i>n</i> ₄₇₁	<i>n</i> ₄₇₂	<i>n</i> ₄₇₃	<i>n</i> ₄₇₄	<i>n</i> ₄₇₅	<i>n</i> ₄₇₆	<i>n</i> ₄₇₇	<i>n</i> ₄₇₈	<i>n</i> ₄₇₉	<i>n</i> ₄₈₀	<i>n</i> ₄₈₁	<i>n</i> ₄₈₂	<i>n</i> ₄₈₃	<i>n</i> ₄₈₄	<i>n</i> ₄₈₅	<i>n</i> ₄₈₆	<i>n</i> ₄₈₇	<i>n</i> ₄₈₈	<i>n</i> ₄₈₉	<i>n</i> ₄₉₀	<i>n</i> ₄₉₁	<i>n</i> ₄₉₂	<i>n</i> ₄₉₃	<i>n</i> ₄₉₄	<i>n</i> ₄₉₅	<i>n</i> ₄₉₆	<i>n</i> ₄₉₇	<i>n</i> ₄₉₈	<i>n</i> ₄₉₉	<i>n</i> ₅₀₀	<i>n</i> ₅₀₁	<i>n</i> ₅₀₂	<i>n</i> ₅₀₃	<i>n</i> ₅₀₄	<i>n</i> ₅₀₅	<i>n</i> ₅₀₆	<i>n</i> ₅₀₇	<i>n</i> ₅₀₈	<i>n</i> ₅₀₉	<i>n</i> ₅₁₀	<i>n</i> ₅₁₁	<i>n</i> ₅₁₂	<i>n</i> ₅₁₃	<i>n</i> ₅₁₄	<i>n</i> ₅₁₅	<i>n</i> ₅₁₆	<i>n</i> ₅₁₇	<i>n</i> ₅₁₈	<i>n</i> ₅₁₉	<i>n</i> ₅₂₀	<i>n</i> ₅₂₁	<i>n</i> ₅₂₂	<i>n</i> ₅₂₃	<i>n</i> ₅₂₄	<i>n</i> ₅₂₅	<i>n</i> ₅₂₆	<i>n</i> ₅₂₇	<i>n</i> ₅₂₈	<i>n</i> ₅₂₉	<i>n</i> ₅₃₀	<i>n</i> ₅₃₁	<i>n</i> ₅₃₂	<i>n</i> ₅₃₃	<i>n</i> ₅₃₄	<i>n</i> ₅₃₅	<i>n</i> ₅₃₆	<i>n</i> ₅₃₇	<i>n</i> ₅₃₈	<i>n</i> ₅₃₉	<i>n</i> ₅₄₀	<i>n</i> ₅₄₁	<i>n</i> ₅₄₂	<i>n</i> ₅₄₃	<i>n</i> ₅₄₄	<i>n</i> ₅₄₅	<i>n</i> ₅₄₆	<i>n</i> ₅₄₇	<i>n</i> ₅₄₈	<i>n</i> ₅₄₉	<i>n</i> ₅₅₀	<i>n</i> ₅₅₁	<i>n</i> ₅₅₂	<i>n</i> ₅₅₃	<i>n</i> ₅₅₄	<i>n</i> ₅₅₅	<i>n</i> ₅₅₆	<i>n</i> ₅₅₇	<i>n</i> ₅₅₈	<i>n</i> ₅₅₉	<i>n</i> ₅₆₀	<i>n</i> ₅₆₁	<i>n</i> ₅₆₂	<i>n</i> ₅₆₃	<i>n</i> ₅₆₄	<i>n</i> ₅₆₅	<i>n</i> ₅₆₆	<i>n</i> ₅₆₇	<i>n</i> ₅₆₈	<i>n</i> ₅₆₉	<i>n</i> ₅₇₀	<i>n</i> ₅₇₁	<i>n</i> ₅₇₂	<i>n</i> ₅₇₃	<i>n</i> ₅₇₄	<i>n</i> ₅₇₅	<i>n</i> ₅₇₆	<i>n</i> ₅₇₇	<i>n</i> ₅₇₈	<i>n</i> ₅₇₉	<i>n</i> ₅₈₀	<i>n</i> ₅₈₁	<i>n</i> ₅₈₂	<i>n</i> ₅₈₃	<i>n</i> ₅₈₄	<i>n</i> ₅₈₅	<i>n</i> ₅₈₆	