An improved rovibrational linelist of formaldehyde, $\text{H}_2^{12}\text{C}^{16}\text{O}$

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Abstract

Published high-resolution rotation-vibration transitions of $\text{H}_2^{12}\text{C}^{16}\text{O}$, the principal isotopologue of methanal, are analyzed using the MARVEL (Measured Active Rotation-Vibration Energy Levels) procedure. The literature results are augmented by new, high-accuracy measurements of pure rotational transitions within the ground, $\nu_3$, $\nu_4$, and $\nu_6$ vibrational states. Of the 16 596 non-redundant transitions processed, which come from 43 sources including the present work, 16 403 could be validated, providing 5029 empirical energy levels of $\text{H}_2^{12}\text{C}^{16}\text{O}$ with statistically well-defined uncertainties. All the empirical rotational-vibrational energy levels determined are used to improve the accuracy of ExoMol’s AYTY line list for hot formaldehyde. The complete list of collated experimental transitions, the empirical energy levels determined, as well as the extended and improved line list are provided as Supplementary Material.

Keywords: Formaldehyde; Line list; Ro-vibrational energy; MARVEL analysis.

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1. Introduction

Formaldehyde, formally methanal, HCHO, is the simplest aldehyde. In the gas phase, formaldehyde is considered to be carcinogenic \[1, 2\]. Since formaldehyde is a trace species in the earth’s atmosphere, formed as a result of photo-oxidation or through incomplete biomass burning, its carcinogenic nature motivated the development of spectroscopic techniques for detecting it in trace quantities \[3\].

The photochemistry and photophysics of formaldehyde, involving several excited electronic states and isomerization processes, leading to the products H₂ + CO or H + HCO, have been investigated in considerable detail \[4–9\], both experimentally and theoretically. The \( \tilde{X}^1A_1 \) and \( \tilde{A}^1A_2 \) electronic states of formaldehyde have been utilized in two-photon stimulated emission pumping (SEP) experiments to derive, for example, a complete set of 27 normal-mode vibrational constants characterizing the \( \tilde{X}^1A_1 \) ground electronic state \[10\]. Thus, in 1984, Field and co-workers \[10\] could legitimately claim that the “unique characteristics of SEP have enabled us to describe the \( E \leq 9300 \text{ cm}^{-1} \) rotation-vibration structure of \( \text{H}_2\text{CO} \tilde{X}^1A_1 \) at a level of detail and completeness which we believe is without precedent for a four-atomic polyatomic molecule”. Nevertheless, though a huge achievement, the accuracy attainable through these spectroscopic constants was a mere 3 cm\(^{-1}\), hardly acceptable by present-day standards.

Over the years, beyond anharmonic (quartic) force field representations \[11\] of the \( \tilde{X}^1A_1 \) PES of formaldehyde \[12–15\], several global PESs have been developed for the \([\text{C,H,H,O}]\) system \[16–22\]. Part of the interest in a global ground-electronic-state \( (S_0) \) PES stems from the existence of further important minima, \textit{cis-} and \textit{trans-H–C–OH}, hydroxycarbene \[17, 20\], on it besides that corresponding to formaldehyde. The \textit{trans}-hydroxycarbene minimum is some 18 000 cm\(^{-1}\) \[23\] above the \( \text{H}_2\text{CO} \) minimum (the global minimum on \( S_0 \) belongs to \( \text{CO} + \text{H}_2 \) \[23\]), separated by a transition state of 10 400 cm\(^{-1}\), measured from the hydroxycarbene side, and through enhanced deep tunneling \textit{trans}-hydroxycarbene rearranges to formaldehyde with a half-life of only two hours \[23\]. The \( \text{CO-H}_2 \) complex has also been the topic of interesting dynamical and spectroscopic studies \[24, 25\].

Formaldehyde has been observed in different flames \[26, 27\], most famously in cold flames, first by Sir Humphry Davy \[26\] in 1817. The spectrum of formaldehyde has been used for its time-resolved monitoring in combustion engines \[28\], for which supporting spectroscopic studies have been performed \[29\].

Formaldehyde is a trace species on Mars \[30\], as well, and it is well known in comets \[31–34\]. Its
infrared absorption spectrum has been observed in protoplanetary disks \[35\]. Interstellar H\textsubscript{2}\textsuperscript{12}C\textsuperscript{16}O was detected 50 years ago \[36\] and many of the formaldehyde lines are now resolved routinely in high-resolution spectroscopic studies of the interstellar medium \[37\]. Interstellar formaldehyde masers have been widely observed \[38–42\].

Much of the laboratory spectroscopy of formaldehyde has focused on electronic (ro-vibrionic) transitions. In fact, formaldehyde was the first polyatomic molecule where the rotational subband structure of vibronic transitions has been successfully analyzed \[43\]. It is probably fair to say that the photodissociation of formaldehyde is one of the most thoroughly understood polyatomic unimolecular reactions \[6, 44\].

The importance of line-by-line information on formaldehyde has led to a large number of laboratory studies of its high-resolution rotational-vibrational spectra \[10, 28, 43–68, 68–107\], involving a diverse set of experimental techniques, such as SEP \[10\], dispersed laser-induced fluorescence \[75\], conventional infrared spectroscopy, with some of the oldest results contained in Refs. \[54, 57, 65, 67, 68\], tunable infrared difference frequency laser spectroscopy \[74\], and sub-Doppler laser Stark and Doppler-limited Fourier-transform spectroscopy \[79\]. Many of the results of these high-resolution experimental studies will be addressed and discussed in detail below.

During the present study our focus is exclusively on transitions within the electronic ground state and we perform a MARVEL (Measured Active Rotational-Vibrational Energy Levels) \[108–110\] analysis of all the measured transitions of H\textsubscript{2}\textsuperscript{12}C\textsuperscript{16}O in its \(\tilde{X}^1A_1\) state. This involves collating all available laboratory spectra and then validating the observed and assigned transitions. The collection of the validated lines is then inverted to give a set of accurate empirical energy levels with statistically significant associated uncertainties. As part of this study, the published spectra are augmented by high-accuracy measurements of pure rotational transitions within the ground, \(\nu_3\), \(\nu_4\), and \(\nu_6\) vibrational states.

Accurate energy levels have a number of uses in spectroscopy, kinetics, and thermochemistry. One of the opportunities is to improve theoretical prediction of rotation-vibration spectra \[111\]. Recently, as part of the ExoMol project \[112\], Al-Refaie et al. \[113\] computed an extensive rotation-vibration line list for hot formaldehyde, which they called AYTY. While this line list is comprehensive and reasonably accurate, its predicted line centers do not meet high resolution standards. The empirical energy levels generated, based partially on literature results and partially on the new measurements performed as part of this study, are used to make this line list suitable for high-resolution observational studies. This is achieved by a one-by-one replacement of the empirically
adjusted energy levels of the AYTY line list by the empirical rovibrational energy levels resulting from our MARVEL-based investigation. Such high-accuracy line lists are required, for example, by astronomers studying exoplanets using high-resolution Doppler-shift spectroscopy [114]. Indeed, experience shows that failed detections can in some cases be attributed to inaccurate line lists [115]. For this reason the ExoMol project decided to refactor its line lists to include empirically determined energy levels wherever possible [116]; this work forms part of this effort.

