

Accurate rest frequencies of methanol maser and dark cloud lines[★]

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Abstract. We report accurate laboratory measurements of selected methanol transition frequencies between 0.834 and 230 GHz in order to facilitate astronomical velocity analyses. New data have been obtained between 10 and 27 GHz and between 60 and 119 GHz. Emphasis has been put on known or potential interstellar maser lines as well as on transitions suitable for the investigation of cold dark clouds. Because of the narrow line widths ($<0.5 \text{ km s}^{-1}$) of maser lines and lines detected in dark molecular clouds, accurate frequencies are needed for comparison of the velocities of different methanol lines with each other as well as with lines from other species. In particular, frequencies for a comprehensive set of transitions are given which, because of their low energy levels ($<20 \text{ cm}^{-1}$ or 30 K), are potentially detectable in cold clouds. Global Hamiltonian fits generally do not yet yield the required accuracy. Additionally, we report transition frequencies for other lines that may be used to test and to improve existing Hamiltonian models.

Key words. masers – molecular data – ISM: molecules – radio lines: ISM – line: identification – line: profiles

1. Introduction and motivation

1.1. Methanol masers

Methanol (CH_3OH) is the molecule with the largest number of known interstellar maser lines. These transitions arise from a wide range of energy levels above the ground state, and modeling their excitation provides important information on their emitting regions. Based on the small number of lines known at the time, Batrla et al. (1986) were the first to suggest that *all* methanol maser transitions belong to either one of two types, named class I and class II by Menten (1991a,b).

Obviously, the lines considered (within each class) have to arise from the same region for excitation modeling to make sense. The first clue that this indeed is the case comes from the observation that different transitions cover very similar LSR velocity ranges. Moreover, in particular for class I maser lines, the frequently very sparse spectra (sometimes showing a single strong feature only) look very similar for different transitions (apart from their intensities); see, e.g., Fig. 1 of Menten (1991b). The conclusion made in the latter reference, that class I methanol masers are associated with interstellar outflows and frequently found far away (up to a pc) from their exciting sources, while class II masers arise from the closest,

warm ($T \sim 150 \text{ K}$), dense ($n \sim 10^{6-7} \text{ cm}^{-3}$) environment of newly formed high-mass stars, has been confirmed by all subsequent observations (see astronomical references in Table 1). This dichotomy is coupled to their excitation: as model calculations show (Leurini et al. 2004a), class I masers arise from basic properties of the methanol molecule via collisional excitation, if no strong far-infrared field is present, i.e. far away from stars. In contrast, class II masers are pumped by infrared radiation (from the embedded objects), most likely via one or more torsionally excited states (e.g., Sobolev & Deguchi 1994).

A common origin of different maser lines has been *directly* proven – so far – in only a few cases: very Long Baseline Interferometry observations of the two strongest class II maser lines, the $5_1 \rightarrow 6_0A^+$ and $2_0 \rightarrow 3_{-1}E$ transitions, at 6.7 and 12.2 GHz, respectively, show that, indeed, maser spots in both lines do arise from identical locations on milliarc-second (few AU) scales (Menten et al. 1992). More recently, Kogan & Slysh (1998) found something similar for class I maser transitions in DR21(OH) by combining their observations of $7_0 \rightarrow 6_1A^+$ at 44.0 GHz with those of $8_0 \rightarrow 7_1A^+$ at 95.2 GHz by Plambeck & Menten (1990).

While such direct imaging certainly proves the coexistence issue, it is available for few lines and few sources only. Thus, a lot of the interpretation depends on comparison of line profiles. Therefore, a need for rest frequency values of the highest possible accuracy is rather obvious.

[★] Tables 1 to 3 are also available in electronic form at the CDS via anonymous ftp to cdsarc.u-strasbg.fr (130.79.128.5) or via <http://cdsweb.u-strasbg.fr/cgi-bin/qcat?J/A+A/428/1019>

Table 1. Methanol maser transitions – maser class, frequencies, lower state energies, line strengths, and laboratory and astronomical references.

