Rotational Spectra of the $X^2\Sigma^+$ states of CaH and CaD [1]

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ABSTRACT

The rotational spectra of the $^2\Sigma^+$ ground states of calcium monohydride and monodeuteride have been recorded in absorption between 250 GHz and 700 GHz. The gas phase free radicals have been produced in a ceramic furnace by the reaction of elemental calcium with molecular hydrogen or deuterium in the presence of an electrical discharge. The molecular constants including the rotational constant, centrifugal distortion constants, spin-rotation constants, and magnetic hyperfine interaction constants have been extracted from the spectra.

Subject headings: microwave, infrared: spectra - interstellar: molecules - laboratory spectra

Calcium hydride is an important astrophysical molecule which has been detected through its electronic transitions in the Sun (Olmstedt 1908; Eagle 1909) and other stars (Öhman 1935). The presence of this free radical is also postulated in the interstellar medium (Oppenheimer and Dalgarno 1974), where atoms such as Na, Mg, Ca, and Fe are believed to play a significant role in maintaining the charge balance in the molecular clouds (Oppenheimer and Dalgarno 1974). The formation of metal hydrides as well as metal oxides could significantly influence the overall concentration of available neutral metal in the molecular clouds, Therefore, the detection of metal hydrides will help in better understanding of the important chemical processes taking place in the interstellar medium. Unfortunate] y, radioastronomical searches for CaH have been hindered by the lack of accurately determined frequencies for its rotational transitions.

CaH was extensively studied in the laboratory (Eagle 1909; Mulliken 1925; Hulthen 1927; Grundstrom 1931, 1932; Watson *et a/. 1935;* Steimle *et al. 1987,* Petitperez *et al.* 1989) following its detection in the Sun (Eagle 1909), and accurate molecular constants were obtained. Knight and Weltner obtained the hyperfine coupling constants of CaH trapped in a low-temperature matrix. Additionally, calcium rnonohydride has been the subject of numerous theoretical investigations (1 lonjou *et al. 1980;* Jeung *et al. 1983;* Petterson *et al. 1983;* Rao *et al.* 1983; Shida *et al. 1987;* Martin 1988) primarily due to unusual features of the $B^2\Sigma^+$ electronic state. This study describes the ground state rotational transitions of both CaH and CaD. The measured low-N rotational transitions of CaH have large hyperfine splittings which allow the determination of the Fermi contact, A_{iso}, and spin dipolar, A_{dip}, hyperfine parameters.

The rotational spectra of CaH and CaD were recorded in absorption using a millimeter spectrometer similar to that described by Birk *et a/.* Klystrons which were phase-locked to a frequency synthesizer were used to drive a Schottky diode multiplier. The second through the fifth harmonics of a 124-134 GHz klystron were used to cover the frequency range 250-650

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GHz. The detector cutoff limited the lowest end of the frequency range to 250 GHz. The emerging radiation from the multiplier was focused in the middle of the absorption cell by a spherical teflon lens, The emerging radiation was collected by an identical lens placed at the opposite extremity of the cell and focused on a 4K InSb detector. The molecular signal was detected using tone burst modulation (Pickett 1991).

The free radicals were produced in a ceramic furnace by the reaction of calcium metal vapor with molecular hydrogen or deuterium in the presence of an electrical discharge, Elemental calcium (Johnson Matthey, 99 % purity) was placed in the middle of the 90 cm long, 5.0 cm diameter ceramic furnace. A quartz liner was used to separate the metal from the alumina wall of the furnace. The cell was pressurized to 100 mtorr with a mixture of 10-20 % H_2 in argon and the central region of the furnace was heated to 7500C. For the deutereted species D_2 was substituted for H_2. A small gas mixture flow was maintained to avoid the build up of impurities. A DC discharge was passed through the mixture between two water-cooled electrodes placed at the extremities of the ceramic tube. The experimental conditions were systematically adjusted to maximize the absorption signal. The best results were obtained at a temperature of $750^\circ C$, 100 mtorr total pressure and a discharge current of 190 mA at 2000 V. With these conditions the electrical discharge remained stable for many hours allowing sufficient spectral integration to obtain a better than 65:1 signal-to-noise ratio for the strongest lines. The well resolved molecular transitions of CaH are 2-2.5 MHz wide with Doppler and pressure broadening equally contributing to the line widths. For the purpose of the fit an uncertainty of 150 kHz was assigned to each rotational line.

