METHANE AND ITS ISOTOPES: CURRENT STATUS AND PROSPECTS FOR IMPROVEMENT†

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Abstract—The compilations of molecular line parameters of methane are continually being updated and improved. In the present article, numerous changes made for the 1991 and 1992 versions of the HITRAN database in the 0–6185 cm^{-1} region are described. An assessment of the deficiencies in the parameters is also given.

INTRODUCTION

Methane is an important and relatively abundant constituent of planetary atmospheres. As a result, remote sensing applications require good knowledge of its spectroscopic line parameters: position v, intensity I, air-broadened line width γ_{air} (HWHM), lower-state transition energy E'', self-broadened line width γ_{self}, temperature dependence of the air-broadened width n, and the air-broadened pressure-shift δ_{air}. In the last decade, laboratory studies have resulted in significant revisions of these molecular line parameters in the public databases.[1-3] This is illustrated in Table 1 which shows a comparison of the CH_4 parameters compiled for the 1982 (AFGL), 1986, 1991 and 1992 HITRAN databases; it displays the total number of bands, lines, wavenumbers (cm^{-1}) covered, the integrated intensity and the minimum i.r. intensity cutoff. The updates focused on adding new weak bands and improving the accuracies of vibration–rotation constants for bands already included in the catalog so that the total integrated absorption changed only slightly.

For the 1991 and 1992 editions of HITRAN, results from new laboratory studies of methane absorption spectra were incorporated in five spectral intervals: (a) 0–579 cm^{-1}, (b) 904–1969 cm^{-1}, (c) 2005–3254 cm^{-1}, (c) 3700–4667 cm^{-1}, and (e) 550–6185 cm^{-1}. Table 2 is a summary of the modifications, given by region and isotope (1 = $^{12}CH_4$, 2 = $^{13}CH_4$, 3 = CH_3D), the references used, the type of revision (change of existing parameters or addition of new ones), the minimum line intensity cutoff, and the type of rotation–vibration notation. For the first two isotopes, measured air-broadened linewidths and air-shifts of over 1300 transitions[4-9] between 1100 and 4600 cm^{-1} were inserted, and their averaged values were extrapolated for transitions not directly measured. A few dozen measurements[10] and estimates were also used for self-broadened linewidths. A small number of CH_3D width measurements[11,12] were introduced with default values set for the majority. Revised predictions based on the theoretical modeling of measured positions and intensities of the two lowest fundamentals of $^{12}CH_4$ and $^{13}CH_4$[13-15] and the four lowest fundamentals of CH_3D[16-18] were included, as were predictions of hot bands[19-21] from 0 to 1978 cm^{-1}. Finally, experimental measurements[22-25] from 3700 to 3900 cm^{-1} and 5500 to 6185 cm^{-1} were added for the first time. A lower minimum intensity criterion was applied to reflect the needs of planetary studies and to anticipate improved sensitivity of atmospheric sensors. With the inclusion of nine new bands and

Table 1. Comparison of the 1982, 1986, 1991 and 1992 methane parameters.

Summations	1982	1986	1991	1992
Total number of bands	23	32	37	37
Total number of lines	13005	17774	46971	47415
Total wavenumbers (cm^{-1}) included	2313	3614	4205	4205
Total absorption$^+$	$1.73x10^{17}$	$1.74x10^{17}$	$1.77x10^{17}$	$1.77x10^{17}$
Minimum IR intensity included$^+$	$3.x10^{24}$	$3.x10^{24}$	$4.x10^{26}$	$4.x10^{26}$

$^+$ The intensities are in units of cm^{-1} / (molecule $\cdot$ cm^{-2}) at 296 K

the revision of the nine existing ones, many lines weaker than 4×10^{-24} cm^{-1}/(molecule·cm^{-2}) were incorporated; as a result, the number of lines changes from 17774 in 1986 to 47415 in 1992. The reference and error code fields were also implemented. As in 1986,[1,2] different notation schemes were used to identify the rotational quantum numbers of CH_4. Between 1991 and 1992, the only changes made were in the 3900–4172 cm^{-1} region,[23] with the insertion of empirical lower state energies of lines and the addition of 444 weak features.

CURRENT STATUS

Positions and intensities by region

In the 0–578 cm^{-1} interval, the 1986 edition contained only 80 CH_3D lines below 101 cm^{-1}. For the present database, the CH_3D entries were not changed, but some 8600 very weak hot band transitions of the $^{12}CH_4$ and $^{13}CH_4$ (ground–ground, v_4–v_4, v_2–v_4) were computed[19,20] using constants based on analyses of the ground states[13] and the v_2/v_4 dyads.[14] However, the more recent improvements of Roche and Champion[26] were not included. The statistics of the analyses indicated that the accuracies for positions were 4×10^{-5} cm^{-1} at best. Accuracies of intensities were difficult to judge, since no measurements were available. The systematic errors in the calculated relative intensities may be as great as 30%.

In the 904–1969 cm^{-1} (dyad) region, all the fundamental bands of the three isotopes were revised, and a smaller minimum intentsity criterion was employed (see Table 2). In Table 3, the resulting atlas for the region is summarized by showing the list of the isotopes, bands and their centers, the sum of the intensities and the number of lines. The positions and intensities of the v_2 and v_4

Table 2. Summary of the 1991 and 1992 revisions for methane and its isotopes.

