

Spectroscopy of the CH Free Radical

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New emission observations of the $A^2\Delta-X^2\Pi$ and $B^2\Sigma^-X^2\Pi$ electronic transitions of the CH free radical were recorded. The $A^2\Delta-X^2\Pi$ and $B^2\Sigma^-X^2\Pi$ data were obtained with a Fourier transform spectrometer and additional measurements of the $A^2\Delta-X^2\Pi$ transition were made with a spectrograph. These line positions were combined with the previous infrared vibration-rotation measurements in a simultaneous fit to determine the molecular parameters for the $X^2\Pi$, $A^2\Delta$, and $B^2\Sigma^-$ states. © 1991 Academic Press, Inc.

INTRODUCTION

CH is one of the most studied free radicals because it occurs in such a wide variety of environments. A partial review of the spectroscopic literature on CH was provided in a previous paper (1). Since 1986, when the vibration-rotation emission spectrum was observed with a Fourier transform spectrometer (1), we have observed an additional vibration-rotation band (4-3) as well as the $A^2\Delta-X^2\Pi$ and $B^2\Sigma^-X^2\Pi$ electronic transitions. In this paper, we take the opportunity to correct an error in the fitting of our previous infrared data and we report a combined fit of all of our CH observations.

There has been considerable spectroscopic, kinetic, and theoretical work on the CH free radical since 1986. The hyperfine structure of the $A^2\Delta-X^2\Pi$ (2) and $C^2\Sigma^+X^2\Pi$ (3) transitions was measured in molecular beam experiments. The hyperfine parameters of the low-lying states in CH were also calculated ab initio by several groups (4-6). The microwave optical double resonance experiments of Steimle *et al.* provided the hyperfine parameters for the $X^2\Pi$ state of ^{13}CH (7).

Tunable far infrared and laser magnetic resonance measurements of the pure rotational transitions of CD (8), CH, and ^{13}CH (9) were made in Boulder. The metastable $a^4\Sigma^-$ state was discovered by Nelis *et al.* (10) by far infrared laser magnetic resonance. This state may be important in the production of ions in flames by the reaction

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TABLE I
Line Positions for the 4-3 Vibration-Rotation Band of CH (in cm^{-1})

J"	R _{1e}	R _{1f}	R _{2e}	R _{2f}
0.5	-	-	-	2417.3613(2)
1.5	2404.7967(16) ^a	2404.6711(-85)	2429.2943(6)	2429.4952(6)
2.5	2427.4996(9)	2427.3204(-34)	2449.4551(0)	2449.7081(-24)
3.5	2448.6388(3)	2448.4071(-2)	2468.8674(-45)	-
4.5	2468.4795(-8)	2468.1974(9)	-	2487.5717(22)
5.5	2487.0703(34)	2486.7409(61)	2504.3913(80)	-
6.5	2504.3913(-29)	2504.0176(-8)	-	2520.7620(98)
7.5	-	2520.0290(-4)	2534.9809(2)	2535.4536(60)
8.5	2535.1936(4)	2534.7430(-17)	-	2548.8321(2)
9.5	-	2548.1338(-60)	-	-

J"	P _{1e}	P _{1f}	P _{2e}	P _{2f}
1.5	-	-	2296.2426(14)	-
2.5	-	-	2279.2365(-53)	2279.0068(-18)
3.5	2280.4625(-11)	2280.6694(55)	2251.7012(-9)	2251.3920(-22)
4.5	2252.0956(54)	2252.3615(-34)	2222.9084(187)	-
5.5	2222.9084(-77)	2223.2650(-20)	2193.1051(30)	2192.6392(0)
6.5	2192.9111(-15)	-	-	-
7.5	-	2162.5969(-11)	-	-

^a Observed-Calculated line positions in units of 10^{-4} cm^{-1} .

$\text{CH}(a^4\Sigma^-) + \text{O} \rightarrow \text{HCO}^+ + e^-$ (11). The microwave spectra of CH have been reviewed by Lovas and Suenram in 1989 (12).

