Microwave Spectra of Molecules of Astrophysical Interest. XX. Methane

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The available data on methane are critically reviewed for information applicable to radio astronomy. Molecular data such as rotational constants, centrifugal distortion constants, and the distortion electric dipole moment are presented for $^{12}CH_4$ and $^{13}CH_4$. Observed microwave, infrared-microwave double resonance, and molecular beam measurements of ($\Delta J = 0$) frequencies are tabulated along with experimental uncertainties which represent estimated 95% confidence limits. For $^{12}CH_4$, these data have been analyzed to predict all Q-branch rotational transitions for $J \leqslant 20$; the predictions are presented with 95% confidence limits which have been calculated from the analysis.

Key words: Distortion dipole transitions; interstellar molecules; methane; microwave spectra; molecular parameters; radio astronomy; rotational transitions.

Contents

1. Introduction

This article is part of a series of critical reviews on the microwave spectra of molecules of interest in radio astronomy. The series has hitherto been concerned with confirmed interstellar species. Methane is an exception in this regard, but a review seems, nevertheless, to be appropriate. CH_4 is an extremely important, very stable molecule and almost certainly has a high interstellar abundance. The possibility of observing CH_4 has stimulated considerable interest among radioastronomers, including a suggestion [1][1] of how anomalous interstellar emission and absorption might occur for specific transitions. Observation of several interstellar lines [2] has been reported for J values ranging from 11 to 20, with the excitation mechanism being described as non-thermal. A tentative detection of a single line in the Jovian atmosphere has been reported [3]. However, all the detected lines show unusual features and their identifications have not yet been confirmed. Indeed, one of these transitions has recently been shown to be due to methyl formate [4]. The great complexity of the microwave spectrum has significantly hindered work on this problem; except for a few low J transitions, the frequencies and line strengths can be calculated only with highly specialized computer routines. A prime purpose of this review is to present information necessary for interstellar searches and the analysis of any astronomical detection.

The absorption mechanism in CH_4 is rather unusual. Because of its tetrahedral symmetry, methane does not possess a permanent dipole moment. The transition dipole moment operator arises from centrifugal distortion effects [5-8] and the magnitude of the distortion dipole moment θ_z^{xy} is typically only $\sim 10^{-5}$ D (1D $= 3.3356 \times 10^{-30}$ C m) in light molecules. On the other hand, the matrix elements of this operator contain an extra factor of roughly J^2 when compared to the matrix elements

[1]Figures in brackets indicate literature references.

of a conventional electric dipole moment operator [7]. At high J values, this factor compensates in part for the small magnitude of the dipole moment itself, but even at $J = 20$ the line strengths are orders of magnitude smaller than the line strengths for most astrophysical detections of interstellar molecules.

Spectra are presented for all transitions in $^{12}CH_4$ with $\Delta J = 0$ and $J \leqslant 20$. The frequencies all fall below 120 GHz. The excitation energies extend up to 2200 cm^{-1}. No limit has been put on this energy for two reasons: first, the possibility of non-thermal interstellar excitation must be considered and second, the transition moment increases rapidly with J. No spectra with $\Delta J = \pm 1$ are presented; the lowest lying such transitions ($J = 2 \leftarrow 1$) are above 600 GHz, are extremely weak compared to the stronger ($\Delta J = 0$) lines, and cannot be predicted to sufficient accuracy from the laboratory data currently available. No spectra for $^{13}CH_4$ are predicted, but enough information is given to calculate these from the corresponding $^{12}CH_4$ lines. To prevent transcription errors, the $^{12}CH_4$ tables of spectra have been copied directly from computer printouts.

1.1. Molecular Parameter Tables

The Hamiltonian for a tetrahedral molecule in its ground vibronic state can be written to degree eight in J as:

$$\mathbf{H} = \mathbf{H}_S + \mathbf{H}_T$$
$$\mathbf{H}_S = B_0 \mathbf{J}^2 - D_S \mathbf{J}^4 + H_S \mathbf{J}^6 + L_S \mathbf{J}^8$$
$$\mathbf{H}_T = [D_T + H_{4T}\mathbf{J}^2 + L_{4T}\mathbf{J}^4]\mathbf{\Omega}_4 + [H_{6T} + L_{6T}\mathbf{J}^2]\mathbf{\Omega}_6 + L_{8T}\mathbf{\Omega}_8.$$

The operators $\mathbf{\Omega}_4$, $\mathbf{\Omega}_6$, and $\mathbf{\Omega}_8$ are functions of $\mathbf{J}$ and its components referred to molecular-fixed axes; they have been defined in several places [10-12]. B_0 is the rotational constant, and the symbols containing D, H, and L represent respectively quartic, sextic, and octic distortion constants. An alternative development of $\mathbf{H}$ has been presented [13]. The relationship between the two formalisms has been given for the operators [14] and the constants [15].

For $^{12}CH_4$, table 1 gives the scalar constants that enter $\mathbf{H}_S$, the tensor constants that enter $\mathbf{H}_T$ and the distortion dipole moment θ_z^{xy}. Because all the microwave lines obey $\Delta J = 0$, the values of B_0, D_S and H_S do not affect the Q-branch frequencies; they affect only the intensities through the excitation energy. These constants have been determined [16,17] from infrared combination-differences using ground state ($\Delta J = 0$) frequencies to eliminate the effect of $\mathbf{H}_T$. The value of L_S could not be evaluated [17]. The values of the tensor distortion constants determine the microwave frequencies. These constants were evaluated by a least-squares analysis of the ten available Q-branch laboratory frequencies, using as weights the reciprocals of the squares of their experimental uncertainties. The details of the iterative analysis are given elsewhere [12,15]. For the scalar constants and the distortion dipole moment, the errors are taken from the literature; for the tensor constants, the error analysis has been done in the current work. All quoted uncertainties are 95% confidence limits.

For $^{13}CH_4$, table 1 gives B_0 and the distortion constants. These have been determined by procedures similar to those used for $^{12}CH_4$. The 95% confidence limits given for the tensor constants can only be taken as very approximate estimates, because the system has only one degree of freedom. They can more reasonably be expected to be similar to or slightly larger than those of $^{12}CH_4$. The distortion dipole moment in $^{12}CH_4$ has not been determined experimentally, but should be close to the $^{12}CH_4$ value.

