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The vibration–rotation emission spectrum of CH($X\,^2\Pi$)

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The vibration–rotation emission spectrum of the $X\,^2\Pi$ state of CH was observed with the McMath Fourier transform spectrometer at Kitt Peak. The 1–0, 2–1, and 3–2 bands were detected in a microwave discharge of allene in Ar and methane in He. A simultaneous fit of all of the line positions provided spectroscopic constants for $v = 0, 1, 2,$ and 3. Equilibrium molecular constants (in cm^{-1}) include $\omega_e = 2860.4118(98)$, $\omega_e x_e = 64.1082(46)$, $\omega_e y_e = 0.2406(10)$, $B_e = 14.458\,62(48)$, $\alpha_e = 0.534\,16(58)$, $\gamma_e = 0.001\,98(15)$, $r_e = 1.119\,83(2)$ Å. An RKR potential curve was calculated from the equilibrium constants.

I. INTRODUCTION

CH, along with NH and OH, is one of the most studied free radicals. CH occurs prominently in a wide variety of energetic environments including the sun,[1-4] stellar atmospheres,[5,6] comets,[7,8] the interstellar medium,[9-12] flames,[13,15] and detonations. The $A\,^2\Delta-X\,^2\Pi$ electronic transitions near 4300 Å, [1-4, 7-10, 13-15] the vibration–rotation spectrum near 3μ,[4-6] and the Λ-doubling transitions near 3.3 GHz[11,12] are commonly used to monitor the presence of CH in laboratory and extraterrestrial sources.

The CH molecule was first detected in 1918.[16] Since then, numerous analyses of the $A\,^2\Delta-X\,^2\Pi$, $B\,^2\Sigma^--X\,^2\Pi$, and $C\,^2\Sigma^+-X\,^2\Pi$ transitions for CH and CD have appeared in the literature.[17] Transitions to Rydberg states were first observed by Herzberg and Johns[18] in the vacuum ultraviolet, and more recently by Chen, Chupka, and Colson[19] using the technique of laser multiphoton ionization.

High-precision data for $v = 0$ of the $X\,^2\Pi$ state are available from laser magnetic resonance experiments,[20] as well as microwave[21] and microwave–optical double resonance[22-24] detection of the Λ-doubling transitions. The difference frequency laser work of Lubic and Amano[25] provided vibrational and rotational constants for $v = 1$ from the fundamental $(1 - 0)$ vibration–rotation band. The spectroscopic constants available for $v = 2$ are from the reanalysis of optical data by Krupp[26] and Brotterund, Lofthus, and Veseth.[27] By modern standards, the data for $v = 2$ are not of very high quality, and no information is available for vibrational levels higher than two.

This lack of data for the ground state vibrational levels means that no accurate experimental ground state potential curve exists. The ground state potential curve is required, e.g., to compute vibrational wave functions for vibration–rotation transition dipole moment calculations and for the calculation of Franck–Condon factors of electronic transitions. Theoretical calculations are available for the potential curve of the $X\,^2\Pi$ state.[28,29]

The vibration–rotation line positions are themselves valuable pieces of information because they allow the identification of CH in the atmospheres of carbon stars and the sun. For example, the absorption lines of the 3–2 band of CH were identified by Lambert[30] in the sun with the aid of the measurements reported here.

The 1–0, 2–1, and 3–2 vibration–rotation emission bands of the $X\,^2\Pi$ state of CH were detected with a high-resolution Fourier transform spectrometer. A simultaneous fit of these data to a $^2\Pi$ Hamiltonian provided spectroscopic parameters for $v = 0, 1, 2,$ and 3. Equilibrium constants were derived and an RKR potential curve was computed for the $X\,^2\Pi$ state.

II. EXPERIMENT

The emission spectrum of the CH radical was excited in an electrodeless quartz discharge tube driven by a 2450 MHz microwave oscillator. A mixture of 2.75 Torr He, 0.030 Torr CH_4, and 0.040 Torr of white phosphorous vapor flowed through the cell. The CH spectrum was found by accident and the phosphorous is, presumably, not required. A vibration–rotation spectrum of CH was also observed in a discharge of 3.3 Torr of argon and 0.80 Torr of allene, but with a reduced signal-to-noise ratio.