Other spectroscopic measurements of CH include the dipole moment (13) of the $A^2\Delta$ state (0.77 D), a reanalysis of the $A^2\Delta-X^2\Pi$ transition (14), and a measurement of isotopic shifts in the rotational lines of the $A^2\Delta-X^2\Pi$ transition (15). CH is widely observed in extraterrestrial sources including the sun (16) and diffuse interstellar clouds (17-20). Highly excited states of CH were found by resonance enhanced multiphoton ionization with the detection of the ion and/or the photoelectron (21-27). Very good ab initio calculations by van Dishoeck (28) are now available for these highly excited states.

The CH molecule is readily detected in hydrocarbon flames (29-32) and shock tubes (33). The formation of the $A^2\Delta$ state by electron impact on methyl halides has been studied (34). Reaction rates of CH can be measured by laser-induced fluorescence (35-37). Radiative lifetimes, rotational energy transfer, and quenching rates of the $A^2\Delta$ state are known (38-44). Even state-to-state energy transfer rates in the ground $X^2\Pi$ state have been measured (45) and theoretically explained (46).

EXPERIMENTAL DETAILS

The 4-3 vibration-rotation band was found in the same spectrum which yielded the 3-2, 2-1, and 1-0 bands previously reported (1). The experimental conditions used can be found in our previous CH paper (1).

The $A^2\Delta-X^2\Pi$ and $B^2\Sigma^-X^2\Pi$ transitions were recorded in two Fourier transform

TABLE II
Measured Line Positions for the $A^2\Delta-X^2\Pi$ Transition of CH (in cm^{-1})^a

0-0 Band						
J	Q_{1fe}	O-C	Q_{1ef}	O-C	R_{1e}	O-C
1.5					23228.008	71
2.5	23172.5904	-17	23172.7567	33	23260.0996	-16
3.5	23175.6443	-4	23176.0206	7	23292.0084	2
4.5	23179.0751	-64	23179.7444	-12	23324.1842	-13
5.5	23183.0698	40	23184.0952	26	23356.7388	-8
6.5	23187.6531	-40	23189.1235	50	23389.6844	-12
7.5	23192.8766	11	23194.8443	27	23423.0066	26
8.5	23198.7229	-3	23201.2625	9	23456.6585	-9
9.5	23205.1907	-8	23208.3690	20	23490.6058	-11
10.5	23212.2631	-15	23216.1415	23	23524.7865	-89
11.5	23219.9212	-1	23224.5540	4	23559.1721	33
12.5			23233.5803	-1	23593.6684	13
13.5	23236.8772	16	23243.1922	72	23628.2235	-25
14.5	23246.1121	53	23253.3248	-32	23662.7895	122
15.5	23255.7812	-75	23263.9616	-35	23697.2505	21
16.5	23265.8722	-36	23275.0447	-18	23731.5567	-59
17.5	23276.3074	-97	23286.5473	303	23765.6314	-62
18.5	23287.0475	-81	23298.3379	227		
19.5	23298.0260	-17	23310.3737	6	23832.7065	-72
20.5	23309.1567	-57	23322.5675	-476	23865.5136	-64
21.5	23320.3947	141	23334.9669	91		
22.5	23331.5915	-24	23347.3079	-7		
23.5	23342.7146	104				

J	R_{1f}	O-C	P_{1e}	O-C	P_{1f}	O-C
1.5	23228.0070	-172				
2.5	23260.2657	32				
3.5	23292.3839	6	23088.1369	13	23088.5123	15
4.5	23324.8480	-14	23062.7172	-9	23063.3828	7
5.5	23357.7674	14	23037.9608	-12	23038.9894	9
6.5	23391.1482	18	23013.9820	-16	23015.4457	10
7.5	23424.9716	25	22990.8426	-51	22992.7976	-156
8.5	23459.1963	1	22968.6032	75	22971.1351	20
9.5	23493.7812	10	22947.2610	42	22950.4316	8
10.5	23528.6750	82	22926.8492	-23	22930.7353	115
11.5	23563.8011	43	22907.3986	49	22912.0221	-7
12.5	23599.1048	-16	22888.8515	-406	22894.3403	75
13.5	23634.5286	9	22871.3326	-170	22877.6383	-148
14.5	23669.9997	112	22854.7627	-14	22861.9579	-197
15.5	23705.4149	27			22847.2923	-24
16.5	23740.7164	-12	22824.4509	223	22833.5861	-7
17.5	23775.8239	58	22810.6408	-52	22820.8283	-19
18.5			22797.7398	-147	22808.9831	-116
19.5			22785.7140	-72	22798.0538	111
20.5			22774.5013	-40	22787.9201	-90
21.5	23912.2480	160			22778.6227	225
22.5	23944.774	-160				
23.5	23976.467	-127				