Class ^a	Transition, $J_k=^b$	Frequency (MHz) ^c	E_ℓ^d (cm ⁻¹)	$S\mu^2$ (D ²)	Laboratory ref. ^e	Astronomical ref. ^f
I? ^g	$1_1 \rightarrow 1_1A^\mp$	834.267(2) ^h	11.705	1.2129	Radford 1972	Ball et al. (1970)
I? ^g	$3_1 \rightarrow 3_1A^\mp$	5005.32079(20) ^h	19.703	0.4693	HD73	Robinson et al. (1973)
II	$5_1 \rightarrow 6_0A^+$	6668.5192(8)	33.876	5.0768	BR95	Menten (1991)
I	$9_{-1} \rightarrow 8_{-2}E$	9936.202(4)	76.102	2.7769	BR95	Slysh et al. (1993)
II	$2_0 \rightarrow 3_{-1}E$	12 178.597(4)	13.556	1.9848	BR95	Batrla et al. (1987)
II	$2_1 \rightarrow 3_0E$	19 967.3961(2)	18.803	0.9244	M 85	Wilson et al. (1985)
II	$9_2 \rightarrow 10_1A^+$	23 121.0242(5)	98.053	3.1467	M 85	Wilson et al. (1984)
I	$3_2 \rightarrow 3_1E$	24 928.707(7)	24.310	2.8073	This work	Barrett et al. (1975)
I	$4_2 \rightarrow 4_1E$	24 933.468(2)	30.764	3.9283	Gaines et al. (1974)	Barrett et al. (1971)
I	$2_2 \rightarrow 2_1E$	24 934.382(5)	19.469	1.5948	Gaines et al. (1974)	Barrett et al. (1975)
I	$5_2 \rightarrow 5_1E$	24 959.0789(4)	38.833	5.0264	M 85	Barrett et al. (1971)
I	$6_2 \rightarrow 6_1E$	25 018.1225(4)	48.514	6.1287	M 85	Barrett et al. (1971)
I	$7_2 \rightarrow 7_1E$	25 124.8719(4)	59.809	7.2483	M 85	Barrett et al. (1971)
I	$8_2 \rightarrow 8_1E$	25 294.4165(2)	72.717	8.3910	M 85	Barrett et al. (1971)
I	$9_2 \rightarrow 9_1E$	25 541.3979(4)	87.239	9.5570	M 85	Menten et al. (1986)
I	$10_2 \rightarrow 10_1E$	25 878.2661(4)	103.373	10.7398	M 85	Matsakis et al. (1980)
I	$12_2 \rightarrow 12_1E$	26 847.233(50)	140.478	13.0919	T95	Wilson et al. (1996)
I	$13_2 \rightarrow 13_1E$	27 472.531(30)	161.449	14.2057	T95	Wilson et al. (1996)
I	$14_2 \rightarrow 14_1E$	28 169.462(30)	184.032	15.2244	T95	Wilson et al. (1996)
I	$15_2 \rightarrow 15_1E$	28 905.812(30)	208.226	16.0977	T95	Wilson et al. (1996)
II	$8_2 \rightarrow 9_1A^-$	28 969.942(50)	83.319	3.0236	T95	Wilson et al. 1993
I	$16_2 \rightarrow 16_1E$	29 636.936(10)	234.031	16.7716	T95	Wilson et al. (1996)
I	$17_2 \rightarrow 17_1E$	30 308.034(10)	261.445	17.1961	T95	Wilson et al. (1996)
I	$4_{-1} \rightarrow 3_0E$	36 169.265(30)	18.803	2.5184	T95	Morimoto et al. (1985)*
II	$7_{-2} \rightarrow 8_{-1}E$	37 703.700(30)	61.930	2.4051	T95	Haschick et al. (1989)
II	$6_2 \rightarrow 5_3A^+$	38 293.268(50)	58.813	0.9488	T95	Haschick et al. (1989)
II	$6_2 \rightarrow 5_3A^-$	38 452.677(50)	58.813	0.9495	T95	Haschick et al. (1989)
I	$7_0 \rightarrow 6_1A^+$	44 069.410(10)	43.694	6.1380	T95	Morimoto et al. (1985)
I	$5_{-1} \rightarrow 4_0E$	84 521.169(10)	25.254	3.0830	This work	Batrla & Menten (1988)*
II	$7_2 \rightarrow 6_3A^-$	86 615.600(5)	68.493	1.3578	This work	Sutton et al. (2001)*
II	$7_2 \rightarrow 6_3A^+$	86 902.949(5)	68.493	1.3596	This work	Sutton et al. (2001)*
I	$8_0 \rightarrow 7_1A^+$	95 169.463(10)	54.888	7.2211	This work	Plambeck & Wright (1988)*
I	$11_{-1} \rightarrow 10_{-2}E$	104 300.414(7)	106.779	3.4141	This work	Voronkov et al. (2004)*
II	$3_1 \rightarrow 4_0A^+$	107 013.803(5)	16.134	3.0088	This work	Val'tts et al. 1995a*
II	$0_0 \rightarrow 1_{-1}E$	108 893.963(7)	5.490	0.9784	This work	Val'tts et al. (1999)*
I	$6_{-1} \rightarrow 5_0E$	132 890.692(10)	33.316	3.6871	T95	Slysh et al. (1997)*
I	$9_0 \rightarrow 8_1A^+$	146 618.794(50)	67.679	8.3288	T95	Menten (1991b)
II	$8_0 \rightarrow 8_{-1}E$	156 488.868(10)	61.930	6.7830	T95	Slysh et al. (1995a)*
II	$2_1 \rightarrow 3_0A^+$	156 602.413(10)	9.681	1.9963	T95	Slysh et al. 1995a*
II	$7_0 \rightarrow 7_{-1}E$	156 828.533(10)	49.035	6.2749	T95	Slysh et al. (1995a)*
II	$6_0 \rightarrow 6_{-1}E$	157 048.625(10)	37.749	5.6636	T95	Slysh et al. (1995a)*
II	$5_0 \rightarrow 5_{-1}E$	157 179.017(10)	28.073	4.9589	T95	Slysh et al. (1995a)*
II	$4_0 \rightarrow 4_{-1}E$	157 246.056(10)	20.009	4.1725	T95	Slysh et al. (1995a)*
II	$1_0 \rightarrow 1_{-1}E$	157 270.851(10)	5.490	1.4611	T95	Slysh et al. (1995a)*
II	$3_0 \rightarrow 3_{-1}E$	157 272.369(10)	13.556	3.3178	T95	Slysh et al. (1995a)*
II	$2_0 \rightarrow 2_{-1}E$	157 276.058(10)	8.717	2.4090	T95	Slysh et al. (1995a)*
I	$8_{-1} \rightarrow 7_0E$	229 758.760(50)	54.266	5.0473	Sastry et al. (1985)	Slysh et al. (2002)*