Bands	Iso Num	Region (cm^{-1})	References			Status	Minimum Intensity	Rovib. Notation
			v	I	γ			
gs–gs	1,2	0000-0313	19	19	4	new	$4.x10^{34}$	J,C,α
dyad–dyad	1,2	0002-0579	20	20	4	new	$4.x10^{29}$	J,C,α
dyad(v_2,v_4)	1,2	0992-1799	14	15	4	chg	$4.x10^{26}$	J,C,α
pentad–dyad$^+$	1	1109-1969	21	21	4	new	$4.x10^{26}$	J,C,α
v_3, v_5, v_6	3	0904-1696	16	16	5,6	chg	$1.x10^{27}$	
v_2, $2v_6$	3	2005-2356	1,17	1,17	def.	new	$1.x10^{28}$	
pentad$^+$	1,2	2255-3254	1,6	1,6	4,7-9	γ only	$3.x10^{24}$	mixed
v_1, v_4, $2v_5$	3	2902-3147	1	1	def.	fixed$^\#$	$3.x10^{24}$	
unassigned	1	3700-4136	22,23	22,23	4,23	new	$4.x10^{25}$	
octad$^+$	1	4136-4667	1,28	1,28	4	γ only	$4.x10^{23}$	J,R,C,n
$2v_3$	1	5891-6106	24	24	4	chg	$4.x10^{23}$	J,R,C,n
$2v_3$	2	5898-6069	24,29	24,29	4	chg	$1.x10^{24}$	J,R,C,n
unassigned	1	5500-6185	24,25	24,25	4,25	new	$1.x10^{24}$	

$^+$ The dyad refers to two states: v_2 and v_4; the pentad refers to the five states: v_1, v_3, $2v_2$, $2v_4$, and v_2+v_4; the octad refers to eight states: $3v_4$, $2v_4+v_2$, v_1+v_4, v_3+v_4, v_4+2v_2, v_1+v_2, v_2+v_3 and $3v_2$. Minimum intensity is given in units of cm^{-1}/ (molecule $\cdot$ cm^{-2}).
$^\#$ A few dozen false entries appearing in the 1986 edition were removed.

Table 3. Summary of the 900–2000 cm^{-1} atlas of methane.

Isotope	Band	cm^{-1}	Σ Intensity	Lines
CH$_3$D	ν_6	1161	0.0362	2081
^{13}CH$_4$	ν_4	1302	1.24	1246
CH$_3$D	ν_3	1306	0.0260	1003
^{12}CH$_4$	$2\nu_4 - \nu_4$	1310	0.908	2397
^{12}CH$_4$	$\nu_2 + \nu_4 - \nu_2$	1310	0.138	1813
^{12}CH$_4$	ν_4	1310	127.500	3198
^{12}CH$_4$	$\nu_1 - \nu_2$	1384	0.00179	342
CH$_3$D	ν_5	1472	0.00876	1873
^{12}CH$_4$	$\nu_3 - \nu_2$	1485	0.00855	768
^{12}CH$_4$	ν_2	1533	1.35	1799
^{13}CH$_4$	ν_2	1533	0.0128	724
^{12}CH$_4$	$2\nu_2 - \nu_2$	1533	0.0021	500
^{12}CH$_4$	$\nu_2 + \nu_4 - \nu_4$	1533	0.0075	1214
^{12}CH$_4$	$\nu_1 - \nu_4$	1607	0.0005	135
^{13}CH$_4$	$\nu_3 - \nu_4$	1710	0.047	1833
^{12}CH$_4$	$2\nu_2 - \nu_4$	1750	0.00054	189

$^+$ The sum of the intensities are in units of cm^{-1}/(molecule · cm^{-2}) at 296K.
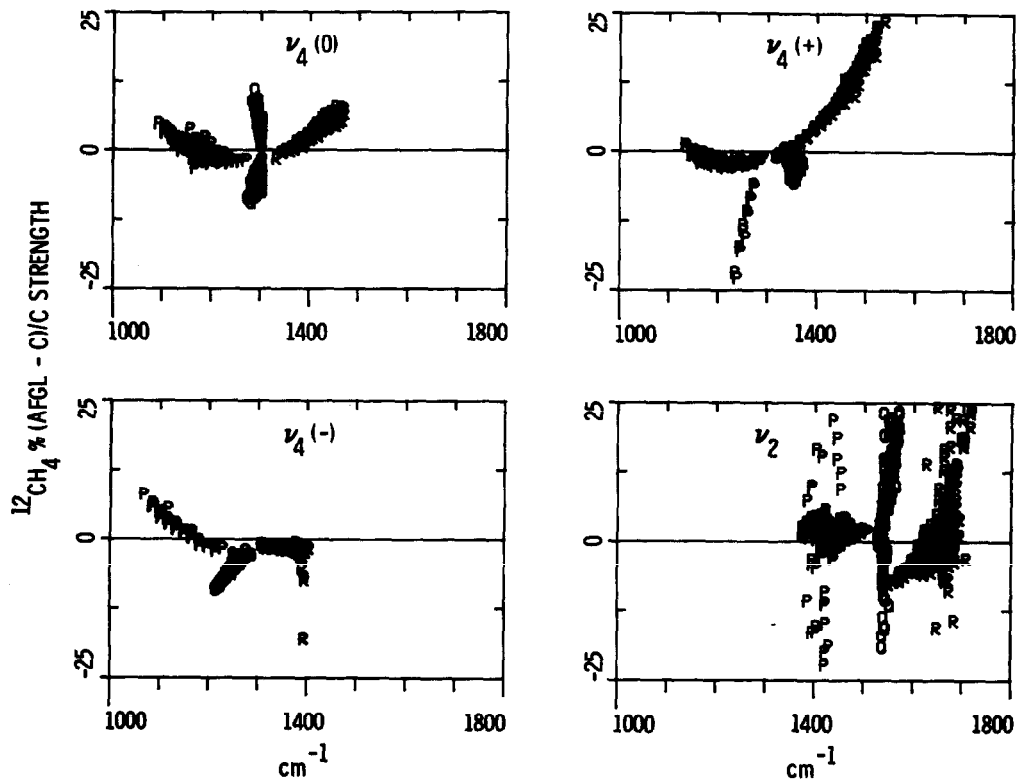

