Tunable Diode Laser Spectra and Assignment of the 748 cm^{-1} Band of Propane

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Dedicated to Professor Dr. H. Dreizler on the Occasion of his 60th Birthday

The rotational structure of the 748 cm^{-1} *c*-type CH_2 -rocking fundamental of propane was analysed using tunable diode laser (TDL) techniques. On grounds of a low-resolution Fourier transform (FTIR) spectrum and of the known ground-state rotational and centrifugal-distortion constants, some 700 transitions were measured and assigned in several regions of the band. The upper-state constants determined in this way allow the prediction of rovibrational frequencies to within 0.003 cm^{-1} , covering quantum states up to $J = 50$ and $K_a = 20$. The band appears unperturbed.

Key words: Propane, Diode laser spectra, Excited state, Rotational constants, Centrifugal distortion constants.

1. Introduction

Propane, $\text{CH}_3\text{CH}_2\text{CH}_3$, is the first and also simplest (most rigid) asymmetric rotor in the alkane series. The next member, butane, shows already trans-gauche rotational isomerism around the central carbon-carbon bond and in turn much more complicated spectra. All asymmetric alkanes absorb near 740 wave numbers, which is due to the in-phase CH_2 rocking fundamental vibration [1]. The central Q branches of the trans and gauche isomers of butane are separated by only 15 cm^{-1} [2, 3] so that a Doppler-limited high-resolution study of the overlapping frequency region, at different temperatures, could possibly provide a way of determining the trans-gauche enthalpy difference. There is current interest in this molecular quantity, as it is, for example, of key importance for understanding the structure and dynamics of polyethylene and related polymers. It seemed natural to first attempt a Doppler-limited study of the CH_2 -rocking region of propane gas, which exhibits stronger rovibrational absorptions than butane. A big advantage is the knowledge of the ground-state rotational constants of the propane molecule from its microwave spectrum [4]. Quite recently, also accurate centrifugal distortion constants have been determined by Best-

mann et al. [5] in a combined microwave Fourier-transform and mm-wave investigation of 45 rotational transitions. Daunt et al. [6] have already reported preliminary results of a combined high resolution FTIR and diode laser study of the 748 cm^{-1} band of propane. However, detailed results have not yet appeared in the literature.

There is also some astrophysical interest in the rovibrational constants of the propane molecule because its infrared signals were detected by Voyager in the atmosphere of Titan [7] and possibly also of Saturn [8]. In addition, IR investigations of interstellar space will be of future importance, and laboratory or computational model spectra are useful to aid assignments. The upper state rotational and centrifugal distortion constants reported in the present work for the 748 cm^{-1} fundamental band of propane are based on 731 diode-laser transitions observed in various sub-bands. Their predicting power, in combination with the known ground-state constants, should be better than 0.003 cm^{-1} for rovibrational transitions involving quantum states J and K_a up to 50 and 20, respectively.

2. Experimental

The basic spectrometer set-up used in this work has been described previously [9]. It is operated with an air-spaced etalon in front of the mode-filter mono-

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Fig. 1. Optical layout of the spectrometer. DL, diode-laser cold head; E, etalon; MC, mirror chopper; G, monochromator grating; RC, reference cell; MRC, White-type cell; D, detector. Using a mirror chopper instead of beam splitters provides more radiation intensity in both the cell and etalon branches, and avoids some resonator effects. The signal path was chosen to be unaffected by the mirror, which has the advantage of easier adjustment of the White cell. The electronics is described in [9].

Fig. 2. Beginning of the RQ_9 , $\Delta K_a = 2$ progression in the CH_2 -rocking band of propane. The J quantum numbers are given. The TDL spectrum shown was digitally filtered, and the diode-current ramp was transferred to the linear frequency abscissa with the computer program described in the text. The marked (*) line is an ammonia absorption at 761.91828 cm^{-1} [14]. The horizontal curve near the bottom of the spectrum served as an intensity threshold for the peak-finding routine, see text (the numbered peak markers were omitted).

chromator so that frequent adjustment and recalibration of the etalon are unnecessary. Meanwhile, the two beam splitters and the beam chopper have been replaced by a mirror-chopper [10], which has the advantage that the whole diode-laser intensity is successively available in both the signal and etalon path. In addition, any background modulation owing to reso-

nator effects in the beam-splitter surfaces is most easily avoided. The measurements on propane have been performed in a White-type cell, and a conventional one in series for calibration purposes. The etalon fringes were interpolated between and relative to the frequencies of accurately known CO_2 , NH_3 , and HCN signals [11–14]. The present optical layout of

Fig. 3. Part of the $\Delta K_c = 2$ progression of the $^PQ_{10}$ sub-branch near 734.7 cm^{-1} . The J quantum numbers are indicated. The frequency increases from left to right, the fringe spacing is 0.014993 cm^{-1} . The frequency of the CO_2 calibration line, $R(17)$ of the hot-band transition $(10^{\circ}0, 02^{\circ}0)_1 - 01^{\circ}1_0$, is 734.7128 cm^{-1} and was calculated with the parameter set given by Paso *et al.* [11]. Some members of several $^PQ_K(J)$ sub-branches are also indicated. The density of lines is low in comparison with PQ_K sub-branches of smaller K values.

the spectrometer is given in Figure 1. The TDL spectra were recorded with approximately 50 m path length in the multiple-reflexion cell and at pressures below 3 mbar. Intensity modulation was preferred to first- or second-derivative diode-current modulation techniques in the dense regions of the spectrum, for better recognition of absorption patterns.