Table 1. Molecular Constants for Methane[a]

Parameter	$^{12}CH_4$	Ref.	$^{13}CH_4$	Ref.
Rotational Constant (cm^{-1})				
B_0	5.2410354(192)	75A,76A	5.24119(20)[b]	76B
Centrifugal Distortion Constants (MHz)[c]				
D_S	3.3240(43)	75A,76A	3.337 (37)[b]	76B
H_S	173.0 (96) x10^{-6}	75A,76A	171. (66) x10^{-6}[b]	76B
D_T	132,943.22 (245)x10^{-6}		132,982.07 (165)x10^{-6}	
H_{4T}	-16.9832(225)x10^{-6}		-16.9870(136)x10^{-6}	
H_{6T}	11.0318(178)x10^{-6}		11.1786(69) x10^{-6}	
L_{4T}	2.028 (60) x10^{-9}		1.976 (29) x10^{-9}	
L_{6T}	-2.670 (73) x10^{-9}		-2.644 (28) x10^{-9}	
L_{8T}	-3.026 (378)x10^{-9}		-2.677 (139)x10^{-9}	
Distortion Dipole Moment (Debye)				
θ_z^{xy}	24.06 (45) x10^{-6}	71		

[a]Uncertainties are 95 percent confidence intervals.

[b]Ref. (80A) lists slightly different values, but no error limits are given and the basis for the newer results are still unpublished.

[c]For the tensor distortion constants, the number of significant figures quoted is necessary to obtain all the calculated frequencies without significant round-off errors.

Table 2. The Observed Spectrum of Methane[a]

Transition	Upper State	Lower State	$^{12}CH_4$ Observed Frequency (Uncertainty)	Ref.	Calculated Frequency (Uncertainty)	$^{13}CH_4$ Observed Frequency (Uncertainty)	Ref.	Calculated Frequency (Uncertainty)
2	F2,1	E,1	7.9703(80)	80B	7.97048(14)			
7	F1,2	F2,2	423.020 (40)	73	423.0278 (45)			
7	F2,2	F1,1	1246.550 (40)	73	1246.546 (13)			
12	E,2	E,1	10321.91 (10)	75B	10321.908 (40)	10324.14 (10)	76C	10324.140(22)
13	E,2	E,1	11261.37 (10)	75B	11261.358 (27)	11265.53 (10)	76C	11265.528(13)
14	E,3	E,2	7861.655 (40)	80C	7861.657 (18)	7865.203(40)	80C	7865.203(8)
14	E,2	E,1	19288.63 (20)	75B	19288.636 (94)	19292.80 (15)	76C	19292.800(34)
15	E,2	E,1	14151.81 (10)	75B	14151.814 (42)	14154.65 (8)	76C	14154.650(17)
16	E,3	E,2	18562.40 (20)	75B	18562.396 (94)	18572.00 (12)	76C	18571.999(27)
18	E,3	E,2	18528.94 (20)	75B	18528.935 (94)	18532.82 (10)	76C	18532.820(23)

[a] All frequencies are in MHz.

1.2. Microwave Spectral Tables

Table 2 contains the measured frequencies of the observed Q-branch transitions of $^{12}CH_4$ and $^{13}CH_4$ along with their frequencies calculated using the tensor distortion constants given in table 1. The experimental uncertainties shown are estimated 95 percent confidence limits. In the cases where the definition of the confidence level was unclear in the original literature, the situation was resolved by consulting the authors involved. The uncertainties shown for the calculated results are 95 percent confidence intervals, as derived [18] from the variance-covariance matrix of the least square fit.

The transitions are labelled by the values of J, C, and t [15] for the upper and lower states. C gives the symmetry species (A_1,A_2,E, F_1 or F_2) in the point group T_d; t is an index (1,2,3...) which numbers the levels of given (J,C) in order of increasing energy. The relationships to the other common systems of notation are given in ref. [15].

The transition labelled $2[F2,1] \leftarrow [E,1]$ should, more correctly, be called an energy spacing, because this is neither electric nor magnetic dipole allowed for a molecule in field-free space. This energy spacing was measured by a molecular-beam avoided-crossing technique and cannot be observed astronomically.

Table 3 contains the predicted frequencies and uncertainties of all electric dipole Q-branch transitions up to $J = 20$. The listed uncertainties are again 95 percent confidence limits, calculated as described for table 2. Because of the very irregular nature of the spectrum the transitions are first sorted with respect to their J value and then listed in order of increasing frequency.

The relationship between the line strength listed in table 3 and the peak intensity of the absorption line is the same as that adopted earlier in this series [19] for problems involving nuclear spin degeneracies. However, because of the tetrahedral symmetry, an explicit definition is required and this is somewhat different in appearance. The line strength $S(J'C't';J''C''t'')$ is defined by

$$S(J'C't';J''C''t'') = \sum_{f\alpha\beta} |\langle\alpha|\tilde{\mu}_f|\beta\rangle|^2/g(\theta_z^{xy})^2.$$

where the summation is over the three molecular-fixed directions f and all components α of $|J'C't'\rangle$ and β of $|J''C''t''\rangle$. g is the nuclear spin statistical weight and takes the values 5,2, and 3 for the allowed transitions $A_1 \longleftrightarrow A_2$, $E \longleftrightarrow E$, and $F_1 \longleftrightarrow F_2$, respectively. The basis functions used here in evaluating S diagonalize the full tensor Hamiltonian given in sec. 1.1. A good approximation to S can be obtained by using the basis which diagonalized only $\mathbf{\Omega}_4$ (10,15,20). In this basis,

$$S(J'C't';J''C''t'') = S_{ab}/g(\theta_z^{xy})^2 \text{ of eq (16) ref. [10]}$$
$$= \Gamma/20g(\theta_z^{xy})^2 \text{ of eq (11a) ref. [20].}$$

The relationship between S and the integrated intensity of the absorption line is given in detail in ref. [10] for Q-branch transitions and in ref. [20] for R-branch transitions. Note that there are two misprints in eq (16a) of ref. [20]. A factor $5g/(J+1)$ was omitted and the K appearing in the argument of F_2 should be K'.