Fig. 1. Comparison of the 1991 and 1992 ^{12}CH$_4$ calculated intensities of ν_2 and ν_4 with the corresponding values from the 1986 HITRAN compilation for some 1200 transitions that were measured and fitted by Brown et al.[15] The notation ($-$,0, $+$) indicate the three degeneracies of the ν_4 fundamental; $R(-)$, $Q(0)$ and $P(+)$ are the allowed transitions.

fundamentals of $^{12}CH_4$ and $^{13}CH_4$ were measured with high precision using the Fourier transform spectrometer located at the McMath telescope, Kitt Peak National Observatory, Arizona and successfully modeled.[14,15] In these studies, the r.m.s. values of the observed minus calculated positions and intensities were $0.00006\,cm^{-1}$ and 3%, respectively. To indicate how the intensities of the dyad changed, the percent differences between the 1986 and 1991 values for the three components of the v_4 ($-,0,+$) and v_2 bands are plotted in Fig. 1.

For CH_3D, the analysis of the positions and intensities of the v_6, v_5 and v_3 fundamentals between 900 and 2000 cm^{-1} was used;[16] the intensities, computed for a 100% sample of the isotope, were multiplied by 5.9×10^{-4} to correspond to the telluric abundance. The r.m.s. values of the observed minus calculated values of the triad analysis of v_6, v_5, and v_3 were $0.0076\,cm^{-1}$ for positions and 7% for intensities. A more recent intensity study of Tarrago et al[27] was not included.

Some 10,000 transitions of nine new hot bands of the main isotope were added. These came from a Ph.D thesis[21] by Ouardi who modeled FTS intensity measurements to provide preliminary predictions of the hot bands of $^{12}CH_4$ arising from the dyad (v_2, v_4) levels as the lower states and five pentad levels ($2v_4$, $v_2 + v_4$, v_1, v_3 and $2v_2$) as the upper states. Because of the large uncertainties associated with modeling the pentad levels, the accuracies in positions were only $0.004\,cm^{-1}$. The
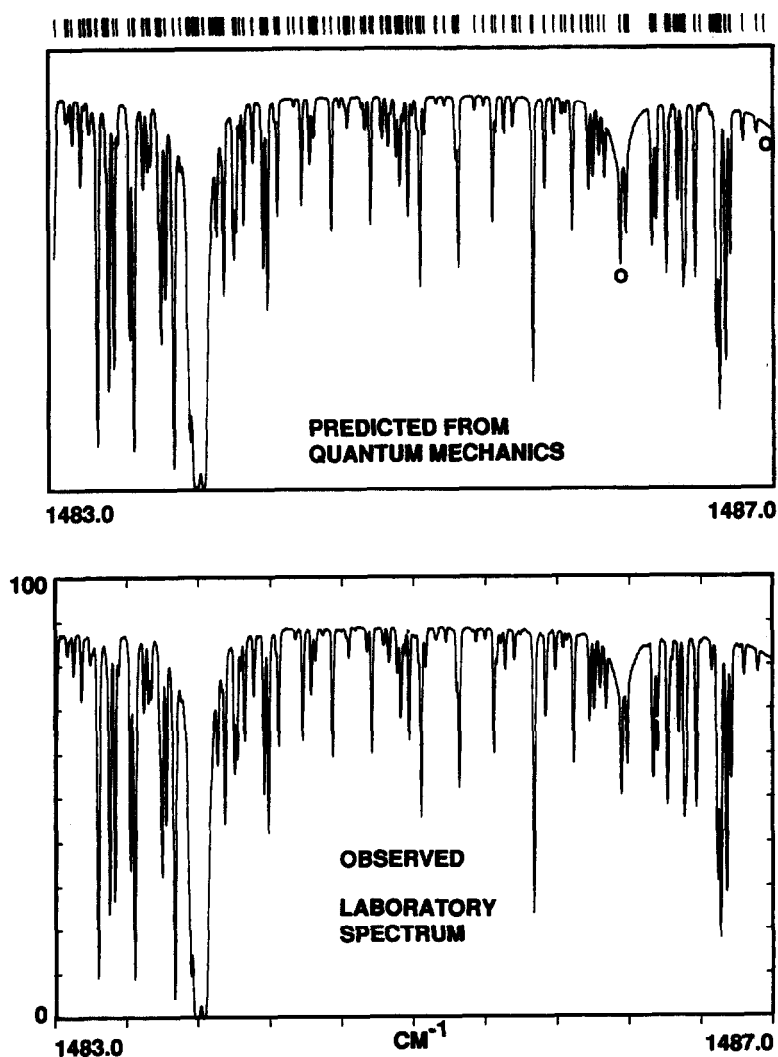

Fig. 2. An indication of the good agreement between the predicted and observed spectra in the region of the v_3–v_2 Q branch. The observed spectrum is recorded with the FTS at Kitt Peak National Observatory/National Solar Observatory with a 193 m path and 10 torr of normal sample methane at room temperature. The predicted spectrum also includes features arising from residual H_2O, which are marked by °. A summary of the bands included in the 1000–2000 cm^{-1} methane atlas is shown in Table 3.

intensities of the hot bands were fitted to experimental data from JPL with estimated accuracies of 4–20%. To indicate the quality of the results, Fig. 2 shows agreement between the predicted and observed spectra in the region of the very weak v_3–v_2 band. The observed spectrum was recorded at $0.0056\,\mathrm{cm}^{-1}$ resolution (unapodized) using the FTS at Kitt Peak; the gas pressure was 10 torr at room temperature and the path was 193 m. Residual water transitions are indicated by °.

