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THE MICROWAVE AND FAR-INFRARED SPECTRA OF THE CH RADICAL[1]

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ABSTRACT

The frequencies, wavelengths, and line strengths for transitions of the CH molecule at microwave and far-infrared wavelengths have been calculated from an analysis of the laser magnetic resonance spectrum. The low-frequency transitions are between lambda-type doublets, while the higher frequency transitions are between different spin-rotation levels.

Subject headings: interstellar: molecules — laboratory spectra — line identifications

It has been known for a long time, from the observation of lines in its optical spectrum, that the free radical CH is a constituent both of stellar atmospheres (Herzberg 1950) and the interstellar gas clouds (Swings and Rosenfeld 1937; McKellar 1941). More recently, its presence in the interstellar medium has been confirmed by radio astronomy through the detection of transitions within the lowest rotational level ($J = \frac{1}{2}$) of the ground $^2\Pi$ state at frequencies around 3.3 GHz (Rydbeck *et al.* 1973; Turner and Zuckerman 1974). The extent of excitation of CH in different sources can be determined by the study of spectroscopic transitions involving higher rotational levels. Such observations can be made in the microwave region or, as has been demonstrated recently for OH (Storey, Watson, and Townes 1981), in the far-infrared. While microwave observations are restricted to the cold molecular cloud regions, the far-infrared spectrum can be used to monitor species in a much greater range of different physical conditions including even the ionized (H II) regions.

The CH radical has been studied at fairly high resolution in the laboratory by optical spectroscopy (Gerö 1941*a*, *b*; Kiess and Broida 1956; Herzberg and Johns 1969). However, much more precise measurements have been made on the molecule in its ground state by laser magnetic resonance (LMR) spectroscopy at far-infrared wavelengths (Evenson, Radford, and Moran 1971; Hougen *et al.* 1978). In these experiments, a molecular transition frequency is tuned into coincidence with that of a fixed frequency laser by application of a variable magnetic field (0–2 teslas). We have recently extended the study of the LMR spectrum and have fitted all the observations together with the frequencies measured by radio astronomers (Rydbeck *et al.* 1974) to a single model Hamiltonian given by Brown *et al.* (1978). A full account of this work is to be published elsewhere (Brown and Evenson 1983).

Zero field frequencies are not measured directly in LMR experiments, but the quality of fit of the data for CH is such that the extrapolation to zero field can be performed reliably. We have computed the frequencies of individual hyperfine transitions involving all rotational levels up to $N = 5$. The results are given in Tables 1 and 2. The former contains the lambda doubling (microwave) transitions, while the latter is concerned with the spin-rotational transitions which, generally speaking, fall in the far-infrared region. The results are also summarized in the diagram in Figure 1, which shows the low-lying energy levels of CH. By an accident of nature, CH is very close to the Hund's coupling case (b) limit ($A = 2B$) in its ground $^2\Pi$ state. Consequently, the large spin splittings usually associated with the spin-orbit interaction (as, for example, in OH) are not found in CH, as is shown in the energy level scheme in Figure 1. The basic pattern of rotational levels can be quite well described in terms of the case (b) quantum number N. Each such N level is further split into a spin-rotation doublet, the two components of which can be distinguished by the value of the quantum number J. The allowed values are $J = N + \frac{1}{2}$ and $J = N - \frac{1}{2}$, sometimes referred to as F_1 and F_2 components respectively (Herzberg 1950). Table 2 is not quite complete in that transitions with $\Delta J = 1, F_2 \leftarrow F_1$ have been omitted. Although these transitions are formally allowed, they are very weak because they also require $\Delta N = 2$ and so would be forbidden in the strict Hund's case (b) limit.