^a Gives the maser type. Interstellar methanol masers are either class I or to II; see text and Menten (1991a,b). ^b The parity of A symmetry transitions is given as superscript. If the parities of the upper (left) and lower (right) state differ, the parities are given as upper and lower superscript, respectively. ^c Numbers in parentheses denote the measurement uncertainties in units of the least significant figures. ^d Lower state level energies are *all* relative to the ground-state (0_0^+) level of the A -symmetry species. The E-type ground state (1_{-1}) level is at a 5.490 cm⁻¹ higher energy. ^e HD73 stands for Heuvel & Dymanus (1973); BR95 for Breckenridge & Kukolich (1995), M 85 for Mehrotra et al. (1985), and T95 for Tsunekawa et al. (1995). ^f Only the first reference reporting *maser* emission in this line is given. An asterisk means that this line was earlier detected in thermal emission or absorption. See Lovas (2004) for relevant references. ^g See Sect. 4.3. for a discussion of these lines. ^h The ¹H hyperfine splitting has been resolved to some extent in the laboratory. For the $J = 1 \rightarrow 1$ transition, four components, spread over 19.4 km s⁻¹, have been observed. The frequency in the table is the one of the strongest component; the intensity weighted average is 1 kHz lower. For the $J = 3 \rightarrow 3$ transition, two components, split by 0.19 km s⁻¹, have been observed.

1.2. Methanol in dark clouds

As mentioned above, methanol is readily found in hot, dense molecular cores in high-mass star-forming regions.

In contrast, few observations of methanol in cold dark clouds have been made. This is partially due to the weakness of the emission, which is optically thin and has a low excitation temperature in such sources, where small $\text{CH}_3\text{OH}/\text{H}_2$ ratios of order 10^{-8} – 10^{-9} are found. Such values can be readily explained by gas phase chemistry models.

The first observations of CH_3OH in cold, dark clouds where made by Friberg et al. (1988), who detected the $k = 0$ and 1 E -type and the $k = 0$ A^+ -type lines of the 2_k-1_k quartet near 96.7 GHz as well as the 48.4 GHz $1_0-0_0A^+$ transition. Sources included the well-studied molecule-rich clouds TMC-1, L134N (=L183), and B335. Turner (1998) added a number of other lines to the still small list of methanol lines observed in dark clouds (see Table 2).

Of particular importance in this context is the detection of enhanced absorption (over-cooling or anti-inversion) of the 12.2 GHz $2_0-3_{-1}E$ line against the cosmic microwave background radiation toward TMC-1 and L183 (Walmsley et al. 1988). No line better demonstrates the class I/II maser dichotomy than this transition, the second most luminous and widespread class II maser line known (Batra et al. 1987), which is pumped by prodigious far-infrared radiation near newly formed high-mass (proto)stars. In class I sources, in contrast, as well as in dark clouds, i.e. in regions devoid of strong far-infrared radiation, this line becomes anti-inverted by the same mechanism, that produces the $J_{k=-1} - (J-1)_{k=0}E$ ($J = 4, \dots, 9$) maser lines (see Table 1; and Leurini et al. 2004a,b).

2. Existing data and new laboratory measurements

Modern millimeter-wavelength spectroscopy of methanol effectively started with the classic paper by Lees & Baker (1968).

An early compilation of line rest frequencies was presented by Lees et al. (1973). Many of the millimeter and submillimeter transition frequencies commonly used by astronomers today are the result of a concerted laboratory measurement/theory effort by the Duke, then Ohio State University group. They used large quantities of measured line frequencies to fit the (many) parameters of an extended internal axis method Hamiltonian, yielding better than 100 kHz accuracy fits to the bulk of the frequencies (Herbst et al. 1984; De Lucia et al. 1989; Anderson et al. 1990).

The published frequencies in the older references had typical uncertainties of 0.1 MHz. At 100 GHz, this corresponds to a velocity uncertainty of 0.3 km s^{-1} , comparable to the line widths of single maser features.

More recently, these measurements have been extended to selected frequency regions between 550 and 1200 GHz by Belov et al. (1995) employing the Cologne Terahertz Spectrometer. Still higher frequency measurements were published e.g. by Matsushima et al. (1994) and Odashima et al. (1995). In the latter laboratory, rather comprehensive measurements have been performed between 7 and 200 GHz

(Tsunekawa et al. 1995). Even further measurements and often model Hamiltonians have been reported in references cited in these articles and the ones mentioned below.