<i>n</i> ₅₈₇	<i>n</i> ₅₈₈	<i>n</i> ₅₈₉	<i>n</i> ₅₉₀	<i>n</i> ₅₉₁	<i>n</i> ₅₉₂	<i>n</i> ₅₉₃	<i>n</i> ₅₉₄	<i>n</i> ₅₉₅	<i>n</i> ₅₉₆	<i>n</i> ₅₉₇	<i>n</i> ₅₉₈	<i>n</i> ₅₉₉	<i>n</i> ₆₀₀	<i>n</i> ₆₀₁	<i>n</i> ₆₀₂	<i>n</i> ₆₀₃	<i>n</i> ₆₀₄	<i>n</i> ₆₀₅	<i>n</i> ₆₀₆	<i>n</i> ₆₀₇	<i>n</i> ₆₀₈	<i>n</i> ₆₀₉	<i>n</i> ₆₁₀	<i>n</i> ₆₁₁	<i>n</i> ₆₁₂	<i>n</i> ₆₁₃	<i>n</i> ₆₁₄	<i>n</i> ₆₁₅	<i>n</i> ₆₁₆	<i>n</i> ₆₁₇	<i>n</i> ₆₁₈	<i>n</i> ₆₁₉	<i>n</i> ₆₂₀	<i>n</i> ₆₂₁	<i>n</i> ₆₂₂	<i>n</i> ₆₂₃	<i>n</i> ₆₂₄	<i>n</i> ₆₂₅	<i>n</i> ₆₂₆	<i>n</i> ₆₂₇	<i>n</i> ₆₂₈	<i>n</i> ₆₂₉	<i>n</i> ₆₃₀	<i>n</i> ₆₃₁	<i>n</i> ₆₃₂	<i>n</i> ₆₃₃	<i>n</i> ₆₃₄	<i>n</i> ₆₃₅	<i>n</i> ₆₃₆	<i>n</i> ₆₃₇	<i>n</i> ₆₃₈	<i>n</i> ₆₃₉	<i>n</i> ₆₄₀	<i>n</i> ₆₄₁	<i>n</i> ₆₄₂	<i>n</i> ₆₄₃	<i>n</i> ₆₄₄	<i>n</i> ₆₄₅	<i>n</i> ₆₄₆	<i>n</i> ₆₄₇	<i>n</i> ₆₄₈	<i>n</i> ₆₄₉	<i>n</i> ₆₅₀	<i>n</i> ₆₅₁	<i>n</i> ₆₅₂	<i>n</i> ₆₅₃	<i>n</i> ₆₅₄	<i>n</i> ₆₅₅	<i>n</i> ₆₅₆	<i>n</i> ₆₅₇	<i>n</i> ₆₅₈	<i>n</i> ₆₅₉	<i>n</i> ₆₆₀	<i>n</i> ₆₆₁	<i>n</i> ₆₆₂	<i>n</i> ₆₆₃	<i>n</i> ₆₆₄	<i>n</i> ₆₆₅	<i>n</i> ₆₆₆	<i>n</i> ₆₆₇	<i>n</i> ₆₆₈	<i>n</i> ₆₆₉	<i>n</i> ₆₇₀	<i>n</i> ₆₇₁	<i>n</i> ₆₇₂	<i>n</i> ₆₇₃	<i>n</i> ₆₇₄	<i>n</i> ₆₇₅	<i>n</i> ₆₇₆	<i>n</i> ₆₇₇	<i>n</i> ₆₇₈	<i>n</i> ₆₇₉	<i>n</i> _{680</}
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Table 4. Symmetry classification of the 2D and 3D isotropic harmonic oscillators for the corresponding vibrational angular momentum index L_2 and the multiplicity index M_i ($i = 3, 4, 0 \leq M_i \leq L_i$), respectively.