The hyperfine components of the N=2-1, N=1 -O transitions of CaH, and the blended features for the N=3-2, N=3-4, N=5-6 transitions of CaD were measured, CaH data consist of three kinds of transitions. The ΔF = AJ = 1 transitions are the strongest and appear well resolved in both N=1-0 and N=2-1 transitions. 'The ΔF = AJ = O and ΔF = O, AJ = 1 transitions are also resolved but their intensity diminishes and the weakest three transitions

could not be reliably measured, The observed CaD transitions appear as partially resolved or unresolved triplets with $\Delta N = \Delta J = 1$, Therefore, the reported CaD frequencies are given as the center of the blended multiplet. The measured rotational transitions for CaH listed together with their assignment are shown in Table I. CaD lines are listed in Table 11 together with the calculated frequencies of the hyperfine components of each measured lines and the weighted average of the unresolved hyperfine multiplet.

The data were analyzed using the Hamiltonian for a Hund's case $(b)\,^2\Sigma^+$ molecule with nuclear spin, I. The case $b_{\beta J}$ for the nuclear spin coupling, was assumed.

$$
\begin{aligned}
\mathbf{H} &= \mathbf{H}_{rfs} + \mathbf{H}_{hfs} \\
\mathbf{H}_{rfs} &= B\mathbf{N}^2 - D\mathbf{N}^4 + H\mathbf{N}^6 + (\gamma + \gamma_D\mathbf{N}^2)\mathbf{N}\cdot\mathbf{S} \\
\mathbf{H}_{hfs} &= A_{iso}\mathbf{I}\cdot\mathbf{S} + A_{dip}[3I_zS_z - \mathbf{I}\cdot\mathbf{S}] + C_I\mathbf{I}\cdot\mathbf{S}
\end{aligned}
$$

where B, D, H, γ, ancl γ_D are the rotational, quartic and sextic centrifugal distortion, and spin-rotation interaction constants. The hyperfine interaction is expressed as the sum of the isotropic and dipolar spin-spin, and nuclear spin-rotation interaction contributions. The value of C_J is not determined from the data and the nuclear spin- rotation term was excluded from the fits. The data do however allow an upper limit of ≤ 100 kHz to be placed on the magnitude of the nuclear spin - rotation interaction constant.

The molecular constants were extracted by least-squares analysis using a spectrum fitting program written by Pickett (Pickett 1991). The CaH data were fitted both individually and together with the high-resolution infrared data obtained in emission using a FT spectrometer (Frum and Pickett 1992). The standard deviation of both fits compares well with the experiment al error. Excellent agreement was found between the molecular constants derived from these individual fits. The molecular constants of CaH arc given in Table 111, A similar data analysis was carried out for CaD using the infrared data of Petitperez *et al.* The

hyperfine constants were held fixed to the calculated values derived from the CaH parameters using isotope relationships, $[A_{iso}, A_{dip}]_D = I_H/I_D \mu_D/\mu_H [A_{iso}, A_{dip}]_H$. These constants together with the rotational, centrifugal distortion, and spin-rotation interaction constants of CaD are also shown in Table III,

The gas phase value of the Fermi contact constant, A''_{iso} is *22* MHz larger than the argon matrix value of 135(1) MHz while the dipolar interaction constant, A_{dip} *is* not significantly different from its matrix value. A similar trend is observed for MgH (Zink *et al. 1990)* where the gas phase values of A_{iso} and A_{dip} are larger by about 10 MHz and 150 kHz than the argon matrix values, respectively,. The effect of the matrix on the hyperfine coupling constants is expected to lower their values and to be more pronounced as the ionicity of the molecular bond increases.