In the 2005–3254 cm⁻¹ (pentad) region, only a few changes were made. For CH_3D, the v_2 band was added,[17,18] and 35 false entries[2] between 2900 and $3150\,\mathrm{cm}^{-1}$ were located (by doing visual comparison of observed laboratory spectra and synthetic spectra based on the parameters) and purged. A few new lines in the v_3 band of $^{13}CH_4$ were inserted.[6] Their intensities were set by finding a ratio of intensities of the added line to another line in the same manifold either in the $^{12}CH_4$ v_3 band or from the original spectral fits. This ratio was then employed with the appropriate $^{13}CH_4$ line intensity already on the linelist to obtain the intensity of the added line. The reference codes were set to 0. In addition, a dozen previously-unassigned lines were identified[6] as v_3 lines of $^{13}CH_4$.

The linelist in this region is still a mixture of prediction for part of the pentad of $^{12}CH_4$ with experimental positions and intensities greater than $4 \times 10^{-24}\,\mathrm{cm}^{-1}/\mathrm{molecule} \cdot \mathrm{cm}^{-2}$ at room temperature (see Refs. 1 and the references therein).† For the measurements, the transition identities have been ascribed, but these may be incorrect in some cases. Lower state energies of the unidentified lines (9% of this region) are either obtained empirically or are artificially set to −1.

In the 3700–4667 cm⁻¹ (octad) region, the 1986 linelist consisted of measurements in the 3900–4667 cm⁻¹ region[1,2,28] for which some assignments were known for three of the eight possible bands arising from the ground state. The list did not include all the transitions that can be observed in atmospheric spectra. In the 1991 edition, line positions and intensities from 4172 to $4666\,\mathrm{cm}^{-1}$ did not change, but new room temperature measurements,[22] made with the Kitt Peak FTS, were added from 3700 to $4136\,\mathrm{cm}^{-1}$ with very weak lines included. Only a few new quantum assignments (11 lines of $3v_4$) were inserted. For the 1992 update, additional weak lines from 4136 to $4172\,\mathrm{cm}^{-1}$ were included, and empirically-determined lower state energies from 3900 to $4172\,\mathrm{cm}^{-1}$ were obtained using cold sample spectra.[23] The experimental accuracies of empirical lower states were usually in the range of 5–10% even for well isolated lines. This large uncertainty could contribute substantial errors for atmospheric applications, depending on the quantum numbers and temperatures involved. To avoid this in the methane linelist, an effective J'' was computed [= $\mathrm{sqrt}(E''/5.2)$] so that a mean calculated ground state energy from Table VIII of Ref. 13 could be used. The lower state energies of unassigned lines from 3700 to $3900\,\mathrm{cm}^{-1}$ were set to a default value of $300.3333\,\mathrm{cm}^{-1}$.

In the 5500–6185 cm⁻¹ region, the 1986 compilation contained only 142 lines of $^{12}CH_4$ and 93 lines of $^{13}CH_4$ calculated for the $2v_3$ bands[1,2,29] in the 5897–6107 cm⁻¹ region. The new list now has over 2000 experimental positions and intensities[24] to represent the methane absorption between 5500 and $6185\,\mathrm{cm}^{-1}$. In comparing the two lists line by line, one finds that the $2v_3$ band intensity effectively increased 11% and that a substantial Herman–Wallis factor was applied to the P and R branch lines. Because only the strongest lines of $^{13}CH_4$ were measured,[24] the new experimental and old predicted values were merged, using measurements where available and scaling the old prediction in proportion to the change in the $^{12}CH_4$ band strength and Herman–Wallis factor. The $^{13}CH_4$ lines with intensities greater than $4 \times 10^{-24}\,\mathrm{cm}^{-1}/(\mathrm{molecule} \cdot \mathrm{cm}^{-2})$ were generally taken from the experimental values. While only 3% of the lines were assigned (to $2v_3$ at $6000\,\mathrm{cm}^{-1}$ and $2v_4 + v_3$ near $5640\,\mathrm{cm}^{-1}$), many of the lower state energies were determined empirically using cold sample spectra[25]; as in the previous region, an effective J'' was computed [= $\mathrm{sqrt}(E''/5.2)$] so that a mean value of ground state energy at each J could be used for the database. A default value of $555.5555\,\mathrm{cm}^{-1}$ was used otherwise. Figure 3 shows synthetic spectra using the new empirical results for the 2.5 and 1.7 μm regions. No parameters were available between 5000 and $5500\,\mathrm{cm}^{-1}$

Air-broadened halfwidths

The air-broadened halfwidths of the methane isotopes were based upon Refs. 4–9. In these studies, experimental widths of some 1300 transitions of v_4, v_2, v_3, $2v_4$, $v_2 + v_4$, $v_1 + v_4$ and $v_3 + v_4$ of $^{12}CH_4$ and the fundamentals of $^{13}CH_4$ were obtained with the Kitt Peak FTS and, in some cases,

