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, $CH_3CH_2CH_3$, 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 polyetheylene 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 Bestmann 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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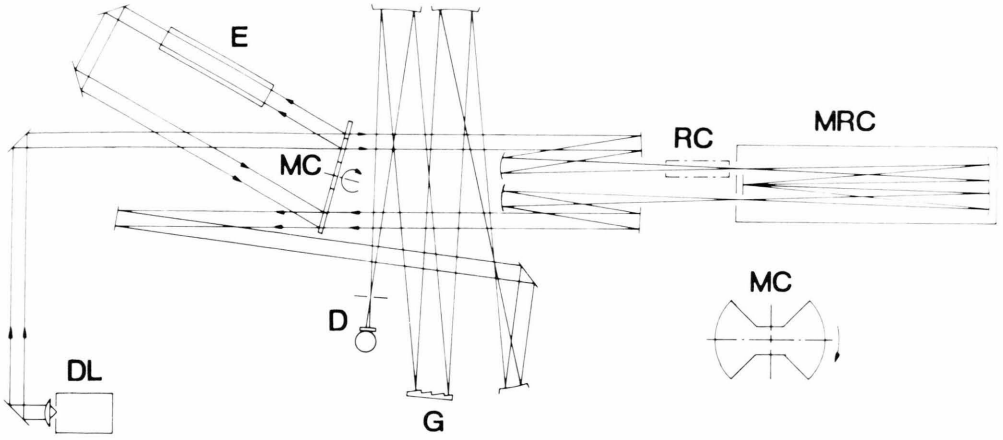

Fig. 1. Optical layout of the spectrometer. DL, diode-laser cold head; E, etalon; MC, mirror chopper; G, monochromator grating; RC, reference cell; MRC, White-type cell; D, detector. Using a mirror chopper instead of beam splitters provides more radiation intensity in both the cell and etalon branches, 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].

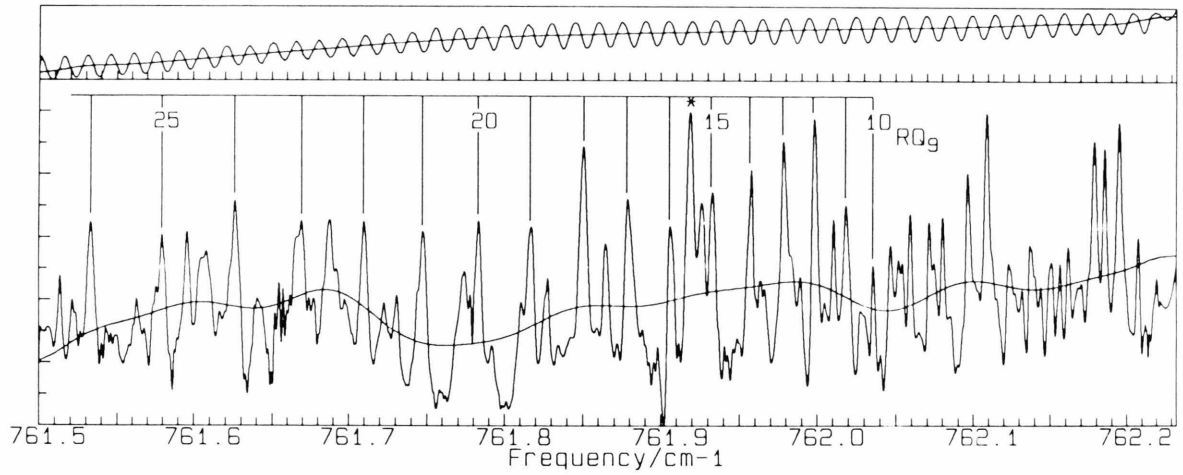

Fig. 2. Beginning of the ${}^{R}Q_9$, $\Delta K_a = 2$ progression in the CH_2-rocking band of propane. The J quantum numbers are given. The TDL spectrum shown was digitally filtered, and the diode-current ramp was transferred to the linear frequency abscissa with the computer program described in the 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 resonator 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