During the progress of this work, an automatic peak finding system was installed, which proved helpful in determining the line positions in the relatively dense spectra [15]. In order to operate it, the infrared intensities as obtained subsequently in the filled and empty cell together with their accompanying etalon signals are stored, as a function of diode laser current, in a microprocessor system. The data are then transferred to the central university computer for efficient digital treatment. After smoothing the etalon transmission signals with the aid of a digital FFT filter [16], a relative frequency scale is obtained which enables the gas absorption profile to be normalized by dividing it by the empty-cell background signal. The result-

ing pattern is better suited especially for the evaluation of relative transition intensities. Any variation in the laser mode characteristic which might have occurred between two successive scans can be taken care of by comparison of the low-pass filter signals of the two etalon transmission curves, as they closely resemble the modes. In the next step, in order to remove noise which may impede analysing line profiles, the normalized signal is also filtered. Finally, the frequencies of line peaks appearing above a given intensity threshold are determined and listed, if possible in relation to a known molecular calibration signal. Figure 2 shows the graphical result of the procedure carried out on part of the RQ_9 branch near 760 cm^{-1} of the CH_2 -rocking fundamental of propane over a linearized frequency axis. It should be noted that the frequency uncertainties caused by the digital filtering are also determined routinely [16]. The frequencies of approximately one half of the transitions analysed in this work were obtained by computer-controlled data acquisition as described, the others by hand.

Fig. 4. The two sub-branches of PQ_7 , J quantum numbers being indicated. The $\Delta K_c = 0$ and $\Delta K_c = 2$ progressions start to separate at $J = 21$. Frequency increases from left to right, fringe distance as in Fig. 3. The CO_2 calibration line, at 739.2849 cm⁻¹, is R(23) from the same hot-band series as already used in Figure 3. Most of the remaining lines belong to different branches and are also assigned (see Table 1).

A 0.05 cm⁻¹ resolution Nicolet FTIR recording, kindly supplied by Professor H. Bürger, Wuppertal, was also at our disposal and proved indispensable for a successful analysis of the laser spectra.

3. Spectral Assignment

The 748 cm⁻¹ band originates from a B vibrational mode in the point group C_{2v} and obeys therefore c -type selection rules. Propane is a $\kappa = -0.909$ nearly prolate rotor, hence assignments of the gross features in the FTIR-spectrum were possible with the aid of the first three terms in the Wang series energy expression [17],

$$E(J, K_a) = \frac{B+C}{2} J(J+1) + \left(A - \frac{B+C}{2} \right) K_a^2 - \frac{1}{4} (B-C) J(J+1) (\delta_{1J} - \delta_{1J-1}) + \dots \quad (1)$$

as well as with the absorption-intensity rules given by Allen and Cross [18]. Some of the sub-band Q branches ${}^PQ_{K_a}$ and ${}^RQ_{K_a}$ show a typical band-head structure at reasonably high J quantum numbers, and their

K_a values were easily assigned on grounds of their pronounced unresolved intensity and regular spacing. Several strong ${}^PQ_{K_a}(J)$ and ${}^RQ_{K_a}(J)$ transitions could also be localized in the FTIR-spectrum with the aid of (1), and assigned with an accuracy of about 0.02 cm⁻¹.

The TDL spectra appeared almost completely resolved in the investigated regions. The assignment of single rovibrational lines was possible by subtracting upper-state interconnected transitions and comparing the corresponding accurately predicted ground-state level differences. For example, the two transitions ${}^RQ_{K_a-1}(J-1)$ and ${}^PQ_{K_a+1}(J+1)$ have the (unknown) upper (J, K_a) state in common, which cancels on subtracting the two frequencies. Figure 3 shows assignments in the ${}^PQ_{10}$, $\Delta K_c = 2$ progression achieved in this way. Figure 4 shows the resolved $\Delta K_c = 0$ band head of the PQ_7 branch near 739.01 cm⁻¹, embedded in the corresponding $\Delta K_c = 2$ progression.

4. Results

Spectra-prediction and least-squares refinement computations have been done in the computer center

Fig. 5. Fortrat (above) and intensity (below) diagrams of the CH_2 -rocking fundamental of propane near 748 cm^{-1} , see text. The lower-state J quantum numbers are given in the ordinate above, the logarithmic scale below is proportional to absorption intensity.

Table 1. Least-squares spectral parameters of the 748 cm^{-1} band of propane as obtained with the 731 transitions listed in Table 2. Errors given in parentheses in units of the last digit are standard deviations. The ground-state rotational and centrifugal distortion constants from [5] were held fixed, and the sextic constants of the upper were constrained to those of the ground state. Φ_J , Φ_{JK} , and φ_K were set to zero and held fixed, in both states. Watson's A reduction and I' representation were used [20].

	Ground state parameters	Upper state ^a parameters	Upper state correlation matrix									
ν_0/cm^{-1}		748.53067(14)	1.000									
A/MHz	29207.48149(313)	29222.14(07)	-0.540	1.000								
B/MHz	8445.96770(71)	8421.10(03)	-0.223	0.080	1.000							
C/MHz	7459.00196(73)	7437.86(04)	-0.139	-0.079	-0.861	1.000						
Δ_J/kHz	7.19296(86)	7.209(39)	0.100	-0.104	-0.306	0.295	1.000					
Δ_{JK}/kHz	-26.9670(83)	-27.08(27)	-0.195	0.161	0.297	-0.241	-0.977	1.000				
Δ_K/kHz	159.845(94)	120.33(58)	-0.110	0.546	-0.212	0.143	0.616	-0.645	1.000			
δ_J/kHz	1.39693(42)	1.422(28)	-0.147	0.113	0.684	-0.630	-0.879	0.859	-0.555	1.000		
δ_K/kHz	3.0585(75)	8.7(27)	0.156	-0.071	-0.233	0.149	0.973	-0.945	0.591	-0.804	1.000	
Φ_{JK}/Hz	0.0296(101)	0.0296										
Φ_{KJ}/Hz	-1.423(168)	-1.423										
Φ_K/Hz	5.52(92)	5.52										
φ_J/Hz	0.00368(28)	0.00368										

^a The standard deviation of the fit was $\sigma = 0.0012\text{ cm}^{-1}$.