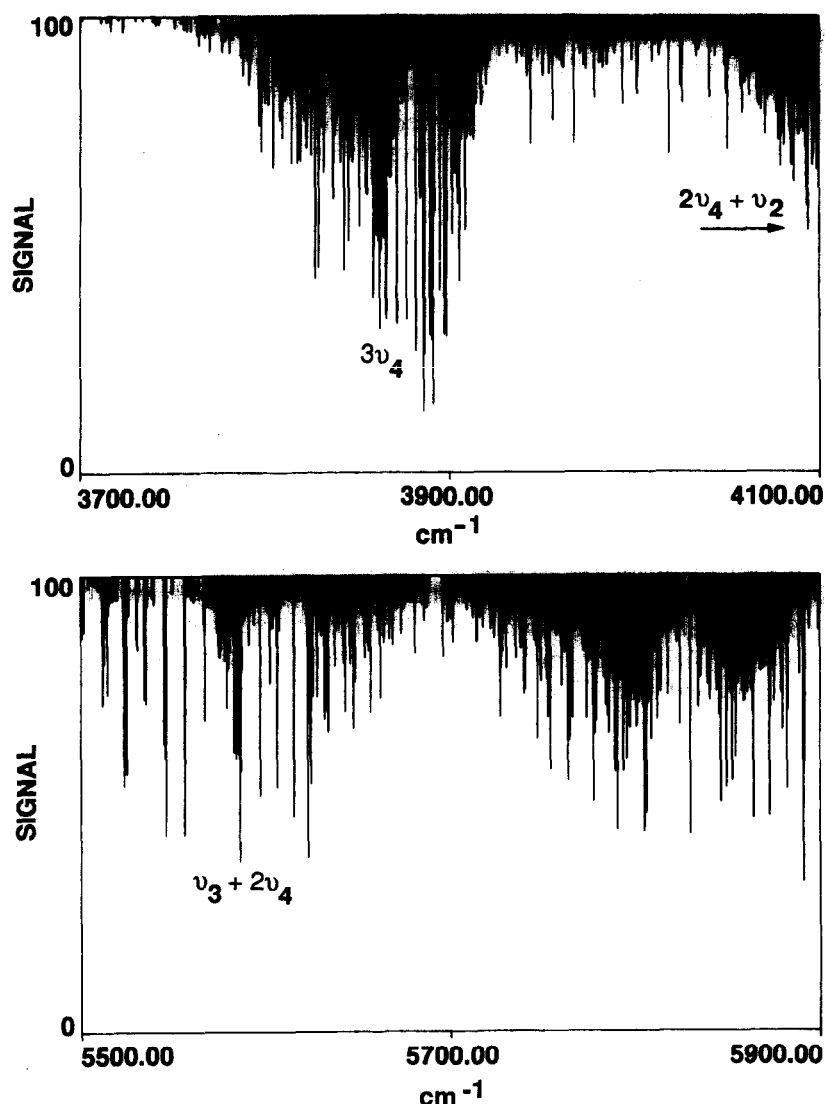†Refs. 46–52 therein are needed to document the 1992 methane linelist completely.

Fig. 3. Calculated spectra at $0.02 \, \text{cm}^{-1}$ resolution (apodized) based on the empirical line parameters of methane. The pressure is 2.0 torr at room temperature and the path is 12.3 m. The two regions are largely unassigned, except for a few R branch lines of the $3v_4$ and $2v_4 + v_3$ bands at low J that can be ascribed by visual inspection. In the interim, the compilation includes experimentally-determined lower state energies.[23,25]

with a TDL at Langley.[1,6,7] These were inserted into the 1991 and 1992 editions, with indicated accuracies between ±3 and 15%.

These measurements were not modeled to achieve new predictions of linewidths based on quantum mechanics, as is available for other minor gases. In the interim, empirical mean values of $^{12}CH_4$ air-broadened widths, reproduced in Table 4, were tabulated[4] to provide widths as a function of J and C ($=A$, F, E) for transitions with known assignments. The uncertainties associated with this tabulation are higher than the experimental accuracy (±20%) because the dependence of the width on transition quantum numbers is ignored. For $^{13}CH_4$ a value of 0.95 times the mean values of $^{12}CH_4$ were used except in the v_3 region. The 5% discrepancy seen between the $^{12}CH_4$ lines and the $^{13}CH_4$ line widths in the v_4 band[4] does not seem to exist in the v_3 band.[6] From 3900 to $6186 \, \text{cm}^{-1}$, widths of unassigned lines with empirically determined lower states were taken from Table 4 using the effective J'' calculated from E'' and assuming that the lines were all "F" species. The widths of the remaining unassigned lines were set to a default value of $0.055 \, \text{cm}^{-1}/\text{atm}$. For CH_3D, the default value $0.060 \, \text{cm}^{-1}/\text{atm}$ was used, except for a dozen experimental values[12,13] for the v_3 and v_6 fundamentals.

Table 4. The mean air-broadened $^{12}CH_4$ widths.

$|m|^+$	A	F	E
0 - 1.5	0.066	0.056	0.061
2 - 3.5	0.066	0.066	0.061
4 - 5.5	0.066	0.063	0.058
6 - 7.5	0.064	0.061	0.056
8 - 9.5	0.058	0.058	0.052
10 - 11.5	0.054	0.053	0.045
12 - 13.5	0.051	0.052	0.041
14 - 15.5	0.047	0.044	0.036
16 - 17.5	0.047	0.044	0.029
18 - 19.5	0.045	0.039	0.028
(default)	0.055		

$^+$ $m = -J''$, $J''+0.5$ and $J''+1$ for P, Q and R, respectively. The widths[4]
are in cm^{-1}/ atm at 296K. For $^{13}CH_4$ lines, the widths are scaled by 0.95.
The default value is 0.06 cm^{-1}/atm for CH$_3$D.