The emission from the discharge tube was observed with the McMath Fourier transform spectrometer of the National Solar Observatory at Kitt Peak. Ten scans were coadded in 70 min of integration. The unapodized resolution was set to 0.02 cm^{-1}. InSb detectors and a silicon filter limited the bandpass to approximately 1800–9000 cm^{-1}.

The spectrum contained emission from the molecules CO, PH, CP, C_2, CH, and P_2. The analyses of the vibration–rotation spectrum of PH[31] and the $A\,^2\Pi-X\,^2\Sigma^+$ electronic transition of CP[32] are published elsewhere. The impurity CO lines were used to calibrate[33] the CH spectrum.

III. RESULTS AND DISCUSSION

The interferogram was transformed by Ladd to provide the spectrum. Some ringing was present, particularly near strong atomic lines, so the spectrum was apodized. The final linewidth of the CH lines was 0.036 cm^{-1}. The line positions were extracted from the spectrum with the data reduction program called DECOMP developed at Kitt Peak. The peak positions were found by fitting a Voigt line shape to each feature using a nonlinear least-squares procedure. Since the strongest lines have a signal-to-noise ratio of about 20, the peak positions have a precision of about 0.002 cm^{-1}. The calibration lines have a signal-to-noise ratio greater than 20, so the absolute accuracy of the strongest CH lines is also ± 0.002 cm^{-1}.

TABLE I. Observed line positions of the vibration–rotation emission spectrum of the $X\,^2\Pi$ state of CH (in cm^{-1}). Observed–calculated line positions, computed with the constants of Table II, are in parentheses.

			1–0 band	
J''[a]	R_{1e}	R_{1f}	R_{2e}	R_{2f}
0.5	$\cdots$	$\cdots$	2796.8826(− 10)	2797.0075(12)
1.5	2785.1080(4)	2784.9787(19)	2812.9725(26)	2813.2007(27)
2.5	2810.9964(− 2)	2810.7981(8)	2836.1105(22)	2836.4004(12)
3.5	2835.2362(− 23)	2834.9739(− 4)	2858.5391(26)	2858.8868(8)
4.5	2858.1400(− 6)	2857.8135(− 25)	2879.8823(− 4)	2880.2812(− 46)
5.5	2879.7533(− 15)	2879.3743(− 5)	2900.0336(13)[b]	2900.4867(27)[b]
6.5	2900.0841(38)[b]	2899.6514(17)	2918.9274(14)	2919.4172(− 45)
7.5	2919.1025(15)[b]	2918.6245(1)	2936.5215(− 7)	2937.0572(− 12)
8.5	2936.8003(39)	2936.2795(22)	2952.7871(− 2)	2953.3629(6)
9.5	2953.1449(− 8)	2952.5852(− 4)	$\cdots$	$\cdots$

			1–0 band	
J''	P_{1e}	P_{1f}	P_{2e}	P_{2f}
1.5	$\cdots$	$\cdots$	2664.8854(37)	2664.7423(− 14)
2.5	2676.3596(− 7)	2676.5015(− 4)	2643.6918(6)	2643.4318(− 2)
3.5	2645.2425(− 9)	2645.4638(− 12)	2613.0658(4)	2612.7230(− 3)
4.5	2613.6122(− 16)	2613.9174(− 3)	2581.0761(− 21)	2580.6503(− 7)
5.5	2581.1915(1)	2581.5800(8)	2548.0781(− 42)	2547.5685(− 1)
6.5	2547.9392(27)	2548.4114(17)	2514.1902(− 4)	2513.5906(14)
7.5	2513.8620(18)	2514.4203(4)	2479.4701(35)	2478.7794(22)
8.5	$\cdots$	2479.6357(− 6)	2443.9566(− 24)	2443.1844(24)
9.5	2443.3550(− 40)	2444.0792(− 128)[b]	$\cdots$	$\cdots$