Table 2. Assignment of rovibrational transitions $\nu_{\text{obs.}}$ and comparison with calculated values $\nu_{\text{calc.}}$ as obtained with the constants in Table 1. The ground-state and upper-state quantum numbers are given in the second and first columns, respectively. $\Delta = \nu_{\text{obs.}} - \nu_{\text{calc.}}$, frequencies in cm⁻¹.

$J' K'_a K'_c$	$J'' K''_a K''_c$	$\nu_{\text{obs.}}$	Δ	$J' K'_a K'_c$	$J'' K''_a K''_c$	$\nu_{\text{obs.}}$	Δ	$J' K'_a K'_c$	$J'' K''_a K''_c$	$\nu_{\text{obs.}}$	Δ
24 18 7	24 19 5	722.5042	0.0023	8 7 1	9 8 1	733.1371	0.0005	23 4 19	24 3 21	738.6800	-0.0007
24 18 6	24 19 4	722.5436	0.0006	7 7 0	8 8 0	733.6821	-0.0012	22 4 19	22 5 17	741.8180	0.0008
38 17 22	38 18 20	723.1572	0.0022	37 6 32	37 7 30	738.5782	-0.0021	22 4 18	23 3 20	739.3400	0.0020
26 14 13	26 15 11	727.7949	-0.0022	36 6 31	36 7 29	738.5957	-0.0007	21 4 17	21 5 17	742.2938	-0.0007
24 14 10	24 15 8	727.9086	-0.0023	35 6 30	35 7 28	738.7366	-0.0008	21 4 16	21 5 16	741.8781	0.0004
24 14 8	24 15 6	727.9560	-0.0009	35 6 30	36 7 30	739.5561	0.0007	20 4 16	20 5 16	742.2158	-0.0005
20 14 7	20 15 5	728.0088	-0.0015	35 6 29	36 5 31	733.7668	0.0010	20 4 16	21 3 18	740.7458	0.0011
19 14 6	19 15 4	728.0394	-0.0012	34 6 28	35 5 30	734.5831	0.0007	20 4 17	20 5 15	741.9246	-0.0006
18 14 5	18 15 3	728.0684	-0.0008	34 6 29	34 7 27	738.7906	-0.0001	19 4 16	19 5 14	741.9579	0.0009
17 14 4	17 15 2	728.0959	-0.0004	33 6 28	33 7 26	738.8355	-0.0022	19 4 15	19 5 15	742.1583	0.0000
19 13 6	20 14 6	718.7748	0.0019	32 6 27	32 7 25	738.8678	-0.0004	18 4 14	18 5 14	742.1197	-0.0010
18 13 5	19 14 5	719.3375	-0.0006	31 6 25	31 7 25	739.0633	-0.0009	18 4 15	18 5 13	741.9852	0.0006
13 13 0	14 14 0	722.1165	-0.0004	31 6 26	31 7 24	738.8957	-0.0006	18 4 14	19 3 16	742.1999	-0.0006
21 12 9	22 13 9	719.0178	0.0019	30 6 25	30 7 23	738.9192	-0.0008	17 4 13	17 5 13	742.0938	-0.0006
20 12 8	21 13 8	719.5814	0.0010	30 6 24	31 7 24	722.3839	-0.0019	17 4 14	18 5 14	732.4184	-0.0002
15 12 3	16 13 3	722.3743	0.0009	29 6 23	30 5 25	738.9774	-0.0007	17 4 17	17 5 12	742.0069	0.0002
14 12 2	15 13 2	722.9308	0.0008	29 6 24	29 7 22	738.9394	-0.0006	17 4 13	18 5 13	732.4931	-0.0013
13 12 1	14 13 1	723.4814	0.0004	29 6 24	30 7 24	722.9396	-0.0013	16 4 13	16 5 11	742.0249	-0.0002
12 12 0	13 13 0	724.0326	0.0009	29 6 23	29 7 23	723.0053	-0.0018	16 4 12	17 5 12	733.0176	-0.0002
24 11 13	25 12 13	718.6974	0.0019	28 6 23	29 7 23	739.0180	0.0000	15 4 11	16 5 11	733.5497	-0.0002
23 11 13	24 12 12	732.0128	0.0011	28 6 22	28 7 22	723.4933	0.0002	15 4 11	15 5 11	742.0735	-0.0010
23 11 12	24 12 11	719.2652	0.0002	27 6 21	28 7 21	738.9581	-0.0007	15 4 12	16 5 12	733.5209	-0.0004
21 11 11	22 12 11	732.7889	0.0009	27 6 22	28 7 22	740.1361	-0.0006	15 4 11	15 5 10	742.0405	-0.0007