L_2	Symmetry 2D	M_i	Symmetry 3D
0	A_1	0	A_1
$3n$	A_1, A_2	$12n + 0$	A_1
$3n \pm 1$	E	$12n + 6$	A_2
		$6n \pm 2$	E
		$4n + 3$	F_1
		$4n + 1$	F_2

n is an arbitrary integer, $n = 1, 2, 3, \dots$

$\dots, 0(1)$. $M_i \leq L_i$ is a multiplicity index used to count states within a given n_i, L_i set, see Boudon, Rey & Loëte (2006). The advantage of this scheme is that the angular momentum indices L_i (for the E -type ν_2 mode) and M_i (for the F -type ν_3 and ν_4 modes) provide a one-to-one correspondence to the symmetry of the corresponding component as listed in Table 4. In fact, such a correspondence is common for the 2D E -type symmetry isotropic harmonic oscillators, see e.g. Bunker & Jensen (1998) and Yurchenko et al. (2005), while the 3D isotropic harmonic oscillator quantum numbers (Hougen 2001) are less common.

The normal mode assignment is in fact reconstructed using the local mode quantum numbers. The easiest way to correlate them is at step 2 of the TROVE calculations, when the three reduced eigenvalue problems in equations (21)–(23) are solved. Indeed, the local mode eigensolutions of the 4D Hamiltonian $\hat{H}^{(1)}$ in equation (21) need to match the combinations of stretching 1D and 3D harmonic oscillators only; the eigenvalues of the 2D bending $\hat{H}^{(2)}$ are easily matched to energies of a 2D isotropic harmonic oscillator; and the eigenvalues of the 3D bending reduced problem for $\hat{H}^{(3)}$ are then correlated solutions of a 3D harmonic oscillator. Once the correlation is established, it is propagated through the multistep assignment procedure along with the local mode quantum numbers. Moreover, the unique vibrational state index i_{vib} can also be used to efficiently re-assign the TROVE local mode quantum numbers to any other quantum numbers scheme, which is possible even in the final data set.

The CH₄ experimental quantum number set usually consists of J, Γ_{tot} , polyad number P in equation (19) and a counting number n , counting different states within the same J, Γ_{tot} , and P . It is an extremely simple, and therefore powerful, set for correlating methane spectroscopic data from different sources. It has been adopted by the community as the methane spectroscopic standard and it was used to classify the experimental data in the recent MARVEL work on CH₄ (Kefala et al. 2024). The disadvantage of the experimental quantum number scheme is that it loses any connection with the physics, such as, e.g. vibrational state, which can be required, e.g. when it is important to know if a given state has a bending or stretching nature, whether it belongs to a forbidden or combination band, and so on.

An important aspect of the ExoMol States file is the state degeneracies $g_i = g_{\text{ns}}(2J + 1)$. For ¹²CH₄, considering the H nuclear spin, the nuclear statistical weight, g_{ns} , takes the symmetry-dependent values 5, 5, 2, 3, and 3 for $A_1, A_2, E, F_1,$ and F_2 , respectively.

The electric dipole transitions obey the following symmetry-determined selection rules:

$$A_1 \leftrightarrow A_2, E \leftrightarrow E, F_1 \leftrightarrow F_2 \quad (28)$$

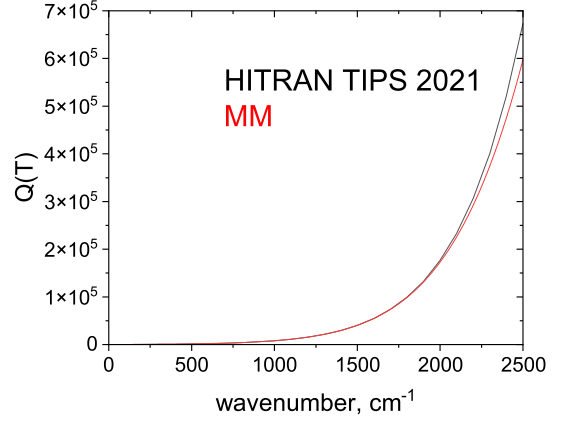


Figure 4. Partition functions of CH₄: HITRAN TIPS 2021 (Gamache et al. 2021) and MM.

with the standard rotational angular momentum, J , selection rules:

$$J \leftrightarrow J \pm 1, J' + J'' \neq 0. \quad (29)$$

5.2 Partition function

A partition function of CH₄ computed using the MM line list is provided as part of the line list package, covering the temperature range from 0 to 2500 K on a grid of 1 K. In Fig. 4, the MM partition function is compared to the HITRAN partition function generated using the TIPS 2021 package (Gamache et al. 2021). The MM partition function closely agrees with TIPS until about $T = 2000$ K, after which it slowly deviates, underestimating the more complete TIPS partition function. Hence, $T = 2000$ K is our estimated upper temperature limit for completeness of the MM line list.