			2–1 band	
J''[c]	R_{1e}	R_{1f}	R_{2e}	R_{2f}
0.5	$\cdots$	$\cdots$	2669.0013(− 10)	2669.1199(27)
1.5	2657.0034(3)	2656.8763(− 19)	2683.7552(12)	2683.9733(4)
2.5	2681.8355(36)	2681.6406(− 14)	2705.8993(13)	2706.1777(7)
3.5	2705.0420(1)	2704.7887(− 15)	2727.3235(− 16)	2727.6604(− 5)
4.5	2726.9276(− 12)	2726.6191(2)	2747.6770(7)	2748.0685(35)
5.5	2747.5444(24)	2747.1780(1)	2766.8376(− 32)	2767.2767(− 14)
6.5	2766.8852(53)	2766.4658(1)	2784.7635(26)	2785.2421(4)[b]
7.5	2784.9221(− 30)	2784.4666(8)	2801.3970(4)	2801.9126(− 23)
8.5	2801.6559(7)	2801.1534(− 33)	2816.7159(1)	2817.2660(23)
9.5	2817.0445(− 11)	2816.5168(10)	$\cdots$	$\cdots$

			2–1 band	
J''	P_{1e}	P_{1f}	P_{2e}	P_{2f}
1.5	$\cdots$	$\cdots$	2540.7135(− 21)	2540.5856(6)
2.5	2552.3696(− 8)	2552.5111(25)	2520.9132(− 10)	2520.6614(− 16)
3.5	2522.3654(− 14)	2522.5830(1)	2491.3354(− 14)	2491.0104(47)[b]
4.5	2491.8350(− 18)	2492.1342(15)	2460.4291(23)	2460.0104(− 39)
5.5	2460.5151(0)	2460.8892(− 26)	2428.5202(− 3)	2428.0278(17)
6.5	2428.3636(− 17)	2428.8256(23)	2395.7268(5)	2395.1475(− 21)
7.5	2395.3990(8)	2395.9405(26)	$\cdots$	$\cdots$

			3–2 band	
J''[d]	R_{1e}	R_{1f}	R_{2e}	R_{2f}
1.5	2530.3620(22)	2530.2379(− 19)	2555.9899(13)	2556.1929(− 58)
2.5	$\cdots$	2553.9456(3)	2577.1414(− 13)	2577.4096(− 2)
3.5	2576.3047(− 4)	2576.0652(16)	2597.5711(15)	2597.8929(28)
4.5	2597.1737(− 5)	2596.8775(4)	2616.2957(8)	2617.2953(7)
5.5	2616.7795(− 17)	2616.4308(− 18)	2635.0898(− 111)[b]	2635.5158(6)
6.5	2635.1161(− 71)[b]	2634.7270(− 1)[b]	2652.0381(− 15)	2652.4956(17)
7.5	2652.1827(8)	2651.7420(− 4)	2667.6995(5)	2668.1862(− 23)
8.5	2667.9333(7)	2667.4550(9)	$\cdots$	$\cdots$

			3–2 band	
J''	P_{1e}	P_{1f}	P_{2e}	P_{2f}
2.5	$\cdots$	$\cdots$	2399.5608(84)	2399.3112(12)
3.5	2400.8988(5)[b]	2401.1078(15)	2371.0052(4)[b]	2370.6852(6)[b]
4.5	$\cdots$	2371.7354(− 27)[b]	$\cdots$	$\cdots$
5.5	$\cdots$	2341.5801(27)[b]	2310.3176(− 25)[b]	2309.8392(− 2)[b]
6.5	2310.1476(4)[b]	$\cdots$	$\cdots$	$\cdots$

[a] Q lines observed: $Q_{1fe}(2.5)$ 2729.5440(− 9); $Q_{1ef}(2.5)$ 2729.8587(− 27); $Q_{2ef}(1.5)$ 2729.7021(14); $Q_{2fe}(1.5)$ 2730.1768(− 22); $Q_{1fe}(1.5)$ 2731.7481(0); $Q_{1ef}(1.5)$ 2731.7920(− 2).

[b] Blended lines. Weight reduced by a factor of 16 in the fit.