The lambda doubling spectrum in Table 1 depends primarily on the one set of very precise measurements for the lowest level by Rydbeck *et al.* (1974) although there is some information on the intervals for higher

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TABLE 1

CALCULATED LAMBDA DOUBLING TRANSITION FREQUENCIES FOR THE CH RADICAL IN ITS GROUND STATE

F_i	TRANSITION[a] J	TRANSITION[a] $F' - F''$	FREQUENCY (MHz)	LINE STRENGTH[b]
F_1 ...	$1\frac{1}{2}$	$2^{-}-2^{+}$	699.6(20)[c]	1.2059
		$2^{-}-1^{+}$	702.5(20)	0.1339
		$1^{-}-2^{+}$	719.9(20)	0.1340
		$1^{-}-1^{+}$	722.8(20)	0.6700
	$2\frac{1}{2}$	$3^{+}-2^{-}$	4836.5(20)	0.3817×10^{-1}
		$3^{+}-3^{-}$	4845.2(20)	0.7639
		$2^{+}-2^{-}$	4867.5(20)	0.5348
		$2^{+}-3^{-}$	4876.2(20)	0.3819×10^{-1}
	$3\frac{1}{2}$	$4^{-}-3^{+}$	11253.2(30)	0.1589×10^{-1}
		$4^{-}-4^{+}$	11266.9(30)	0.5564
		$3^{-}-3^{+}$	11289.0(30)	0.4293
		$3^{-}-4^{+}$	11302.6(30)	0.1589×10^{-1}
	$4\frac{1}{2}$	$5^{+}-4^{-}$	19933.3(30)	0.8080×10^{-2}
		$5^{+}-5^{-}$	19949.9(30)	0.4367
		$4^{+}-4^{-}$	19971.8(30)	0.3559
		$4^{+}-5^{-}$	19988.4(30)	0.8085×10^{-2}
	$5\frac{1}{2}$	$6^{-}-5^{+}$	30842.5(40)	0.4658×10^{-2}
		$6^{-}-6^{+}$	30860.9(40)	0.3591
		$5^{-}-5^{+}$	30882.8(40)	0.3031
		$5^{-}-6^{+}$	30901.2(40)	0.4662×10^{-2}
F_2 ...	$\frac{1}{2}$	$0^{-}-1^{+}$	3263.794[d]	0.3334
		$1^{-}-1^{+}$	3335.481[d]	0.6666
		$1^{-}-0^{+}$	3349.193[d]	0.3334
	$1\frac{1}{2}$	$1^{+}-2^{-}$	7274.4(10)	0.1327
		$1^{+}-1^{-}$	7323.9(10)	0.6634
		$2^{+}-2^{-}$	7347.2(10)	1.1941
		$2^{+}-1^{-}$	7396.7(10)	0.1327
	$2\frac{1}{2}$	$2^{-}-3^{+}$	14714.7(20)	0.3801×10^{-1}
		$2^{-}-2^{+}$	14757.0(20)	0.5319
		$3^{-}-3^{+}$	14779.4(20)	0.7599
		$3^{-}-2^{+}$	14821.8(20)	0.3800×10^{-1}
	$3\frac{1}{2}$	$3^{+}-4^{-}$	24391.0(30)	0.1586×10^{-1}
		$3^{+}-3^{-}$	24429.7(30)	0.4279
		$4^{+}-4^{-}$	24451.8(30)	0.5547
		$4^{+}-3^{-}$	24490.5(30)	0.1585×10^{-1}
	$4\frac{1}{2}$	$4^{-}-5^{+}$	36279.5(40)	0.8079×10^{-2}
		$4^{-}-4^{+}$	36315.9(40)	0.3553
		$5^{-}-5^{+}$	36337.9(40)	0.4360
		$5^{-}-4^{+}$	36374.3(40)	0.8076×10^{-2}

[a] Quantum numbers for the upper and lower states are denoted by single and double primes respectively. The superscripts on the F quantum numbers values indicate the parities of the states involved in accordance with the definition in Brown *et al.* 1978.

[b] For definition, see eq. (1).

[c] Estimated uncertainty in units of the last quoted decimal place (1 σ).

