The Rotational Spectrum of Propane Centrifugal Distortion Analysis

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The ground state rotational spectrum of propane has been investigated between 6.4 and 26.5 GHz with a microwave Fourier transform spectrometer and between 140 and 300 GHz with a millimeter-wave spectrometer. High J transitions have been measured and fitted to a centrifugally distorted Hamiltonian including some sextic coefficients. The results of the analysis are sufficiently accurate for the prediction of all strong transitions of astrophysical interest.

The ground state rotational spectrum of propane ($CH_3CH_2CH_3$) was first measured by Lide [1] who determined the dipole moment, the rotational constants for several isotopic species and a complete r_s structure. The dipole moment was then remeasured with a greater accuracy using a parallel plate cell [2]. The first two torsional excited states were measured by Scharpen [3] and later analyzed by Hirota et al. [4] and by Trinkaus et al. [5]; the barrier to internal rotation is about 13.2 kJ/mole (3.2 kcal/mole).

Propane has already been identified in the Voyager IR spectrum of Titan [6] and tentatively in that of Saturn [7]; it presence in interstellar space is also probable. But only seven transitions with $J \leqq 6$ have been measured for the ground state of the most abundant isotopic species, which is insufficient to determine the centrifugal distortion constants and to predict a rotational spectrum.

For these reasons we have measured the rotational spectrum of propane and carried out a complete centrifugal distortion analysis so that accurate measurements and predictions would be available for the radio astronomers.

Detecting high J transitions with a Stark spectrometer would be difficult due to the very small value of the dipole moment (0.085 D, [2]).

The measurements were made with a microwave Fourier transform (MWFT) spectrometer [8, 9a–c] in the region 6.4 to 26.5 GHz and a video or source modulation spectrometer [10] in the region 140 to 300 GHz. The measurements with the MWFT spectrometer were made at temperatures of approximately −40 °C and pressures below 2 mT, with the millimeterwave spectrometer all spectra were measured at −60 °C and pressures of about 20 mTorr. The accuracy is about 10 to 20 kHz for the MWFT spectrometer and between 30 and 150 kHz for the millimeterwave spectrometer.

The measured lines are given in Table 1. Almost all the centimeterwave lines measured by MWFT were found split by internal rotation. On the other hand no splitting could be satisfactorily resolved in the millimeter region due to Doppler broadening. The internal rotation analysis will be reported elsewhere [11]. For the split lines the unperturbed frequency $\nu_0 = (\nu_{AA} + 2\nu_{AE})/3$ has been used. To derive the molecular parameters the spectrum was fitted to the Hamiltonian of Watson (Eq. (68) of [12]) using the I^r representation in the A-reduction (Program ZFAP6, Author V. Typke). The rotational constants, the quartic and four sextic centrifugal distortion constants were determined. They are given in Table 2 together with their standard deviation. A list of predicted lines may be obtained upon request to one of the authors (J.D.).

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Table 1. Measured ground state transitions of propane (in MHz).