^a Observed minus calculated line positions are in units of 10^{-4} cm^{-1} .

emission experiments and the $A^2\Delta-X^2\Pi$ transition was also measured with the Oregon grating spectrograph. In the first Fourier transform measurement, a Cossart source (47) was used with a trace of CH_4 in 2 Torr of Ar gas on the low pressure side of the capillary discharge. The current was about 100 mA. The emission from the lamp was focused onto the entrance aperture of the McMath Fourier transform spectrometer of the National Solar Observatory at Kitt Peak. Three scans were coadded in 22 min of integration at a resolution of 0.071 cm^{-1} . Two cooled photomultiplier detectors (RCA 31034) and CuSO_4 filters limited the spectral band pass to approximately 2800–5800 Å. In the second experiment, the pressure in the Cossart cell was about 0.7 Torr and the other experimental parameters were very similar. For this experiment, 12 scans were coadded in 85 min of integration.

TABLE II—Continued

J	R _{2f}	O-C	R _{2a}	O-C	Q _{2ef}	O-C
0.5	23247.5241	-53	23247.6493	87		
1.5	23267.3831	17	23267.6254	-13	23180.4563	-3
2.5	23296.9053	-6	23297.3957	-35	23180.8797	14
3.5	23327.8103	2	23328.6259	0	23182.9343	17
4.5	23359.5419	26	23360.7512	1	23186.0336	-4
5.5	23391.8921	-4	23393.5742	24	23189.9974	-4
6.5	23424.7570	17	23426.9694	-25	23194.7962	579
7.5	23458.0425	-12	23460.8658	12	23200.2032	-3
8.5	23491.6800	-50	23495.1776	31	23206.3536	-8
9.5	23525.6079	-31	23529.8275	-30	23213.1615	48
10.5	23559.7587	38	23564.7618	-5	23220.5775	2
11.5	23594.0421	-69	23599.8999	12	23228.5972	153
12.5	23628.4211	-28	23635.1770	106	23237.1325	-16
13.5	23662.7899	-177	23670.4983	87		
14.5	23697.1139	-112	23705.7901	12		
15.5	23731.3027	55	23740.9911	101	23265.663	8
16.5	23765.2509	104	23775.9708	-70	23275.9699	3
17.5	23798.893	271	23810.683	-31		
18.5	23832.090	111	23845.0099	34		
19.5	23864.7680	-98			23308.4607	-44
20.5	23896.856	28	23912.054	23	23319.5771	-44
21.5	23928.169	-179	23944.540	1	23330.7017	23
22.5	23958.667	164	23976.158	-71	23341.7076	-128

J	Q _{2fa}	O-C	P _{2f}	O-C	P _{2a}	O-C
1.5	23180.7043	25				
2.5	23181.3721	6	23093.9503	-31	23094.4421	-46
3.5	23183.7338	-145	23066.9027	-22	23067.7166	-41
4.5	23187.2481	24	23041.1569	4	23042.3644	-38
5.5	23191.6754	-17	23016.4928	6	23018.1712	-6
6.5	23196.9536	-12	22992.8273	-163	22995.0572	-30
7.5	23203.0262	-2	22970.1919	55	22973.0062	-12
8.5	23209.8421	-21	22948.5198	56	22952.0091	52
9.5	23217.3644	-123	22927.8196	-67	22932.0549	88
10.5	23225.5812	-44	22908.1254	19	22913.1434	121
11.5	23234.4376	46	22889.3872	-180	22895.2681	127
12.5	23243.8752	-36	22871.6699	15	22878.4019	-98
13.5	23253.8765	-29	22854.9058	-9	22862.5897	1
14.5	23264.3819	-58	22839.1129	34	22847.7556	-189
15.5	23275.3445	-73	22824.2575	-35		
16.5	23286.7075	-71	22810.3503	100	22821.0775	-21
17.5	23298.4153	18	22797.3233	31		
18.5	23310.3724	-70	22785.1594	-72		
19.5	23322.5340	-22				
20.5	23334.8099	104				
21.5	23347.0692	-73				