2. Methods

2.1. MARVEL

Details about the MARVEL technique [108–110], built upon the theory of spectroscopic networks (SNs) [117–119], and the xMARVEL code, introduced in Refs. 110 and 120, have been given in several recent publications [110, 118, 120–122]. MARVEL has been used to treat the laboratory

![Figure 1: Vibrational fundamentals of $\tilde{X}^1{A}_1$ H$_2^{12}$C$^{16}$O, with their symmetry species and the types of bands indicated. The arrows representing atomic motions during the normal-mode vibrations are not proportional to the actual displacements.](image-url)
spectroscopic data of nine isotopologues of water \([111, 123–126]\), as well as of diatomics \([127–131]\), triatomics \([132–135]\), tetramotics \([136–138]\), and beyond \([139]\). Thus, it is sufficient to give only a relatively brief discussion about MARVEL here.

Of importance to the present study, the MARVEL protocol yields empirical rovibronic energies with well-defined provenance and statistically-sound uncertainties. It always starts with the construction of a SN using the dataset of measured and assigned transitions collated from the literature. Then, a sophisticated inversion of the transitions is performed, yielding empirically determined rovibrational energy levels, with associated uncertainties, within each component of the SN. The inversion process expedites the validation of the experimental information through utilization of several elements of network theory.

The xMARVEL procedure \([110, 120]\) has been used extensively during the present study to treat experimental rovibrational transitions of \(\text{H}_2^{12}\text{C}^{16}\text{O}\). The corresponding xMARVEL input and output data files are provided as supplementary material.

2.2. Quantum numbers

The xMARVEL procedure requires as input spectral lines assigned with a unique set of quantum numbers. The equilibrium structure of formaldehyde on its ground electronic state has \(C_{2v}\) point-group symmetry (with irreducible representations, irreps, \(A_1, A_2, B_1,\) and \(B_2\), which are the same for the isomorphic \(C_{2v}(M)\) molecular-symmetry group); it is an asymmetric-top, semirigid molecule. The vibration-rotation motions of formaldehyde can be well represented by a set of six vibrational normal-mode quantum numbers, \([v_1, v_2, v_3, v_4, v_5, v_6]\), arranged in standard order \([140]\), and the three standard “rigid-rotor” quantum numbers \([141]\), \((J, K_a, K_c)\). See Fig. 1 for a pictorial representation of the normal modes of \(\text{H}_2^{12}\text{C}^{16}\text{O}\). Rotational states with \(K_a \approx J\) which differ only in their \(K_c\) quantum number lie close in energy and often give rise to two very-closely-spaced transitions, a phenomenon known as \(K\)-doubling or asymmetry splitting.

The electric-dipole-allowed transitions are described as \(A_1 \leftrightarrow A_2\) and \(B_1 \leftrightarrow B_2\). These selection rules are derived from symmetry relations. Namely, the two nuclear-spin isomers of \(\text{H}_2^{12}\text{C}^{16}\text{O}\), \(\text{para}\) and \(\text{ortho}\), correspond to \(v_4 + v_5 + v_6 + K_a\) being even ( irreps A) or odd ( irreps B), respectively, while the subscripts of the irreps are 1 or 2 depending on whether \(v_5 + v_6 + K_a + K_c\) is even or odd, respectively.

Table 1: Pure rotational Lamb-dip lines of \(\text{H}_2^{12}\text{C}^{16}\text{O}\) measured during this study with 2 kHz \((6.67 \times 10^{-8} \, \text{cm}^{-1})\) accuracy.
our MARVEL treatment, we have recorded a set of 89 pure rotation transitions in the ground band both for the upper and the lower state.

| σ_{new}/cm^{-1} | Line assignment | σ_{fit}/cm^{-1} |
|------------------|-----------------|-----------------|
| 9.390727 127     | ν_{0}, 4_{1,4} ← 3_{1,3} | 9.390727 53(33) [76] |
| 9.694153 448     | ν_{0}, 4_{0,4} ← 3_{0,3} | 9.694153 31(33) [76] |
| 9.714646 159     | ν_{0}, 4_{2,3} ← 3_{2,2} | 9.714646 7(67) [72] |
|                  |                  | 9.714646 0(67) [74] |
| 9.719405 248     | ν_{0}, 4_{3,2} ← 3_{3,1} | 9.719407(10) [76] |
| 9.719536 101     | ν_{0}, 4_{3,1} ← 3_{3,0} | 9.719532 8(33) [85] |
| 9.738339 080     | ν_{0}, 4_{2,2} ← 3_{2,1} | 9.738339 0(67) [72] |
| 10.034829 847    | ν_{0}, 4_{1,3} ← 3_{1,2} | 10.034830 00(33) [76] |

\(^{n}\) In the first and last columns, the new, σ_{new}, and the best previous, σ_{fit}, transition wavenumbers are reported, respectively. The “Line assignment” column contains the assignments of the lines in the form of ν_{0}, J'_{K_a,K_c} ← J''_{K_a,K_c}, where J_{K_a,K_c} denote the rotational assignment and ν_{0} refers to the ground vibrational band both for the upper and the lower state.

### 2.3. New rotational measurements

In order to increase the number of available experimental data of H_{2}^{12}C^{16}O, and thus improve our MARVEL treatment, we have recorded a set of 89 pure rotational transitions in the ground and some vibrationally excited states. The measurements were performed using the frequency-modulation millimeter/submillimeter spectrometer in Bologna. The instrumental setup of the spectrometer is detailed elsewhere [142, 143]; here we provide only a brief description.

### Table 2: Rotational lines of H_{2}^{12}C^{16}O measured during this study with 20 kHz (6.67 × 10^{-7} cm^{-1}) accuracy.\(^{n}\)