The spontaneous emission rates presented in table 3 are the Einstein coefficients

$$A = 64\pi^4\nu^3(\theta_z^{xy})^2 S(J'C't';J''C''t'')/3hc^3(4\pi\epsilon_0)(2J'+1).$$

If ν is entered in MHz and θ_z^{xy} in Debye, this becomes

$$A = 1.16395\times10^{-20}\nu^3(\theta_z^{xy})^2 S(J'C't';J''C''t'')/(2J'+1).$$

In these equations, the prime refer to the upper level and the double primes to the lower level. These coefficients are given explicitly because there is such a large range in ν for transitions with a given J that the line strengths themselves can be misleading in comparing different transitions.

To check the calculations, the frequencies of the lines were evaluated twice using independent tetrahedral programs, designated "Reading" and "U.B.C.", which are based on different algorithms [21,22]. The results were identical. The line strengths in table 3 were obtained with the Reading program. The values calculated with this program differ slightly from those obtained in earlier works on Q-branch [10] and R-branch [20] transitions because these works used the basis which diagonalizes only $\mathbf{\Omega}_4$. If H_{6T},L_{6T} and L_{8T} are set equal to zero so that the two basis sets become identical, then the Reading line strengths agree with the results of ref. [10] for $\Delta J = 0$ and with the results of ref. [20] for $\Delta J = \pm 1$. These checks are brought to the reader's attention because the two major sources of Q-branch line strengths in the literature, namely refs. [10] and [23], disagree with each other, with the former being correct.

TABLE 3. THE CALCULATED Q-BRANCH SPECTRUM OF $^{12}CH_4$

J	TRANSITION UPPER STATE	LOWER STATE	CALCULATED FREQUENCY (UNCERTAINTY) IN MHZ	LINE STRENGTH	SPONTANEOUS EMISSION RATE IN S-1	ENERGY LEVELS IN CM-1 UPPER STATE	LOWER STATE
3	(F2,1)	-(F1,1)	31.8645(0.0005)	3.150E+02	9.810E-24	62.877	62.876
4	(F2,1)	-(F1,1)	159.1045(0.0024)	1.021E+03	3.077E-21	104.780	104.775
5	(F2,1)	-(F1,1)	107.5934(0.0016)	2.397E+02	1.829E-22	157.128	157.124
5	(F1,2)	-(F2,1)	329.5192(0.0046)	4.354E+03	9.542E-20	157.139	157.128
6	(F1,1)	-(F2,2)	134.7950(0.0017)	8.250E+03	1.047E-20	219.941	219.937
6	(A1,1)	-(A2,1)	760.839(0.009)	1.287E+04	2.938E-18	219.945	219.920
6	(F1,1)	-(F2,1)	785.839(0.010)	3.116E+03	7.838E-19	219.941	219.915
7	(F2,1)	-(F1,1)	106.7691(0.0016)	5.023E+02	2.746E-22	293.126	293.123
7	(F1,2)	-(F2,2)	423.0278(0.0045)	1.777E+04	6.041E-19	293.178	293.164
7	(F2,2)	-(F1,1)	1246.546(0.013)	1.824E+03	1.587E-18	293.164	293.123
7	(F1,2)	-(F2,1)	1562.804(0.017)	9.589E+03	1.644E-17	293.178	293.126
8	(F1,2)	-(F2,1)	566.744(0.008)	1.770E+03	1.277E-19	376.805	376.786
8	(F2,2)	-(F1,2)	644.276(0.006)	4.900E+04	5.193E-18	376.826	376.805
8	(F2,1)	-(F1,1)	1563.543(0.015)	2.900E+03	4.393E-18	376.786	376.734
8	(E,2)	-(E,1)	2567.496(0.023)	1.479E+04	9.923E-17	376.821	376.735
8	(F2,2)	-(F1,1)	2774.563(0.025)	6.769E+03	5.730E-17	376.826	376.734
9	(F2,1)	-(F1,1)	101.4490(0.0025)	2.226E+02	8.244E-23	470.720	470.717
9	(F2,2)	-(F1,3)	301.5218(0.0022)	7.564E+04	7.353E-19	470.865	470.855
9	(A2,1)	-(A1,1)	1257.746(0.012)	1.058E+05	7.466E-17	470.873	470.831
9	(F2,2)	-(F1,2)	1792.092(0.014)	1.676E+04	3.420E-17	470.865	470.805
9	(F1,2)	-(F2,1)	2546.379(0.020)	6.100E+03	3.572E-17	470.805	470.720
9	(F1,3)	-(F2,1)	4036.949(0.029)	1.647E+04	3.844E-16	470.855	470.720
9	(F2,2)	-(F1,1)	4439.920(0.032)	3.199E+03	2.545E-16	470.865	470.717
10	(F1,1)	-(F2,2)	426.5756(0.0051)	1.003E+04	2.499E-19	575.184	575.170
10	(F2,3)	-(F1,2)	768.403(0.006)	1.370E+05	1.994E-17	575.285	575.260
10	(F1,2)	-(F2,2)	2689.430(0.018)	1.006E+04	6.279E-17	575.260	575.170
10	(F2,3)	-(F1,1)	3031.257(0.017)	4.111E+04	3.674E-16	575.285	575.184
10	(F1,1)	-(F2,1)	3946.718(0.023)	5.050E+03	9.961E-17	575.184	575.053
10	(A1,1)	-(A2,1)	5014.097(0.035)	3.878E+04	1.569E-15	575.223	575.056
10	(F1,2)	-(F2,1)	6209.572(0.034)	1.723E+04	1.323E-15	575.260	575.053
10	(E,2)	-(E,1)	6614.904(0.036)	1.473E+04	1.368E-15	575.272	575.051
11	(F2,1)	-(F1,1)	70.3851(0.0027)	1.063E+02	1.086E-23	689.708	689.705
11	(F1,3)	-(F2,3)	952.095(0.010)	2.692E+05	6.807E-17	690.049	690.018
11	(F2,3)	-(F1,2)	1822.278(0.028)	4.998E+03	8.860E-18	690.018	689.957
11	(F1,2)	-(F2,2)	2396.516(0.016)	2.769E+04	1.117E-16	689.957	689.877
11	(E,2)	-(E,1)	4600.354(0.019)	6.773E+04	1.932E-15	690.040	689.886
11	(F2,2)	-(F1,1)	5142.242(0.024)	2.287E+03	9.112E-17	689.877	689.705
11	(F1,3)	-(F2,2)	5170.889(0.023)	2.506E+04	1.015E-15	690.049	689.877