The Fourier transform spectra were calibrated to an absolute accuracy of about $\pm 0.001 \text{ cm}^{-1}$ with the argon atomic line positions of Norlen (48). The observed CH linewidths were about 0.12 cm^{-1} , consistent with Doppler broadening with a translational temperature of about 600 K. Since the maximum signal-to-noise ratio was about 50, the strong, unblended low- J CH lines have an accuracy of about $\pm 0.002 \text{ cm}^{-1}$. However, many lines were blended or they were considerably weaker with a typical accuracy of $\pm 0.01 \text{ cm}^{-1}$.

The $A^2\Delta-X^2\Pi$ emission spectra recorded in Oregon used a direct current flowing afterglow seeded with a small amount of acetylene downstream of the discharge. The spectrograph was a Czerny-Turner grating instrument with a 1.9-m focal length Newtonian collimating mirror, a 350-mm by 175-mm plane diffraction grating and a 7-m focal length focusing mirror. The slit was $15 \mu\text{m}$ wide. Spectra were recorded on Kodak 103a0 photographic plates which had been hypersensitized by baking in an atmosphere of 8% hydrogen and 92% nitrogen for 2 hr at 50°C . Wavelength calibration was provided by an iron-neon hollow cathode lamp which was focused and directed onto the slit next to the CH signal using a right-angle prism.

TABLE II—Continued

1-1 Band						
J	Q_{1fe}	O-C	Q_{1ef}	O-C	R_{1e}	O-C
1.5					23232.5330	91
2.5			23179.3259	-132	23262.6719	-31
3.5	23181.3726	-52	23181.7332	-53	23292.3841	22
4.5	23183.6986	146	23184.3222	-12	23322.0821	-14
5.5	23186.2495	-49	23187.2445	9	23351.8755	25
6.5	23189.1233	-146	23190.5458	-4	23381.7663	124
7.5	23192.3521	81	23194.1944	-443	23411.6946	-4
8.5	23195.8564	-62	23198.3194	109	23441.6484	14
9.5	23199.6753	39	23202.7460	152	23471.527	-230
10.5	23203.7198	-192	23207.4678	-35	23501.3457	100
11.5	23208.0160	-107	23212.4934	54	23530.9495	204
12.5	23212.4932	45	23217.7416	99		
13.5	23217.0432	-296	23223.1543	78		
J	R_{1f}	O-C	P_{1e}	O-C	P_{1f}	O-C
1.5	23232.5331	-112				
2.5	23262.8327	36				
3.5	23292.7466	40	23097.8831	-47	23098.2577	92
4.5	23322.7166	-64	23072.6839	41	23073.3111	-82
5.5	23352.8613	-9	23047.8559	11	23048.8438	-3
6.5	23383.1663	41	23023.5135	-58	23024.9202	-74
7.5	23413.5997	101	22999.7321	41	23001.6410	184
8.5	23444.1003	74	22976.4964	-154	22978.9404	-172
9.5	23474.6127	33	22953.8615	-255		
10.5	23505.0580	-100				
13.5	23595.286	49				
J	R_{2f}	O-C	R_{2e}	O-C	Q_{2ef}	O-C
0.5	23251.9656	53	23252.0733	67		
1.5	23269.6983	48	23269.9245	-17	23186.7662	-43
2.5	23297.0999	-85	23297.5819	19	23186.4304	7
3.5	23325.5896	43	23326.3677	3	23187.4182	133
4.5	23354.5817	0	23355.7454	3	23189.1235	-23
5.5	23383.8870	-59	23385.5066	-1	23191.4076	18
6.5	23413.3910	-53	23415.5337	63	23194.1259	-266
7.5	23442.9971	12	23445.7290	200	23197.3074	39
8.5			23475.9800	180	23200.7987	-85
9.5	23502.1278	-110	23506.1952	-36	23204.6030	-116
10.5	23531.5135	18	23536.3255	-50	23208.6699	-53
11.5			23566.283	179	23212.9482	124
12.5			23595.881	-255		