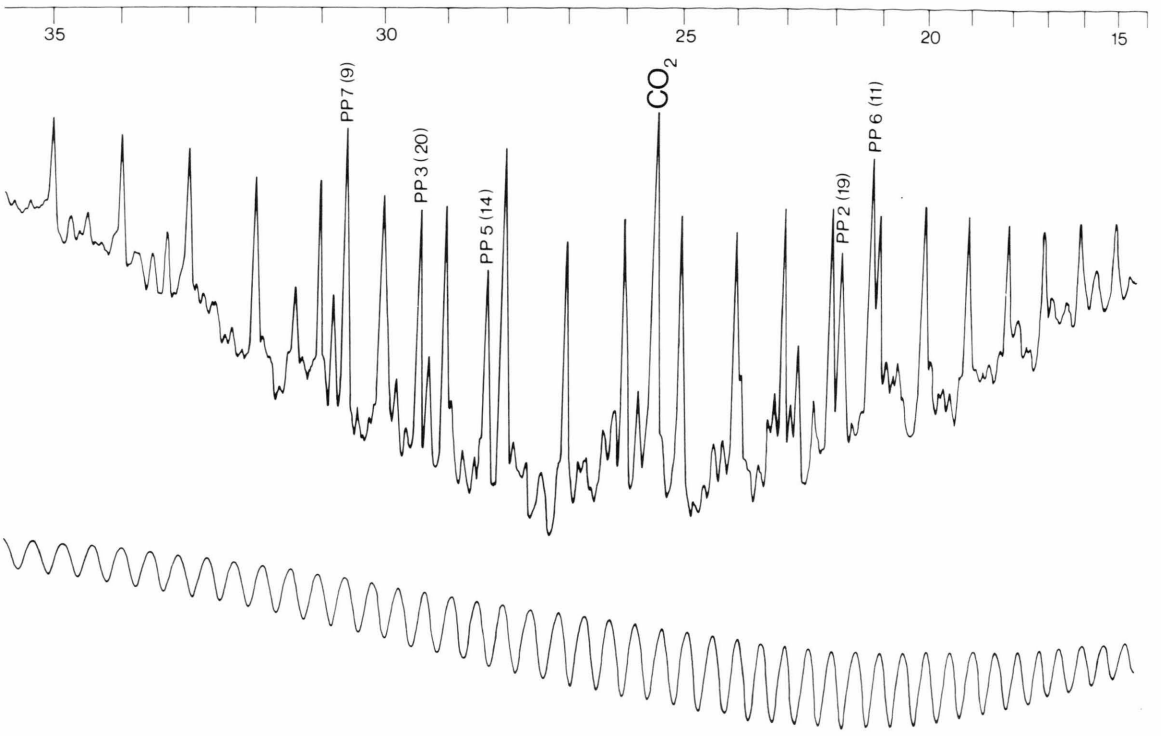

Fig. 3. Part of the $\Delta K_c = 2$ progression of the $^PQ_{10}$ sub-branch near 734.7 cm^{-1}. The J quantum numbers are indicated. The frequency increases from left to right, the fringe spacing is 0.014993 cm^{-1}. The frequency of the CO_2 calibration line, R(17) of the hot-band transition $(10^00, 02^00)_{II} - 01^10$, is 734.7128 cm^{-1} and was calculated with the parameter set given by Paso et al. [11]. Some members of several $^PP_K(J)$ 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 resulting 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.