TABLE 3. (CONTINUED)

J	TRANSITION UPPER STATE	TRANSITION LOWER STATE	CALCULATED FREQUENCY (UNCERTAINTY) IN MHZ	LINE STRENGTH	SPONTANEOUS EMISSION RATE IN S-1	ENERGY LEVELS IN CM-1 UPPER STATE	ENERGY LEVELS IN CM-1 LOWER STATE
11	(F1,2)	-(F2,1)	7468.373(0.039)	3.841E+04	4.687E-15	689.957	689.708
11	(F2,3)	-(F1,1)	9361.036(0.037)	2.181E+04	5.241E-15	690.018	689.705
11	(F1,3)	-(F2,1)	10242.746(0.041)	6.240E+02	1.964E-16	690.049	689.708
12	(F1,3)	-(F2,3)	467.9236(0.0050)	3.921E+05	1.083E-17	815.132	815.116
12	(F1,2)	-(F2,1)	534.493(0.015)	3.496E+03	1.439E-19	814.884	814.867
12	(A1,2)	-(A2,1)	1637.170(0.025)	4.677E+05	5.531E-16	815.144	815.089
12	(F1,3)	-(F2,2)	3700.473(0.023)	4.039E+04	5.516E-16	815.132	815.008
12	(F2,2)	-(F1,2)	3710.007(0.025)	6.651E+04	9.154E-16	815.008	814.884
12	(F2,1)	-(F1,1)	6553.357(0.026)	1.685E+03	1.278E-16	814.867	814.648
12	(F2,3)	-(F1,2)	6942.556(0.021)	6.123E+04	5.522E-15	815.116	814.884
12	(F1,3)	-(F2,1)	7944.973(0.026)	2.966E+04	4.009E-15	815.132	814.867
12	(E,2)	-(E,1)	10321.908(0.040)	5.001E+04	1.482E-14	814.993	814.649
12	(F2,2)	-(F1,1)	10797.857(0.038)	3.639E+04	1.235E-14	815.008	814.648
12	(A2,1)	-(A1,1)	13279.654(0.043)	2.861E+04	1.806E-14	815.089	814.646
12	(F2,3)	-(F1,1)	14030.406(0.039)	4.636E+03	3.451E-15	815.116	814.648
13	(F2,1)	-(F1,1)	44.8658(0.0025)	3.430E+01	7.729E-25	949.843	949.842
13	(F2,2)	-(F1,3)	960.579(0.006)	7.679E+04	1.699E-17	950.337	950.305
13	(F1,4)	-(F2,3)	1048.906(0.017)	6.272E+05	1.806E-16	950.522	950.487
13	(F2,3)	-(F1,3)	5470.077(0.036)	2.638E+04	1.078E-15	950.487	950.305
13	(F1,4)	-(F2,2)	5558.404(0.020)	7.848E+04	3.363E-15	950.522	950.337
13	(F2,2)	-(F1,2)	6009.731(0.018)	4.804E+04	2.602E-15	950.337	950.136
13	(A2,1)	-(A1,1)	6935.069(0.052)	2.247E+05	1.870E-14	950.385	950.154
13	(F1,2)	-(F2,1)	8796.275(0.036)	1.553E+03	2.638E-16	950.136	949.843
13	(F2,3)	-(F1,2)	10519.229(0.026)	5.514E+04	1.602E-14	950.487	950.136
13	(E,2)	-(E,1)	11261.358(0.027)	5.476E+04	1.952E-14	950.505	950.129
13	(F1,3)	-(F2,1)	13845.427(0.042)	6.135E+04	4.064E-14	950.305	949.843
13	(F2,2)	-(F1,1)	14850.872(0.042)	4.271E+04	3.491E-14	950.337	949.842
13	(F2,3)	-(F1,1)	19360.370(0.053)	6.808E+03	1.233E-14	950.487	949.842
13	(F1,4)	-(F2,1)	20364.410(0.045)	2.817E+02	5.937E-16	950.522	949.843
14	(F1,1)	-(F2,2)	383.571(0.014)	2.937E+03	3.851E-20	1095.632	1095.619
14	(F2,4)	-(F1,3)	1138.766(0.025)	9.974E+05	3.422E-16	1096.171	1096.133
14	(F2,3)	-(F1,2)	3364.710(0.024)	1.481E+05	1.311E-15	1095.981	1095.869
14	(F1,3)	-(F2,3)	4543.435(0.055)	8.649E+03	1.885E-16	1096.133	1095.981
14	(F1,2)	-(F2,2)	7493.364(0.016)	2.149E+04	2.101E-15	1095.869	1095.619
14	(E,3)	-(E,2)	7861.657(0.018)	1.463E+05	1.651E-14	1096.157	1095.895
14	(F2,4)	-(F1,2)	9046.911(0.021)	4.585E+04	7.888E-15	1096.171	1095.869
14	(F2,3)	-(F1,1)	10474.504(0.045)	1.852E+05	4.946E-14	1095.981	1095.632
14	(F1,1)	-(F2,1)	11396.688(0.090)	9.910E+02	3.408E-16	1095.632	1095.252

TABLE 3. (CONTINUED)