| σ_{new}/cm^{-1} | Line assignment | σ_{new}/cm^{-1} | Line assignment | σ_{new}/cm^{-1} | Line assignment |
|------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 9.396103 294     | ν_{3}, 4_{1,4} ← 3_{1,3} | 12.098165 470     | ν_{4}, 5_{3,3} ← 4_{3,2} | 9.694153 398     | ν_{0}, 4_{0,4} ← 3_{0,3} |
| 9.720532 400     | ν_{3}, 4_{0,4} ← 3_{0,3} | 12.098598 600     | ν_{4}, 5_{3,2} ← 4_{3,1} | 9.714646 044     | ν_{0}, 4_{2,2} ← 3_{2,1} |
| 9.745845 447     | ν_{3}, 4_{2,3} ← 3_{2,2} | 12.129667 850     | ν_{4}, 5_{3,1} ← 4_{2,2} | 9.719450 501     | ν_{0}, 4_{3,2} ← 3_{3,1} |
| 9.753700 377     | ν_{3}, 4_{3,2} ← 3_{3,1} | 12.432459 250     | ν_{4}, 5_{1,4} ← 4_{4,1} | 9.719535 726     | ν_{0}, 3_{1} ← 3_{3,0} |
| 9.753599 167     | ν_{3}, 4_{3,1} ← 3_{3,0} | 9.366709 450      | ν_{0}, 4_{1,4} ← 3_{1,3} | 9.738339 087     | ν_{0}, 4_{2,2} ← 3_{2,1} |
| 9.773007 973     | ν_{3}, 4_{2,2} ← 3_{2,1} | 9.682101 847      | ν_{0}, 4_{0,4} ← 3_{0,3} | 9.834452 846     | ν_{0}, 22_{2,20} ← 23_{0,23} |
| 10.088575 460    | ν_{3}, 4_{1,3} ← 3_{1,2} | 9.697356 479      | ν_{0}, 4_{2,3} ← 3_{2,2} | 10.034829 710     | ν_{0}, 4_{1,3} ← 3_{1,2} |
| 11.739822 940    | ν_{3}, 4_{0,5} ← 4_{1,4} | 9.696151 729      | ν_{0}, 4_{3,2} ← 3_{3,1} | 10.248367 590     | ν_{0}, 9_{2,7} ← 10_{0,10} |
| 12.129667 850    | ν_{3}, 5_{0,5} ← 4_{0,4} | 9.696255 862      | ν_{0}, 4_{3,1} ← 3_{3,0} | 10.364365 470     | ν_{0}, 18_{3,15} ← 19_{1,18} |
| 12.178445 400    | ν_{3}, 5_{2,4} ← 4_{2,3} | 9.718870 594      | ν_{0}, 4_{2,2} ← 3_{2,1} | 10.448342 040     | ν_{0}, 37_{4,33} ← 37_{4,34} |
| 12.192149 190    | ν_{3}, 5_{4,2} ← 4_{4,1} | 10.029447 240     | ν_{0}, 4_{1,3} ← 3_{1,2} | 10.555863 330     | ν_{0}, 11_{1,10} ← 11_{1,11} |
| 12.192149 190    | ν_{3}, 5_{4,1} ← 4_{4,0} | 11.704713 210     | ν_{0}, 5_{1,5} ← 4_{1,4} | 10.896074 830     | ν_{0}, 19_{2,17} ← 19_{2,18} |
| 12.194013 170    | ν_{3}, 5_{3,3} ← 4_{3,2} | 12.086508 690     | ν_{0}, 5_{0,5} ← 4_{0,4} | 11.212427 070     | ν_{0}, 28_{3,25} ← 28_{3,26} |
| 12.194571 510    | ν_{3}, 5_{3,2} ← 4_{3,1} | 12.120488 600     | ν_{0}, 5_{2,4} ← 4_{2,3} | 11.733738 380     | ν_{0}, 5_{1,5} ← 4_{1,4} |
| 12.232626 840    | ν_{3}, 5_{2,3} ← 4_{2,2} | 12.109817 660     | ν_{0}, 5_{1,2} ← 4_{1,1} | 12.073937 490     | ν_{0}, 8_{2,6} ← 9_{0,9} |

Continued on next page
The radiation source is a Gunn diode (80–115 GHz) that is frequency- and phase-stabilized via a phase-lock-loop and is driven by a centimeter-wave synthesizer referenced to a 5 MHz rubidium atomic clock. Spectral coverage between 240 and 420 GHz is obtained by coupling the Gunn diode to passive multipliers. Then, the electromagnetic radiation is frequency-modulated at \( f = 48 \) kHz and fed into a glass absorption cell (3 m optical path length) filled with formaldehyde vapors at pressure between 0.5 and 20 \( \mu \)bar; specifically, pressures between 0.5 and 20 \( \mu \)bar were used to record ground state lines with intensities spanning almost six orders of magnitude, while 10–15 \( \mu \)bar were used to observe the vibrational excited states. The sample of H\(_2\)CO was freshly obtained before each measurement from the vapors of solid, room-temperature paraformaldehyde. The output radiation was finally detected by a Schottky barrier diode, demodulated by a lock-in amplifier set at twice the modulation-frequency (2\( f \) scheme), filtered, and analog-to-digitally converted.

A small sub-set of measurements have been performed exploiting the Lamb-dip technique \([14]\). In this respect, the optics of the spectrometer were adequately set up in a double-pass configuration (as detailed in \([14]\)), \( f \) was set to 1 kHz, and a low-pressure of H\(_2\)CO was used (0.5 \( \mu \)bar).

The new measurements consist of (a) two complete \( a \)-type \( ^q R \)-branch transitions (\( J = 4 \) \( \leftarrow \) 3 and 5 \( \leftarrow \) 4) within the \( \nu_0, \nu_3, \nu_4, \) and \( \nu_6 \) bands, where \( \nu_0 \) denotes the ground vibrational state, and (b) about 20 ground-state \( P \) and \( Q \) transitions with \( \Delta K_a = 0 \) or 2, with integrated intensity

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Table 2 – Continued from previous page

| \( \sigma_{\text{new}}/\text{cm}^{-1} \) | Line assignment | \( \sigma_{\text{new}}/\text{cm}^{-1} \) | Line assignment | \( \sigma_{\text{new}}/\text{cm}^{-1} \) | Line assignment |
|-------------------------------------|-----------------|-------------------------------------|-----------------|-------------------------------------|-----------------|
| 12.604848 190                      | \( \nu_3, 5_{1,4} \leftarrow 4_{1,3} \) | 12.109817 660                     | \( \nu_6, 5_{1,4} \leftarrow 4_{1,0} \) | 12.099570 770                     | \( \nu_5, 5_{0,5} \leftarrow 4_{0,4} \) |
| 9.389443 381                       | \( \nu_4, 4_{1,4} \leftarrow 3_{1,3} \) | 12.121054 530                     | \( \nu_6, 5_{3,3} \leftarrow 4_{3,2} \) | 12.139927 050                     | \( \nu_5, 5_{2,4} \leftarrow 4_{2,3} \) |
| 9.649643 518                       | \( \nu_4, 4_{0,4} \leftarrow 3_{0,3} \) | 12.121422 250                     | \( \nu_6, 5_{3,2} \leftarrow 4_{3,1} \) | 12.145176 040                     | \( \nu_5, 4_{2,4} \leftarrow 4_{4,1} \) |
| 9.670558 195                       | \( \nu_4, 4_{2,3} \leftarrow 3_{2,2} \) | 12.163422 430                     | \( \nu_6, 5_{2,3} \leftarrow 4_{2,2} \) | 12.145176 040                     | \( \nu_5, 4_{1,1} \leftarrow 4_{4,0} \) |
| 9.677770 970                       | \( \nu_4, 4_{3,2} \leftarrow 3_{3,1} \) | 12.532770 030                     | \( \nu_6, 5_{1,4} \leftarrow 4_{1,3} \) | 12.150912 170                     | \( \nu_5, 3_{3,3} \leftarrow 4_{3,2} \) |
| 9.677893 765                       | \( \nu_4, 4_{3,1} \leftarrow 3_{3,0} \) | 8.237600 872                      | \( \nu_6, 2_{1,2,19} \leftarrow 2_{2,0,22} \) | 12.151369 510                     | \( \nu_5, 3_{3,2} \leftarrow 4_{3,1} \) |
| 9.693290 175                       | \( \nu_4, 4_{2,2} \leftarrow 3_{2,1} \) | 8.600996 014                      | \( \nu_6, 3_{5,3,32} \leftarrow 3_{6,1,35} \) | 12.187211 040                     | \( \nu_5, 2_{3,2} \leftarrow 4_{2,2} \) |
| 9.949961 352                       | \( \nu_4, 4_{1,3} \leftarrow 3_{1,2} \) | 8.615829 497                      | \( \nu_6, 10_{2,8} \leftarrow 11_{0,11} \) | 12.441481 610                     | \( \nu_5, 1_{2,11} \leftarrow 12_{1,12} \) |
| 11.726529 220                      | \( \nu_5, 5_{1,5} \leftarrow 4_{1,4} \) | 8.798468 478                      | \( \nu_6, 3_{6,1,32} \leftarrow 3_{6,4,33} \) | 12.538447 510                     | \( \nu_5, 1_{5,2} \leftarrow 4_{1,3} \) |
| 12.045134 760                      | \( \nu_5, 5_{0,5} \leftarrow 4_{0,4} \) | 8.815102 825                      | \( \nu_6, 10_{1,9} \leftarrow 10_{1,10} \) | 12.795269 680                     | \( \nu_5, 20_{2,18} \leftarrow 20_{2,19} \) |
| 12.084311 370                      | \( \nu_5, 5_{2,4} \leftarrow 4_{2,3} \) | 9.160256 575                      | \( \nu_6, 18_{2,16} \leftarrow 18_{2,17} \) |                               |                               |
| 12.093976 360                      | \( \nu_4, 5_{4,2} \leftarrow 4_{4,1} \) | 9.390727 004                      | \( \nu_6, 4_{1,4} \leftarrow 3_{1,3} \) |                               |                               |
| 12.093963 030                      | \( \nu_4, 5_{4,1} \leftarrow 4_{4,0} \) | 9.461197 252                      | \( \nu_6, 27_{3,24} \leftarrow 27_{3,25} \) |                               |                               |