5.3 Opacities

Temperature- and pressure-dependent opacities of CH₄ have been generated using the ExoMolOP procedure (Chubb et al. 2021) for the MM line list. These are provided for four exoplanet atmospheric retrieval codes ARCIS (Min et al. 2020), TauREx (Al-Refaie et al. 2021), NEMESIS (Irwin et al. 2008), and petitRADTRANS (Mollière et al. 2019). For the line broadening, we assumed an 85 percent H₂ and 15 percent He atmosphere and Voigt line profile with the following parameters: $\gamma_{\text{H}_2} = 0.12 \text{ cm}^{-1}$, $n_{\text{H}_2} = 0.5$, $\gamma_{\text{He}} = 0.05 \text{ cm}^{-1}$, and $n_{\text{He}} = 0.5$.

6 SPECTROSCOPIC ILLUSTRATIONS

We use the MM line list to simulate spectra of CH₄ to demonstrate the accuracy of the line positions, the quality of the line intensities, as well as its completeness especially at high temperatures. To this end, we compare simulated spectra either with experimental or theoretical spectra from the literature or other data bases.

We start with a comparison against the HITRAN spectrum of ¹²CH₄ at $T = 296$ K. Figs 5 and 6 provides detailed comparisons of MM and HITRAN ‘stick’ spectra at $T = 296$ K, where absorption coefficients (cm per molecule) are plotted as sticks as functions of the wavenumber covering the region between 2700 and 12000 cm^{-1} . There is very good agreement between MM and HITRAN below 6200 cm^{-1} , where all the lines shown are MARVELized, also nicely illustrating the completeness of the CH₄ MARVEL energies in this