The highest accuracy measurements available for lines in the radio frequency and centimeter wavelength ranges, where high accuracy is most important, were made by Radford (1972), Heuvel & Dymanus (1973), and Gaines et al. (1974), employing beam-maser spectroscopy. Later, Mehrotra et al. (1985) and Breckenridge & Kukulich (1995) employed microwave Fourier transform (MWFT) spectroscopy.

In this paper, we present a compilation of frequencies of all known class I and II methanol maser lines. Values with the highest accuracy published were chosen in general. In addition, we used spectrometers available in Cologne and Kiel for accurate measurements of selected methanol transition frequencies.

3. Cologne and Kiel laboratory measurements

The frequency region between 60 and 119 GHz has been investigated in Cologne employing AM-MSP1 and AM-MSP2 millimeter wave synthesizers (Analytik & Meßtechnik GmbH, Chemnitz, Germany) as sources and a Schottky diode detector. Details of the spectrometer were described by Winnewisser et al. (2000). The absorption cell was about 3.5 m long. In order to obtain accurate line positions, low pressures (0.1–1.0 Pa) and a large number of data points were used. Figures 1 and 2 demonstrate the very good signal-to-noise ratio and the smoothness of the baseline for strong to moderately weak transitions.

Two waveguide microwave Fourier transform spectrometers were used for the measurements in Kiel which cover the regions of roughly 8–18 and 18–26 GHz. Further details on the spectrometer are given by Krüger et al. (1993) and Meyer et al. (1991).

Table 1 presents our compilation of laboratory frequencies of all known interstellar methanol maser lines. References for the first astronomical detection of *maser*¹ emission are also given for each line. The latest version of Frank Lovas' "NIST Recommended Rest Frequencies for Observed Interstellar Molecular Microwave Transitions", Revision 2002 (Lovas 2004), proved an invaluable resource in compiling it. We augmented this table with high accuracy rest frequencies obtained by us and other groups where appropriate. The methanol transition frequencies and uncertainties in the Lovas (2004) compilation are the *calculated values* from Xu & Lovas (1997); see also the discussion. The Xu & Lovas (1997) data are also available online in the Cologne Database for Molecular Spectroscopy, CDMS, described in Müller et al. (2001) and Müller et al. (2004).

Table 2 gives frequencies for strong transitions with lower state energies below 20 cm^{-1} and frequencies below 200 GHz for which laboratory frequencies with less than 30 kHz uncertainties are known. Note that some transitions may be both in Tables 1 and 2.

¹ In some transitions narrow maser emission is observed as well as broader (quasi)thermal emission.

Table 2. Accurately known methanol transitions detected or potentially detectable in dark clouds, frequencies, lower state energies, line strengths, and laboratory and dark cloud references.