\(^{a}\) \( \sigma_{\text{new}} \) denotes newly measured transition wavenumbers. The line assignments are given in the form of \( \nu_i, J_{K_a,K_c}^{\prime} \leftarrow J_{K_a,K_c}^{\prime\prime} \), where \( \nu_i \) and \( J_{K_a,K_c} \) represent the vibrational and the rotational assignment of the measured lines, respectively, \( \nu_0 \) refers to the ground vibrational state, while \( \nu_3, \nu_4, \) and \( \nu_6 \) designate vibrational fundamentals (see Fig. 1).
between $10^{-23}$ and $10^{-27}$ cm molecule$^{-1}$.

The uncertainty of our measurements is estimated to be in the range of 2–20 kHz. We label the seven Lamb-dip transitions of Table 1 with the reference tag 21AlTeYuMe, and the others as 21AlTeYuMe_S2, see Table 2.

2.4. Artificial transitions

In the absence of transitions linking the *ortho* and *para* nuclear-spin isomers, the measured transitions form two distinct principal components (PC) 118 in the SN of H$_2$^{12}C$^{16}$O. As usual 111 during MARVEL analyses of experimental transitions of species having more than one nuclear-spin isomer, the *ortho* and *para* principal components are linked using artificial transitions, colloquially called magic numbers, taken possibly from effective Hamiltonian fits (EH) 122.

For H$_2$^{12}C$^{16}$O, the wavenumber of the unmeasurable rotational transition $1_{1,1} \leftarrow 0_{0,0}$, reported in 146 as 10.539 039 1 cm$^{-1}$, is utilized as a magic number. Since the very accurate empirical (MARVEL) energies of the pure rotational states $1_{0,1}$, $2_{0,2}$, and $3_{0,3}$, that is, 2.429 612 60(33), 7.286 404 28(47), and 14.565 513 07(58) cm$^{-1}$, respectively, are reproduced by the EH-predicted values, see the fourth column of Table 3 of Ref. 146, with unsigned deviations of $8.26 \times 10^{-7}$, $2.20 \times 10^{-6}$, and $4.37 \times 10^{-6}$ cm$^{-1}$, respectively, the average of these unsigned deviations, $2.3 \times 10^{-6}$ cm$^{-1}$, is adopted as a conservative estimate for the uncertainty of the magic number. In addition, 11 artificial transitions were used to link the largest floating components to the PCs. These transitions form bridges between the principal components and the floating components of disconnected higher-$J$ transitions. In fact, these transitions link the ground state to series of states with $K_a = 8$, $K_a = 10$, and $K_a = 11$. The values of these artificial transitions are taken from the effective Hamiltonian study of 88NaReDaJo 87.

First-principles computations are capable of estimating small energy splittings very accurately 122; thus, we decided to add the $J_{J,0/1}$ separations as virtual lines to the dataset. They are part of a source tagged as ‘21virt’ (see Table 3). These virtual transitions are distributed into four segments, based on the magnitude of the splittings and thus on their assumed uncertainties. Through these virtual lines 199 further rovibrational energy levels could be determined: the experimentally unavailable states of certain $J_{J,0/1}$ pairs.

Table 3: Data source segments and their characteristics for the H$_2$^{12}C$^{16}$O molecule$^a$
| Segment tag | Range | A/N/V | ESU | MSU | LSU | Recalib. Factor |
|------------|-------|-------|-----|-----|-----|----------------|
| 72TuToTh  | 0.483 28–0.483 28 | 1/1/1 | 2.67e-09 | 2.67e-09 | 2.67e-09 | 2.67e-09 |
| 71TuToTh  | 0.141 30–0.165 74 | 3/3/3 | 3.67e-09 | 3.67e-09 | 5.34e-09 | |
| 81ChGu   | 0.002 373–0.002 305 | 14/9/9 | 6.67e-09 | 1.00e-08 | 3.34e-08 | |
| 73ChGu   | 0.000 003–0.966 50 | 23/21/21 | 1.00e-08 | 1.00e-08 | 3.66e-07 | |
| 66Takami | 0.000 022–0.001 829 | 12/10/10 | 1.67e-08 | 3.15e-08 | 6.44e-07 | |
| 73ChGu   | 0.000 005–0.002 305 | 39/39/35 | 3.34e-08 | 3.34e-08 | 1.33e-07 | |
| 96BoDePoLi | 0.000 003–0.708 93 | 23/21/21 | 1.00e-08 | 1.00e-08 | 3.66e-07 | |
| 77ChGu   | 0.000 005–0.002 305 | 39/39/35 | 3.34e-08 | 3.34e-08 | 1.33e-07 | |
| 96BoDePoLi | 0.000 003–0.708 93 | 23/21/21 | 1.00e-08 | 1.00e-08 | 3.66e-07 | |
| 96BoDePoLi | 0.000 003–0.708 93 | 23/21/21 | 1.00e-08 | 1.00e-08 | 3.66e-07 | |
| 96BoDePoLi | 0.000 003–0.708 93 | 23/21/21 | 1.00e-08 | 1.00e-08 | 3.66e-07 | |
| 21AlTeYuMe | 9.390 7–10.035 | 7/7/7 | 7.00e-08 | 7.00e-08 | 1.33e-07 | |
| 17MuLe   | 0.163 02–0.164 94 | 3/3/2 | 8.34e-07 | 8.34e-07 | 1.00e-06 | |
| 03BrMuLeWi | 27.793–66.778 | 136/136/136 | 1.00e-06 | 1.00e-06 | 2.74e-05 | |
| 09MaPeJaBa | 5.016 8–30.115 | 172/172/171 | 1.00e-06 | 1.00e-06 | 1.33e-05 | |
| 21virt   | 0.000 020–0.000 009 | 178/171/171 | 1.00e-06 | 1.00e-06 | 2.11e-04 | |
| 07TcPeLa | 0.553 19–1.979 8 | 15/15/15 | 1.47e-06 | 1.47e-06 | 7.86e-06 | |
| 51LaSt   | 0.245 59–2.429 6 | 18/18/18 | 1.67e-06 | 2.40e-06 | 2.03e-05 | |
| 56Erlandss | 2.429 6–7.528 5 | 9/8/8 | 1.67e-06 | 1.60e-06 | 2.79e-05 | |
| 88NaReDaJo | 0.000 18–0.000 9 | 178/178/178 | 1.00e-06 | 1.00e-06 | 5.55e-06 | |
| 21virt   | 0.000 005–0.000 009 | 157/157/157 | 1.00e-06 | 1.00e-06 | 2.78e-03 | |
| 72Nerf   | 1.610 6–10.035 | 15/15/15 | 1.47e-06 | 1.47e-06 | 7.86e-06 | |
| 51LaSt   | 0.245 59–2.429 6 | 18/18/18 | 1.67e-06 | 2.40e-06 | 2.03e-05 | |
| 56Erlandss | 2.429 6–7.528 5 | 9/8/8 | 1.67e-06 | 1.60e-06 | 2.79e-05 | |
| 64OTaMo  | 0.000 153–2.437 1 | 70/49/49 | 1.67e-06 | 1.80e-06 | 2.66e-05 | |
| 79CaHeDe | 10.539–10.539 | 1/1/1 | 2.30e-06 | 2.30e-06 | 2.30e-06 | |
| 72JoLoKi | 0.000 153–4.504 1 | 314/312/312 | 2.00e-04 | 1.19e-04 | 2.01e-02 | |
| 78DaWiBe | 0.000 006–10.029 | 84/82/82 | 6.67e-06 | 6.67e-06 | 2.31e-05 | |
| 73ChFrOk | 0.553 19–1.979 8 | 7/7/7 | 1.67e-05 | 1.67e-05 | 2.67e-05 | |
| 85TiKuHu  | 4.211 6–5.224 0 | 100/100/100 | 1.00e-04 | 1.10e-04 | 1.16e-02 | |
| 82BrJoMcWo | 1.693 1–1.793 4 | 248/248/248 | 4.00e-04 | 1.59e-04 | 8.99e-04 | |
| 79BrHuPi  | 2.700 0–3.000 2 | 319/318/318 | 5.00e-04 | 3.27e-04 | 4.52e-02 | |
| 81Swas   | 1.707 1–1.746 9 | 76/76/76 | 5.00e-04 | 6.50e-04 | 3.38e-03 | |
| 88CUVa   | 2.867 2–2.880 4 | 24/22/22 | 5.00e-04 | 3.48e-04 | 7.22e-03 | |
| 94ItNaTa  | 2.276 2–5.536 3 | 320/320/320 | 5.00e-04 | 3.91e-04 | 5.56e-03 | |
| 10JLaTeGa | 1.675 0–3.089 8 | 782/781/781 | 5.00e-04 | 1.62e-04 | 6.45e-03 | 1.000 001 293 |
| 07TcPeLa | 0.000 006–10.029 | 84/84/84 | 2.10e-04 | 1.00e-04 | 2.25e-03 | |
| 07TcPeLa | 927.68–1.812 1 | 402/410/101 | 8.00e-04 | 1.04e-04 | 5.00e-03 | |
| 06BrUtHa  | 2.756 2–2.864 6 | 147/143/143 | 1.00e-03 | 1.00e-03 | 3.82e-02 | |
| 09CiMaCl | 4.350 9–4.360 6 | 49/46/36 | 1.00e-03 | 1.00e-03 | 7.97e-03 | |