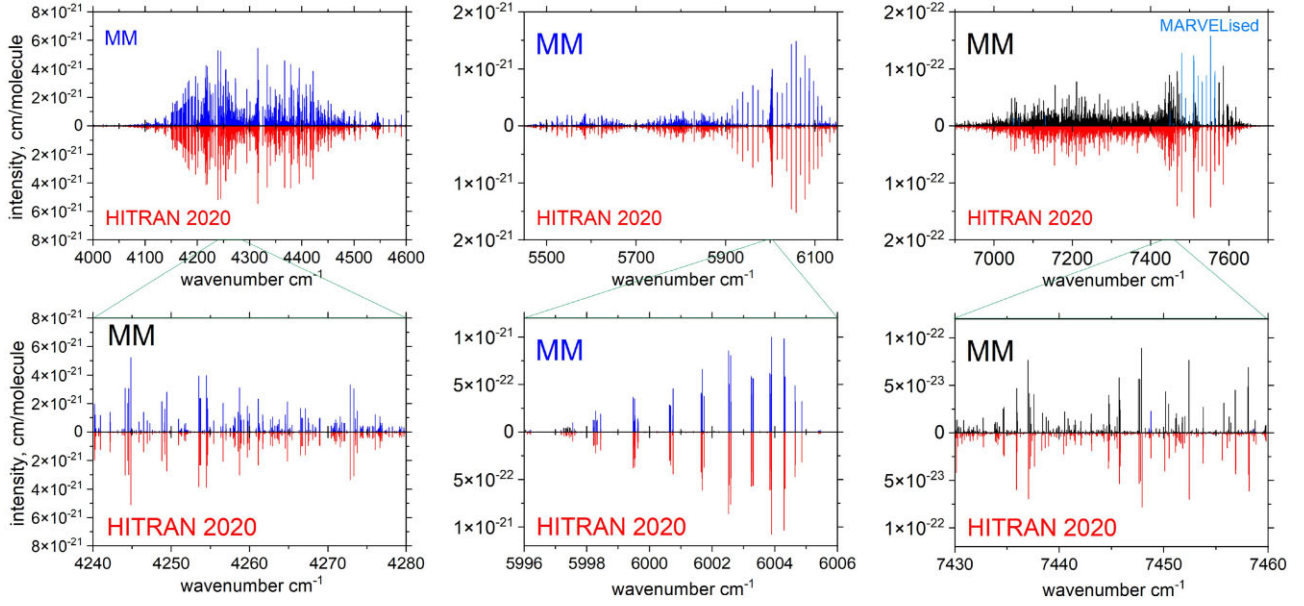


Figure 5. Absorption stick spectra of CH_4 calculated using the MM line list at $T = 296$ K and compared to HITRAN (polyads 3, 4, 5). All blue sticks (light or dark) correspond to MARVELized transitions, while the black sticks correspond to the calculated MM transitions. Insets zoom in in some selected regions.

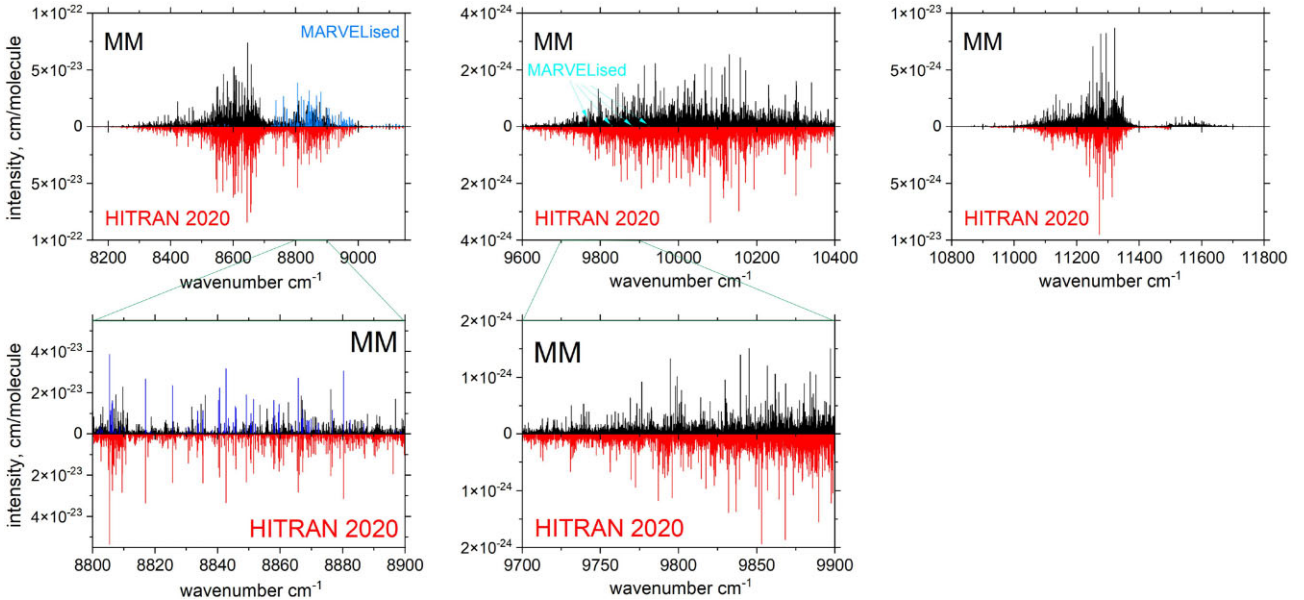


Figure 6. Absorption stick spectra of CH_4 calculated using the MM line list at $T = 296$ K and compared to HITRAN (polyads 6, 7, 8). All blue sticks (light or dark) correspond to MARVELized transitions, while the black sticks correspond to the calculated MM transitions. Insets zoom in in some selected regions.

region. The MM spectrum below 2700 cm^{-1} agrees with HITRAN as well or better. The incompleteness of the CH_4 MARVEL data set, and therefore of the assigned experimental data available in the literature, is evident above 8200 cm^{-1} . The agreement of the MM line positions with HITRAN also deteriorates for polyads six and seven, which again reflects the limited experimental data used in the refinement of our PES. Our intensities, which are based on *ab initio* DMSs, agree reasonably well with the HITRAN data even at very high wavenumbers, which is illustrated in Fig. 7, where we compare the HITRAN and MM line intensities as a ratio $I_{\text{HITRAN}}/I_{\text{calc}}$ averaged over lines within 58 vibrational bands for 204 127 (out of 309 683) lines we could establish the correlation with. The averaging

included all sub-bands corresponding to different symmetries and vibrational angular momentum quantum numbers l_2, l_3, l_4 of each vibrational state $(\nu_1, \nu_2, \nu_3, \nu_4)$. The majority of points are safely within 5 per cent.