Maser ^a	Transition, J_k^b	Frequency (MHz) ^c	E_l^d (cm ⁻¹)	$S\mu^2$ (D ²)	Laboratory ref. ^e	Dark cloud ref. ^f
I?	$1_1 \rightarrow 1_1 A^\mp$	834.267(2)	11.705	1.2129	Radford (1972)	<i>Slysh et al. (1995b)</i>
	$2_1 \rightarrow 2_1 A^\mp$	2502.7785(10)	14.904	0.6725	HD73	ND
I?	$3_1 \rightarrow 3_1 A^\mp$	5005.32079(20)	19.703	0.4693	HD73	<i>Kalenskii et al. (2004)</i>
II	$2_0 \rightarrow 3_{-1} E^f$	12 178.595(3)	13.556	1.9848	Gaines et al. (1974)	Walmsley et al. (1988)
II	$2_1 \rightarrow 3_0 E$	19 967.3961(2)	18.803	0.9224	M 85	
I	$2_2 \rightarrow 2_1 E$	24 934.382(5)	19.469	1.5948	Gaines et al. (1974)	
I	$4_{-1} \rightarrow 3_0 E$	36 169.265(30)	18.803	2.5184	T95	
	$1_0 \rightarrow 0_0 A^+$	48 372.4558(7)	0.000	0.8086	HD73	Friberg et al. (1988)
	$1_0 \rightarrow 0_0 E$	48 376.892(10)	9.122	0.8084	T95	<i>Kaifu et al. (2004)</i>
	$1_0 \rightarrow 2_{-1} E$	60 531.489(10)	8.717	1.4742	This work	NO
	$1_1 \rightarrow 2_0 E$	68 305.640(20)	13.963	0.4573	This work	
	$2_1 \rightarrow 1_1 A^+$	95 914.309(5)	11.705	1.2141	This work	
	$2_{-1} \rightarrow 1_{-1} E$	96 739.362(5)	5.490	1.2133	This work	Friberg et al. (1988)
	$2_0 \rightarrow 1_0 A^+$	96 741.375(5)	1.614	1.6171	This work	Friberg et al. (1988)
	$2_0 \rightarrow 1_0 E$	96 744.550(5)	10.736	1.6167	This work	Friberg et al. (1988)
	$2_1 \rightarrow 1_1 E$	96 755.511(5)	16.241	1.2443	This work	Menten et al. (1988)
	$2_1 \rightarrow 1_1 A^-$	97 582.804(7)	11.733	1.2141	This work	
II	$3_1 \rightarrow 4_0 A^+$	107 013.803(5)	16.134	3.0088	This work	
II	$0_0 \rightarrow 1_{-1} E$	108 893.963(7)	5.490	0.9784	This work	Turner (1998)
	$2_2 \rightarrow 1_1 E$	121 689.975(10)	16.241	2.8297	T95	
	$3_1 \rightarrow 2_1 A^+$	143 865.801(10)	14.904	2.1584	T95	
	$3_0 \rightarrow 2_0 E$	145 093.707(10)	13.963	2.4249	T95	
	$3_{-1} \rightarrow 2_{-1} E$	145 097.370(10)	8.717	2.1569	T95	Turner (1998)
	$3_0 \rightarrow 2_0 A^+$	145 103.152(10)	4.840	2.4257	T95	Turner (1998)
	$3_1 \rightarrow 2_1 E$	145 131.855(10)	19.469	2.2119	T95	
	$3_1 \rightarrow 2_1 A^-$	146 368.342(50)	14.988	2.1585	T95	
II	$2_1 \rightarrow 3_0 A^+$	156 602.413(10)	9.681	1.9963	T95	
II	$1_0 \rightarrow 1_{-1} E$	157 270.851(10)	5.490	1.4611	T95	
II	$3_0 \rightarrow 3_{-1} E$	157 272.369(10)	13.556	3.3178	T95	
II	$2_0 \rightarrow 2_{-1} E$	157 276.058(10)	8.717	2.4090	T95	
	$1_1 \rightarrow 1_0 E$	165 050.195(10)	10.736	1.3466	T95	
	$2_1 \rightarrow 2_0 E$	165 061.156(10)	13.963	2.2373	T95	
	$3_1 \rightarrow 3_0 E$	165 099.271(10)	18.803	3.1170	T95	
	$3_2 \rightarrow 2_1 E$	170 060.581(10)	19.469	3.1205	T95	ND
	$4_1 \rightarrow 3_1 A^+$	191 810.509(10)	19.703	3.0352	T95	ND
	$4_0 \rightarrow 3_0 E$	193 415.367(10)	18.803	3.2327	T95	ND
	$4_{-1} \rightarrow 3_{-1} E$	193 441.610(10)	13.556	3.0330	T95	ND
	$4_0 \rightarrow 3_0 A^+$	193 454.361(10)	9.681	3.2342	T95	ND
	$4_1 \rightarrow 3_1 A^-$	195 146.760(10)	19.870	3.0353	T95	ND

For nomenclature see also notes to Table 1. ^a I and II mean that these lines are class I and II maser transitions, respectively, in some non-dark cloud regions (see Table 1). ^f Only references reporting the first detection of a line in cold ($T \approx 10$ K) dark clouds are listed. For non-dark cloud astronomical references to first detections, see Lovas (2003). “ND” means that no astronomical detection is reported in the latter reference; “NO” means that the line is not observable from the ground. ^g This line appears in enhanced absorption (i.e. is over-cooled) against the cosmological microwave background radiation. References in italics report observations of a given line that did not yield its detection.

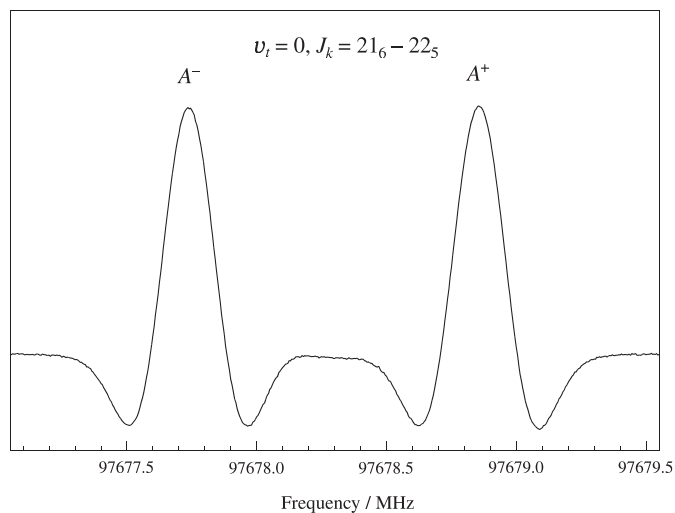


Fig. 1. Section of the millimeter wave spectrum of CH₃OH showing asymmetry splitting in the $\nu_t = 0$, $J_k = 21_6 - 22_5$ transitions of A symmetry. Each line appears approximately as a second derivative of a Gaussian because of the $2f$ -modulation employed to reduce noise and baseline effects.