RESULTS AND DISCUSSION

The 4-3 vibration-rotation band was identified with the help of the constants obtained from the ATMOS observations of the sun (16). Table I lists our newly identified 4-3 band measurements. The ATMOS lines for the 1-0 through 4-3 bands complement our work because we observe mainly low- J transitions, while the much hotter (5000 K) solar measurements provide the high- J transitions. The two data sets were integrated and fitted together. If there were two unblended measurements for the same line, the slightly more accurate laboratory measurement was chosen.

The 0-0, 1-1, and 2-2 bands were measured for the $A^2\Delta-X^2\Pi$ transition (Table II) in three different spectra. The measurements were integrated into a single data set, again favoring the Fourier transform measurements in the case of multiple determinations of a line position.

The 2-2 band assignments of the $A^2\Delta-X^2\Pi$ transition required some care because no previous modern observations were available at the time this work was completed. Recently, Bembenek *et al.* (14) have reanalyzed the $A^2\Delta-X^2\Pi$ transitions and our 2-2 band assignments are in agreement with theirs. Our 0-0 band measurements also

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TABLE II—Continued

J	Q _{2f₀}	O-C	P _{2f}	O-C	P _{2₀}	O-C
1.5	23187.0324	292				
2.5	23186.9119	106	23103.4963	-104	23103.9863	80
3.5	23188.1858	-12	23076.7247	-15	23077.5009	-74
4.5	23190.2914	23	23050.9438	-16	23052.1070	-17
5.5	23193.0271	75	23025.9490	-9	23027.5628	-8
6.5	23196.2885	50	23001.6410	-244	23003.7911	-53
7.5	23200.0203	38	22978.0689	93	22980.7452	-275
8.5			22955.1049	-98	22958.4550	-168
9.5	23208.6699	-47	22932.7941	-227		
10.5	23213.5012	72	22911.1664	154		
11.5	23218.5758	101				
12.5	23223.8301	20				

2-2 Band

J	R _{1₀}	O-C	R _{1f}	O-C	Q _{1₀}	O-C
1.5	23169.4838	51	23169.4832	-122		
2.5	23197.3077	-95	23197.4682	53	23118.1865	14
3.5	23224.3421	33	23224.6712	-122	23119.1486	-8
4.5	23250.9534	7	23251.5531	-127	23119.8357	41
5.5	23277.2365	4			23120.3303	-376
6.5					23120.7711	-227
7.5					23121.1228	179
8.5					23121.3065	314

J	Q _{1f}	O-C	P _{1₀}	O-C	P _{1f}	O-C
2.5	23118.3276	-33				
3.5	23119.4976	36	23040.0433	259		
4.5	23120.4256	-191	23014.6253	-170	23015.2572	19
5.5	23121.3065	-112	22989.2545	77	22990.1893	-73
6.5	23122.1547	77	22963.9887	631		
7.5	23122.9236	-25	22938.7244	34		
8.5	23123.6104	-164				

J	R _{2f}	O-C	R _{2₀}	O-C	Q _{2f}	O-C
0.5	23188.7963	-126	23188.9166	53		
1.5	23204.0610	159	23204.2503	-158	23125.4771	86
2.5	23228.8479	-210	23229.3052	-150	23124.0115	124
3.5	23254.3166	101	23255.0806	239	23123.3932	-80
4.5	23279.8292	23			23123.1067	-126
5.5					23122.9203	-432
6.5					23122.8244	-65

J	Q _{2₀}	O-C
1.5	23125.6765	-130
2.5	23124.4583	79
3.5	23124.1546	32
4.5	23124.2187	-179
5.5	23124.4583	-560
6.5	23124.8773	-23

Satellite lines for the A²Δ-X²Π transition of CH (in cm⁻¹).