Self-broadened halfwidths

Measured self-broadened linewidths[10] for 61 allowed R (0–12) branch lines of v_4 were put into the 1991 edition. For all other methane lines, the air-broadened values in Table 4 were scaled to provide a crude estimate; the scaling factors, shown in Table 5, were tabulated from the ratio of self-broadened values[10] to corresponding air-widths[4] for 53 transitions. The mean ratio of self- to air-broadened halfwidths was 1.37 (±0.09). The scatter arises not from measurement error, but rather from transition quantum number dependence. Widths of unassigned lines above 3900 cm^{-1} with empirically measured lower state energies were determined by computing the effective J'' and assuming the species to be F. For unidentified lines, the value of 0.075 cm^{-1}/atm was used. All estimated self-broadened halfwidths were rounded to the nearest 0.001 cm^{-1}/atm. The CH$_3$D lines were set to a default value of 0.08 cm^{-1}/atm. The uncertainties associated with the estimates are thought to be $\pm25\%$.

Temperature dependence of γ_{air}

In the 1986 edition, the temperature dependence of the halfwidth "n" was set to three different values according to symmetry species, using the results of Varanasi et al.[30] However, other studies[31-36] did not confirm this conclusion, so for the 1991 and 1992 editions, a mean value of 0.75 has been selected for all lines.

Pressure shifts δ_{air}

Pressure shifts of methane in air were implemented for the first time. The measurements with accuracies of perhaps ±0.0005 cm^{-1}/atm^{-1} for $^{12}CH_4$ and $^{13}CH_4$[4-9] were inserted directly for over 1300 lines. Unfortunately, no simple relationship between pressure shift and rotational quantum number was perceived in any of these studies. Lines not measured in these studies were given default values based on the mean values obtained in each spectral region: -0.003 cm^{-1}/atm between 900 and 2356 cm^{-1}, -0.006 cm^{-1}/atm between 1900 and 3254 cm^{-1} and -0.0081 cm^{-1}/atm above 3700 cm^{-1}. Again, the mean averages are considered to be crude estimates. For example, the studies

Table 5. Self-broadened widths conversion.

Species	$\gamma_{self} = \gamma_{air} \cdot F$
Assigned	where F =
A	$1.458 - 0.0449 \times J'' + 0.00449 \times (J'')^2$
F	$1.174 + 0.0216 \times J''$
E	$1.199 + 0.0284 \times J''$
Unassigned	0.075 (default)
CH$_3$D	0.080 (default)

of the v_2 and v_4 regions indicate a mean pressure shift of -0.0028 (± 0.0030) cm^{-1}/atm.[4] Since these mean values are approximately proportional to vibrational transition energy, the lines from 0 to 580 cm^{-1} were all assigned pressure shifts of zero. However, the shifts for lines near 6000 cm^{-1} are set to -0.008 rather than a value of -0.012, as suggested by a frequency extrapolation. Inadvertently, the shifts of CH_3D were set to -0.003 for v_2 or -0.006 cm^{-1} for $2v_6$.

Error and reference codes

The error codes were implemented in the 1991 and 1992 editions. However, for positions and intensities, the indicated codes are rather subjectively determined; they should be viewed as the probable errors rather than systematic evaluations of the uncertainties. For widths, the error code is for the air-broadened parameter. If measurements are used, then the error code corresponds to twice the standard deviation from random errors in the original fits to the experimental data. Widths based on the mean tabulations of Table 4 were given one default error code.

Rotation–vibration notation for assignments

Detailed explanations and examples of methane notation are more appropriately given else-where,[37-40] but certain aspects are highlighted here for the convenience of the database users. At present, there are three different ro-vibrational notation schemes for methane transitions; examples of these are shown in Table 6 for the E levels of the methane pentad at J equal 7. All schemes have J and C ($=A_1,A_2,E,F_1,F_2$) with the general selection rule of $\Delta J = 0$, ± 1 and $\Delta C \neq 0$ for the transitions. In the older set, the energy levels are labelled by five quantum numbers: J, R, C, n and the vibration code v. The value of n is an index that is incremented through levels of the same J, R, and C in ascending or descending order of energy to express an additional selection rule for strong "allowed" ($\Delta R = 0$ and $\Delta n = 0$) and weak "forbidden" ($\Delta R \neq 0$ and/or $\Delta n \neq 0$) transitions. These are most applicable to the i.r. active fundamentals v_3 and v_4 and a few of their overtones such as $2v_4$. The newer studies, based on the formalism of Champion,[37] indicate that R is generally not a valid quantum number. This is the case even for $v_2 + v_4$; in this state, the three i.r. active and the three i.r. inactive degeneracies mix above J equal 3, giving rise to transitions of almost equal intensity so that selection "rules" of allowed and forbidden transitions are essentially defunct.

Table 6. Rotational notation for the pentad levels.