J	TRANSITION UPPER STATE	TRANSITION LOWER STATE	CALCULATED FREQUENCY (UNCERTAINTY) IN MHZ	LINE STRENGTH	SPONTANEOUS EMISSION RATE IN S-1	ENERGY LEVELS IN CM-1 UPPER STATE	ENERGY LEVELS IN CM-1 LOWER STATE
14	(F1,3)	(F2,2)	15401.509(0.037)	7.607E+04	6.457E-14	1096.133	1095.619
14	(F2,4)	(F1,1)	16156.705(0.029)	3.853E+03	3.776E-15	1096.171	1095.632
14	(A1,1)	(A2,1)	17257.924(0.072)	8.473E+04	1.012E-13	1095.829	1095.253
14	(F1,2)	(F2,1)	18506.482(0.086)	6.876E+04	1.013E-13	1095.869	1095.252
14	(E,2)	(E,1)	19288.636(0.094)	6.361E+04	1.061E-13	1095.895	1095.251
14	(F1,3)	(F2,1)	26414.626(0.107)	2.639E+03	1.130E-14	1096.133	1095.252
14	(E,3)	(E,1)	27150.293(0.094)	2.706E+03	1.253E-14	1096.157	1095.251
15	(F2,1)	(F1,1)	25.8384(0.0019)	1.020E+01	3.824E-26	1250.837	1250.836
15	(F2,4)	(F1,4)	559.050(0.014)	1.392E+06	5.288E-17	1252.046	1252.027
15	(F2,3)	(F1,2)	1683.665(0.042)	1.755E+04	1.820E-17	1251.646	1251.590
15	(A2,2)	(A1,1)	1785.875(0.048)	1.503E+06	1.861E-15	1252.061	1252.001
15	(F1,3)	(F2,3)	4810.686(0.048)	3.427E+05	8.294E-15	1251.807	1251.646
15	(F2,4)	(F1,3)	7169.628(0.037)	6.167E+04	4.940E-15	1252.046	1251.807
15	(F1,2)	(F2,2)	8652.431(0.029)	2.043E+04	2.877E-15	1251.590	1251.301
15	(F1,4)	(F2,3)	11421.264(0.031)	1.118E+05	3.620E-14	1252.027	1251.646
15	(F2,4)	(F1,2)	13663.978(0.041)	5.528E+04	3.065E-14	1252.046	1251.590
15	(F2,2)	(F1,1)	13961.601(0.180)	5.015E+02	2.966E-16	1251.301	1250.836
15	(E,2)	(E,1)	14151.814(0.042)	2.368E+05	1.459E-13	1251.779	1251.307
15	(F1,3)	(F2,2)	15146.781(0.038)	1.436E+05	1.085E-13	1251.807	1251.301
15	(A1,1)	(A2,1)	21303.440(0.074)	1.001E+05	2.104E-13	1252.001	1251.291
15	(F1,4)	(F2,2)	21757.359(0.047)	2.552E+04	5.712E-14	1252.027	1251.301
15	(F1,2)	(F2,1)	22588.194(0.183)	9.397E+04	2.354E-13	1251.590	1250.837
15	(F2,3)	(F1,1)	24297.697(0.219)	8.421E+04	2.626E-13	1251.646	1250.836
15	(F1,3)	(F2,1)	29082.544(0.181)	9.311E+02	4.978E-15	1251.807	1250.837
15	(F1,4)	(F2,1)	35693.122(0.209)	1.577E+03	1.559E-14	1252.027	1250.037
15	(F2,4)	(F1,1)	36278.010(0.198)	1.261E+03	1.309E-14	1252.046	1250.836
16	(F1,2)	(F2,1)	281.934(0.016)	1.036E+03	4.741E-21	1417.128	1417.119
16	(F2,4)	(F1,4)	1147.500(0.035)	2.016E+06	6.218E-16	1418.136	1418.098
16	(F1,3)	(F2,3)	1626.815(0.006)	3.722E+05	3.272E-16	1417.806	1417.752
16	(A1,2)	(A2,1)	8570.848(0.099)	7.945E+05	1.021E-13	1417.864	1417.578
16	(F1,3)	(F2,2)	8620.376(0.025)	1.837E+05	2.402E-14	1417.806	1417.519
16	(F2,4)	(F1,3)	9894.134(0.073)	9.734E+04	1.925E-14	1418.136	1417.806
16	(F1,4)	(F2,3)	10373.448(0.087)	4.669E+04	1.064E-14	1418.098	1417.752
16	(F2,2)	(F1,2)	11706.065(0.068)	2.662E+04	8.719E-15	1417.519	1417.128
16	(F2,1)	(F1,1)	16958.511(0.341)	2.874E+02	2.862E-16	1417.119	1416.553
16	(F1,4)	(F2,2)	17367.009(0.091)	8.732E+04	9.339E-14	1418.098	1417.519
16	(E,3)	(E,2)	18562.396(0.094)	1.089E+05	1.423E-13	1418.118	1417.498
16	(F2,3)	(F1,2)	18699.626(0.069)	2.669E+05	3.563E-13	1417.752	1417.128

TABLE 3. (CONTINUED)