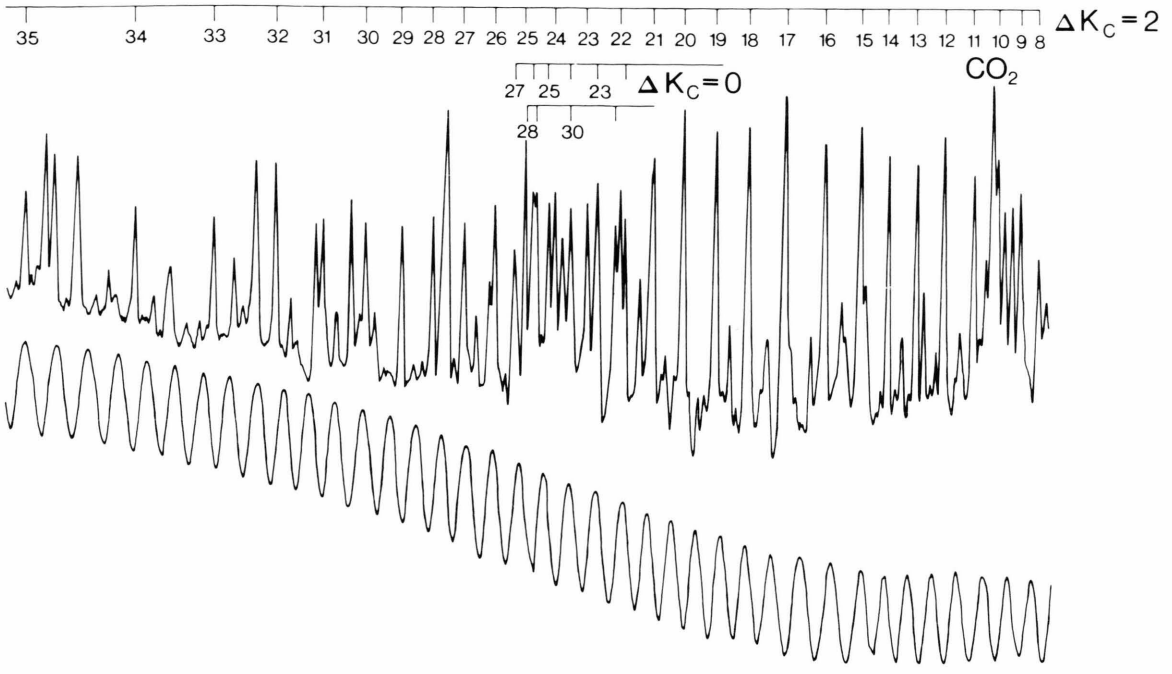

Fig. 4. The two sub-branches of $^{P}Q_{7}$, J quantum numbers being indicated. The $\Delta K_c = 0$ and $\Delta K_c = 2$ progressions start to separate at $J = 21$. Frequency increases from left to right, fringe distance as in Fig. 3. The CO_2 calibration line, at 739.2849 cm^{-1}, is R(23) from the 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 undispensible 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 $\varkappa = -0.909$ 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],

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

as well as with the absorption-intensity rules given by Allen and Cross [18]. Some of the sub-band Q branches $^{P}Q_{K_a}$ and $^{R}Q_{K_a}$ 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 $^{P}P_{K_a}(J)$ and $^{R}R_{K_a}(J)$ 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 $^{R}Q_{K_a-1}(J-1)$ and $^{P}Q_{K_a+1}(J+1)$ have the (unknown) upper (J, K_a) state in common, which cancels on subtracting the two frequencies. Figure 3 shows assignments in the $^{P}Q_{10}$, $\Delta K_c = 2$ progression achieved in this way. Figure 4 shows the resolved $\Delta K_c = 0$ band head of the $^{P}Q_{7}$ 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