[d] Astronomical determination, Rydbeck *et al.* 1974.

TABLE 2

CALCULATED SPIN-ROTATION TRANSITION FREQUENCIES FOR THE CH RADICAL IN ITS GROUND STATE

TRANSITION[a]			FREQUENCY (GHz)	VACUUM WAVELENGTH (μm)	LINE STRENGTH[b]
$F_i' - F_i''$	$J' - J''$	$F' - F''$			
		A. $\Delta N = 1, \Delta J = 1$ Transitions			
F_1–F_1	$2\frac{1}{2}$–$1\frac{1}{2}$	3^-–2^+	1656.9596(30)[c]	180.9292	2.3070
		2^-–2^+	1656.9683(30)	180.9283	0.1647
		2^-–1^+	1656.9712(30)	180.9280	1.4831
		3^+–2^-	1661.1052(30)	180.4777	2.3090
		2^+–1^-	1661.1159(30)	180.4765	1.4844
		2^+–2^-	1661.1361(30)	180.4743	0.1649
F_1–F_1	$3\frac{1}{2}$–$2\frac{1}{2}$	4^+–3^-	2525.5226(30)	118.7051	3.5271
		3^+–2^-	2525.5276(30)	118.7049	2.6127
		3^+–3^-	2525.5362(30)	118.7045	0.1306
		4^-–3^+	2531.9443(30)	118.4041	3.5284
		3^-–2^+	2531.9490(30)	118.4038	2.6137
		3^-–3^+	2531.9800(30)	118.4024	0.1306
F_1–F_1	$4\frac{1}{2}$–$3\frac{1}{2}$[d]	5^-–4^+	3376.7959(60)	88.7802	4.6405
		4^-–3^+	3376.7987(60)	88.7801	3.6913
		4^-–4^+	3376.8124(60)	88.7797	0.1054
		5^+–4^-	3385.4789(60)	88.5525	4.6414
		4^+–3^-	3385.4816(60)	88.5524	3.6921
		4^+–4^-	3385.5174(60)	88.5514	0.1054
F_1–F_1	$5\frac{1}{2}$–$4\frac{1}{2}$[d]	6^+–5^-	4219.8033(60)	71.04418	5.7099
		5^+–4^-	4219.8052(60)	71.04415	4.7437
		5^+–5^-	4219.8217(60)	71.04387	0.8777×10^{-1}
		6^-–5^+	4230.7144(60)	70.86095	5.7107
		5^-–4^+	4230.7161(60)	70.86092	4.7443
		5^-–5^+	4230.7546(60)	70.86028	0.8781×10^{-1}
F_2–F_2	$1\frac{1}{2}$–$\frac{1}{2}$	1^-–1^+	2006.7478(30)	149.3922	0.1671
		1^-–0^+	2006.7615(30)	149.3912	0.3342
		2^-–1^+	2006.7973(30)	149.3885	0.8355
		1^+–1^-	2010.7362(30)	149.0959	0.1679
		1^+–0^-	2010.8079(30)	149.0906	0.3357
		2^+–1^-	2010.8090(30)	149.0905	0.8392
F_2–F_2	$2\frac{1}{2}$–$1\frac{1}{2}$	2^+–2^-	2585.8396(30)	115.9362	0.1651
		3^+–2^-	2585.8819(30)	115.9343	2.3105
		2^+–1^-	2585.8891(30)	115.9340	1.4853
		2^-–2^+	2593.2495(30)	115.6049	0.1652
		3^-–2^+	2593.3142(30)	115.6021	2.3125
		2^-–1^+	2593.3223(30)	115.6017	1.4866
F_2–F_2	$3\frac{1}{2}$–$2\frac{1}{2}$[d]	3^-–3^+	3407.1561(60)	87.98906	0.1307
		4^-–3^+	3407.1948(60)	87.98806	3.5284
		3^-–2^+	3407.1985(60)	87.98796	2.6136
		3^+–3^-	3416.8064(60)	87.74055	0.1308
		4^+–3^-	3416.8671(60)	87.73899	3.5297
		3^+–2^-	3416.8711(60)	87.73888	2.6146
F_2–F_2	$4\frac{1}{2}$–$3\frac{1}{2}$	4^+–4^-	4238.4781(60)	70.73116	0.1055
		5^+–4^-	4238.5145(60)	70.73055	4.6410
		4^+–3^-	4238.5168(60)	70.73051	3.6917
		4^-–4^+	4250.3423(30)	70.53372	0.1055
		5^-–4^+	4250.4006(30)	70.53275	4.6420
		4^-–3^+	4250.4030(30)	70.53271	3.6925