J	TRANSITION UPPER STATE - LOWER STATE	CALCULATED FREQUENCY (UNCERTAINTY) IN MHZ	LINE STRENGTH	SPONTANEOUS EMISSION RATE IN S-1	ENERGY LEVELS IN CM-1 UPPER STATE	LOWER STATE
16	(F1,3)-(F2,1)	20608.375(0.075)	1.587E+05	2.836E-13	1417.806	1417.119
16	(E,2)-(E,1)	28329.924(0.404)	1.158E+05	5.376E-13	1417.498	1416.553
16	(F2,2)-(F1,1)	28946.510(0.416)	1.087E+05	5.383E-13	1417.519	1416.553
16	(F1,4)-(F2,1)	29355.008(0.118)	3.722E+04	1.922E-13	1418.098	1417.119
16	(F2,4)-(F1,2)	30220.574(0.087)	1.847E+03	1.041E-14	1418.136	1417.128
16	(A2,1)-(A1,1)	30750.113(0.464)	1.041E+05	6.180E-13	1417.578	1416.552
16	(F2,3)-(F1,1)	35940.071(0.408)	3.084E+03	2.924E-14	1417.752	1416.553
16	(E,3)-(E,1)	46892.321(0.410)	1.616E+03	3.403E-14	1418.118	1416.553
16	(F2,4)-(F1,1)	47461.020(0.395)	8.860E+02	1.934E-14	1418.136	1416.553
17	(F2,1)-(F1,1)	14.1139(0.0015)	2.675E+00	1.448E-27	1592.358	1592.357
17	(F1,5)-(F2,4)	1148.797(0.042)	2.852E+06	8.325E-16	1594.381	1594.343
17	(F2,2)-(F1,3)	1161.649(0.042)	3.034E+04	9.156E-18	1593.560	1593.521
17	(F1,4)-(F2,3)	4424.896(0.044)	6.069E+05	1.012E-14	1594.024	1593.877
17	(F2,4)-(F1,4)	9555.722(0.190)	1.107E+04	1.859E-15	1594.343	1594.024
17	(F2,3)-(F1,3)	10652.547(0.049)	8.773E+04	2.042E-14	1593.877	1593.521
17	(E,3)-(E,2)	13154.373(0.162)	1.964E+05	8.606E-14	1594.365	1593.926
17	(F1,4)-(F2,2)	13915.794(0.064)	4.996E+05	2.592E-13	1594.024	1593.560
17	(F1,5)-(F2,3)	15129.415(0.178)	5.457E+04	3.638E-14	1594.381	1593.877
17	(F2,2)-(F1,2)	15392.433(0.192)	1.864E+04	1.308E-14	1593.560	1593.047
17	(F1,2)-(F2,1)	20654.389(0.623)	1.735E+02	2.944E-16	1593.047	1592.358
17	(A2,1)-(A1,1)	21837.924(0.179)	4.030E+05	8.080E-13	1593.783	1593.054
17	(F1,5)-(F2,2)	24620.313(0.185)	1.252E+04	3.596E-14	1594.381	1593.560
17	(F2,4)-(F1,3)	24633.165(0.216)	1.449E+05	4.169E-13	1594.343	1593.521
17	(F2,3)-(F1,2)	24883.330(0.199)	2.746E+05	8.143E-13	1593.877	1593.047
17	(E,2)-(E,1)	26486.115(0.208)	2.458E+05	8.791E-13	1593.926	1593.043
17	(F1,3)-(F2,1)	34885.172(0.788)	1.399E+05	1.143E-12	1593.521	1592.358
17	(F2,2)-(F1,1)	36060.935(0.814)	1.305E+05	1.178E-12	1593.560	1592.357
17	(F2,4)-(F1,2)	38863.948(0.243)	1.501E+04	1.697E-13	1594.343	1593.047
17	(E,3)-(E,1)	39640.489(0.229)	1.726E+04	2.069E-13	1594.365	1593.043
17	(F2,3)-(F1,1)	45551.833(0.816)	3.499E+03	6.367E-14	1593.877	1592.357
17	(F1,4)-(F2,1)	49962.615(0.780)	2.083E+02	5.002E-15	1594.024	1592.358
17	(F2,4)-(F1,1)	59532.451(0.795)	1.301E+02	5.285E-15	1594.343	1592.357
17	(F1,5)-(F2,1)	60667.134(0.756)	1.267E+03	5.445E-14	1594.381	1592.358
18	(F1,1)-(F2,2)	175.516(0.016)	4.087E+02	4.024E-22	1779.027	1779.021
18	(F1,4)-(F2,5)	550.707(0.024)	3.820E+06	1.162E-16	1780.744	1780.726
18	(A1,2)-(A2,2)	1689.717(0.078)	3.930E+06	3.453E-15	1780.760	1780.704
18	(F1,3)-(F2,3)	4134.891(0.175)	4.712E+04	6.066E-16	1780.119	1779.981
18	(F2,4)-(F1,3)	5687.920(0.094)	1.215E+06	4.073E-14	1780.309	1780.119

TABLF 3. (CONTINUED)

J	TRANSITION UPPER STATE - LOWER STATE	CALCULATED FREQUENCY (UNCERTAINTY) IN MHZ	LINE STRENGTH	SPONTANEOUS EMISSION RATE IN S-1	ENERGY LEVELS IN CM-1 UPPER STATE	LOWER STATE
18	(F2,3)-(F1,2)	10592.000(0.103)	1.166E+05	2.523E-14	1779.981	1779.628
18	(F1,4)-(F2,4)	13051.392(0.346)	6.918E+04	2.801E-14	1780.744	1780.309
18	(F1,2)-(F2,2)	18187.840(0.375)	8.860E+03	9.707E-15	1779.628	1779.021
18	(F2,5)-(F1,3)	18188.606(0.326)	1.309E+05	1.434E-13	1780.726	1780.119
18	(E,3)-(E,2)	18528.935(0.094)	6.571E+05	7.612E-13	1780.266	1779.648
18	(F2,4)-(F1,2)	20414.812(0.102)	3.250E+05	5.036E-13	1780.309	1779.628
18	(F1,4)-(F2,3)	22874.204(0.458)	7.140E+04	1.556E-13	1780.744	1779.981
18	(F1,1)-(F2,1)	24753.007(1.063)	9.482E+01	2.619E-16	1779.027	1778.202
18	(F2,3)-(F1,1)	28604.324(0.433)	4.052E+05	1.727E-12	1779.981	1779.027
18	(F1,3)-(F2,2)	32914.731(0.466)	3.249E+05	2.110E-12	1780.119	1779.021
18	(F2,5)-(F1,2)	32915.497(0.400)	6.735E+04	4.374E-13	1780.726	1779.628
18	(A2,2)-(A1,1)	33274.672(0.464)	2.002E+05	1.343E-12	1780.704	1779.594
18	(F2,4)-(F1,1)	38427.136(0.412)	6.319E+03	6.530E-14	1780.309	1779.027
18	(A1,1)-(A2,1)	41735.723(1.404)	1.707E+05	2.260E-12	1779.594	1778.202
18	(F1,2)-(F2,1)	42765.331(1.427)	1.638E+05	2.333E-12	1779.628	1778.202
18	(E,2)-(E,1)	43370.954(1.441)	1.617E+05	2.402E-12	1779.648	1778.201
18	(F2,5)-(F1,1)	50927.821(0.474)	9.815E+03	2.361E-13	1780.726	1779.027
18	(F1,4)-(F2,2)	51654.044(0.469)	8.145E+03	2.044E-13	1780.744	1779.021
18	(F1,3)-(F2,1)	57492.223(1.508)	1.691E+03	5.852E-14	1780.119	1778.202
18	(E,3)-(E,1)	61899.889(1.464)	1.434E+03	6.193E-14	1780.266	1778.201
18	(F1,4)-(F2,1)	76231.535(1.378)	5.325E+02	4.296E-14	1780.744	1778.202
18	(A1,2)-(A2,1)	76700.112(1.361)	1.409E+03	1.158E-13	1780.760	1778.202
19	(F2,1)-(F1,1)	7.3733(0.0013)	6.601E-01	4.571E-29	1974.036	1974.036
19	(F2,3)-(F1,2)	1027.003(0.096)	9.985E+03	1.869E-18	1975.755	1975.720
19	(F1,5)-(F2,5)	1064.395(0.062)	5.147E+06	1.072E-15	1977.210	1977.175
19	(F2,4)-(F1,4)	2281.232(0.028)	1.373E+06	2.816E-15	1976.646	1976.570
19	(A2,2)-(A1,1)	9591.458(0.239)	2.207E+06	3.365E-13	1976.713	1976.393
19	(F2,4)-(F1,3)	12243.031(0.176)	4.136E+05	1.311E-13	1976.646	1976.237
19	(F1,3)-(F2,3)	14474.904(0.222)	2.000E+05	1.048E-13	1976.237	1975.755
19	(F1,5)-(F2,4)	16919.385(0.628)	9.239E+04	7.731E-14	1977.210	1976.646
19	(F2,5)-(F1,4)	18136.222(0.669)	6.143E+04	6.332E-14	1977.175	1976.570
19	(F1,2)-(F2,2)	21360.910(0.685)	5.758E+03	9.697E-15	1975.720	1975.008
19	(F1,4)-(F2,3)	24436.702(0.229)	6.586E+05	1.661E-12	1976.570	1975.755
19	(F2,4)-(F1,2)	27744.938(0.274)	3.507E+05	1.294E-12	1976.646	1975.720
19	(F2,5)-(F1,3)	28098.021(0.822)	9.001E+04	3.450E-13	1977.175	1976.237
19	(F2,2)-(F1,1)	29127.845(1.716)	4.865E+01	2.077E-16	1975.008	1974.036
19	(E,3)-(E,2)	29909.965(0.851)	1.520E+05	7.027E-13	1977.193	1976.195
19	(E,2)-(E,1)	35525.498(0.881)	4.892E+05	3.790E-12	1976.195	1975.010