19 11 9	19 12 7	732.1387	0.0012	27 6 21	28 7 21	739.0105	-0.0003	14 4 11	15 5 10	734.0697	-0.0006
18 11 8	18 12 6	732.1676	0.0006	27 6 22	28 7 22	739.0116	-0.0010	14 4 11	14 5 9	742.0547	-0.0014
17 11 6	18 12 6	732.1360	-0.0004	26 6 20	27 7 20	740.1361	-0.0006	13 4 10	14 5 10	734.6146	0.0019
17 11 7	17 12 5	732.1961	-0.0009	26 6 21	27 7 21	739.0105	-0.0003	13 4 10	13 5 8	742.0660	0.0000
16 11 5	17 12 5	732.1935	-0.0011	26 6 20	26 7 20	740.1361	-0.0006	13 4 10	14 5 10	742.0786	0.0000
15 11 5	15 12 3	732.2441	0.0010	26 6 21	26 7 19	738.9763	-0.0011	12 4 8	12 5 8	742.0838	0.0001
14 11 4	15 12 2	732.2889	0.0015	26 6 22	27 7 22	742.2239	-0.0001	11 4 8	11 5 6	742.0907	-0.0007
13 11 3	13 12 1	732.2889	0.0015	25 6 19	25 7 19	739.0335	-0.0014	10 4 6	10 5 6	738.1034	-0.0016
13 11 2	14 12 2	724.8532	0.0015	25 6 20	26 7 20	739.0105	-0.0003	9 4 5	9 5 5	742.1134	-0.0001
12 11 1	12 12 0	732.3101	-0.0007	24 6 18	24 7 18	739.9937	-0.0010	8 4 4	8 5 4	742.1245	-0.0008
12 11 0	13 12 0	732.4050	0.0008	24 6 19	25 7 19	739.0105	-0.0003	7 4 4	7 5 4	742.1348	-0.0012
11 11 0	12 12 0	725.9562	-0.0007	23 6 17	23 7 17	739.0295	-0.0013	6 4 3	6 5 3	742.1439	0.0001
38 10 29	38 11 27	732.8207	0.0000	23 6 18	23 7 16	739.0478	-0.0013	5 4 2	5 5 2	742.1522	-0.0017
36 10 27	36 11 25	732.9043	-0.0004	22 6 16	22 7 16	739.0692	-0.0006	4 4 0	5 5 0	739.5036	-0.0007
35 10 26	35 11 24	732.9456	-0.0003	22 6 17	22 7 15	739.0999	-0.0009	3 4 0	4 5 0	742.5097	-0.0024
34 10 25	34 11 23	732.9864	-0.0003	21 6 15	21 7 14	739.0873	-0.0009	25 3 28	26 4 28	734.3484	0.0000
33 10 24	33 11 22	733.0273	-0.0002	21 6 16	21 7 14	739.0861	-0.0015	25 3 24	26 4 22	738.7065	0.0002
31 10 22	31 11 20	733.1064	0.0006	20 6 14	20 7 13	739.1174	-0.0021	23 3 21	23 4 19	741.8646	0.0010
30 10 21	30 11 19	733.1455	0.0006	19 6 13	19 7 12	739.1260	-0.0021	22 3 20	22 4 22	741.7191	0.0009
28 10 19	28 11 17	733.2231	-0.0007	18 6 12	17 11	739.1557	-0.0023	22 3 20	23 2 22	742.2054	0.0000
27 10 18	27 11 16	733.2597	-0.0003	18 6 13	18 7 11	739.1454	-0.0021	22 3 19	22 4 21	739.0051	-0.0002
26 10 16	27 11 16	718.9494	-0.0013	17 6 12	17 11	739.1657	-0.0023	21 3 19	22 2 21	742.0167	-0.0006
25 10 15	26 11 15	719.5154	0.0001	16 6 11	16 7 10	739.2033	-0.0014	21 3 18	22 2 20	739.3495	0.0022
25 10 16	25 11 14	733.3311	-0.0003	15 6 10	15 7 9	739.2208	-0.0003	20 3 17	21 4 17	732.9100	0.0001
24 10 14	25 11 14	733.3921	-0.0001	14 6 9	14 7 8	732.3503	-0.0019	19 3 17	20 4 17	732.4321	-0.0003
21 10 12	21 11 10	733.4618	0.0001	12 6 6	13 7 6	732.3503	-0.0019	19 3 16	20 4 16	740.1942	0.0005
20 10 10	20 11 10	722.3374	-0.0009	12 6 7	12 7 5	739.2567	-0.0012	18 3 15	19 4 15	733.8096	0.0005
20 10 11	20 11 9	733.4924	-0.0004	11 6 5	12 7 5	732.8988	-0.0017	18 3 16	19 4 16	733.0539	0.0014
19 10 9	20 11 9	722.4986	-0.0015	11 6 6	12 7 6	732.9100	-0.0017	17 3 14	18 4 14	734.2643	0.0014