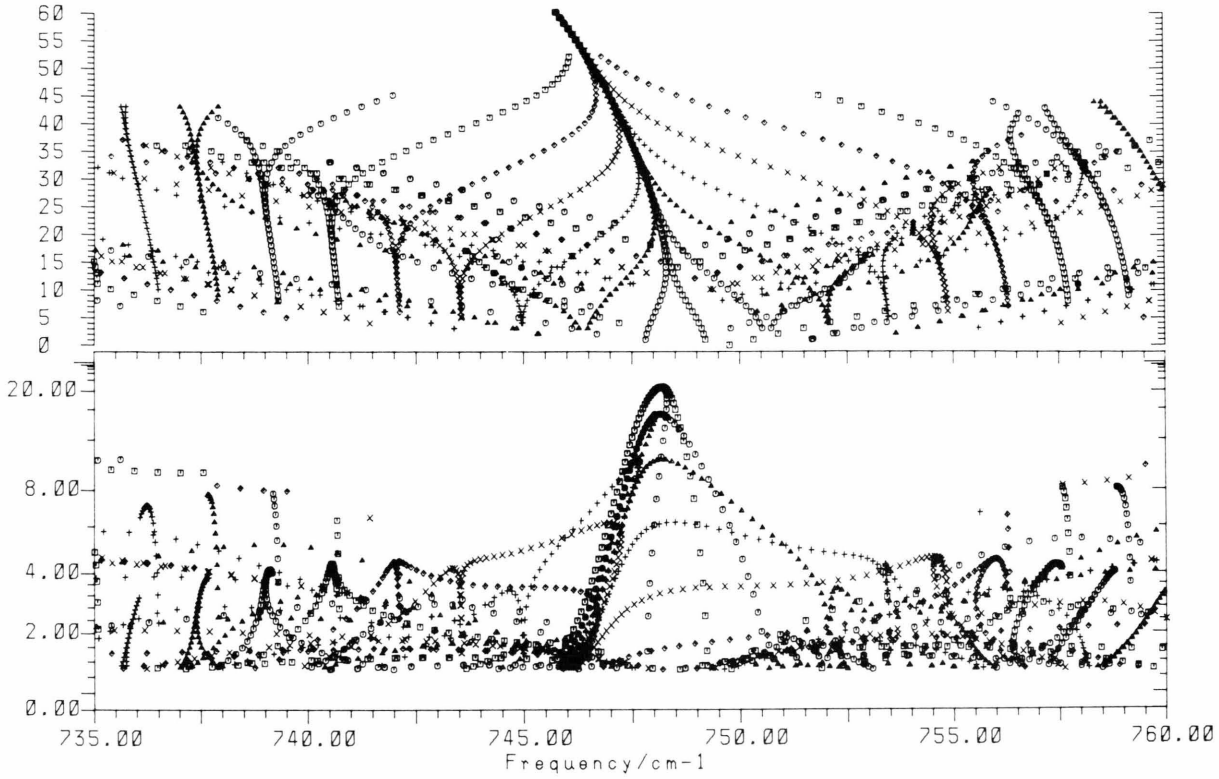

Fig. 5. Fortrat (above) and intensity (below) diagrams of the CH_2-rocking fundamental of propane near 748 cm^{-1}, see text. The lower-state J quantum numbers are given in the ordinate above, the logarithmic scale below is proportional to absorption intensity.

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-stante 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^r 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 $\sigma = 0.0012$ cm^{-1}.

Table 2. Assignment of rovibrational transitions $\nu_{obs.}$ and comparison with calculated values $\nu_{calc.}$ 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. $\Delta = \nu_{obs.} - \nu_{calc.}$, frequencies in cm^{-1}.