[c] Q lines observed: $Q_{1fe}(2.5)$ 2603.5065(− 122)[b]; $Q_{2ef}(1.5)$ 2603.7072(21)[b]; $Q_{2fe}(1.5)$ 2604.1527(− 76)[b]; $Q_{1fe}(1.5)$ 2605.6851(− 81)[b]; $Q_{1ef}(1.5)$ 2605.7252(− 47)[b]; $Q_{2fe}(0.5)$ 2605.8820(− 3); $Q_{2ef}(0.5)$ 2605.6856(130)[b].

[d] Q lines observed: $Q_{2ef}(1.5)$ 2479.1403(− 58); $Q_{1ef}(2.5)$ 2479.2102(− 12); $Q_{2fe}(1.5)$ 2479.5758(− 20).

TABLE II. Molecular constants (in cm^{-1}) for the $X\,^2\Pi$ state of CH with one standard error in parentheses.

Constants	$v = 0$	$v = 1$	$v = 2$	$v = 3$
T_v	0.0	2732.977 29(74)	5339.903 4(11)	7822.221 9(16)
B_v	14.192 103(91)^b	13.661 706(78)	13.135 800(37)	12.613 20(14)
$10^4 \times D_v$	14.530(20)^b	14.363(17)	14.163(19)	13.902(37)
$10^8 \times H_v$	10.8(29)^b	9.9(10)	10.6(11)	5.1(26)
A_v	28.146 7^a	28.339 6(23)	28.530 3(43)	28.673(25)
$10^3 \times \gamma_v$	$-25.54(50)^b$	$-23.18(39)$	$-21.57(38)$	20.31(37)
$10^4 \times \gamma_{D_v}$	0.38(11)^b	0.0	0.0	0.0
$10^3 \times q_v$	38.682 8^a	37.424(67)	35.951(48)	34.511(68)
$10^6 \times q_{D_v}$	-15.26^a	$-19.8(19)$	$-14.70(52)$	$-13.38(83)$
$10^8 \times q_{H_v}$	0.321^a	3.9(13)	0.0	0.0
$10^3 \times p_v$	33.489^a	32.07(36)	31.11(48( )	30.16(69)
$10^6 \times p_{D_v}$	-9.12^a	$-9.9(51)$	$-10.6(62)$	$-20.5(97)$
$10^8 \times p_{H_v}$	0.109^a	0.0	0.0	0.0

^{a} Fixed to the value of Brazier and Brown, Ref. 23.
^{b} The values of Brazier and Brown (Ref. 23) are $B_0 = 14.192\,3801(24)$; $D_0 = 14.6186(11) \times 10^{-4}$; $H_0 = 11.67 \times 10^{-8}$ (fixed); $\gamma_0 = -0.025\,721\,5(94)$; and $\gamma_{D_0} = 5.27(80) \times 10^{-6}$ cm^{-1}.

TABLE III. Equilibrium vibrational and rotational constants of the $X\,^2\Pi$ state of CH (in cm^{-1}).

Constant	This work	Ab initio^a	Constant	This work	Ab initio^a
B_e	14.458 62(48)	14.39	ω_e	2860.4118(98)	2841.7
α_e	0.534 16(58)	0.532	$\omega_e x_e$	64.1082(46)	64.4
γ_e	0.001 98(15)	$\cdots$	$\omega_e y_e$	0.2406(10)	
r_e	1.119 83(2) Å	1.122 Å			

^{a} Reference 28.

Three vibration–rotation bands were observed: 1–0, 2–1, and 3–2. The observed line positions and rotational assignments are provided in Table I. The assignments were straightforward with the help of the previous work. The vibration–rotation transitions are $^2\Pi$–$^2\Pi$, with each $^2\Pi$ state belonging to Hund's case (b).[34]

For each value of quantum number N ($\widehat{N} = \widehat{J} - \widehat{S}$), there are four nearly degenerate energy levels, e or f,[35] $J = N \pm \frac{1}{2}$.[34] This produces a characteristic quartet pattern for each N and provides a convenient signature[5] for the presence of CH in an infrared spectrum. The P and R branches are strong, and a few low-J Q-branch lines were also found. The lines of Table I are ordered by J rather than N: for the F_1 levels $N = J - \frac{1}{2}$, while for the F_2 levels $N = J + \frac{1}{2}$.[34]