We also calculated the line intensity , $I_{fi}(T)$, for the low—N rotational transitions of $^2\Sigma^+$ ground states of CaH and CaD according to

$$I_{fi}(T) = (8\pi/3hc)\nu_{fi}S_{fi}\mu_z^2[e^{-E''/kT} - e^{-E'/kT}]/Q_{rs}$$

where $\nu_{fi}, S_{fi}, \mu_z, E'', E'$, and Q_{rs} are the transition frequency, line strength, the component of the dipole moment along the internuclear axis, lower and upper state energies and the rotation-spin partition function, respectively. The rotational line strengths, the energies, and the line intensity (reported as $log(I_T)$), calculated for $\mu_z = 1$ D and T = 300K are given in Tables IV and V. The calculated line frequencies shown in this table have one standard deviation included in the parentheses.

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Table I. Measured transitions of CaH (MHz).

N'	J'	F'	N''	J''	F''	Exp.Freq.	o.-c.
1	1.5	2	0	0.5	1	254176.466	0.047
1	1.5	1	0	0.5	0	254232.162	0.081
1	0,5	1	0	0.5	1	252162.958	-0.031
2	1.5	1	1	0.5	1	506316.463	0.114
2	2.5	3	1	1.5	2	507566.372	-0.127
2	2.5	2	1	1.5	1	507575.889	-0.142
2	1.5	2	1	0.5	1	506252.618	-0.127
2	1$5	1	1	0.5	0	506263.000	0.085
2	1.5	2	1	1,5	2	507474.670	0.145

Table II. Measured transitions of **CaD** (MHz).

N'	J'	F'	N''	J''	F''	Exp.Freq.	Avg.talc.	o.- c.	Calc.Freq
3	2.5	3.5	2	1.5	2.5				391084.131
3	2.5	2.5	2	1.5	1.5	391084.351	391084.390	-0.039	391084.143
3	2.5	1.5	2	1.5	0.5				391085.504
3	3.5	4.5	2	2.5	3.5				391757.075
3	3.5	3.5	2	2.5	2.5	391757.872	391757.828	0.044	391758.403
3	3.5	2.5	2	2.5	1.5				391757,812
4	3.5	4.5	3	2.5	3.5				521395.238
4	3,5	3.5	3	2.5	2.5	521395.494	521395.418	0.076	521395.244
4	3.5	2.5	3	2.5	1.5				521395.996
4	4,5	5.5	3	3.5	4.5				522066.638
4	4.5	4.5	3	3.5	3.5	522067.050	522067.076	-0.026	522067.376
4	4.5	3.5	3	3.5	2.5				522067.397
5	4.5	5.5	4	3.5	4,5				651565.926
5	4.5	4.5	4	3.5	3.5	651566.021	651566.051	-0.030	651565.930
5	4.5	3.5	4	3.5	2.5				651566.407
5	5.5	6.5	4	4.5	5.5				652235.827
5	5.5	5.5	4	4.5	4.5	652236,101	652236.113	-0.012	652236,297
5	5.5	4.5	4	4.5	3.5				652236.309

Table III. Molecular constants of **CaH** and **CaD** (in MHz).

Constant	CaH	CaD
B_0	126772.916(19)[a]	65263.188(19)
D_0	5.5457(15)	-1.46262(44)
$H_0 \, x \, 104$	1,889(36)	0.2210(95)
γ_0	1306.10(12)	672.86(32)
γ_D	-0.145(12)	-0.0456(59)
A_{iso}	157.19(23)	24.1480[b]
A_{dip}	1.39(16)	0.23[b]

a. One standard deviation is included **in parentheses**

b. Fixed to the values calculated from the Call **constants**
using isotope relationships.

Table IV. Line intensities of the low$-N$ rotational transitions of $X^2\Sigma^+$ state of CaH.