State	J	C	R	n	n	α	Energy cm^{-1}
$2v_4$	7	E	5	1	1	1	2827.895
	7	E	6	1	2	2	2854.061
	7	E	7	1	3	3	2874.613
	7	E	7	1	4	4	2891.703
	7	E	8	1	5	5	2924.460
	7	E	8	2	6	6	2930.176
	7	E	9	1	7	7	2970.814
v_2+v_4	7	E			1	8	3088.128
	7	E			2	9	3088.757
	7	E			3	10	3092.381
	7	E			4	11	3123.789
	7	E			5	12	3136.014
	7	E			6	13	3161.477
	7	E			7	14	3170.489
	7	E			8	15	3173.594
v_1	7	E	7	1	1	16	3210.234
v_3	7	E	6	1	1	17	3306.000
	7	E	7	1	2	18	3309.903
	7	E	8	2	3	19	3314.129
	7	E	8	1	4	20	3314.930
$2v_2$	7	E			1	21	3364.327
	7	E			2	22	3366.702
	7	E			3	23	3370.663

To be able to model bands like these, two other approaches are used depending on whether the band is treated as an isolated state or as one of a "polyad" set.[38] In both cases, the levels previously indexed separately as a function of R and v are now counted together in order of *increasing* energy, as shown in Table 6. In the isolated band situation, levels are labelled by J, C, n, and v. For example, Table III of Hilico et al[39] shows how the index numbering changes for all the levels of v_4 and v_3 below J equal 14 if the R quantum number is invalid, but the vibrational identity is maintained. In the polyad case, the quantum numbers are J, C, and α, with v being given for convenience. In labelling the energy levels, the vibrational identification is ignored so that the index "α" is numbered not in just one vibrational state, but throughout the polyad set of bands that are in interaction. For the dyad, all the levels of a particular J and C of v_4 are counted first, followed by those of v_2 (until the levels of the two states begin to intermingle above $J = 23$). For the pentad, the five bands are indexed together, starting with $2v_4$, as seen in Table 6.

In the HITRAN database, all the entries below 2461 cm^{-1} are given with the polyad notations. Above 3700 cm^{-1}, the notation appears to be the old isolated band scheme, although for $v_3 + v_4$ the notation is somewhat contrived (since the quantum numbers are really J, S, R, C, n and v). In the pentad region, the ^{12}CH$_4$ lines are generally given with the polyad notation, and the ^{13}CH$_4$ lines and the hot bands are listed with the old isolated band scheme. Future studies will eventually result in the removal of all the old isolated band entries, leaving states labeled by either the polyad notation for well-understood regions (dyad and pentad) or the new isolated band scheme in region where only a partial analysis has been completed (the octad and above). For those who use the database for remote sensing, the notation is of little consequence. Those who apply it to interpret laboratory studies can contact the authors (Champion, Brown) for assistance in converting from one set to another.

Deficiencies

Despite numerous changes, the methane line parameters are still incomplete and/or inaccurate. The specific flaws are listed in Table 7 by region and depicted schematically in Fig. 4; the diagram indicates the availability of measurements and calculations of the four essential parameters (v, I, γ, E'') for five spectral regions between 0 and 6200 cm^{-1}. The regions are labeled by the "polyad" scheme, which indicates the number of vibrational states that fall in each region: (a) rotational: 0–578 cm^{-1}; (b) dyad containing v_2 and v_4: 900–2000 cm^{-1}; (c) pentad containing $2v_4$, $v_2 + v_4$, v_1, v_3 and $2v_2$: 2000–3300 cm^{-1}; (d) octad containing $3v_4$, $2v_4 + v_2$, $v_1 + v_4$, $v_3 + v_4$,

Table 7. What is wrong with the 1992 methane compilation.

| Region (cm^{-1})	Comments
0 - 600	Intensities to ±30%?; no experimental data
900 - 2000	Hot band predictions: v to ± 0.004 cm^{-1}, intensities to ± 20%
2000 - 2350	CH$_3$D: v to ± 0.002 cm^{-1}
2300 - 3300	Mix of empirical data and ^{12}CH$_4$ prediction; some assignments missing or wrong Poor and incomplete catalog of the isotopes and of the hot bands
3700 - 4170	Only empirical data with experimental lower states
4170 - 4700	Missing weak lines (I< 10^{-23}), empirical data with missing or wrong assignments
5100 - 5500	No data for features that appear in atmospheric spectra
5500 - 6180	Only empirical data with experimental lower states
7200 - 7700	No data for features that appear in atmospheric spectra
all regions:	Self-broadened widths extrapolated from few measurements and no accurate models for the width and pressure shift measurements
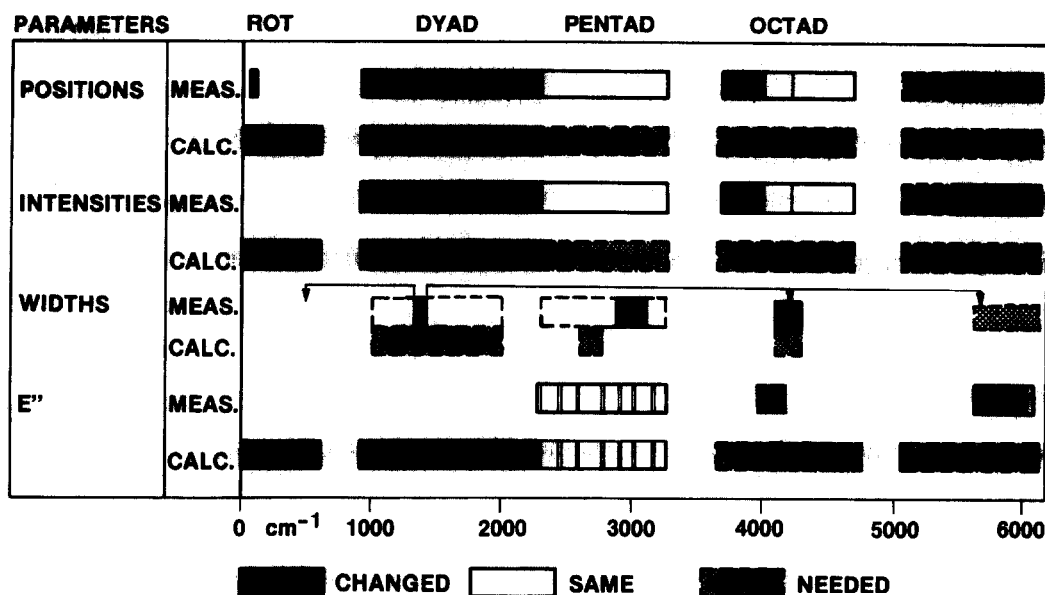
Fig. 4. The status of the 1991 methane positions, intensities, air-broadened widths and lower state energies. "Meas." indicates experimental measurements, while "calc." indicates the availability of successful modeling of the measurements to Hamiltonian models.