TABLE 2—*Continued*

TRANSITION[a]			FREQUENCY (GHz)	VACUUM WAVELENGTH (μm)	LINE STRENGTH[b]
$F_i' - F_i''$	$J' - J''$	$F' - F''$			
		B. $\Delta N = 1, \Delta J = 0$ Transitions			
F_2–F_1	$1\frac{1}{2}$–$1\frac{1}{2}$	1^-–2^+	1470.6861(30)	203.8453	0.3363×10^{-1}
		1^-–1^+	1470.6890(30)	203.8449	0.1681
		2^-–2^+	1470.7356(30)	203.8384	0.3028
		2^-–1^+	1470.7385(30)	203.8380	0.3359×10^{-1}
		1^+–1^-	1477.2901(30)	202.9340	0.1652
		1^+–2^-	1477.3104(30)	202.9313	0.3303×10^{-1}
		2^+–1^-	1477.3630(30)	202.9240	0.3301×10^{-1}
		2^+–2^-	1477.3832(30)	202.9213	0.2974
F_2–F_1	$2\frac{1}{2}$–$2\frac{1}{2}$	2^+–2^-	2399.6070(30)	124.9340	0.1344
		2^+–3^-	2399.6156(30)	124.9335	0.9603×10^{-2}
		3^+–2^-	2399.6493(30)	124.9318	0.9577×10^{-2}
		3^+–3^-	2399.6580(30)	124.9313	0.1921
		2^-–2^+	2409.4965(30)	124.4212	0.1322
		2^-–3^+	2409.5275(30)	124.4196	0.9446×10^{-2}
		3^-–2^+	2409.5613(30)	124.4179	0.9429×10^{-2}
		3^-–3^+	2409.5922(30)	124.4163	0.1890
F_2–F_1	$3\frac{1}{2}$–$3\frac{1}{2}$[d]	3^-–3^+	3281.2778(60)	91.36455	0.1079
		3^-–4^+	3281.2915(60)	91.36416	0.4001×10^{-2}
		4^-–3^+	3281.3165(60)	91.36347	0.3981×10^{-2}
		4^-–4^+	3281.3302(60)	91.36309	0.1401
		3^+–3^-	3294.4186(60)	91.00011	0.1063
		3^+–4^-	3294.4543(60)	90.99912	0.3937×10^{-2}
		4^+–3^-	3294.4793(60)	90.99843	0.3924×10^{-2}
		4^+–4^-	3294.5151(60)	90.99745	0.1378
F_2–F_1	$4\frac{1}{2}$–$4\frac{1}{2}$[d]	4^+–4^-	4142.9959(60)	72.36127	0.8953×10^{-1}
		4^+–5^-	4143.0124(60)	72.36098	0.2037×10^{-2}
		5^+–4^-	4143.0323(60)	72.36064	0.2021×10^{-2}
		5^+–5^-	4143.0488(60)	72.36035	0.1100
		4^-–4^+	4159.3400(60)	72.07693	0.8815×10^{-1}
		4^-–5^+	4159.3785(60)	72.07626	0.2004×10^{-2}
		5^-–4^+	4159.3983(60)	72.07592	0.1993×10^{-2}
		5^-–5^+	4159.4368(60)	72.07525	0.1083
		C. $\Delta N = 0, \Delta J = 1$ Transitions			
F_1–F_2	$1\frac{1}{2}$–$\frac{1}{2}$	1^+–1^-	532.7233(15)[e]	562.7545	0.1655
		2^+–1^-	532.7262(15)	562.7515	0.8274
		1^+–0^-	532.7950(15)	562.6788	0.3309
		2^-–1^+	536.7613(15)	558.5210	0.8312
		1^-–1^+	536.7815(15)	558.4999	0.1662
		1^-–0^+	536.7953(15)	558.4857	0.3324
F_1–F_2	$2\frac{1}{2}$–$1\frac{1}{2}$[d]	3^-–2^+	178.8768(60)	1675.972	0.2415×10^{-1}
		2^-–2^+	178.8855(60)	1675.891	0.1732×10^{-2}
		2^-–1^+	178.9583(60)	1675.209	0.1551×10^{-1}
		3^+–2^-	191.0692(60)	1569.026	0.2407×10^{-1}
		2^+–2^-	191.1001(60)	1568.772	0.1718×10^{-2}
		2^+–1^-	191.1497(60)	1568.365	0.1546×10^{-1}
F_1–F_2	$3\frac{1}{2}$–$2\frac{1}{2}$[d]	4^+–3^-	111.0852(60)	2698.763	0.7507×10^{-2}
		3^+–3^-	111.0988(60)	2698.430	0.2813×10^{-3}
		3^+–2^-	111.1636(60)	2696.858	0.5552×10^{-2}
		4^-–3^+	137.1315(60)	2186.168	0.7491×10^{-2}
		3^-–3^+	137.1672(60)	2185.598	0.2765×10^{-3}
		3^-–2^+	137.2096(60)	2184.923	0.5541×10^{-2}