18 10 8	19 11 8	733.4563	0.0002	10 6 4	11 7 4	733.4458	-0.0017	16 3 14	17 4 14	734.2603	0.0013
17 10 7	18 11 6	733.5752	-0.0001	10 6 5	10 7 3	739.2874	-0.0004	16 3 13	17 4 13	734.7125	0.0008
16 10 6	17 11 6	733.6465	0.0000	9 6 4	9 7 2	739.3104	-0.0002	15 3 12	16 4 12	738.7505	0.0016
15 10 5	16 11 5	733.6875	0.0001	8 6 2	9 7 2	734.5330	0.0007	8 3 5	9 4 5	739.7615	-0.0019
14 10 4	15 11 4	725.6810	-0.0005	8 6 3	9 7 3	734.5330	0.0007	7 3 4	8 4 4	739.2949	0.0018
12 10 3	13 11 3	733.7046	0.0014	7 6 1	8 7 1	735.0756	0.0023	7 3 5	8 4 5	739.2913	0.0005
11 10 2	12 11 2	727.8818	-0.0001	37 5 33	37 6 31	738.5900	-0.0004	6 3 4	7 4 4	741.4487	-0.0003
43 9 35	43 10 33	734.1108	-0.0007	35 5 30	36 6 30	732.6268	0.0000	27 2 25	28 3 25	728.1087	-0.0013
42 9 34	42 10 32	734.1218	-0.0008	35 5 30	35 6 30	742.2977	0.0002	25 2 24	26 3 24	728.1521	0.0027
42 9 33	42 10 31	734.1489	-0.0010	35 5 30	36 6 30	722.2997	-0.0026	22 2 20	23 3 20	732.4273	0.0011
42 9 34	42 10 32	734.1416	-0.0005	35 5 30	36 6 30	722.2997	-0.0026	20 2 19	20 3 17	741.7095	-0.0021
41 9 33	41 10 31	734.1567	-0.0006	34 5 29	35 6 29	722.2409	-0.0023	20 2 18	21 3 18	733.9026	-0.0011
40 9 31	40 10 29	734.2088	-0.0002	33 5 28	34 6 28	723.1371	-0.0023	19 2 17	20 3 17	734.5762	0.0006
40 9 32	40 10 30	734.2058	-0.0002	32 5 28	33 6 28	722.5046	-0.0019	19 2 18	19 3 16	742.2435	0.0000
38 9 30	38 10 28	734.2726	0.0006	31 5 27	32 6 27	723.1139	0.0001	17 2 17	18 3 17	741.6795	-0.0001
37 9 28	37 10 26	734.2726	0.0006	31 5 27	31 6 25	740.0685	0.0008	16 2 15	17 3 15	735.0285	0.0012
36 9 29	37 10 27	734.3076	0.0002	30 5 26	30 6 24	740.1786	-0.0009	16 2 14	17 3 16	741.9307	-0.0010
36 9 28	36 10 26	734.3413	0.0016	29 5 25	29 6 23	742.3861	-0.0003	15 2 14	16 3 15	742.2202	-0.0012
35 9 27	35 10 25	734.3763	0.0020	29 5 25	29 6 23	740.2612	0.0010	15 2 13	16 3 14	738.8559	0.0001
34 9 26	34 10 24	734.4121	0.0018	28 5 24	28 6 22	740.8508	0.0010	10 2 8	11 3 8	739.3245	0.0012
33 9 25	33 10 23	734.4482	0.0014	28 5 23	28 6 21	740.7578	0.0004	10 2 9	11 3 9	738.9120	-0.0014
32 9 24	32 10 22	734.4832	0.0021	26 5 22	26 6 20	740.6862	0.0014	9 2 6	9 3 6	740.2840	0.0013
31 9 23	31 10 21	734.5192	-0.0015	25 5 21	25 6 19	740.4155	0.0015	7 2 6	8 3 6	740.6553	0.0004
30 9 22	30 10 20	734.5547	0.0016	24 5 20	24 6 18	740.4455	0.0021	5 2 3	6 3 3	741.8058	0.0006
29 9 21	29 10 19	734.5904	0.0010	24 5 20	24 6 18	740.4706	0.0015	5 2 4	6 3 4	741.7691	0.0001
29 9 20	30 10 20	718.6373	0.0015	23 5 19	23 6 17	740.4941	-0.0016	21 1 20	22 2 20	732.1569	-0.0004
28 9 19	29 10 19	719.2083	-0.0014	22 5 18	22 6 16	740.5670	-0.0003	19 1 19	20 2 19	733.9546	-0.0005
28 9 20	28 10 18	734.6245	0.0017	22 5 18	23 6 20	742.1872	0.0002	19 1 18	20 2 18	732.6185	-0.0015
27 9 19	27 10 17	734.6597	0.0007	21 5 17</							