$v_4 + 2v_2$, $v_1 + v_2$, $v_2 + v_3$ and $3v_2$: 3650–4800 cm^{-1}; and (e) (tetradecad: $4v_4$, $v_2 + 3v_4$, $2v_4 + v_1$, $2v_4 + v_3$, $2v_2 + 2v_4$, $v_1 + v_2 + v_4$, $2v_1$, $v_2 + v_3 + v_4$, $3v_2 + v_4$, $v_1 + v_3$, $v_1 + 2v_2$, $2v_3$, $2v_2 + v_3$, $4v_2$) 5000–6350 cm^{-1}. In the lowest and highest cm^{-1} regions, the deficiencies exist because laboratory measurements have not been done (rotational region, 5100–5500, 7200–7700 cm^{-1} and beyond). In two intervals (3700–4700 and 5500–6185 cm^{-1}), there are many experimental positions, strengths and even some widths measured to good accuracies (0.0001 cm^{-1} for v, $\pm3\%$ for I,γ), but the theoretical fitting of these values to Hamiltonian models is so intractable that even the assignment of the regions is incomplete; users must therefore rely totally on the laboratory measurements. In other regions (2200–3300 cm^{-1}), the theoretical analyses provide a general understanding of the assignments and the interactions that occur, but the resulting calculations fail to reproduce all the experimental data, particularly at higher values of J. For these, interim linelists concocted by mixing predicted and measured values must be used for now. Only in the lower fundamental regions are calculations successful (as is the norm for most other molecules in the compilations).

PROSPECTS FOR IMPROVEMENT

A few of the problems listed in Table 7 will be corrected in the near future. In the pentad region, new analyses of positions and intensities of the five interacting bands of $^{12}CH_4$ and $^{13}CH_4$ are underway. The fourth order Hamiltonian to the i.r. and Raman line positions[40] has been successfully applied to fit almost 1200 transitions of $^{13}CH_4$ assigned through J equal to 15 with an r.m.s. of 0.0007 cm^{-1}. The modeling of the measured intensities to the second order dipole moment expansion[41] is in progress, along with the corresponding studies of the main isotope. The prediction of the pentad energy levels then will provide improved line positions of the pentad—dyad hot bands in the 1000–2000 cm^{-1}. The major difficulty to overcome is that the fourth order model implemented thus far fails to reproduce the higher J data, and for even the terrestrial applications, the fundamentals must be fitted through J equal 24.

In the octad region, a new study of intensities[42] of the $v_2 + v_3$ band of $^{12}CH_4$ will allow some of the empirical results in the 4400–4700 cm^{-1} region to be replaced with calculated values that include much weaker transitions. However, at present only three of the eight bands in the region are assigned. It is clear that the final good prediction of the region can be achieved only through the simultaneous fitting of all eight states together. This analysis is needed in order to predict hot bands

arising from the levels of the octad–dyad from 2000 to 3400 cm^{-1} and octad–pentad from 1000 to 2000 cm^{-1}.

There are also studies in progress to measure and interpret line widths and shifts. Fox et al[43-46] have measured selected lines in v_3 and $3v_3$ using up to nine different broadening agents. A few studies (Varanasi and Chudamani[47] and Smith et al[48]) indicate that the shifts vary with temperature (so that a new parameter might be needed in the database). Some of the present authors are currently reducing measurements for self-(Benner), air-(Brown) and hydrogen-(Margolis) broadening of methane. Finally, Gamache has recently undertaken the theoretical modeling of the air-broadened measurements.

In the long term, the improvements of other deficiencies depend on the level of support for research. The straightforward but time-consuming empirical approach provides initial parameters for a region (in principle, two remaining regions needed for terrestrial applications could be measured). However, this method is generally inadequate because the temperature dependencies of the intensities are not always correct, even when the empirical lower states are measured. In addition, it is impossible to measure accurately all the weak transitions needed. The modeling of laboratory positions and intensities to theory is essential in order to predict all the transitions, ground state and hot band, that arise from a set of energy levels. The theoretical understanding of methane and spherical rotors, summarized elsewhere,[38] has advanced considerably. However, application of the models to all the bands observed by remote sensing applications is time-consuming. At present, there are too few research groups working on methane; indeed, a number of groups who contributed in the 1980s have now become inactive. It is not likely that rapid progress will be achieved unless greater resources are brought to bear.

Note added in proof

An error was made in converting the prediction of the v_2/v_4 dyad of $^{12}CH_4$ and $^{13}CH_4$ into HITRAN format in that the vibrational code v' was reversed for two dozen pairs of levels. The specific levels involved are given in Table 7 of Rothman et al (this issue). As a result, the intensity statistics in Table 2 of Rothman et al are not consistent with the correct values shown in Table 3 of the present article. These errors will be rectified with the next update.

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