TABLE 2—*Continued*

TRANSITION[a]			FREQUENCY (GHz)	VACUUM WAVELENGTH (μm)	LINE STRENGTH[b]
$F_i' - F_i''$	$J' - J''$	$F' - F''$			
		C. $\Delta N = 0, \Delta J = 1$ Transitions (*cont.*)			
F_1–F_2	$4\frac{1}{2}$–$3\frac{1}{2}$[d]	5^-–4^+	71.0139(60)	4221.602	0.3310×10^{-2}
		4^-–4^+	71.0304(60)	4220.619	0.7701×10^{-4}
		4^-–3^+	71.0912(60)	4217.011	0.2627×10^{-2}
		5^+–4^-	115.4156(60)	2597.504	0.3305×10^{-2}
		4^+–4^-	115.4541(60)	2596.638	0.7449×10^{-4}
		4^+–3^-	115.4928(60)	2595.769	0.2624×10^{-2}

[a] Quantum numbers for the upper and lower states are denoted by single and double primes respectively. The superscripts on the F quantum number values indicate the parities of the states involved in accordance with the definition in Brown *et al.* 1978.

[b] For definition, see eq. (1).

[c] Estimated uncertainty in units of the last quoted decimal place (1 σ).

[d] Transition not directly studied in the LMR spectrum.

[e] Calculated frequency more reliable because it is based on observation with three separate laser lines.