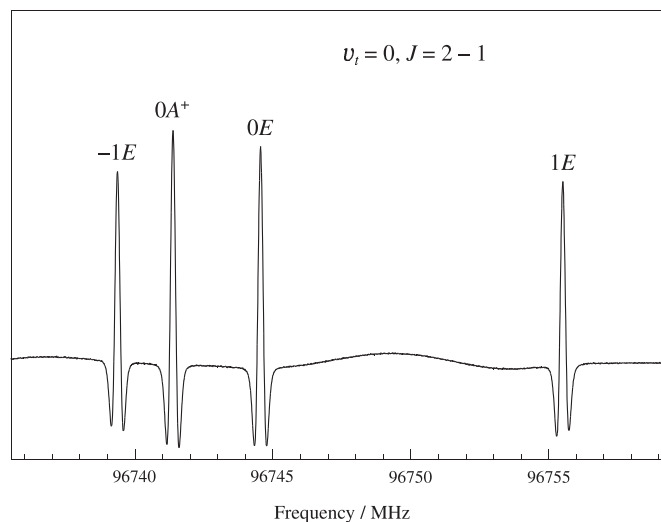


Fig. 2. Section of the millimeter wave spectrum of CH₃OH showing part of the $\nu_t = 0$, $J = 2 - 1$ a -type transitions ($\Delta K = 0$) which are observable in dark clouds. The k values and the symmetry are indicated. See also caption to Fig. 1.

Only very few transitions have larger uncertainties (of the order 50 kHz).

Finally, Table 3 summarizes the remaining transition frequencies determined in the course of the present study. These frequencies, together with the newly measured ones in Tables 1 and 2, may be useful for improving existing methanol Hamiltonians.

4. Discussion and conclusions

4.1. Comparison with earlier results

The newly obtained transition frequencies are generally much more accurate than previously published values, sometimes by more than a factor of 10. Moreover, they agree generally well within experimental uncertainties both with older measurements summarized in Xu & Lovas (1995) and with more recent measurements from Tsunekawa et al. (1995). Specifically, among the new lines in Tables 1 and 2 there is only one for which the agreement is not quite within estimated uncertainties with either data. The value of 86 615.760 MHz in Xu & Lovas (1995) originates from Sastry et al. (1985) and has an uncertainty of 100 kHz in that paper. Tsunekawa et al. (1995) give 86 615.578 MHz with an uncertainty of 10 kHz. Both values differ slightly from our value of 86 615.600(5) kHz. But since experimental uncertainties are usually given as 1σ values, agreement “only” within twice or three times the larger uncertainties should not be of major concern. Moreover, our current value is in excellent agreement with the calculated value of 86 615.602(14) kHz in Xu & Lovas (1995). Also, the $J = 2 \rightarrow 1$ transition frequencies around 96 GHz given in Table 2 agree within 1 to 4 kHz with *calculated* values in Xu & Lovas (1995). In most instances, this is less than *both* the experimental and the calculated uncertainties.

The agreement of the transition frequencies in Table 3 with calculated values in Xu & Lovas (1995) is mostly

within 50 kHz or three times the calculated uncertainties, whichever is larger; only some high J lines show larger deviations. This level of agreement is satisfactory. It should be pointed out that the calculated frequencies and uncertainties not only in Xu & Lovas (1995), but for all Hamiltonian models depend on the quality of the model employed and on the quality of the input data. Since the input data in Xu & Lovas (1995) has an accuracy of 50 or 100 kHz for the most part it cannot be expected that the predictions are much better than this *in general* – irrespective of the predicted uncertainties. Moreover, while predictions are *usually* reliable in cases of interpolation, extrapolations should always be viewed with caution.

In addition, most transitions in Table 3 had been measured already by Tsunekawa et al. (1995). The agreement is almost always good to very good, meaning within three and one times the combined experimental uncertainties, respectively. There are, however, lines with larger deviations: for the $17_{-2} \rightarrow 17_1 E$ line they report 111 626.846(30) MHz while we measured 111 626.449(15) MHz. The latter value is in good agreement with 111 626.530(100) MHz measured by Sastry et al. (1985) and with 111 626.550(35) MHz calculated by Xu & Lovas (1995). Therefore, we suspect a typographical error by Tsunekawa et al. A bigger discrepancy occurred for the $32_2 \rightarrow 32_1 E$ transition. Tsunekawa et al. (1995) report 12 198.200(50) MHz. No line was measured at that position in the course of the present investigation. Pearson communicated an alternative position almost 200 MHz lower for this transition from an ongoing investigation into the ro-torsional spectrum of CH₃OH, a reassignment for the line at 14 446.665 MHz, supposedly the $31_2 \rightarrow 31_1 E$ transition, as well as an alternative position for the latter. Lines with very good signal-to-noise ratio could be measured within 100 kHz of the predictions.