$J' K'_a K'_c$	$J'' K''_a K''_c$	$v_{\text{obs.}}$	Δ	$J' K'_a K'_c$	$J'' K''_a K''_c$	$v_{\text{obs.}}$	Δ	$J' K'_a K'_c$	$J'' K''_a K''_c$	$v_{\text{obs.}}$	Δ
8 2 7	7 1 7	755.3109	-0.0002	26 5 21	26 4 23	754.6734	-0.0006	40 7 33	40 6 35	756.4671	-0.0011
8 2 6	7 1 6	754.6164	-0.0004	26 5 21	25 4 21	767.3326	-0.0005	41 7 34	41 6 36	756.3583	-0.0010
9 2 7	8 1 7	755.1244	-0.0013	27 5 22	26 4 22	767.6705	-0.0021				
9 2 6	8 1 6	755.9584	-0.0008	27 5 22	25 4 22	767.0014	-0.0006	10 8 2	9 7 2	764.4679	-0.0025
10 2 9	9 1 9	756.6201	-0.0008	28 5 23	28 4 25	754.9573	-0.0016	11 8 3	10 7 3	764.9814	-0.0021
10 2 8	9 1 8	755.6495	-0.0005	28 5 23	27 4 23	768.0135	-0.0007	12 8 4	11 7 4	765.4936	-0.0021
11 2 10	10 1 10	756.1971	-0.0011	28 5 23	27 4 21	755.4448	-0.0005	16 8 8	15 7 8	767.5233	-0.0011
12 2 11	11 1 11	756.7117	-0.0021	29 5 24	28 4 24	768.7642	-0.0008	17 8 9	16 7 9	768.0286	-0.0014
12 2 11	11 1 13	753.2162	-0.0011	29 5 24	29 4 26	755.1677	-0.0004	18 8 10	17 7 10	768.5249	-0.0008
12 2 12	11 1 10	753.0581	-0.0007	30 5 25	29 4 25	768.7310	-0.0022	29 8 21	28 7 21	773.8617	-0.0002
16 2 14	15 1 12	754.2580	-0.0018	30 5 25	30 4 28	755.4348	-0.0010	29 8 22	28 7 22	773.8649	-0.0001
17 2 16	16 1 16	761.6041	-0.0012	31 5 26	31 4 28	755.7580	-0.0012	30 8 22	29 7 22	774.3267	-0.0002
18 2 17	17 1 15	753.3371	-0.0003	32 5 28	31 4 28	771.7263	-0.0013	30 8 23	29 7 23	774.3320	-0.0001
18 2 17	17 1 14	753.3373	-0.0002	33 5 29	33 4 30	772.9918	-0.0019	33 8 26	32 7 24	773.4661	-0.0017
19 2 17	18 1 15	755.8179	-0.0013	34 5 30	33 4 30						
20 2 18	19 1 16	756.2495	-0.0002	36 5 32	35 4 32	774.3155	-0.0002	9 9 0	8 8 0	765.3899	-0.0015
21 2 19	20 1 17	756.6336	-0.0009	36 5 31	35 4 31	771.6621	-0.0016	13 9 4	12 8 4	767.4402	-0.0011
21 2 20	20 1 20	764.6290	-0.0002	37 5 32	36 4 32	772.3062	-0.0018	14 9 5	13 8 5	767.9497	-0.0007
22 2 21	21 1 21	765.3931	-0.0002	38 5 33	37 4 33	772.9976	-0.0019	15 9 6	14 8 6	768.4566	-0.0003
23 2 21	22 1 21	765.0270	-0.0011					22 9 13	21 8 13	771.9549	-0.0011
25 2 24	24 1 24	767.6908	-0.0006	6 6 1	6 5 1	756.3388	-0.0004	23 9 14	22 8 14	772.4459	-0.0006
26 2 24	25 1 24	767.5444	-0.0006	7 6 2	7 5 2	756.3271	-0.0002	24 9 15	23 8 15	772.9349	-0.0005
27 2 25	26 1 25	768.3667	-0.0002	8 6 3	8 5 3	756.3138	-0.0003	25 9 16	24 8 16	773.4234	-0.0016
				9 6 4	9 5 4	756.2981	-0.0001	26 9 17	25 8 17	773.9066	-0.0008
3 3 1	2 2 1	753.6706	-0.0008	10 6 5	10 5 5	756.2809	-0.0007	35 9 27	34 10 25	753.0020	-0.0016
3 3 0	2 2 0	753.6668	-0.0019	10 6 4	10 5 5	756.2809	-0.0007	36 9 28	35 10 26	753.4989	-0.0007
4 3 1	3 2 1	754.1925	-0.0016	11 6 5	11 5 5	756.2605	-0.0004				
4 3 2	3 2 2	754.1985	-0.0016	12 6 6	12 5 6	756.2379	-0.0003	10 10 0	9 9 0	767.3454	-0.0001
6 3 4	5 2 4	755.2531	-0.0003	12 6 6	12 5 8	756.2379	-0.0003	11 10 0	11 9 2	767.0172	-0.0010
7 3 7	6 2 6	756.3228	-0.0010	12 6 6	11 5 6	762.6208	-0.0020	11 10 1	10 9 1	767.8582	-0.0015
8 3 6	7 2 6	756.8658	-0.0022	12 6 6	11 5 6	755.7223	-0.0013	12 10 2	11 9 2	768.0735	-0.0005
9 3 7	8 2 7	756.8658	-0.0022	14 6 8	14 5 10	756.1836	-0.0006	13 10 4	13 9 4	761.9787	-0.0001
16 3 19	16 2 15	753.1479	-0.0019	15 6 9	15 5 11	756.1531	-0.0007	14 10 5	14 9 5	761.9060	-0.0004
17 3 14	16 4 12	753.0024	-0.0024	16 6 11	16 5 11	756.1169	-0.0007	15 10 6	15 9 6	761.9326	-0.0003
17 3 14	17 2 16	753.4543	-0.0002	17 6 12	17 5 12	761.9194	-0.0014	16 10 7	16 9 7	767.9060	-0.0005
17 3 15	16 2 15	761.6080	-0.0011	17 6 12	16 5 12	764.6409	-0.0016	17 10 8	17 9 8	761.8779	-0.0005
18 3 15	17 2 13	753.4543	-0.0002	17 6 12	16 5 12	756.1193	-0.0005	19 10 10	19 9 10	761.8161	-0.0007
18 3 15	18 2 17	753.8229	-0.0013	17 6 12	16 5 12	761.9270	-0.0005	19 10 11	19 9 11	771.9120	-0.0007
19 3 16	18 4 14	754.3246	-0.0027	17 6 12	16 5 12	765.1393	-0.0021	20 10 10	19 9 10	772.4105	-0.0011
20 3 17	19 2 17	761.8699	-0.0018	17 6 12	16 5 12	765.1393	-0.0021	20 10 11	20 9 11	761.7825	-0.0005
21 3 18	20 4 16	755.9884	-0.0018	18 6 13	18 5 13	754.9400	-0.0002	21 10 12	21 9 12	767.7455	-0.0005
22 3 18	20 4 16	755.6453	-0.0003	18 6 13	18 5 13	756.0320	-0.0000	21 10 11	20 9 11	772.9070	-0.0013