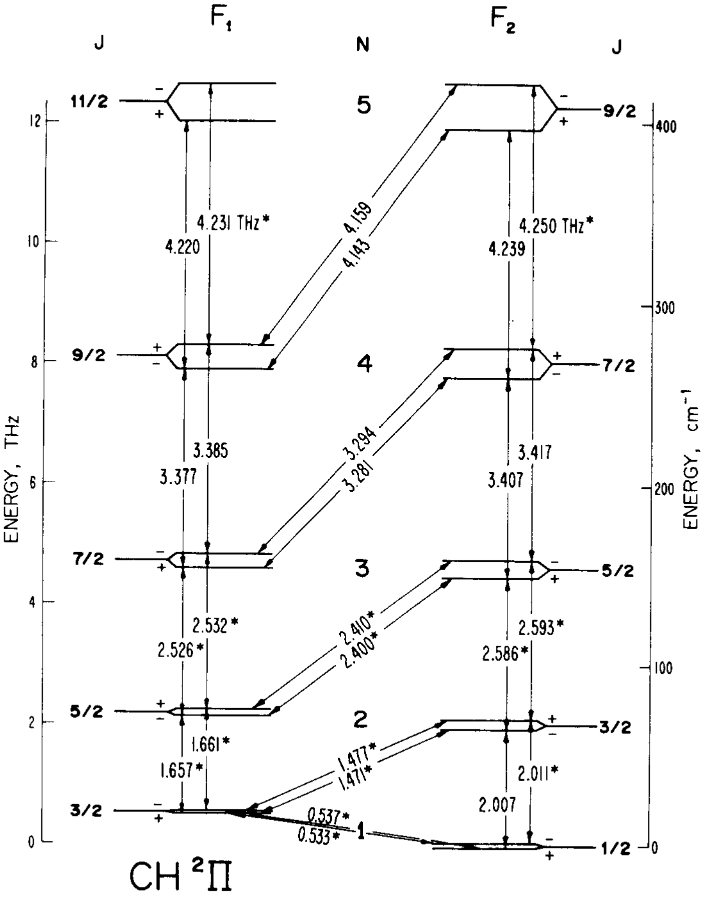

FIG. 1.—The low-lying energy levels of the CH radical, connected by electric dipole transitions (+ ↔ −) in the microwave and far-infrared regions. The parity doubling (lambda doubling) has been exaggerated by a factor of 20 for the sake of clarity. The transition frequencies are given in THz. The transitions observed in the LMR experiment are marked with an asterisk.

levels in the LMR spectrum. We therefore attach a progressively increasing uncertainty to the calculated lambda doubling frequencies as the levels involved become farther away from the lowest. The frequencies of transitions between levels studied directly in the far-infrared LMR experiment are not strongly model dependent and so are quite reliable, with an estimated uncertainty (1 σ) of 3 MHz. The calculated frequencies of the other spin-rotational transitions in Table 2 depend on the validity of the model used to fit the data and are therefore less reliable (± 6 MHz). The line strengths of the transitions are also given in Tables 1 and 2. The line strength $S_{F'F''}$ can be used to assess the relative intensity of an individual transition. It is defined by

$$S_{F'F''} = \left| \left\langle \gamma' F' \middle\| \mathfrak{D}^{(1)}_{\cdot q}(\omega)^* \middle\| \gamma F \right\rangle \right|^2, \qquad (1)$$

where the quantity on the right-hand side is the reduced matrix element of the rotation matrix (Brink and Satchler 1968) and γ stands for subsidiary quantum numbers. The intensity of a line in absorption can be obtained by multiplying the line strength by the square of the dipole moment μ (1.46 debyes for CH, Phelps and Dalby 1966), by the transition frequency, and by the population factor for the lower level. The Einstein A-coefficients for spontaneous emission from state i to j can also be calculated from the line strengths by use of

$$A_{i\to j} = \left(16\pi^3 \nu_{ij}/3\varepsilon_0 h c^3\right)(2F_i + 1)^{-1} S_{ij}\mu^2. \qquad (2)$$

It is hoped that the information contained in Tables 1 and 2 will be useful to astronomers in the search for additional transitions in the CH radical. Both optical and radio astronomy have shown that CH is largely confined to its lowest, $J = \frac{1}{2}$, level in the interstellar clouds (McKellar 1941; Rydbeck, Elldér, and Irvine 1973; Turner and Zuckerman 1974). One would therefore confidently expect that the transitions from this level at 533 and 537 μm ($F_1 \leftarrow F_2, J = 1\frac{1}{2} \leftarrow \frac{1}{2}$) can be detected in such sources. We are currently making a companion study of CD, with a view to providing the corresponding information for this molecule.

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