Table 3. Other methanol transitions measured in the course of the present investigation.

v_t	Transition, $J_k = {}^b$	Frequency (MHz) ^c		v_t	Transition, $J_k = {}^b$	Frequency (MHz) ^c	
0	$4_3 \rightarrow 5_2 A^-$	10 058.268(2)		1	$2_{-1} \rightarrow 1_{-1} E$	96 501.705(10)	
0	$32_2 \rightarrow 32_1 E$	11 841.902(1)	ND	1	$2_0 \rightarrow 1_0 A^+$	96 513.675(10)	
0	$31_2 \rightarrow 31_1 E$	14 407.777(1)	ND	1	$2_1 \rightarrow 1_1 A^-$	96 588.582(5)	
0	$32_8 \rightarrow 31_9 E$	14 446.665(1)	ND	0	$21_6 \rightarrow 22_5 A^-$	97 677.738(5)	
0	$30_2 \rightarrow 30_1 E$	16 941.190(1)	ND	0	$21_6 \rightarrow 22_5 A^+$	97 678.857(7)	
0	$6_1 \rightarrow 6_1 A^\mp$	17 513.342(2)x	ND	0	$15_1 \rightarrow 15_1 A^\mp$	99 602.078(10)	ND
0	$29_2 \rightarrow 29_1 E$	19 390.121(6)	ND	0	$9_{-2} \rightarrow 9_1 E$	101 737.173(20)	
1	$10_1 \rightarrow 11_2 A^+$	20 970.651(1)		0	$10_{-2} \rightarrow 10_1 E$	102 122.667(10)	
1	$12_2 \rightarrow 11_1 A^-$	21 550.300(6)		0	$11_{-2} \rightarrow 11_1 E$	102 658.046(7)	
0	$28_2 \rightarrow 28_1 E$	21 708.662(5)	ND	0	$22_{-2} \rightarrow 22_2 E$	102 704.298(20)	ND
0	$27_2 \rightarrow 27_1 E$	23 854.261(6)	ND	1	$15_{-2} \rightarrow 16_{-3} E$	102 957.691(7)	
0	$26_2 \rightarrow 26_1 E$	25 787.125(10)	ND	0	$12_{-2} \rightarrow 12_1 E$	103 381.146(5)	
1	$10_1 \rightarrow 11_2 A^-$	26 120.584(10)	ND	0	$13_{-3} \rightarrow 12_{-4} E$	104 060.657(10)	
0	$8_2 \rightarrow 9_1 A^+$	66 947.895(20)	ND	0	$13_{-2} \rightarrow 13_1 E$	104 336.562(7)	
0	$11_1 \rightarrow 10_2 A^-$	76 247.283(5)		0	$10_4 \rightarrow 11_3 A^-$	104 354.819(5)	
0	$5_0 \rightarrow 4_1 E$	76 509.668(7)		0	$10_4 \rightarrow 11_3 A^+$	104 410.446(5)	
0	$15_{-2} \rightarrow 15_2 E$	78 254.011(20)	ND	0	$13_1 \rightarrow 12_2 A^+$	105 063.691(5)	
0	$7_2 \rightarrow 8_1 A^-$	80 993.241(7)		0	$14_{-2} \rightarrow 14_1 E$	105 576.290(10)	
0	$17_{-2} \rightarrow 17_2 E$	81 318.424(20)	ND	0	$15_{-2} \rightarrow 15_1 E$	107 159.820(10)	
0	$18_{-2} \rightarrow 18_2 E$	83 792.561(10)	ND	0	$26_0 \rightarrow 26_{-1} E$	109 136.883(7)	
0	$13_{-3} \rightarrow 14_{-2} E$	84 423.776(5)		0	$16_{-2} \rightarrow 16_1 E$	109 153.107(10)	
1	$13_{10} \rightarrow 13_{11} E$	84 930.946(10)	ND	0	$23_{-2} \rightarrow 23_2 E$	110 060.492(20)	ND
1	$14_{10} \rightarrow 14_{11} E$	85 346.076(7)	ND	0	$18_0 \rightarrow 17_3 E$	111 254.256(20)	U
0	$6_{-2} \rightarrow 7_{-1} E$	85 568.084(10)		0	$7_2 \rightarrow 8_1 A^+$	111 289.550(10)	
1	$15_{10} \rightarrow 15_{11} E$	85 773.092(7)	ND	0	$17_{-2} \rightarrow 17_1 E$	111 626.449(15)T	
0	$19_{-2} \rightarrow 19_2 E$	87 066.748(10)	ND	0	$14_{-3} \rightarrow 15_2 E$	112 490.953(15)	ND
0	$14_1 \rightarrow 14_1 A^\mp$	87 241.339(10)	ND	0	$16_1 \rightarrow 16_1 A^\mp$	112 745.243(10)	ND
0	$8_{-4} \rightarrow 9_{-3} E$	89 505.808(5)		0	$25_0 \rightarrow 25_{-1} E$	113 408.094(7)	ND
0	$20_{-2} \rightarrow 20_2 E$	91 254.686(10)	ND	0	$18_{-2} \rightarrow 18_1 E$	114 650.861(5)	
1	$1_0 \rightarrow 2_1 E$	93 196.673(10)		0	$19_{-3} \rightarrow 20_0 E$	115 800.166(20)	ND
1	$10_{-7} \rightarrow 11_{-6} E$	94 022.734(10)	ND	0	$24_0 \rightarrow 24_{-1} E$	117 636.228(10)	NO
0	$8_3 \rightarrow 9_2 E$	94 541.765(5)	ND	1	$10_2 \rightarrow 9_3 E$	118 156.280(10)	NO
0	$19_7 \rightarrow 20_6 A$	94 814.987(10)	ND	1	$8_1 \rightarrow 9_2 A^+$	118 207.927(5)	NO
1	$2_1 \rightarrow 1_1 A^+$	96 396.040(7)		0	$19_{-2} \rightarrow 19_1 E$	118 293.492(5)	NO
0	$21_{-2} \rightarrow 21_2 E$	96 446.619(15)		1	$17_6 \rightarrow 18_5 A$	118 481.011(5)	NO
1	$2_1 \rightarrow 1_1 E$	96 492.152(7)		0	$24_{-2} \rightarrow 24_2 E$	118 522.453(15)	NO
1	$2_0 \rightarrow 1_0 E$	96 493.540(10)					