*Continued on next page*
Table 3 – Continued from previous page

| Segment tag | Range / cm⁻¹ | A/N/V | ESU | MSU | LSU | Recalib. Factor |
|-------------|--------------|-------|-----|-----|-----|-----------------|
| 07SaBaHiRi [99] | 5.597.8–5.698.3 | 424/422/418 | 1.50e-03 | 1.00e-03 | 9.08e-03 |
| 17TaAdNg [107] | 3.398.7–3.529.7 | 786/786/785 | 1.60e-03 | 1.11e-03 | 3.66e-02 |
| 73Toth [65] | 3.428.2–3.507.4 | 299/299/298 | 3.00e-03 | 2.83e-03 | 4.23e-02 |
| 77AlJoMc [68] | 945.23–1.540.0 | 991/922/904 | 5.00e-03 | 3.94e-03 | 4.57e-02 |
| 77AlJoMc [69] | 1.483.0–1.518.1 | 70/70/70 | 5.00e-03 | 4.14e-03 | 3.57e-02 |
| 76NaYaKu [149] | 2.643.9–3.011.8 | 184.8/184.5/171.1 | 3.00e-02 | 1.68e-02 | 9.89e-02 |

*Tags denote segments used in this study. The column ‘Range’ indicates the range (in cm⁻¹) corresponding to validated wavenumbers within the transition list. A is the number of assigned transitions, N is the number of non-redundant lines (with distinct wavenumbers or labels), and V is the number of validated transitions obtained at the end of the xMAREV analysis. In the heading of this table, ESU, MSU, and LSU denote the estimated, the median, and the largest segment uncertainties, respectively, in cm⁻¹. Rows are arranged in the order of the ESUs with the restriction that the segments of the same data source should be listed consecutively.*

3. The rovibrational database

3.1. Overview

Tables 3 and 4 present an overview of the experimental information considered during this project. Each experimental source is given a tag composed of the last two digits of the year of publication and letters of the names of up to the first four co-authors.

Table 3 summarizes the sources included in our final MARVEL analysis and gives statistical information about the transitions these sources contain. We utilized data from 43 literature sources,
including this work, yielding 19,831 transitions, of which 16,596 are non-redundant.

Table 4 lists sources that were not included in the final analysis. A number of other older sources [47, 51, 55] were also excluded from the present analysis, as their measurements have been superseded by those of significantly more accurate studies.

3.2. Source-specific comments

A significant problem we faced during the data collection was that there are several publications [92, 94, 95] for \( \text{H}_2\text{\textsuperscript{12}}\text{\textsuperscript{16}}\text{O} \) where the authors did not provide the direct measured data in their original paper and when approached they turned down our request to send the measured data forming the basis of their existing publication. Similar problems, and related issues, have been highlighted in a recent paper by Gordon et al. [150]. Seemingly it is not straightforward to include old data into new data compilations.

Another significant issue is that a number of sources do not provide a clear statement about the uncertainties of the observed lines. Thus, we had to estimate them by various means, which included comparisons with other sources as well as combination-difference relations. Such sources include 76NaYaKu [149], 82BrJoMcWo [79], 88ClVa [82], 85TiChKuHu [80], 77AlJoMc [68], 77AlJoMcba [69], and 10JaLaTcGa [103]. Since the authors of 10JaLaTcGa state that their line positions were not calibrated, we used an xMARVEL facility to calibrate the wavenumbers of the measured transitions published in 10JaLaTcGa. This gave a calibration factor of 1.000 001 148 for this source.

64OkTaMo [52] provides high-resolution pure rotational transitions between levels in vibrationally excited states. However, 78DaWiBe [72] found it necessary to reassign the vibrational states in this source; we have adopted and in fact validated the assignments of 78DaWiBe.

76NaYaKu [149] is an older and relatively low-resolution source, which nonetheless contains lines for which no data are available from alternative sources. The authors used a compact, non-standard notation for the assignments, which had to be unpicked. A total of 134 lines could not be validated and thus were removed. Transitions involving high \( K_a \) states did not resolve the \( K\)-doublets, i.e., the \( K_c \) quantum number. For these transitions we used two lines corresponding to both possible transitions.