TABLE IV. RKR turning points for the $X\,^2\Pi$ state of CH.

v	E_v (cm^{-1})	$R_{\min}$ (Å)	$R_{\max}$ (Å)
0.0	1 415.9663	1.018 78	1.246 24
0.5	2 798.3015	0.983 09	1.307 75
1.0	4 148.9436	0.957 85	1.359 31
1.5	5 468.0728	0.937 94	1.406 06
2.0	6 755.8697	0.921 38	1.450 00
2.5	8 012.5146	0.907 16	1.492 15
3.0	9 238.1881	0.894 71	1.533 13
3.5	10 433.0705	0.883 64	1.573 34
4.0	11 597.3423	0.873 67	1.613 07

All of the lines of Table I were reduced to the molecular constants of Table II in a simultaneous nonlinear least-squares fit of the four vibrational energy levels ($v = 0$–3). The effective $^2\Pi$ Hamiltonian of Brown et al.[36] was utilized. An explicit listing of the matrix elements of this Hamiltonian with Hund's case (a) basis functions is provided, e.g., in a paper by Amiot, Maillard, and Chauville.[37]

The initial fits were made holding the molecular constants for $v = 0$ fixed at the values determined by Brazier and Brown.[23] These constants were determined from the laser magnetic resonance data in the far infrared[20] and Λ-doubling transitions in the microwave region.[21,23] In the nearly final fits small systematic residuals remained and some of the constants for $v = 0$ were allowed to vary in order to reproduce the infrared data. For the final fit B_0, D_0, H_0, γ_0, and γ_{D_0} were allowed to vary, while the Λ-doubling constants and A_0 were fixed to the values determined by Brazier and Brown.[23]

TABLE V. Rotational constants calculated from the potential curve of Table IV (in cm^{-1}).

Constant	$v = 0$	1	2	3	4
B_v	14.1926	13.6608	13.1349	12.6107	12.0869
$10^4 \times D_v$	14.66	14.41	14.19	13.90	13.55
$10^8 \times H_v$	11.5	11.2	10.3	8.6	5.4
$10^{12} \times L_v$	-13.6	-13.0	-4.1	11.9	45.2

TABLE VI. Term values (in cm^{-1}) for $X\,^2\Pi$ state of CH computed with the constants of Table II.