For nomenclature see notes to Table 1. Tsunekawa et al. (1995) give 111 626.846(30) MHz for the frequency of the line marked with T; we suspect a typographical error, see Sect. 4.1, where also some assignments for $J > 30$ are discussed. Heuvel & Dymanus (1973) give 17 513.34127(20) MHz for the unsplit position of the line marked with x. All lines, except those marked “ND” have been detected in astronomical sources. See Lovas (2004) for references to first detections. “ND” means that no astronomical detection is reported in the latter reference. “U” means that this line is listed as unidentified in Lovas (2004).

4.2. Astronomical impact

On occasion, astronomical measurements have been used to propose improved rest frequencies compared to the ones obtained in the laboratory. While it may be sometimes easy to obtain very precise astronomical line frequencies, the

determination of *accurate* positions (i.e. the absolute line position) is significantly more difficult. Nevertheless, astronomical observations have pointed at deficiencies in the accuracy of laboratory rest frequencies and have provided improved values in several instances. In fact, the laboratory measurements by Gaines et al. (1974) were sparked by seemingly different

velocity shifts for the E -symmetry, $k = 2 \rightarrow 1$, $\Delta J = 0$ transitions with $J = 6$ and 7 observed by Chui et al. (1974). The greatly improved transition frequencies of Gaines et al. (1974) resolved these discrepancies.

Friberg et al. (1988) proposed an improved rest frequency of the $2_0-1_0A^+$ line by comparison with the velocities of other lines with more accurately known frequencies. However, their shift from 96 741.42 MHz to 96 741.39 MHz was close to the extrapolated uncertainty of 0.04 MHz. On the other hand, Turner (1998) found no need for a revised rest frequency; his downward shift by 8 kHz was well within the uncertainty of 32 kHz. Our new frequency implies an even larger downward shift of 45 kHz, see Table 2, which is in perfect agreement with the calculated position from Xu & Lovas (1997), see above.

To give just one example of the impact our (in many cases revised) frequencies have on the interpretation of maser data, we mention that Val'ts et al. (1995) proposed a revision of the 107 013.85(10) MHz rest frequency by Lees & Baker (1968) to 107 013.67 MHz. The present results clearly show that that shift is too large. In fact, our value of 107 013.803(5) MHz, see Table 1, is well within the uncertainties of Lees & Baker (1968). Indeed, when critically examining their revised velocities, e.g., that of the strongest maser feature in W3(OH) and the thermal emission components in Orion-KL, with literature values of other methanol lines, we believe that the value presented here is the most appropriate.

4.3. A note on the low frequency $\Delta J = 0$ lines

The identification of certain lower- J , $\Delta J = 0$, transitions as masers is uncertain. Given the large linewidths and extended emission distribution observed in the Galactic center region (and only there), the $1_1A^- \rightarrow 1_1A^+$ line, the first interstellar methanol transition discovered, does clearly not show high gain maser action. However, the fact that it appears in emission against a high brightness temperature continuum background indicates that it must be weakly inverted, like low quantum number transitions from various other complex molecules found near the Galactic center; see Menten (2004). Optical depth estimates are of order 10^{-3} (see Gottlieb et al. 1979), which implies certainly no strong maser action. The same arguments apply to the $3_1A^- \rightarrow 3_1A^+$ line, which is also seen in emission toward Sgr B2 and at least one other location in the Galactic center region, G0.5–0.1 (Sgr B1; Mezger & Smith 1976). Recent calculations on CH₃OH excitation predict these lines and other $J_kA^- \rightarrow J_kA^+$ lines to be very weak class I masers under certain conditions (Leurini et al. 2004a).

5. Summary

The present manuscript provides accurate transition frequencies for methanol maser as well as dark cloud lines, several of which have been determined in the course of the present investigation. This compilation of methanol lines should be useful for velocity analyses of methanol masers and of dark clouds. Moreover, the newly determined transition frequencies will be useful for improving existing Hamiltonian models for

methanol. This is of particular importance for obtaining improved methanol rest frequencies in the 26–54 GHz region for which it may be difficult to improve the data in the laboratory.

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