88NaReDaJo [87] gives only calculated line positions and residuals; thus, the observed frequencies were reconstructed from this information. Similarly, the tables in 79BrHuPi [74] are of very poor quality and their line frequency data could only be accurately reconstructed by extensive comparison with HITRAN [151]; 88ClVa [82] also provides a small portion of 79BrHuPi’s spectrum in readable form.

02BaCoHaPe [90] recorded a spectrum of the \( 5\nu_2 \) overtone; this spectrum was analyzed by 07SaBaHaRi [90], who also provided the data (C.M. Western, private communication, 2020). These studies did not contain an estimated uncertainty; thus, an estimated value of 0.0015 cm\(^{-1}\) was adopted on the basis of combination difference relations.
72JoLoKi [59] presents an extensive compilation of early microwave experiments on formaldehyde. Although this is a secondary source, some data were taken from here as the primary sources are not available to us. 72JoLoKi also contains tabulations of hyperfine-resolved transitions for the $1_{01} - 1_{11}$, $2_{11} - 2_{12}$, and $3_{12} - 3_{13}$ rotational lines. Other microwave studies, including 59TaShSh [46], 70TuThTo [56], 71TuToTh [58], 72TuToTh [61], and 17MuLe [106] also present hyperfine-resolved data. Within the present study we completely neglect hyperfine effects and, where necessary, use central, hyperfine-unresolved line positions.

4. Results and Discussion

4.1. Validation

According to Table 3, we considered for validation 16,596 non-redundant transitions measured for H$_2^{12}$C$_{16}$O. 13 of these transitions are artificial (see above) and 143 do not attach to the principal components, they remain parts of floating components. The transitions of the giant components of the SN of H$_2^{12}$C$_{16}$O were validated using several techniques.

193 transitions, including a few which did not obey the selection rules governing electric-dipole-allowed transitions, were removed at the first stage of validation. In almost all cases these transitions were ones for which alternative, validated wavenumber entries were available from other sources. The number of validated transitions within each segment is given in Table 3. The transitions which could not be validated are retained in the transitions list given in the supplementary data, but they are given there as a negative wavenumber entry, which means that they are ignored during the processing of the data by xMARVEL. Therefore, these transitions do not contribute to the final empirical energy levels.

The other important step in the validation process involved comparisons with the AYTY line list [113]. These comparisons were performed iteratively between the empirical (xMARVEL) and the AYTY energy levels. During the first phase, the comparisons identified a number of issues with the original xMARVEL dataset in the form of incorrect quantum numbers or scanning errors. Once these were corrected, only a few lines were found for which the upper states had no reasonable match within the AYTY list. These transitions are augmented with a comment ‘theoretical mismatch’ in the MARVEL XML file given in the supplementary material. Those excluded lines which violate the electric-dipole selection rules have the comment ‘wrong labels’ in the XML file. At the end, we were able to validate 16,403 of the collected transitions.

4.2. Final energies

The MARVEL analysis yielded, in total, 5,029 validated empirical rovibrational energies for H$_2^{12}$C$_{16}$O; they are provided in the supplementary material. The highest rotational quantum number is $J_{\text{max}} = 38$ and the empirical energies go up to 6188 cm$^{-1}$; there are transitions which probe energy levels higher than this but none of them are assigned. Thus, all empirical energy levels are
Table 5: MARVEL-based vibrational band origins (VBO) of H$_2^{12}$C$^{16}$O and their literature counterparts obtained from accurate effective Hamiltonian fits.

| Band | Symmetry | VBO(MARVEL) | $N_0$ | $N_{RL}$ | $J_{\text{max}}$ | VBO(lit) |
|------|----------|-------------|------|---------|----------------|----------|
| $\nu_0$ | a$_1$ | 0.0 | 31 | 525 | 38 | 0.0 |
| $\nu_4$ | b$_1$ | 1.16 725 676(10) | 6 | 346 | 30 | 1.16 725 68(2) |
| $\nu_5$ | b$_2$ | 1.24 904 442(10) | 3 | 405 | 30 | 1.24 904 91(2) |
| $\nu_3$ | a$_1$ | 1.50 000 7450(10) | 4 | 382 | 30 | 1.50 000 76(2) |
| $\nu_2$ | a$_1$ | 1.74 600 914(10) | 4 | 446 | 37 | 1.74 600 89(1) |
| $2\nu_4$ | a$_1$ | – | 0 | 65 | 11 | 2.32 752 39(5) |
| $\nu_4 + \nu_6$ | a$_2$ | – | 0 | 47 | 11 | 2.42 297 01(50) |
| $2\nu_6$ | a$_1$ | – | 0 | 81 | 25 | 2.49 354 3(5) |
| $\nu_3 + \nu_4$ | b$_1$ | – | 0 | 15 | 10 | 2.56 704 86(13) |
| $\nu_3 + \nu_5$ | b$_2$ | 2.71 9156 64(50) | 2 | 232 | 25 | 2.71 9155 75(10) |
| $\nu_4$ | a$_1$ | 2.78 245 69(50) | 2 | 440 | 36 | 2.78 245 69(10) |
| $\nu_5$ | b$_2$ | 2.84 332 354(12) | 4 | 388 | 35 | 2.84 332 35(6) |
| $\nu_2 + \nu_4$ | b$_1$ | – | 0 | 153 | 23 | 2.90 968 5(20) |
| $2\nu_3$ | a$_1$ | – | 0 | 38 | 25 | 2.99 987 3(5) |
| $\nu_2 + \nu_6$ | b$_2$ | 3.00 065 74(50) | 1 | 100 | 21 | 3.00 065 65(10) |
| $2\nu_2$ | a$_1$ | 3.47 172 08(78) | 2 | 373 | 31 | 3.47 171 8(4) |
| $\nu_4 + \nu_5$ | b$_1$ | 3.94 153 08(10) | 1 | 30 | 10 | – |
| $\nu_3 + \nu_5$ | b$_2$ | 3.99 518 6(10) | 1 | 35 | 9 | – |
| $\nu_2 + \nu_5$ | b$_2$ | 4.33 509 894(10) | 1 | 170 | 24 | – |
| $2\nu_2 + \nu_6$ | b$_2$ | – | 0 | 207 | 26 | 4.73 420 78(50) |
| $3\nu_2$ | a$_1$ | – | 0 | 176 | 26 | 5.17 759 52(70) |
| $2\nu_5$ | a$_1$ | 5.65 196 4(15) | 1 | 179 | 20 | – |

*aThe VBO values are in cm$^{-1}$. The uncertainties of the last VBO digits are given in parentheses. The symmetry of the band, the number of transitions determining a particular VBO ($N_0$), as well as the number of rotational levels ($N_{RL}$) and the maximum $J$ value within a given vibrational band are also displayed.

The VBO values are well below the minima corresponding to hydroxymethylene. A large number of further experimental studies are needed to reach that dynamically important and interesting region. The region covered is also considerably more limited than that covered by SEP measurements in the 1980s.

Table 5 presents the vibrational band origins (VBO) and a summary of the number of empirical rovibrational energy levels determined for each vibrational state. The bands $2\nu_3 + \nu_6$, $\nu_2 + \nu_5$, and $\nu_2 + \nu_3 + \nu_4$, which have a combined total of only 6 levels, have been omitted from the table. Table 5 also gives term values of this and previous studies, i.e., levels with $J = 0$ for given vibrational bands.