J'	K'_a	K'_c	J''	K''_a	K''_c	$\nu_{obs.}$	Δ
24	18	7	24	19	5	722.5042	0.0023
23	18	6	23	19	4	722.5436	0.0006
38	17	22	38	18	20	723.1572	0.0022
26	14	13	26	15	11	727.7949	-0.0022
23	14	10	23	15	8	727.9086	-0.0023
21	14	8	21	15	6	727.9760	-0.0009
20	14	7	20	15	5	728.0088	-0.0015
19	14	6	19	15	4	728.0394	-0.0012
18	14	5	18	15	3	728.0684	-0.0008
17	14	4	17	15	2	728.0959	-0.0004
19	13	6	20	14	6	718.7748	0.0019
18	13	5	19	14	5	719.3375	-0.0006
13	13	0	14	14	0	722.1165	-0.0004
21	12	9	22	13	9	719.0178	0.0019
20	12	8	21	13	8	719.5814	0.0010
15	12	3	16	13	3	722.3743	0.0009
14	12	2	15	13	2	722.9308	-0.0014
13	12	1	14	13	1	723.4814	0.0008
12	12	0	13	13	0	724.0326	0.0009
24	11	13	25	12	13	718.6974	0.0019
23	11	13	23	12	11	732.0128	0.0011
23	11	12	24	12	12	719.2652	0.0002
21	11	11	21	12	9	732.0789	0.0005
19	11	9	19	12	7	732.1387	0.0012
18	11	8	18	12	6	732.1676	0.0006
17	11	6	18	12	6	722.6360	-0.0006
17	11	7	17	12	5	732.1961	-0.0009
16	11	5	17	12	5	723.1935	-0.0011
15	11	5	15	12	3	732.2441	0.0010
14	11	4	14	12	2	732.2687	-0.0007
13	11	3	13	12	1	732.2889	0.0005
13	11	2	14	12	2	732.8532	0.0015
12	11	2	12	12	0	732.3101	-0.0007
12	11	1	13	12	1	725.4050	0.0008
11	11	0	12	12	0	725.9562	-0.0007
38	10	29	38	11	27	732.8207	0.0000
36	10	27	36	11	25	732.9043	-0.0004
35	10	26	35	11	24	732.9456	-0.0003
34	10	25	34	11	23	732.9864	0.0000
33	10	24	33	11	22	733.0273	-0.0002
31	10	22	31	11	20	733.1064	0.0006
30	10	21	30	11	19	733.1455	0.0006
28	10	19	28	11	17	733.2231	-0.0007
27	10	18	27	11	16	733.2597	-0.0003
26	10	16	27	11	16	718.9494	-0.0013
26	10	17	26	11	15	733.2959	-0.0004
25	10	15	26	11	15	719.5154	0.0001
25	10	16	25	11	14	733.3311	-0.0003
23	10	14	23	11	12	733.3991	-0.0007
21	10	12	21	11	10	733.4618	0.0001
20	10	10	21	11	10	722.3374	-0.0009
20	10	11	20	11	9	733.4924	-0.0004
19	10	9	20	11	9	722.8986	-0.0015
18	10	8	19	11	8	723.4563	0.0002
17	10	8	17	11	6	733.5752	-0.0001
17	10	7	18	11	7	724.0144	0.0001
16	10	6	17	11	6	724.5710	0.0002
15	10	6	15	11	4	733.6241	0.0000
14	10	5	14	11	3	733.6465	0.0002
14	10	4	15	11	4	725.6810	-0.0005
12	10	3	12	11	1	733.6875	0.0001
11	10	2	11	11	0	733.7046	0.0014
10	10	0	11	11	0	727.8818	-0.0001
43	9	35	43	10	33	734.1108	-0.0007
43	9	34	43	10	34	734.1218	-0.0014
42	9	33	42	10	33	734.1489	-0.0010
42	9	34	42	10	32	734.1416	-0.0005
41	9	33	41	10	31	734.1727	0.0003
40	9	31	40	10	31	734.2088	-0.0002
40	9	32	40	10	30	734.2058	-0.0002
38	9	30	38	10	28	734.2726	0.0006
37	9	28	37	10	28	734.3076	0.0009
37	9	29	37	10	27	734.3076	0.0002
36	9	28	36	10	26	734.3413	0.0016
35	9	27	35	10	25	734.3763	0.0020
34	9	26	34	10	24	734.4121	0.0018
33	9	25	33	10	23	734.4482	0.0014
32	9	24	32	10	22	734.4832	0.0021
31	9	23	31	10	21	734.5192	0.0017
30	9	22	30	10	20	734.5547	0.0016
29	9	21	29	10	19	734.5904	0.0010
29	9	20	30	10	20	718.6373	0.0015
28	9	19	29	10	19	719.2083	-0.0014
28	9	20	28	10	18	734.6245	0.0017
27	9	19	27	10	17	734.6597	0.0007
26	9	18	26	10	16	734.6932	0.0009
25	9	17	25	10	15	734.7270	0.0002
24	9	16	24	10	14	734.7584	0.0012
23	9	15	23	10	13	734.7901	0.0011
22	9	13	23	10	13	722.5995	0.0001
22	9	14	22	10	12	734.8208	0.0012
21	9	12	22	10	12	723.1635	-0.0016
21	9	13	21	10	11	734.8510	0.0009
20	9	12	20	10	10	734.8804	0.0004
19	9	11	19	10	9	734.9075	0.0012
18	9	10	18	10	8	734.9340	0.0015
18	9	9	19	10	9	724.8428	-0.0010
17	9	9	17	10	7	734.9596	0.0017
17	9	8	18	10	8	725.4014	-0.0020
16	9	8	16	10	6	734.9841	0.0017
15	9	7	15	10	5	735.0077	0.0014
12	9	3	12	10	3	728.1653	0.0023