0-0 Band			1-1 Band			
J	O-C		J	O-C		
1.5	23229.7477	127	^R Q _{1fe}	1.5	23185.3085	-46
2.5	23261.2437	-73		1.5	23185.0872	68
2.5	23174.4976	102	^O P _{1f}	2.5	23185.3085	19
3.5	23177.1672	-25		2.5	23102.2866	-16
1.5	23229.7477	-105	^R Q _{1ef}	3.5	23076.3686	-166
2.5	23261.4201	78		2.5	23101.8196	30
3.5	23293.1865	-108		3.5	23293.1921	125
4.5	23325.4362	-9		1.5	23234.2273	-71
5.5	23358.1767	-88		2.5	23263.9613	91
2.5	23174.3265	4	^O P _{1e}	3.5	23293.5492	89
3.5	23176.8011	66				
1.5	23178.9661	-17	^O R _{2₀}			
1.5	23178.7237	12	^O R _{2f}			
3.5	23182.1225	40				
2.5	23092.2169	-25	^F Q _{2f}			
3.5	23065.7664	113				
4.5	23040.3454	29				
2.5	23092.7166	40	^F Q _{2₀}			
3.5	23066.5729	20				
4.5	23041.5512	-30				

TABLE III

Measured Line Positions for the $B^2\Sigma^- - X^2\Pi$ Transition (in cm^{-1})

0-0 Band						
J	P ₂	O-C	P ₁	O-C	Q ₁	O-C
0.5			25698.2278	-74		
1.5	25680.3491	-37	25656.5907	-46	25705.5902	24
2.5	25650.3381	-22	25620.8454	-8	25700.6576	-3
3.5	25616.5756	-9	25582.8211	19	25697.7992	10
4.5	25579.5354	-2	25542.0293	32	25679.4339	25
5.5	25539.3428	43	25498.2985	50	25663.6300	29
6.5	25496.0072	12	25451.5148	15	25644.3539	4
7.5	25449.5100	4	25401.5767	-9	25621.5270	-16
8.5	25399.7871	10	25348.3591	-111	25599.0305	-39
9.5	25346.7351	-69	25291.7449	-76	25564.7160	-45
10.5	25290.2503	-25	25231.5369	-220	25530.4007	-35
11.5	25230.1590	-34	25167.5763	-158	25491.8771	92
12.5	25166.2941	146			25448.8678	108
13.5					25401.0946	189
14.5					25348.1698	-131

J	Q ₂	O-C	R ₂	O-C	R ₁	O-C
0.5	25723.4079	-150				
1.5	25706.8543	-18	25756.0838	-62		
2.5	25695.9788	20	25776.4275	115	25797.0675	105
3.5	25682.5947	43	25792.7352	20	25808.7525	40
4.5	25666.1592	25	25805.4199	92	25817.2144	102
5.5	25646.4522	13	25814.4178	-446	25822.1333	-88
6.5	25623.3100	15	25819.7980	-14	25823.3784	402
7.5	25596.5653	-44	25821.2957	154	25820.5741	31
8.5	25566.0530	-77				
9.5	25531.5831	-12	25811.9103	-94		
10.5	25492.9189	49	25800.5884	-250		
11.5	25449.7854	-34				
12.5	25401.9159	72				
13.5	25348.8892	-404				

1-0 Band						
J	P ₂	O-C	P ₁	O-C	Q ₁	O-C
0.5			27493.2579	90		
1.5	27475.3607	-58	27448.6360	23	27497.6280	-72
2.5	27442.3986	109	27406.9201	13	27486.7419	-36
3.5	27402.6728	87	27359.8939	109	27468.8877	48
4.5	27356.6150	-53	27306.9503	-78	27444.3915	11
5.5	27304.2908	-67	27247.8618	49	27413.2190	-35
6.5	27245.5908	-105			27375.2055	168

J	Q ₂	O-C	R ₂	O-C	R ₁	O-C
0.5	27515.4606	-7				
1.5	27492.9324	37	27542.1795	19	27559.7839	-50
2.5	27473.0374	-32	27553.5026	19	27561.9923	32
3.5	27447.5350	125	27557.6669	-253	27558.2941	-169
4.5	27415.7179	-12	27555.0491	431		
5.5	27377.2302	-171				