Table 5 contains term values for 14 vibrational band origins, including the six fundamentals, determined during this study. The term values of the $\nu_2$, $\nu_3$, and $\nu_4$ fundamentals are determined.
Figure 2: The upper-state energies of the experimental transitions used in this work, against corresponding lower-state energies of $\text{H}_2^{12}\text{C}^{16}\text{O}$. The vertical bars along the horizontal axis show the lower state energies, while the horizontal bars along the vertical axis give the upper state energies. Each circle represents a particular transition, with the size proportional to the number of transitions supporting the corresponding upper state. This value ranges from 1 (dark blue) to 102 (red).

particularly accurately, in part because in these cases the upper states have been subjected to high-accuracy microwave studies; indeed, such studies for $\nu_3$ and $\nu_4$ form part of the present work. We note that these fundamentals are all characterized by at least three transitions. In contrast, the term values of the combination bands are much less accurate and determined by only one, or in one case two, transitions. It is important to note that the fundamentals of Ref. [68] result from effective-Hamiltonian calculations, which may yield higher apparent accuracy than the present MARVEL treatment.

Figure 2 provides a visual representation of the spectroscopic network of $\text{H}_2^{12}\text{C}^{16}\text{O}$, showing the upper-state energies of the measured transitions against corresponding lower-state energies, and giving a visual impression of the number of transitions linking them.

4.3. Protected formaldehyde lines

The National Academies of Sciences, Engineering, and Medicine (NASEM) maintains a list of key long-wavelength transitions relevant for astrophysical studies [152]. This list contains six
transitions belonging to H$_2^{12}$C$^{16}$O; they are given in Table 6. Some previous MARVEL studies, notably on water [110, 120] and ammonia [138], allowed the accuracy, to which some of these lines were known, to be improved using MARVEL. In the case of H$_2^{12}$C$^{16}$O, however, we find that the uncertainties in our MARVEL-determined frequencies simply match those of the current best laboratory determinations; for a discussion how these uncertainties are determined, see Ref. [110]. Nevertheless, Table 6 is still useful as it shows all highly-accurate studies of the NASEM-protected lines.

5. Updated AYTY line list

The AYTY line list [113] of H$_2^{12}$C$^{16}$O contains approximately 10 billion transitions linking 10.3 million rotational-vibrational states. These states are those with $J \leq 70$ which lie up to 10 000 cm$^{-1}$ above the ground state. As part of this study, we replace those energy levels of the AYTY list which are determined empirically by the MARVEL process.

The rovibrational states were matched on the basis of quantum numbers and then checked using the energies. As a result, 367 779 transition frequencies are determined using the empirical energy levels of this study. Of these, 183 673 lie above the dynamic HITRAN intensity cutoff [153]. These numbers should be compared to the 16 596 non-redundant transitions which form the

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### Table 6: Pure rotational frequencies of H$_2^{12}$C$^{16}$O lines under protection by the National Academies of Sciences, Engineering, and Medicine (NASEM) [152] and their various experimental and empirical determinations. The uncertainties of the last few frequency digits are indicated in parentheses.

| $f_{\text{NASEM}}$/GHz | Line assignment | $f_{\text{MARVEL}}$/GHz | $f_{\text{expt}}$/GHz |
|------------------------|----------------|------------------------|----------------------|
| 4.82966                | $\nu_0, 1_{1,0} \leftrightarrow 1_{1,1}$ | 4.829 659 960(50) | 4.829 659 960(50) [58] |
|                        |               | 4.829 660 0(10)       | 85                   |
|                        |               | 4.829 649 0(50)       | 62                   |
|                        |               | 4.829 660 0(10)       | 59                   |
| 14.488                 | $\nu_0, 2_{1,1} \leftrightarrow 2_{1,2}$ | 14.488 478 810(80) | 14.488 478 810(80) [61] |
|                        |               | 14.488 479 0(10)     | 85                   |
|                        |               | 14.488 650(20)       | 52                   |
|                        |               | 14.488 650(50)       | 45                   |
|                        |               | 14.488 65(10)        | 62                   |
| 140.84                 | $\nu_0, 2_{1,2} \leftrightarrow 1_{1,1}$ | 140.839 502(10) | 140.839 502(10) [85] |
|                        |               | 140.839 526(32)     | 60                   |
|                        |               | 140.839 300(50)     | 148                  |
| 145.603                | $\nu_0, 2_{0,2} \leftrightarrow 1_{0,1}$ | 145.602 949(10) | 145.602 949(10) [85] |
|                        |               | 145.602 966(34)     | 60                   |
|                        |               | 145.603 100(50)     | 148                  |
| 150.498                | $\nu_0, 2_{1,1} \leftrightarrow 1_{1,0}$ | 150.498 334(10) | 150.498 334(10) [85] |
|                        |               | 150.498 355(34)     | 60                   |
|                        |               | 150.498 200(50)     | 148                  |
| 218.222                | $\nu_0, 3_{0,3} \leftrightarrow 2_{0,3}$ | 218.222 192(10) | 218.222 192(10) [85] |
|                        |               | 218.222 186(49)     | 60                   |
|                        |               | 218.221 600(50)     | 148                  |
Table 7: Extract from the H$_2$CO state file. The full table is available from [www.exomol.com](http://www.exomol.com).

| I  | $E/\text{cm}^{-1}$ | $g$ | $J$ | $\delta/\text{cm}^{-1}$ | $\tau/\text{s}$ | $\nu_1$ | $\nu_2$ | $\nu_3$ | $\nu_4$ | $\nu_5$ | $\nu_6$ | $\Gamma_{\nu_1}$ | $\Gamma_{\nu_2}$ | $\Gamma_{\nu_3}$ | $\Gamma_{\nu_4}$ | $\Gamma_{\nu_5}$ | $\Gamma_{\nu_6}$ | $K$ | $\tilde{E}_{\text{AYTY}}/\text{cm}^{-1}$ |
|----|-----------------|----|----|----------------|-------------|-------|-------|-------|-------|-------|-------|-------------|-------------|-------------|-------------|-------------|-------------|-----|----------------|
| 1  | 0.000000        | 0  | 0  | 0               | 1           | A1    | 0     | 0     | 0     | 0     | 0     | 0           | 0           | 0           | 0           | 0           | 0           | Ma | 0.000000       |
| 2  | 1500.174503     | 1  | 0  | 0               | 0.000100    | A1    | 0     | 0     | 0     | 0     | 0     | 0           | 0           | 1           | 1           | 0           | 0           | 1   | 1500.129955    |
| 3  | 1746.09136      | 1  | 0  | 0               | 0.000100    | A1    | 0     | 1     | 0     | 0     | 0     | 0           | 0           | 0           | 0           | 0           | 0           | 0   | 1746.045388    |
| 4  | 2327.497142     | 1  | 0  | 0               | 0.200000    | A1    | 0     | 0     | 0     | 0     | 0     | 0           | 0           | 0           | 0           | 0           | 0           | 2   | 2327.497142    |
| 5  | 2494.32937      | 1  | 0  | 0               | 0.200000    | A1    | 0     | 0     | 0     | 0     | 0     | 0           | 0           | 0           | 0           | 0           | 0           | 1   | 2494.32937     |
| 6  | 2782.456913     | 1  | 0  | 0               | 0.000500    | A1    | 0     | 0     | 0     | 0     | 0     | 0           | 0           | 0           | 0           | 0           | 0           | 1   | 2782.410923    |
| 7  | 2999.006647     | 1  | 0  | 0               | 0.000500    | A1    | 0     | 0     | 0     | 0     | 0     | 0           | 0           | 0           | 0           | 0           | 0           | 2   | 2999.006647    |
| 8  | 3238.937891     | 1  | 0  | 0               | 0.000500    | A1    | 0     | 0     | 0     | 0     | 0     | 0           | 0           | 0           | 0           | 0           | 0           | 2   | 3238.937891    |
| 9  | 3471.720843     | 1  | 0  | 0               | 0.000500    | A1    | 0     | 0     | 0     | 0     | 0     | 0           | 0           | 0           | 0           | 0           | 0           | 2   | 3471.719306    |
| 10 | 3825.967015     | 1  | 0  | 0               | 0.000500    | A1    | 0     | 0     | 0     | 0     | 0     | 0           | 0           | 0           | 0           | 0           | 0           | 2   | 3825.967015    |
| 11 | 3936.435541     | 1  | 0  | 0               | 0.000500    | A1    | 0     | 0     | 0     | 0     | 0     | 0           | 0           | 0           | 0           | 0           | 0           | 2   | 3936.435541    |
| 12 | 4058.101422     | 1  | 0  | 0               | 0.000500    | A1    | 0     | 0     | 0     | 0     | 0     | 0           | 0           | 0           | 0           | 0           | 0           | 2   | 4058.101422    |