TABLE 3. (CONTINUED)

J	TRANSITION UPPER STATE	LOWER STATE	CALCULATED FREQUENCY (UNCERTAINTY) IN MHZ	LINE STRENGTH	SPONTANEOUS EMISSION RATE IN S-1	ENERGY LEVELS IN CM-1 UPPER STATE	LOWER STATE
19	(F1,3)	-(F2,2)	36862.816(0.881)	4.212E+05	3.646E-12	1976.237	1975.008
19	(A1,1)	-(A2,1)	41668.338(0.925)	3.950E+05	4.937E-12	1976.393	1975.003
19	(F2,5)	-(F1,2)	43599.928(0.793)	9.909E+04	1.419E-12	1977.175	1975.720
19	(F1,5)	-(F2,3)	43637.320(0.682)	5.839E+03	8.382E-14	1977.210	1975.755
19	(F1,4)	-(F2,2)	46824.615(0.880)	3.117E+04	5.528E-13	1976.570	1975.008
19	(F1,2)	-(F2,1)	50481.381(2.393)	1.982E+05	4.406E-12	1975.720	1974.036
19	(F2,3)	-(F1,1)	51515.758(2.412)	1.946E+05	4.598E-12	1975.755	1974.036
19	(E,3)	-(E,1)	65435.463(0.916)	9.931E+03	4.807E-13	1977.193	1975.010
19	(F1,3)	-(F2,1)	65983.288(2.580)	6.301E+02	3.127E-14	1976.237	1974.036
19	(F1,5)	-(F2,2)	66025.232(0.902)	5.815E+03	2.892E-13	1977.210	1975.008
19	(F1,4)	-(F2,1)	75945.087(2.570)	8.083E+02	6.117E-14	1976.570	1974.036
19	(F2,4)	-(F1,1)	78233.692(2.554)	7.513E+02	6.216E-14	1976.646	1974.036
19	(F2,5)	-(F1,1)	94088.682(2.409)	6.174E+01	8.885E-15	1977.175	1974.036
19	(F1,5)	-(F2,1)	95145.704(2.369)	6.552E+02	9.750E-14	1977.210	1974.036
20	(F1,2)	-(F2,1)	105.481(0.019)	1.265E+02	2.439E-23	2180.947	2180.944
20	(F2,5)	-(F1,5)	1011.410(0.080)	6.806E+06	1.157E-15	2183.712	2183.678
20	(F1,3)	-(F2,3)	2490.119(0.153)	1.887E+05	4.787E-16	2182.477	2182.394
20	(F2,4)	-(F1,4)	5359.401(0.120)	2.058E+06	5.205E-14	2183.087	2182.908
20	(F1,4)	-(F2,3)	15424.813(0.409)	2.197E+05	1.325E-13	2182.908	2182.394
20	(F1,5)	-(F2,4)	17721.022(1.154)	1.140E+04	1.042E-14	2183.678	2183.087
20	(F2,4)	-(F1,3)	18294.095(0.266)	8.994E+05	9.049E-13	2183.087	2182.477
20	(F1,3)	-(F2,2)	19857.001(0.434)	1.428E+05	1.837E-13	2182.477	2181.814
20	(E,4)	-(E,3)	21369.723(1.044)	1.890E+05	3.031E-13	2183.697	2182.984
20	(F2,5)	-(F1,4)	24091.834(1.066)	4.598E+04	1.057E-13	2183.712	2182.908
20	(A1,2)	-(A2,1)	25878.577(0.659)	1.230E+06	3.503E-12	2182.708	2181.844
20	(F2,2)	-(F1,2)	25990.236(1.192)	4.294E+03	1.239E-14	2181.814	2180.947
20	(F1,4)	-(F2,2)	32791.694(0.555)	6.203E+05	3.594E-12	2182.908	2181.814
20	(F2,1)	-(F1,1)	34006.333(2.680)	2.532E+01	1.636E-16	2180.944	2179.810
20	(E,3)	-(E,2)	35454.851(0.599)	5.666E+05	4.150E-12	2182.984	2181.801
20	(F2,5)	-(F1,3)	37026.527(1.302)	2.644E+04	2.205E-13	2183.712	2182.477
20	(F1,5)	-(F2,3)	38505.236(1.486)	1.947E+05	1.827E-12	2183.678	2182.394
20	(F2,3)	-(F1,2)	43357.118(1.614)	5.737E+05	7.685E-12	2182.394	2180.947
20	(F1,3)	-(F2,1)	45952.717(1.610)	4.860E+05	7.750E-12	2182.477	2180.944
20	(F1,5)	-(F2,2)	55872.117(1.331)	4.442E+04	1.273E-12	2183.678	2181.814
20	(E,4)	-(E,2)	56824.574(1.343)	5.244E+04	1.581E-12	2183.697	2181.801
20	(F1,4)	-(F2,1)	58887.411(1.650)	4.004E+04	1.344E-12	2182.908	2180.944
20	(E,2)	-(E,1)	59698.722(3.864)	2.339E+05	8.179E-12	2181.801	2179.810
20	(F2,2)	-(F1,1)	60102.050(3.867)	2.320E+05	8.277E-12	2181.814	2179.810