12	9	4	12	10	2	735.0702	0.0013
31	8	24	32	9	24	718.9239	-0.0016
30	8	23	31	9	23	719.4869	0.0001
24	8	16	25	9	16	722.8727	-0.0014
23	8	15	24	9	15	723.4340	-0.0004
21	8	13	22	9	13	724.5567	-0.0006
19	8	11	20	9	11	725.6759	-0.0008
15	8	7	16	9	7	727.9009	-0.0005
14	8	6	15	9	6	728.4529	0.0008
33	7	27	34	8	27	719.2541	-0.0012
32	7	26	33	8	26	738.9904	-0.0002
17	7	10	18	8	10	728.1840	0.0028
9	7	2	10	8	2	732.5948	-0.0020
8	7	1	9	8	1	733.1371	0.0005
7	7	0	8	8	0	733.6821	-0.0012
37	6	32	37	7	30	738.5782	-0.0021
36	6	31	36	7	29	738.6669	-0.0012
36	6	30	37	7	30	719.5607	0.0004
35	6	30	35	7	28	738.7366	-0.0008
35	6	30	36	7	30	719.5561	0.0007
35	6	29	36	5	31	733.7668	0.0010
34	6	28	35	5	30	734.5831	0.0007
34	6	29	34	7	27	738.7906	-0.0001
33	6	28	33	7	26	738.8355	-0.0022
32	6	27	32	7	25	738.8678	-0.0004
31	6	25	31	7	25	739.0633	-0.0009
31	6	26	31	7	24	738.8957	-0.0006
30	6	25	31	7	25	722.3839	-0.0019
30	6	25	30	7	23	738.9192	-0.0008
30	6	24	31	7	24	722.4754	0.0007
29	6	23	30	5	25	738.6437	-0.0021
29	6	24	29	7	22	738.9394	-0.0006
29	6	24	30	7	24	722.9396	-0.0013
29	6	23	30	7	23	723.0053	-0.0018
29	6	23	29	7	23	739.0180	0.0000
28	6	23	29	7	23	723.4933	0.0002
28	6	22	28	7	22	739.0116	-0.0010
28	6	23	28	7	21	738.9581	-0.0007
27	6	21	28	5	23	740.1361	-0.0006
27	6	21	27	7	21	739.0105	-0.0003
27	6	21	28	7	21	724.0774	0.0003
27	6	22	28	7	22	724.0490	-0.0009
27	6	22	27	7	20	738.9763	-0.0011
26	6	20	27	7	20	724.6229	-0.0011
26	6	20	26	7	20	739.0163	-0.0010
26	6	21	26	7	19	738.9937	-0.0010
26	6	21	27	7	21	724.6033	-0.0008
25	6	19	25	7	19	739.0254	-0.0008
24	6	18	24	7	18	739.0385	-0.0014
24	6	19	24	7	17	739.0295	-0.0013
23	6	17	23	7	17	739.0535	-0.0016
23	6	18	23	7	16	739.0478	-0.0013
22	6	16	22	7	16	739.0692	-0.0006
22	6	17	22	7	15	739.0663	-0.0009
21	6	15	21	7	15	739.0873	-0.0009
21	6	16	21	7	14	739.0861	-0.0015
20	6	15	20	7	13	739.1063	-0.0021
19	6	14	19	7	12	739.1260	-0.0021
18	6	13	18	7	11	739.1454	-0.0017
17	6	12	17	7	10	739.1657	-0.0023
16	6	11	16	7	9	739.1851	-0.0022
15	6	10	15	7	8	739.2033	-0.0014
14	6	9	14	7	7	739.2208	-0.0003
13	6	8	13	7	6	739.2388	-0.0004
12	6	6	13	7	6	732.3503	-0.0019
12	6	7	12	7	5	739.2567	-0.0012
11	6	6	11	7	4	739.2731	-0.0013
11	6	5	12	7	5	732.8988	-0.0020
10	6	4	11	7	4	733.4458	-0.0017
10	6	5	10	7	3	739.2874	-0.0004
9	6	3	10	7	3	733.9910	-0.0009
9	6	4	9	7	2	739.3014	-0.0002
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36	5	30	36	6	30	722.2997	-0.0026
34	5	29	35	6	29	722.7240	-0.0027
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28	5	24	29	6	24	724.8843	-0.0015
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27	5	22	27	6	22	740.7578	0.0004
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26	5	22	26	6	20	740.4155	0.0015
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24	5	20	24	6	18	740.4706	0.0015
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23	5	18	23	4	20	742.1872	0.0002
22	5	18	22	6	16	740.5098	0.0005
21	5	17	21	6	15	740.5249	0.0015
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20	5	16	20	6	14	740.5408	0.0008
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19	5	15	19	6	13	740.5552	0.0013
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17	5	13	17	6	11	740.5864	0.0001
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32	4	29	33	5	29	723.0821	-0.0022
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28	4	25	28	5	23	740.8917	0.0001
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25	4	22	26	5	22	727.7966	-0.0030