22 3 19	21 4 18	756.2865	-0.0018	19 6 14	19 5 14	755.9832	-0.0012	22 10 13	22 9 13	761.7083	-0.0007
22 3 20	21 4 18	754.4737	-0.0018	19 6 14	19 5 15	755.9962	-0.0002	22 10 12	21 9 12	771.4038	-0.0006
22 3 20	21 2 20	765.0076	-0.0004	20 6 15	20 5 15	755.9270	-0.0004	23 10 13	22 9 13	773.8961	-0.0003
24 3 21	23 2 21	764.5426	-0.0002	20 6 15	20 5 15	755.9270	-0.0004	23 10 14	23 9 14	761.6683	-0.0003
24 3 22	23 2 22	755.1930	-0.0019	21 6 16	21 5 17	755.9002	-0.0018	24 10 15	24 9 15	761.6251	-0.0009
25 3 22	24 2 22	765.3040	-0.0017	22 6 17	22 5 17	755.9002	-0.0018	25 10 16	25 9 16	762.5796	-0.0004
27 3 25	26 2 25	768.6607	-0.0009	22 6 17	22 5 17	767.5875	-0.0002	28 10 28	27 11 26	753.0294	-0.0002
33 3 31	32 2 31	773.1854	-0.0019	22 6 17	22 5 17	755.7893	-0.0013	16 11 5	15 10 5	771.8501	-0.0012
				23 6 18	23 5 18	767.5543	-0.0009	17 11 6	16 10 6	772.3540	-0.0018
4 4 0	3 3 0	755.6218	-0.0016	23 6 18	23 5 18	755.7050	-0.0017	18 11 7	17 10 7	772.8567	-0.0018
5 4 1	4 3 1	756.1437	-0.0003	23 6 18	23 5 19	755.7926	-0.0010	19 11 8	18 10 8	773.3597	-0.0002
5 4 2	4 3 2	753.4853	-0.0019	24 6 19	24 5 19	761.9988	-0.0006	20 11 9	19 10 9	773.3888	-0.0001
6 4 2	5 3 4	753.4749	-0.0013	24 6 19	24 5 19	768.4737	-0.0011	21 11 10	20 10 10	774.3558	-0.0003
6 4 3	5 3 3	753.4727	-0.0014	24 6 19	24 5 19	755.6067	-0.0017	25 11 15	25 10 15	763.0388	-0.0003
6 4 6	5 3 6	756.6644	-0.0008	25 6 20	25 5 20	754.9400	-0.0002	26 11 16	26 10 16	762.9946	-0.0005
7 4 3	6 3 5	753.4624	-0.0008	25 6 20	25 5 20	755.4902	-0.0002	27 11 17	27 10 17	762.9444	-0.0003
8 4 5	8 3 5	753.4346	-0.0021	26 6 21	26 5 21	755.3558	-0.0004	28 11 18	28 10 18	762.8969	-0.0002
8 4 6	8 3 6	753.4446	-0.0021	26 6 21	26 5 21	755.3558	-0.0004	29 11 19	29 10 19	762.8448	-0.0004
9 4 6	9 3 6	753.4081	-0.0008	26 6 21	26 5 22	755.6340	-0.0018	30 11 20	30 10 20	762.7906	-0.0006
9 4 5	9 3 7	753.4298	-0.0022	27 6 22	27 5 22	755.1992	-0.0003	31 11 21	31 10 21	762.7336	-0.0003
10 4 6	10 3 7	753.3722	-0.0000	27 6 22	27 5 22	755.1992	-0.0003	32 11 22	32 10 22	762.6740	-0.0005
10 4 7	10 3 8	753.4329	-0.0004	28 6 23	28 5 23	755.5872	-0.0006	33 11 23	33 10 23	762.6181	-0.0004
11 4 8	11 3 8	753.3233	-0.0009	28 6 23	28 5 23	755.0173	-0.0021	36 11 26	36 10 26	762.4089	-0.0009
11 4 7	11 3 9	753.3960	-0.0022	29 6 24	29 5 24	755.0173	-0.0021				
12 4 9	12 3 10	753.2847	-0.0010	29 6 24	29 5 24	754.4818	-0.0001	12 12 1	12 11 1	764.8907	-0.0014
12 4 8	12 3 9	753.3826	-0.0010	30 6 25	30 5 26	755.9347	-0.0018	13 12 2	13 11 2	771.7741	-0.0011
13 4 10	13 3 10	753.1824	-0.0010	30 6 25	30 5 26	755.5119	-0.0015	13 12 1	12 11 1	771.7741	-0.0011
14 4 11	14 3 11	753.0683	-0.0009	30 6 25	30 5 26	755.0353	-0.0003	13 12 2	13 11 2	764.8717	-0.0003
14 4 11	14 3 10	753.0787	-0.0012	31 6 26	31 5 27	755.4547	-0.0012	14 12 2	13 11 2	772.2833	-0.0019
15 4 12	15 3 12	752.9537	-0.0005	31 6 26	31 5 27	755.4547	-0.0012	15 12 3	14 11 3	764.8500	-0.0019
15 4 11	15 3 13	753.3752	-0.0002	31 6 26	31 5 26	754.2780	-0.0004	15 12 3	14 11 3	772.7917	-0.0015
16 4 13	16 3 13	753.4329	-0.0004	32 6 27	32 5 28	755.9720	-0.0004	16 12 4	15 11 4	764.8265	-0.0005
17 4 14	17 3 14	762.3852	-0.0001	32 6 27	32 5 27	754.9614	-0.0004	17 12 5	16 11 5	764.8011	-0.0005
17 4 13	16 3 13	761.9245	-0.0005	32 6 27	32 5 27	772.4335	-0.0007	17 12 6	17 11 6	764.7749	-0.0003
18 4 14	18 3 14	753.4674	-0.0004	33 6 28	33 5 29	771.8651	-0.0007	17 12 5	16 11 5	773.8037	-0.0005
18 4 14	17 3 14	762.3240	-0.0007	33 6 28	33 5 29	754.9614	-0.0004	18 12 6	17 11 6	774.0770	-0.0004
19 4 15	19 3 17	753.5885	-0.0002	33 6 28	33 5 29	772.9435	-0.0016	19 12 7	18 11 7	774.3071	-0.0001
19 4 15	18 3 15	762.7187	-0.0002	33 6 28	33 5 29	755.6322	-0.0023	19 12 8	19 11 8	764.7166	-0.0002
20 4 16	20 3 18	753.7137	-0.0024	34 6 29	34 5 30	773.4673	-0.0009	20 12 9	20 11 9	764.6841	-0.0003
21 4 18	20 3 18	753.1181	-0.0020	34 6 29	34 5 30	773.1643	-0.0012	21 12 9	21 11 9	752.9621	-0.0012
21 4 18	20 3 18	764.6220	-0.0011	35 6 30	35 5 31	755.7378	-0.0009	21 12 10	21 11 10	764.6511	-0.0006
22 4 19	22 3 19	764.1816	-0.0014	35 6 30	35 5 31						