Fig. 8 shows the coverage of the MARVELization of MM in more detail. Using 23 292 MARVELized states only, the $T = 296$ K MM spectrum of CH_4 results in 1 371 651 experimental-quality lines. This is much larger than the 82 173 experimentally assigned transitions used to produce the MARVEL energy set. The HITRAN 2020 line list for $^{12}\text{CH}_4$ contains 309 864 lines. Fig. 8 is a great illustration of the MARVEL methodology that leads to over one million transitions of experimental quality. It should be noted, however, that even with

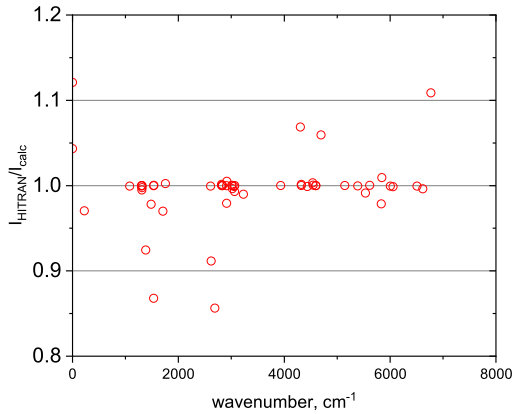


Figure 7. Average intensity ratio $I_{\text{HITRAN}}/I_{\text{calc}}$ between the HITRAN and the MM line intensities with 58 bands.

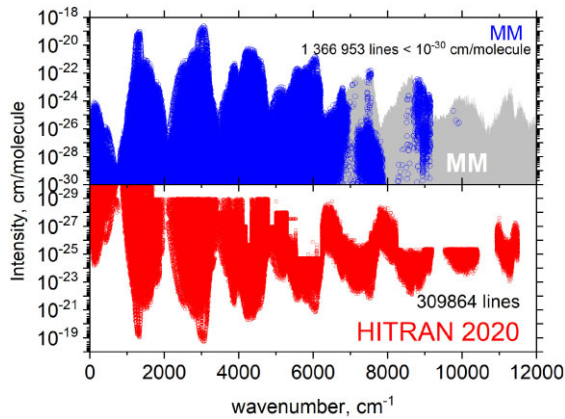


Figure 8. Comparison of the HITRAN (bottom) and MM (top) $T = 296$ K spectra. The dark (blue) points on the top display show line intensities (cm per molecule) computed for the MARVELized states only, while the light (grey) area indicates the full coverage in the MM line list.

this extension, the experimental data set is far from complete, even at room temperature. As is also seen in Fig. 8, the spectroscopic range above 7000 cm^{-1} is poorly represented by experiment, especially by assigned experiment. Although HITRAN provides good coverage up to 9000 cm^{-1} and some coverage up to $11\,500\text{ cm}^{-1}$, the vast majority of these lines are only provided with approximate low state energies needed for the temperature variation of the HITRAN intensities. We hope that our line list will help assign experimental data on CH₄ and in turn lead to improved theoretical models.

Currently, the most comprehensive (accurate and complete) line lists for CH₄ are from TheoReTS (Rey, Nikitin & Tyuterev 2017), McCaSDa@VAMDC (Ba et al. 2013), and HITEMP (Hargreaves et al. 2020). The latter is a compilation of the $T = 296$ K HITRAN line list for ¹²CH₄ and the TheoReTS line list by Rey, Nikitin & Tyuterev (2017). Fig. 9 shows simulations of absorption spectra of CH₄ at $T = 1000$ K, $T = 1500$ K, and $T = 2000$ K at low resolution (1 cm^{-1}) generated using the HITEMP, TheoReTS, and MM line lists. The TheoReTS spectra, based on the TheoReTS line list for CH₄ by Rey, Nikitin & Tyuterev (2017), were computed by combining two contributions, (i) strong lines and (ii) temperature dependent continuum (Hargreaves et al. 2015). While there is generally good agreement between the three spectra at $T = 1000$ K and $T = 1500$ K, where MM is reasonably close both to HITEMP and TheoReTS,

at the higher temperature of $T = 2000$ K all three line lists show significant deviation from each other especially at higher frequencies as well as between the bands. These discrepancies can be most likely attributed to the level of completeness of the line lists, with the TheoReTS based on the largest and HITEMP on the smallest number of transitions in these regions.