Freq(1σ unc.)/MHz	Line Str.	$\log(I_{300})$	E/cm^{-1}	N'	J'	F'	N''	J''	F''
252163.006(116)	0.6295	−2,8839	0.0052	1	0.5	1	0	0.5	1
252216.449(199)	0.3333	−3.1598	0.0052	1	0.5	0	0	0.5	1
252320,193(238)	0,3705	−3.1134	0.0000	1	0.5	1	0	0.5	0
254074.899(153)	0.3705	−3.1075	0.0052	1	1.5	1	0	0.5	1
254176.418(64)	1.6667	−2.4541	0.0052	1	1.5	2	0	0.5	1
254232,087(1 10)	0.6295	−2,8768	0.0000	1	1.5	1	0	0.5	0
504239,323(196)	0.2882	−2.6475	8.4837	2	1.5	2	1	1.5	2
504302.936(203)	0.0333	−3.5843	8.4837	2	1.5	1	1	1.5	2
504340.843(218)	0.0269	−3.6765	8.4803	2	1.5	2	1	1.5	1
504404.455(254)	0.1853	−2.8392	8.4803	2	1.5	1	1	1.5	1
506252.736(79)	1.6848	−1.8772	8.4165	2	1.5	2	1	0.5	1
506262.905(1 17)	0.6667	−2,2798	8.4183	2	1.5	1	1	0,5	0
506316.349(137)	0.3147	−2.6057	8.4165	2	1.5	1	1	0.5	1
507474,520(126)	0.2118	−2.7759	8.4837	2	2.5	2	1	1,5	2
507566.506(78)	2.8000	−1.6545	8.4837	2	2.5	3	1	1,5	2
507576.039(80)	1.7878	−1.8493	8.4803	2	2.5	2	1	1.5	1
509487,933(214)	0.0005	−5,4443	8.4165	2	2.5	2	1	0,5	1
756056.793(313)	0.1848	−2.5326	25.4143	3	2.5	3	2	2.5	3
756124,549(299)	0.0095	−3.8204	25.4143	3	2.5	2	2	2.5	3
756148.779(303)	0.0075	−3.9243	25.4112	3	2.5	3	2	2.5	2
756216.535(317)	0.1412	−2.6493	25.4112	3	2.5	2	2	2.5	2
759383.976(174)	2.8077	−1.3470	25.3033	3	2.5	3	2	1.5	2
759388.119(174)	1.8000	−1.5401	25.3054	3	2.5	2	2	1.5	1
759451.732(185)	0.1922	−2.5116	25.3033	3	2.5	2	2	1.5	2
760602. 170(1 74)	0.1485	−2.6224	25.4143	3	3.5	3	2	2,5	3
760690.1 18(1 73)	3.8571	−1.2079	25.4143	3	3.5	4	2	2.5	3
760694.155(174)	2.8513	−1.3391	25.4112	3	3.5	3	2	2.5	2
763929.352(300)	0.0001	−5.6601	25.3033	3	3.5	3	2	1.5	2

Table V. Line intensities of the low−N rotational transitions of $X^2\Sigma^+$ state of CaD.