J'	K'_a	K'_c	J''	K''_a	K''_c	f_{obs}	$f_{calc-obs}$	J'	K'_a	K'_c	J''	K''_a	K''_c	f_{obs}	$f_{calc-obs}$
1	1	0	1	0	1	21748.336	0.026	16	5	11	15	6	10	22862.335	− 0.014
2	0	2	1	1	1	11013.957	− 0.022	16	5	12	15	6	9	22786.504	0.008
2	1	1	2	0	2	22769.712	0.021	17	2	15	16	3	14	211766.984	0.065
3	1	2	3	0	3	24365.424	0.025	17	2	16	16	1	15	280971.706	0.047
5	1	4	4	2	3	22933.883	− 0.047	17	3	14	16	4	13	142672.637	0.045
5	3	2	6	2	5	11319.926	0.089	17	2	16	17	1	17	140620.619	0.034
5	3	3	6	2	4	8954.356	0.056	18	2	17	17	1	16	293185.436	0.048
6	5	2	5	4	1	286689.990	− 0.048	18	6	13	17	7	10	12061.849	0.041
7	2	5	6	3	4	8308.367	− 0.075	18	6	12	17	7	11	12070.750	0.032
7	3	4	6	2	5	218618.306	− 0.035	18	1	17	18	0	18	140017.440	− 0.094
7	3	5	6	2	4	216117.906	− 0.032	18	8	10	19	7	13	14825.050	− 0.008
7	4	4	8	3	5	20658.616	0.084	18	8	11	19	7	12	14824.591	− 0.015
7	4	3	8	3	6	21001.378	0.058	19	0	19	18	1	18	287574.584	0.065
8	2	6	7	1	7	211481.852	0.047	19	1	18	18	2	17	289146.451	0.072
8	2	6	7	3	5	26133.102	− 0.046	19	1	19	18	0	18	288365.749	0.048
8	2	7	7	3	4	19250.841	− 0.063	19	3	17	18	4	14	145856.220	− 0.011
8	4	4	8	3	5	148136.610	− 0.146	19	3	17	19	2	18	143622.180	− 0.014
9	1	9	8	0	8	146601.280	− 0.019	21	4	18	20	5	15	147044.370	0.089
9	4	5	8	3	6	291944.025	0.013	21	9	13	22	8	14	9282.039	0.023
9	4	6	8	3	5	291586.293	0.000	26	9	18	25	10	15	12435.726	0.026
9	4	5	9	3	6	147728.480	− 0.075	26	9	17	25	10	16	12435.726	0.067
10	0	10	9	1	9	147538.060	− 0.056	26	1	25	26	0	26	219527.413	− 0.034
10	3	7	9	4	6	12381.975	− 0.053	26	2	25	26	1	26	220436.493	− 0.006
10	4	6	10	3	7	147116.440	− 0.086	26	6	20	26	5	21	220215.357	− 0.046
10	5	5	11	4	8	15332.518	0.053	26	11	15	27	10	18	14384.156	0.020
11	2	10	10	1	9	212660.630	− 0.055	27	4	23	26	5	22	293477.608	− 0.064
11	3	8	10	2	9	288181.882	0.057	27	5	22	26	6	21	216107.921	− 0.086
11	4	7	11	3	8	146232.500	− 0.073	27	3	24	27	2	25	141387.150	− 0.004
12	3	10	11	2	9	283543.557	− 0.029	27	6	21	27	5	22	217127.058	− 0.019
12	4	8	12	3	9	145001.150	− 0.055	28	3	26	28	2	27	212717.237	0.037
12	6	7	13	5	8	25916.482	0.046	28	5	23	28	4	24	144760.500	− 0.019
12	6	6	13	5	9	25926.020	0.041	28	6	22	28	5	23	213455.847	− 0.047
13	3	11	12	2	10	295099.457	0.018	29	3	27	29	2	28	221631.655	− 0.038
13	4	10	12	5	7	17119.532	− 0.032	29	5	24	29	4	25	140209.001	0.037
13	4	9	12	5	8	17441.045	− 0.040	29	12	18	30	11	19	8877.344	0.050
13	4	9	13	3	10	143346.340	0.007	31	4	28	31	3	29	214833.358	0.041
13	6	7	14	5	10	9745.337	0.009	32	4	28	32	3	29	142955.170	0.050
13	6	8	14	5	9	9725.283	0.008	32	5	28	32	4	29	211188.559	0.102
14	0	14	13	1	13	211446.958	0.038	33	3	30	33	2	31	214776.052	0.100
14	1	14	13	0	13	215513.772	0.045	33	5	29	33	4	30	216255.769	0.058
14	2	12	13	3	11	146021.260	0.051	34	5	30	34	4	31	221857.648	− 0.028
14	4	10	14	3	11	141203.180	− 0.082	36	5	31	36	4	32	141025.107	0.018
15	1	14	14	2	13	217297.294	0.037	37	5	32	37	4	33	147362.080	− 0.130
15	7	8	16	6	11	20374.586	− 0.008	39	8	31	39	7	32	296256.010	0.014
15	7	9	16	6	10	20372.438	− 0.005	41	8	33	41	7	34	288605.341	− 0.032

Table 2. Rotational, centrifugal distortion constants and correlation matrix for propane[a].

A/MHz	29 207.48149	(313)	1.000												
B/MHz	8 445.96770	(71)	0.294	1.000											
C/MHz	7 459.00196	(73)	0.084	0.599	1.00										
Δ_J/kHz	7.19296	(86)	0.176	0.743	0.743	1.000									
Δ_{JK}/kHz	− 26.9670	(83)	0.399	0.418	0.155	0.422	1.000								
Δ_K/kHz	159.845	(94)	0.701	−0.216	−0.297	−0.223	−0.147	1.000							
δ_J/kHz	1.39693	(42)	0.223	0.364	−0.462	−0.032	0.423	0.076	1.000						
δ_K/kHz	3.0585	(75)	0.026	0.081	−0.098	0.083	0.457	−0.101	0.410	1.000					
Φ_{JK}/Hz	0.0296	(101)	0.087	0.275	0.123	0.350	0.575	−0.213	0.275	0.268	1.000				
Φ_{KJ}/Hz	− 1.423	(168)	0.114	−0.082	−0.116	−0.175	−0.039	0.155	0.026	0.061	−0.826	1.000			
Φ_K/Hz	5.52	(92)	0.484	−0.126	−0.176	−0.096	−0.086	0.751	0.070	−0.076	0.341	−0.496	1.000		
φ_J/Hz	0.00368	(28)	0.200	0.305	−0.395	−0.004	0.516	0.039	0.954	0.606	0.328	0.042	0.042	1.000	

[a] The uncertainties shown in parantheses are in units of the last digit and are standard errors. Representation I^r in the A-reduction has been used. The standard deviation of the fit was 57 kHz.

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