1-1 Band						
J	P ₂	O-C	P ₁	O-C	Q ₁	O-C
0.5			24761.4231	-38		
1.5	24743.5981	34			24765.8692	31
2.5	24712.6773	-40	24680.2084	60	24757.0463	-0
3.5	24676.1125	27	24637.4339	95	24742.3410	-21
4.5	24634.2763	-82	24589.8099	85	24722.0808	15
5.5	24587.2344	-50	24537.0481	-4	24696.2013	-4
6.5					24664.5166	14

J	Q ₂	O-C	R ₂	O-C	R ₁	O-C
0.5	24783.6398	-43			24828.2477	-430
1.5	24762.9887	-59	24810.4088	31	24829.8611	189
2.5	24746.3448	-10				
3.5	24725.0943	-33	24831.1310	-69		
4.5	24698.6104	-3	24832.6616	-87		
5.5	24666.5026	-19	24828.2477	82		

TABLE IV
Molecular Constants for the $X^2\Pi$ State of CH (in cm^{-1})

Constant	v = 0	v = 1	v = 2	v = 3	v = 4
T_v	0.0	2732.97814(48)	5339.90441(76)	7822.22091(109)	10180.9997(15)
B_v	14.192330(30) ^b	13.661754(30)	13.135801(34)	12.613444(39)	12.093088(47)
$10^3 \times D_v$	1.46083(26)	1.43747(27)	1.41590(30)	1.39663(31)	1.38007(36)
$10^7 \times H_v$	1.1215(89)	1.0845(91)	1.0480(92)	1.0066(87)	0.9482(93)
$10^{12} \times L_v$	-8.75(116)	-9.13(103)	-9.97(90)	-11.24(77)	-12.46(77)
A_v	28.1468022 ^a	28.3383(24)	28.5277(50)	28.6913(131)	28.888(22)
$10^2 \times \gamma_v$	-2.513(31)	-2.341(31)	-2.179(32)	-2.041(32)	-1.868(35)
$10^6 \times \gamma_{Dv}$	4.28(167)	4.29(154)	4.52(143)	5.18(132)	4.62(125)
$10^2 \times p_v$	3.3918(187)	3.185(22)	3.062(27)	2.914(32)	2.802(42)
$10^6 \times p_{Dv}$	-8.39(103)	-5.80(95)	-5.11(90)	-4.30(87)	-4.00(103)
$10^9 \times p_{Mv}$	1.09 ^a	0.0	0.0	0.0	0.0
$10^2 \times q_v$	3.86766(170)	3.7280(20)	3.5895(24)	3.4514(27)	3.3119(34)
$10^5 \times q_{Dv}$	-1.5233(141)	-1.4839(142)	-1.4437(142)	-1.4024(139)	-1.3480(167)
$10^3 \times q_{Mv}$	2.99(25)	2.86(22)	2.728(194)	2.619(170)	2.265(191)

^a Fixed to the values of Ref. 49.

^b One standard deviation uncertainty.

agree with the very accurate measurements of Brazier and Brown (49), but our observations are more extensive.

The 0-0, 1-0, and 1-1 bands of the $B^2\Sigma^- - X^2\Pi$ transition were observed by Fourier transform emission spectroscopy. The line positions are listed in Table II.

The previous investigations of the $B^2\Sigma^- - X^2\Pi$ transition are by Shidei (50) and Gerö (51) as well as Herzberg and Johns (52). Term values of the $B^2\Sigma^-$ state are provided by Elander *et al.* (53) and Botterud *et al.* (54). The $B^2\Sigma^-$ potential curve has a barrier to dissociation and the emission breaks off because of predissociation (52, 53). Elander *et al.* combined the spectroscopic data for the $B^2\Sigma^-$ state with some

TABLE V
Molecular Constants for the $A^2\Delta$ State of CH (in cm^{-1})

Constant	v = 0	v = 1	v = 2
T_v	23173.4622(8)	25913.7467(23)	28460.7451(47)
B_v	14.578957(45)	13.910842(146)	13.18626(43)
$10^3 \times D_v$	1.56460(42)	1.6037(22)	1.6652(74)
$10^8 \times H_v$	9.216(129)	6.38(85)	3.12 ^a
$10^{11} \times L_v$	-2.040(129)	0.0	0.0
A_v	-1.09958(112)	-1.0696(31)	-1.0460(50)
$10^2 \times \gamma_v$	4.255(37)	4.011(91)	4.031(158)
$10^5 \times \gamma_{Dv}$	-1.301(175)	-1.06(82)	-0.599 ^a
$10^6 \times p_v$	1.02(78)	0.0	0.0
$10^8 \times q_v$	-6.6(20)	0.0	0.0

^a fixed.