Another important benchmark is provided by Wong et al. (2019), who reported experimental cross sections of ¹²CH₄ at a set of temperatures from 295 to 1000 K in the range 5500 to 8900 cm^{-1} . In their paper they demonstrated excellent agreement of the TheoReTS line list with the experimental cross sections across the entire range of wavenumbers and temperatures. In Fig. 10, we compare the MM simulations at $T = 1000$ K on a grid of 0.0075 cm^{-1} to the CH₄ cross sections at the resolution of 2 cm^{-1} by Wong et al. (2019). The agreement with the experiment for this hot spectrum is comparable with the quality of TheoReTS demonstrated in Wong et al. (2019). It is interesting that the experimental cross sections in 8200 – 8900 cm^{-1} region are systematically higher than both TheoReTS and MM. We currently do not have an explanation for this discrepancy.

7 CONCLUSION

An extensive ro-vibrational line list for the main isotopologue of methane MM is presented. The line list is meant to replace the ExoMol 10to10 and 30to10 CH₄ line lists from 2014; it is both more complete and more accurate. It contains over 50 billion transitions and covers the frequency range from 0 to $12\,000\text{ cm}^{-1}$ with rotational excitation up to $J = 60$. With the lower energy cutoff of $10\,000\text{ cm}^{-1}$, it should be complete up to 1500 K, with lower wavenumbers ($\sim 7000\text{ cm}^{-1}$), complete up to 2000 K. In fact, we show that at high temperatures (>1000 K) it is significantly more complete than the HITEMP line list for CH₄. The line list is based on a new empirical PES, which was refined by fitting to the experimentally derived energies of CH₄, and on a new kinetic energy operator, represented by a Taylor expansion in terms of nine curvilinear coordinates. For intensities, a new high level CCSD(T) dipole moment of CH₄ was used. The accuracy of the line list is further improved via the MARVELization procedure, where the computed energies are replaced by the experimentally derived values [from Kefala et al. (2024)]. This is the ExoMol strategy to replace energies, not line positions, which provides a more consistent as well as more global solution. Indeed, using the MARVELized energy levels only, i.e. states characterized by experimental quality, we were able to generate near $1000\,000$ new lines of that quality.

A room temperature spectrum computed with MM compares well with HITRAN CH₄ data, both in terms of the line positions and intensities, including the very many unassigned transitions in HITRAN. Indeed, Kefala et al. (2024) list about 50 high resolution measurements of CH₄ spectra which are either complete unassigned or only partially assigned. Our line list can undoubtedly help provide quantum number assignments for a significant number of these works as well providing updates for HITRAN. Our improvement is not the last word in the line list provision for methane. Analysis of the high wavenumber CH₄ spectra, especially above $>7000\text{ cm}^{-1}$, will lead to more experimentally derived energies and facilitate further improvement of the PES of CH₄. We hope the turn-around time between the experiment, analysis and theory can now be made more efficient and quicker than 10 yr ago.

In order to facilitate the usage in the exoplanetary applications, as part of the MM ExoMol line list package, we also provide a set of