of this university with the package CDA 4/6 [19] which allows to carry out centrifugal distortion analysis including quartic and sextic terms in Watson's notation. The I' representation in the A reduction was used [20].

The rovibrational parameters obtained in this way, together with the corresponding ground-state constants [5] which were held fixed, are collected in Table 1, and the measured and computed transition frequencies used in the fitting routine can be compared in Table 2. It was necessary to include sextic centrifugal-distortion constants, which we constrained to the values given by Bestmann *et al.* [5] for the ground state. More data, especially transitions between higher J and K_a levels would be required for an independent determination of the upper-state sextic constants. The experimental accuracy of the TDL transition frequencies not determined by computer is limited to approximately 0.002 cm^{-1} by uncertainties in the determination of line and fringe maxima, by residual nonlinearities in the frequency scale as caused by temperature perturbations, and sometimes by the overlap of neighbouring absorptions. The over-all agreement between observed and calculated frequencies seems to confirm this estimate. The computer-determined frequencies should be more accurate as some of the error contributions are reduced. Only strong and clearly recognized transitions were used for the fit, hence all were equally weighted. In a separate least-squares run, the ground-state parameters were also allowed to adjust to the IR frequencies. Their final values agreed with the microwave results within three standard deviations.

The strong correlation between A and A_K in Table 1 might indicate the presence of Coriolis coupling between rovibrational levels of the 748 cm^{-1} CH_2 rocking mode and those of near-by modes of suitable symmetry. This has been investigated in more detail [21], but Coriolis effects were found to be negligible within the present range of K_a levels.

Using the spectral parameters of Table 1, we have computed the Fortrat- and intensity diagrams of the spectral regions close to the center at $(748.5307 \pm 0.0004)\text{ cm}^{-1}$. They are, since they informatively show the gradual appearance of asymmetry perturbations with increasing J , reproduced in the upper and lower parts of Figure 5. Nearby transitions have been recorded as separate entries when they were more than 10^{-3} cm^{-1} apart, otherwise their intensities were added. This causes interruption of the J progression in

some of the Q branches at higher K_a , in the intensity diagram below. The highest branch appearing partly on the right is $^R\text{Q}_8$, the lowest complete one on the left is $^P\text{Q}_9$. The negative slope of the Q branches in the low- J region of the Fortrat diagram arises from the fact that $B + C$ in (1) is larger in value in the vibrational ground state than in the excited state. After K doubling has become dominant in a Q branch, it is seen that one of the two sub-branches at given K_a readily progresses towards the band center with increasing J . These transitions obey the selection rule $\Delta K_c = 0$, hence their decreasing off-set from the center frequency is caused by the increasing oblate properties of the rotor in its low K_a , high J quantum states.

5. Conclusion

The results of this work show that combination of medium-resolved Fourier-transform and high resolution tunable diode laser spectrometry may lead to a complete understanding and assignment of the rovibrational structure of polyatomic asymmetric rotors, at least in the near-symmetric-rotor case. The advantage of the TDL technique is its fast access to selected regions of the spectrum and immediate accurate knowledge of the frequency of a single transition.

The present investigation also encourages to try an analogous analysis of the CH_2 -rocking region of the *n*-butane system. With the electron-diffraction structure of trans-butane [22], an asymmetry parameter of $\kappa = -0.98$ is predicted, indicating that (1) holds even better for this more complicated molecule than for propane. The K_a quantum numbers of the Q branch sub-bands are indeed readily assigned in the medium resolved FTIR spectrum near 733 cm^{-1} . Highly overlapped J progressions are to be expected owing to the small values of the B and C rotational constants of trans-butane. Analysis of the *gauche*-butane spectra, on the other hand, is expected to be more difficult because of the higher asymmetry ($\kappa = -0.847$) of this molecule. However, its rotational spectrum was recently detected and the ground-state spectroscopic constants were determined [23] which, as obvious from the present paper, is of invaluable help in understanding high-resolution IR spectra.

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ground-state data in [5] prior to publication. G. Tränkle has stimulated improvements in the spectrometer set-up.

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