TABLE VI
Molecular Constants for $B^2\Sigma^-$ State of CH (in cm^{-1})

Constant	$v = 0$	$v = 1$
T_v	25712.5101(9)	27507.5239(20)
B_v	12.640178(60)	11.15745(48)
$10^3 \times D_v$	2.13069(80)	3.107(29)
$10^7 \times H_v$	-4.031(30)	-30.9(45)
$10^2 \times \gamma_v$	-2.710(33)	-2.112(50)

lifetime measurements to derive a potential curve (53). Our Fourier transform measurements (Table III) are more accurate than the previous spectroscopic work.

A combined fit of the vibration-rotation data (1-0 to 4-3 bands), the $A^2\Delta-X^2\Pi$ transition (0-0, 1-1, and 2-2 bands), and the $B^2\Sigma^-X^2\Pi$ transition (0-0, 1-0, and 1-1 bands) was carried out. The effective Hamiltonian of Brown *et al.* (55) was used

TABLE VII
Equilibrium Molecular Constants for CH in the $X^2\Pi$, $A^2\Delta$, and $B^2\Sigma^-$ States (in cm^{-1})

Constant	$X^2\Pi$	$A^2\Delta$	$B^2\Sigma^-$
B_e^a	14.45981(15)	14.8918*	13.3815*
α_e	0.53657(27)	0.6116*	1.4827*
$10^3 \gamma_e$	3.33(13)	28.23*	-
$10^4 \epsilon_e$	-2.15(18)	-	-
D_e^b	1.47355(28)	1.5435(29)	1.6425*
$10^2 \beta_e$	-2.586(28)	4.21(50)	97.63*
$10^3 \delta_e$	1.123(57)	-	-
A_e^c	28.05212(97)	-1.1134(14)	-
α_A	0.1894(19)	0.280(17)	-
ω_e^d	2860.7512*	2933.5706*	-
$\omega_e x_e$	64.4390*	96.6431*	-
$\omega_e y_e$	0.3637*	-	-
$10^2 \omega_e z_e$	-1.542*	-	-

^a $B_v = B_e - \alpha_e(v+1/2) + \gamma_e(v+1/2)^2 + \epsilon_e(v+1/2)^3$

^b $D_v = D_e + \beta_e(v+1/2) + \delta_e(v+1/2)^2$

^c $A_v = A_e + \alpha_A(v+1/2)$

^d $G(v) = \omega_e(v+1/2) - \omega_e x_e(v+1/2)^2 + \omega_e y_e(v+1/2)^3 + \omega_e z_e(v+1/2)^4$

^e exact fit

for the ${}^2\Pi$ and ${}^2\Sigma^-$ vibrational states. An explicit listing of the matrix elements of this Hamiltonian is provided for the ${}^2\Pi$ state by Amiot *et al.* (56), while ${}^2\Sigma^+$ matrix elements are tabulated by Douay *et al.* (57). For the $A^2\Delta$ vibrational states, the effective Hamiltonian of Brown *et al.* (58) is utilized, along with their case (a) matrix elements.

A weighted nonlinear least-squares fit of our data provided the spectroscopic constants of Tables IV, V, and VI. A copy of the input data set and the final fit (including term values) can be obtained from one of the authors (PFB) on an IBM compatible floppy disk. The constants of Table IV for the $X^2\Pi$ state supersede those previously reported from the infrared measurements. The constants for $v=0$ in Table IV differ slightly from our previous determination (1) because we now include the solar data of Mélen *et al.* (16) and because we have corrected a small typographical error in the computer code for the matrix elements of H in the original program. The molecular constants of Tables IV–VI were used to determine the equilibrium molecular constants of Table VII.

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