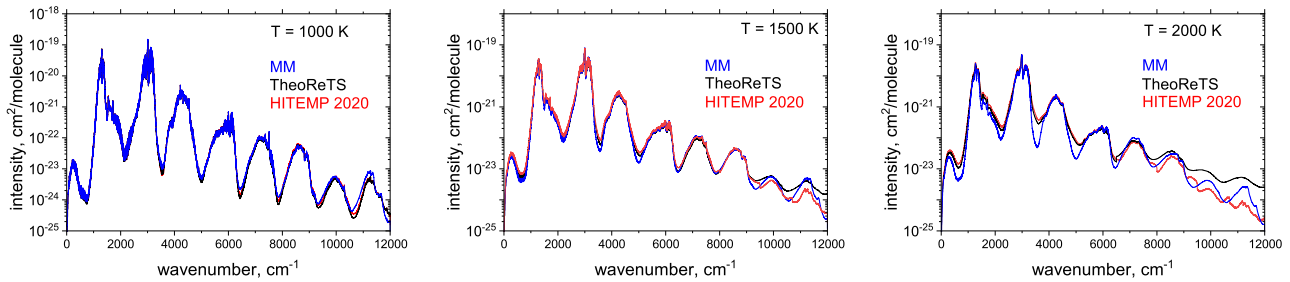


Figure 9. Absorption spectra of CH₄ simulated using the MM, TheoReTS and HITEMP line lists at $T = 1000$ K, $T = 1500$ K and $T = 2000$ K on a grid of 1 cm^{-1} . A Gaussian line profile with a half width at maximum (HWHM) of 1 cm^{-1} was used.

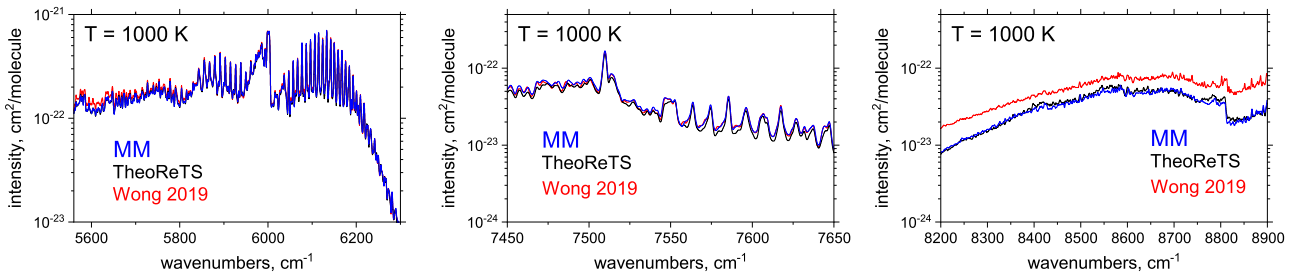


Figure 10. Comparison of the theoretical high temperature ($T = 1000$ K) MM cross sections of CH₄ with the experimental cross sections by Wong et al. (2019). Here we use the 2 cm^{-1} resolution data set of Wong et al. (2019), while the theoretical cross sections were generated using a Lorentzian line profile with a HWHM of 1 cm^{-1} .

atmospheric opacities for four mainstream codes, ARCIS, TauREx, NEMESIS, and petitRADTRANS.

A feature of the MARVEL procedure is its active nature which means that once new sets of assigned transitions become available these can be added to the existing MARVEL data set and the MARVEL procedure can be re-run. The ExoMol data structure means that line lists can then be updated in a straightforward fashion without the need for the expensive re-calculation transition probabilities (Einstein-A coefficients); updates like this have already been made for number of key molecules, for example AlO (Bowesman et al. 2021), H₃⁺, and its isotopologues (Bowesman et al. 2023), and twice for formaldehyde (H₂CO; Abdoulanziz et al. 2021; Germann et al. 2024). The current MM line list is highly accurate in far- and mid-infrared region but loses accuracy at near-infrared wavelengths. Not due to lack of measured methane spectra in this region but the lack of assignments of these spectra. As we and others address this issue and assign these spectra, the results will be used to systematically improve the MM line list.

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DATA AVAILABILITY

The states, transition, opacity, and partition function files for the CH₄ line lists can be downloaded from www.exomol.com. The open access programs TROVE and EXOCROSS are available from github.com/exomol.

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SUPPORTING INFORMATION

Supplementary data are available at [MNRAS](https://www.mnras.org) online.

CH₄_band.centres.corrections is a list of TROVE *J* = 0 energy term values and corresponding empirical energy shifts (EBSC).

SM_ch4_MM_pes_dms.zip contains subroutines and input files for the refined PES and *ab initio* DMS of CH₄.

12C-1H4_MM_model.inp is a TROVE input file containing the potential parameters as well as the TROVE configuration parameters. Supplementary data are available at MNRAS online. This includes the spectroscopic model in the form of the TROVE input file (), containing all parameters as well as the experimentally derived energy term values of CH₄ used in the fit.

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