TABLE 3. (CONTINUED)

J	TRANSITION UPPER STATE	LOWER STATE	CALCULATED FREQUENCY (UNCERTAINTY) IN MHZ	LINE STRENGTH	SPONTANEOUS EMISSION RATE IN S-1	ENERGY LEVELS IN CM-1 UPPER STATE	LOWER STATE
20	(A2, 1)	-(A1, 1)	61002.703(3.874)	2.297E+05	8.570E-12	2181.844	2179.809
20	(F2, 4)	-(F1, 2)	64141.332(1.633)	1.867E+03	8.095E-14	2183.087	2180.947
20	(F2, 3)	-(F1, 1)	77468.931(4.269)	6.936E+02	5.299E-14	2182.394	2179.810
20	(F1, 5)	-(F2, 1)	81967.834(1.732)	6.961E+02	6.300E-14	2183.678	2180.944
20	(F2, 5)	-(F1, 2)	82873.764(1.668)	8.018E+03	7.500E-13	2183.712	2180.947
20	(E, 3)	-(E, 1)	95153.573(4.266)	1.120E+03	1.585E-13	2182.984	2179.810
20	(F2, 4)	-(F1, 1)	98253.145(4.255)	5.817E+02	9.068E-14	2183.087	2179.810
20	(E, 4)	-(E, 1)	116523.296(3.961)	3.924E+02	1.020E-13	2183.697	2179.810
20	(F2, 5)	-(F1, 1)	116985.578(3.945)	2.365E+02	6.223E-14	2183.712	2179.810

Spontaneous emission lifetimes have appeared in several previous papers. Three different lifetimes are given in ref. [1] for ($\Delta J = -1$) transitions. In seconds, these are: 2.1×10^3 for $12(A1,1)\rightarrow11(A2,1)$; 8.3×10^3 for $12(A1,2)\rightarrow11(A2,1)$; 1×10^9 for $4(F1,1)\rightarrow3(F2,1)$. The corresponding numbers from both the Reading and U.B.C. programs are 5.9×10^5, 2.3×10^6 and 1.3×10^9 *s*. The disagreement stems in part from the misprint mentioned above in ref. [20], the work which formed the basis of the ($\Delta J = -1$) calculations in ref. [1]. The ($\Delta J = 0$) *A*-coefficients in table 1 of ref [1] agree with those given here in table 3, with the exception of that for $12(A2,1)\rightarrow12(A1,1)$. In spite of these corrections, the arguments and conclusions given in ref. [1] stand unaltered. The ($\Delta J = 0$) *A*-coefficients in table 1 of ref. [2] do not agree with those given here in table 3. Spontaneous emission lifetimes are given in ref. [9] for several low J ($\Delta J = -1$) transitions. These agree with the current values.

No counterpart of table 3 is given for $^{13}CH_4$. The frequencies $^{13}\nu(JC't';JC''t'')$ can be calculated from the corresponding values $^{12}\nu$ for $^{12}CH_4$ by using second order perturbation theory [12].

$$^{13}\nu(JC't';JC''t'') - {}^{12}\nu(JC't';JC''t'')$$
$$+ [\Delta D_T + \Delta H_{4T}J(J+1) + \Delta L_{4T}J^2(J+1)^2]$$
$$\times[f(JC't') - f(JC''t'')]$$
$$+ [\Delta H_{6T} + \Delta L_{6T}J(J+1)][g(JC't') - g(JC''t'')]$$
$$+[(H^2_{6T}/D_T)_{C-13} - (H^2_{6T}/D_T)_{C-12}][\tilde{g}(JC't') - \tilde{g}(JC''t'')]$$
$$+ \Delta L_{8T}[h(JC't') - h(JC''t'')]$$

Tables are available for f and g in ref. [11] and for $\tilde{g}$ and h in ref. [12]. If all the figures given for the constants in table 1 and for the $^{12}\nu$ in table 3 are used, then the perturbation values of $^{13}\nu$ agree to $\lesssim$ 25 kHz with those obtained directly. The 95% confidence limits for the $^{13}CH_4$ frequencies calculated in this way should be equal to or slightly larger than the corresponding $^{12}CH_4$ confidence limits. The line strengths and *A*-coefficients for $^{13}CH_4$ should also be very close to the ^{12}C values.

1.3. List of Symbols and Conversion Factors

a. Symbols

B_0	Rotational constant.
D	Quartic distortion constant.
H	Sextic distortion constant.
L	Octic distortion constant.
ΔD	$D(^{13}CH_4)$–$D(^{12}CH_4)$.
ΔH	$H(^{13}CH_4)$–$H(^{12}CH_4)$.
ΔL	$L(^{13}CH_4)$–$L(^{12}CH_4)$.
θ^{xy}_z	Centrifugal distortion dipole moment as defined in eq (9), ref. [10].
$\boldsymbol{\Omega}_l$	Tensor angular momentum operator of degree ℓ in **J** and its molecule-fixed components.
J	Total angular momentum quantum number exclusive of nuclear spin.
C	Symmetry species of level in group T_d.
t	Index numbering levels of given J, C in order of increasing energy.
S	Line strength.
$f(JCt)$	Eigenvalue of $\boldsymbol{\Omega}_4$ for state J,C,t.
$g(JCt)$	Expectation value of $\boldsymbol{\Omega}_6$ for states J,C,t in the representation which diagonalizes only $\boldsymbol{\Omega}_4$.
$h(JCt)$	Expectation value of $\boldsymbol{\Omega}_8$ for state J,C,t in the representation which diagonalizes only $\boldsymbol{\Omega}_4$.
$\tilde{g}(JCt)$	Second order perturbation correction factor for state J,C,t.
(...)	Parentheses in the numerical listings contain measured or estimated uncertainties. These should be interpreted as: 10,321.908(0.040) MHz≡10,321.908 (40) MHz ≡10,321.908 ± 0.040 MHz.

b. Conversion Factor

$c = 2.99792458\times10^8$ m s^{-1}.

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