$a$: I: state identifier; $\tilde{E}$: state term value; $g$: state degeneracy; $J$: state rotational quantum number; $\delta$: energy uncertainty; $\tau$: lifetime; $\Gamma_{\text{tot}}$: total symmetry in $C_{2v}(M)$; $v_1 - v_6$: normal mode vibrational quantum numbers; $\Gamma_{\nu_1}$: symmetry of vibrational contribution in $C_{2v}(M)$; $K_a$ and $K_c$: rotational quantum numbers; $|C_{2i}|$: largest coefficient used in the assignment; $n_1 - n_6$: TROVE vibrational quantum numbers; K: data kind indicating if the term value is based on the MARVEL (‘Ma’) or the AYTY energy list (‘Ca’); $\tilde{E}_{\text{AYTY}}$: original AYTY state term value.

input to the original spectroscopic network of H$_2^{12}$C$^{16}$O. It can be seen that this process leads to a significant increase in the number of transitions whose line centres are determined to high-resolution experimental accuracy.

Obviously, 5029 empirically determined energy levels is only a small portion of the 10.3 million entries in the original AYTY line list. We therefore had to estimate the (significantly larger) uncertainties associated with the calculated energy levels. This is important, not least because it allows transitions that are predicted with high accuracy to be easily identified. We estimated the uncertainties, in cm$^{-1}$, of the computed levels using the formula

$$\delta = 0.1 (v_1 + v_2 + v_3 + v_4 + v_5 + v_6) + 0.005J(J+1).$$

This update is in line with the requirements of the 2020 release of ExoMol and is designed to facilitate the use of the data in high-resolution studies by quantifying the uncertainty associated with each transition and hence identifying those known with the required accuracy for a given study.

Table 7 gives a small portion of the updated ExoMol States file in standard ExoMol format. The complete file along with the AYTY Trans file, which is unchanged by the current procedure, can be obtained from the ExoMol website (www.exomol.com).

The HITRAN database contains limited data on H$_2^{12}$C$^{16}$O: besides pure rotations it covers only two bands. Figure 3 gives a comparison for these regions. The agreement is very good and shows that our MARVEL analysis is largely sufficient to cover these regions. Figure 4 illustrates the relative (in)completeness of the HITRAN and our MARVEL data sets when used to simulate the room temperature spectra of H$_2^{12}$C$^{16}$O. There are a number of missing bands in HITRAN and the
Figure 3: Room-temperature \((T = 296 \, K)\) spectra of \(\text{H}_2\text{C}^{16}\text{O}\) in three different regions covered by HITRAN 2016 [151]. The upper panels, in blue, show stick spectra simulated using the MARVEL energy term values from this work and the Einstein-\(A\) coefficients from the AYTY line. The lower panels, in red, show the corresponding spectra taken from HITRAN 2016.

Figure 4: Room temperature \((T = 296 \, K)\) spectra of \(\text{H}_2\text{C}^{16}\text{O}\) from three different sources: lower panel, HITRAN 2016 [151]; upper panel, this work (see caption of Fig. 3) where possible or else from the AYTY line list.

database can now be supplemented with our synthetic line list constructed using the line positions determined to experimental accuracy using MARVEL and AYTY transition intensities.

The AYTY line list was actually designed for treating formaldehyde in hot environments. In order to illustrate the lack of experimental data at high temperatures, Fig. 5 shows \(T = 1000 \, K\) absorption spectra simulated with the same three source as above: MARVEL line positions (this work) combined with the AYTY Einstein-\(A\) coefficients, the HITRAN line list, and the AYTY line list. It is clear that at high temperatures only AYTY provides the spectroscopic coverage required for high temperatures and that known laboratory spectra are not capable of giving a complete representation of hot formaldehyde.
Figure 5: High temperature ($T = 1000$ K) spectra of $\text{H}_2^{12}\text{C}^{16}\text{O}$ from three different sources: HITRAN 2016 \cite{151}, AYTY \cite{113}, and this work (see also caption to Fig. 3).

6. Summary and Conclusions

Apart from a few sources where the authors were reluctant to provide their published results for analysis \cite{92,94,95}, all literature lines measured for $\text{H}_2^{12}\text{C}^{16}\text{O}$ have been collected and analyzed during this study. The information contained in the literature sources was augmented by new measurements results, including seven Lamb-dip lines and 82 further lines, all corresponding to rotational transitions within the ground, $\nu_3$, $\nu_4$, and $\nu_6$ vibrational states. The analysis utilized the Measured Active Rotational-Vibration Levels (MARVEL) approach and the xMARVEL code. A characteristic of MARVEL is that it is an “active” approach, which means that should new sources, or even existing sources that have not been included, became available it is straightforward to include them in a renewed analysis and produce an updated version of the line-by-line database assembled for $\text{H}_2^{12}\text{C}^{16}\text{O}$.

Of the total of 19,831 transitions processed, which come from 43 sources including this work, 16,403 could be validated, providing 5029 empirical energy levels of $\text{H}_2^{12}\text{C}^{16}\text{O}$ with statistically well-defined uncertainties. Our newly-determined empirical rotational-vibrational energy levels are used to improve the accuracy of ExoMol’s AYTY line list for hot formaldehyde \cite{113}. This improved line list is available as supplementary material, along with the xMARVEL files, containing all the rovibrational transitions collated, whether validated or not, as well as all the empirical energy levels derived during this study.

It is the stated plan of the ExoMol project \cite{112} to update all ExoMol line lists to include both
empirical energy levels, where available, and uncertainties for all the energy levels; thus allowing the uncertainty associated with any transition to be estimated. These data will become a standard part of the ExoMol line list and also form input for the new ExoMolHR database, which provides data only on lines of higher intensity whose wavelengths are known to high accuracy. So far only a limited number of ExoMol line lists are available with specified uncertainties in the energy levels. These include important line lists for which MARVEL data were already available, namely those for water [156], AlH [157], $^{12}$C$_2$ [131], $^{12}$C$_2$H$_2$ [158] and $^{48}$Ti$^{16}$O [158], and recently produced line lists including those for CO$_2$ [159], H$_3$O$^+$ [160] and NH$_3$ [161]. The present study is the first in a series where a MARVEL analysis is performed with the intention of updating an available line list.

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