J	$v = 0$		$v = 1$		$v = 2$		$v = 3$	
	F_{1e}	F_{2e}	F_{1e}	F_{2e}	F_{1e}	F_{2e}	F_{1e}	F_{2e}
0.5	$\cdots$	14.2751	$\cdots$	2746.0949	$\cdots$	5351.8743	$\cdots$	7 833.0769
1.5	32.1802	81.2132	2763.9487	2811.1587	5369.6582	5415.0973	7850.7501	7 894.4651
2.5	87.5884	167.4675	2817.2878	2894.1831	5420.9518	5494.9127	7900.0180	7 971.0859
3.5	172.0444	281.1177	2898.5850	3003.5758	5499.1197	5600.0811	7975.0794	8 072.0554
4.5	284.9712	422.4976	3007.2829	3139.6543	5603.6269	5730.9009	8075.4248	8 197.6507
5.5	426.0916	591.5719	3143.1118	3302.3803	5734.2117	5887.3305	8200.8011	8 347.8258
6.5	595.1753	788.1897	3305.8464	3491.6043	5890.6538	6069.2211	8350.9929	8 522.4314
7.5	791.9862	1012.1376	3495.2556	3707.1157	6072.7262	6276.3651	8525.7771	8 721.2607
8.5	1016.2659	1263.1567	3711.0872	3948.6598	6280.1807	6508.5123	8724.9081	8 944.0641
9.5	1267.7281	1540.9487	3953.0623	4215.9440	6512.7423	6765.3756	8948.1133	9 190.5549
10.5	1546.0559	1845.1794	4220.8738	4508.6407	6770.1080	7046.6349	9195.0906	9 460.4120
11.5	1850.9007	2175.4804	4514.1853	4826.3897	7051.9454	7351.9387	9465.5077	9 753.2815
12.5	2181.8820	2531.4502	4832.6314	5168.7991	7357.8936	7680.9057	9759.0018	10 068.7777
J	F_{1f}	F_{2f}	F_{1f}	F_{2f}	F_{1f}	F_{2f}	F_{1f}	F_{2f}
0.5	$\cdots$	14.3859	$\cdots$	2746.2017	$\cdots$	5351.9772	$\cdots$	7 833.1760
1.5	32.1565	81.4580	2763.9283	2811.3922	5369.6419	5415.3190	7850.7378	7 894.6751
2.5	87.4264	167.9602	2817.1333	2894.6560	5420.8065	5495.3651	7899.8817	7 971.5177
3.5	171.6684	281.9327	2898.2237	3004.3594	5498.7753	5600.8330	7974.7519	8 072.7749
4.5	284.3060	423.7084	3006.6427	3140.8187	5603.0138	5732.0203	8074.8390	8 198.7231
5.5	425.0635	593.2501	3142.1220	3303.9942	5733.2615	5888.8837	8199.8910	8 349.3149
6.5	593.7123	790.4049	3304.4382	3493.7342	5889.2999	6071.2722	8349.6942	8 524.3989
7.5	790.0183	1014.9570	3493.3620	3709.8266	6070.9039	6278.9759	8524.0270	8 723.7662
8.5	1013.7257	1266.6446	3708.6427	3952.0154	6277.8277	6511.7416	8722.6463	8 947.1644
9.5	1264.5507	1545.1664	3950.0030	4220.0069	6509.7994	6769.2791	8945.2818	9 194.3039
10.5	1542.1795	1850.1850	4217.1363	4513.4735	6766.5188	7051.2647	9191.6344	9 464.8604
11.5	1846.2668	2181.3282	4509.7063	4832.0560	7047.6572	7357.3430	9461.3748	9 758.4765
12.5	2176.4357	2538.1909	4827.3468	5175.3648	7352.8575	7687.1284	9754.1436	10 074.7623

The changes in the constants for $v = 0$ are quite small, but are larger than the uncertainty estimates in Table II and the uncertainties quoted by Brazier and Brown.[23]

The rotational and vibrational constants of Table II were fitted to the customary expressions[34]

$$B_v = B_e - \alpha_e (v + \tfrac{1}{2}) + \gamma_e (v + \tfrac{1}{2})^2,$$

$$G(v) = \omega_e (v + \tfrac{1}{2}) - \omega_e x_e (v + \tfrac{1}{2})^2 + \omega_e y_e (v + \tfrac{1}{2})^3$$

in order to extract equilibrium constants (Table III). The *ab initio* values of Meyer and Rosmus[28] are included in Table III for comparison purposes. The B_e value (Table III) provides an equilibrium bond distance $r_e = 1.119\,83(2)$ Å. The three vibrational constants are an exact fit to the three vibrational intervals (Table II), so the uncertainties of Table III are derived from a simple error analysis and are not statistical errors. The rules for the propagation of errors were used to project the initial uncertainties in the band origins into the final vibrational constants.

The equilibrium constants of Table III were used to predict the RKR[38] potential curve for the $X\,^2\Pi$ state of CH. Some of the RKR points are listed in Table IV. The dissociation energy (D_0^0) of CH is 3.46 eV[39] (27 950 cm^{-1}), so the RKR curve of Table IV covers about one-third of the complete potential.

The RKR points were input to Hutson's centrifugal distortion program,[40] and calculated values of B, D, H, and L for $v = 0$–4 are provided in Table V. The calculated potential predicts the experimental constants (Table II) with reasonable, but not spectroscopic, accuracy. The "inverted pertur-

bation approach"[41] was not attempted in order to improve the potential curve. Note that the values in Tables IV and V for $v > 3$ are extrapolations.

Finally, in Table VI the term values for $v = 0$–3 are provided. The term values were computed with the constants of Table II. The term values are useful for calculating lines not reported in Table I, calculating the spectra of the overtone transitions and for extrapolating the observed measurements to slightly higher J.

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