Freq(1σ unc.)/MHz	Line Str.	log(I_{300})	E/cm^{-1}	N'	J '	F'	N "	J "	F''
129831.487(314)	0.7169	−3.8617	0.0012	1	0,5	1.5	0	0.5	1.5
129843.296(315)	0.5876	−3.9480	0.0012	1	0.5	0.5	0	0.5	1.5
129867.709(314)	0,6165	−3.9270	0.0000	1	0.5	1.5	0	0.5	0.5
129879,518(315)	0.0790	−4,8191	0.0000	1	0.5	0.5	0	0,5	0.5
130824.924 (1 56)	0.0790	−4.8128	0,0012	1	1.5	0.5	0	0.5	1.5
130837.144(156)	0.6165	−3.9206	0.0012	1	1.5	1.5	0	0.5	1.5
130856.866(156)	2.0000	−3.4093	0.0012	1	1.5	2.5	0	0,5	1.5
130861.146(156)	0.5876	−3.9412	0.0000	1	1.5	0.5	0	0.5	0.5
130873.366(1 56)	0.7169	−3.8548	0,0000	1	1.5	1.5	0	0.5	0.5
25964 1.362(596)	0.3283	−3.6125	4.3661	2	1.5	2.5	1	1.5	2.5
259653.275(596)	0.0634	−4.3264	4.3661	2	1.5	1.5	1	1.5	2.5
259661.084 (596)	0.0590	−4.3582	4.3655	2	1.5	2.5	1	1.5	1.5
259672.997(596)	0.1498	−3.9532	4.3655	2	1.5	1.5	1	1.5	1.5
259680.232(596)	0.0616	−4.3387	4.3655	2	1.5	0.5	1	1.5	1.5
259685.218(596)	0.0590	−4.3575	4.3651	2	1.5	1.5	1	1.5	0,5
259692.453(596)	0.0790	-4.2308	4.3651	2	1.5	0.5	1	1.5	0.5
260666,741(142)	2.0128	−2.8215	4.3319	2	1.5	2.5	1	0.5	1.5
260666,845(142)	0.7457	−3.2528	4.3323	2	1.5	1.5	1	0.5	0.5
260674.080(142)	0.5876	−3.3562	4.3323	2	1.5	0.5	1	0.5	0.5
260678.654(142)	0.5821	−3.3603	4.3319	2	1.5	1.5	1	0.5	1.5
260685.889(142)	0.0717	−4.2698	4.3319	2	1.5	0.5	1	0.5	1.5
261313.445(142)	0.0166	−4.9040	4.3661	2	2.5	1,5	1	1.5	2.5
261325.522(142)	0.3917	−3.5302	4.3661	2	2.5	2.5	1	1.5	2.5
261333.167(142)	0.3881	−3.5342	4.3655	2	2.5	1.5	1	1.5	1.5
261342.138(142)	3.2000	−2.6180	4.3661	2	2.5	3.5	1	1.5	2.5
261345.244(142)	2.0082	−2.8203	4.3655	2	2,5	2.5	1	1.5	1.5
261345,387(142)	1.1953	−3.0457	4.3651	2	2.5	1.5	1	1.5	0.5
262327.014(596)	0.0000	−7.6891	4.3323	2	2.5	1.5	1	0.5	0.5
262350.900(596)	0.0001	−7.0990	4.3319	2	2.5	2.5	1	0.5	1.5

Table V. — continued.

Freq(1σ unc.)/MHz	Line Str.	$\log(I_{300})$	E/cm^{-1}	N'	J'	F'	N"	J"	F"
389383.354 (81 2)	0.2062	−3,4851	13.0836	3	2.5	3.5	2	2.5	3.5
389395.280(812)	0.0185	−4,5317	13.0836	3	2.5	2.5	2	2.5	3.5
389399.970(812)	0.0171	−4.5658	13.0830	3	2.5	3.5	2	2.5	2.5
389411.896(812)	0.1368	−3,6632	13.0830	3	2.5	2.5	2	2.5	2.5
389420,493(812)	0.0187	−4,5285	13.0830	3	2.5	1.5	2	2.5	2.5
389423,973(812)	0.0176	−4,5529	13.0826	3	2.5	2.5	2	2.5	1.5
389432.570(812)	0.0994	−3.8019	13.0826	3	2.5	1.5	2	2.5	1.5
391084.131(116)	3.2052	−2.2897	13,0268	3	2.5	3,5	2	1.5	2.5
391084.143(116)	2.0194	−2.4903	13,0272	3	2.5	2.5	2	1.5	1.5
391085.504(116)	1.2000	−2,7163	13,0275	3	2.5	1.5	2	1.5	0.5
391092.739(116)	0.3806	−3.2150	13.0272	3	2.5	1.5	2	1.5	1.5
391096.056(116)	0.3791	−3.2167	13.0268	3	2.5	2.5	2	1.5	2.5
391104,653(116)	0.0156	−4.6015	13.0268	3	2.5	1.5	2	1.5	2.5
391729.754(116)	0.0060	−5.0183	13.0836	3	3.5	2.5	2	2.5	3.5
391741.787(116)	0.2836	−3.3415	13.0836	3	3,5	3.5	2	2.5	3.5
391746.371(116)	0.2825	−3.3432	13.0830	3	3.5	2.5	2	2.5	2.5
391757.075(116)	4.2857	−2.1622	13.0836	3	3.5	4.5	2	2.5	3.5
391758.403(116)	3.1450	−2.2966	13.0830	3	3.5	3.5	2	2.5	2.5
391758.448(116)	2.2830	−2.4357	13.0826	3	3.5	2.5	2	2.5	1.5
393442,563(812)	0.0000	−7,3162	13.0268	3	3.5	3.5	2	1.5	2.5