24	4	21	25	5	21	728.4035	0.0008
24	4	21	24	5	19	741.6377	0.0021
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23	4	19	24	3	21	738.6800	-0.0007
22	4	19	22	5	17	741.8180	0.0008
22	4	18	23	3	20	739.3400	0.0020
21	4	17	21	5	17	742.2938	-0.0007
21	4	18	21	5	16	741.8781	0.0004
20	4	16	20	5	16	742.2158	-0.0005
20	4	16	21	3	18	740.7458	0.0011
20	4	17	20	5	15	741.9246	-0.0006
19	4	16	19	5	14	741.9579	0.0009
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18	4	14	18	5	14	742.1197	-0.0010
18	4	15	18	5	13	741.9852	0.0006
18	4	14	19	3	16	742.1999	-0.0006
17	4	13	17	5	13	742.0938	-0.0006
17	4	14	18	5	14	732.4184	-0.0002
17	4	14	17	5	12	742.0069	0.0002
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16	4	13	16	5	11	742.0249	-0.0002
16	4	12	17	5	12	733.0176	-0.0002
15	4	11	16	5	11	733.5497	-0.0002
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7	3	4	8	4	4	739.2949	0.0018
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19	1	18	20	2	18	733.9546	-0.0005
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17	1	17	18	2	17	734.2378	0.0010
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9	1	9	10	2	9	740.2958	0.0018
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19	0	19	20	1	19	732.7929	-0.0011
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12	0	12	13	1	12	738.8918	-0.0006
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19	0	19	18	1	17	753.1969	-0.0001
20	0	20	19	1	18	753.3159	-0.0008
21	0	21	20	1	19	753.4379	0.0004
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13	1	12	12	2	10	753.4571	0.0021
14	1	13	13	2	11	753.8349	0.0006
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16	1	15	15	2	13	754.4512	0.0001
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20	1	19	19	2	17	755.1790	-0.0011
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22	1	21	21	0	21	765.2920	-0.0017
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30	5	25	29	4	25	768.7310	0.0022
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31	5	26	31	4	28	755.7580	-0.0012
32	5	28	31	4	28	771.7263	0.0013
33	5	28	33	4	30	756.5839	0.0008
34	5	30	33	4	30	772.9918	0.0019
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36	5	31	35	4	31	771.6621	0.0016
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20	6	14	20	5	16	755.9492	-0.0006
20	6	15	20	5	15	755.9270	-0.0014
21	6	15	21	5	17	755.9002	-0.0018
21	6	16	21	5	16	755.8619	-0.0005
22	6	17	21	5	17	767.5875	-0.0002
22	6	17	22	5	17	755.7893	-0.0013
22	6	16	21	5	16	767.5543	0.0009
23	6	17	22	5	17	768.0174	0.0024
23	6	18	23	5	18	755.7050	-0.0017
23	6	17	23	5	19	755.7926	-0.0010
24	6	19	23	5	19	768.5488	0.0006
24	6	18	23	5	18	768.4737	0.0011
24	6	19	24	5	19	755.6067	-0.0017
25	6	19	25	5	21	755.6844	-0.0013
25	6	20	25	5	20	755.4902	0.0002
26	6	21	26	5	21	755.3558	0.0004
26	6	20	26	5	22	755.6340	-0.0018
27	6	21	26	7	19	753.3985	0.0019
27	6	22	27	5	22	755.1992	-0.0003
27	6	21	27	5	23	755.5872	-0.0006
28	6	22	28	5	24	755.5500	-0.0009
28	6	23	28	5	23	755.0173	-0.0021
29	6	23	28	7	21	754.4818	0.0001
30	6	25	29	7	23	754.9347	-0.0018
30	6	24	30	5	26	755.5119	0.0015
30	6	24	29	7	22	755.0353	-0.0003
31	6	26	30	7	24	755.4547	-0.0012
31	6	26	30	5	26	771.9321	0.0004
31	6	26	31	5	26	754.2780	-0.0003
32	6	27	31	7	25	755.9720	0.0004
32	6	26	32	5	28	755.5614	-0.0003
32	6	27	31	5	27	772.4335	0.0007
33	6	27	32	5	27	771.8651	0.0007
33	6	28	32	7	26	756.4874	0.0010
33	6	28	32	5	28	772.9435	0.0016
33	6	27	33	5	29	755.6322	-0.0023
34	6	29	33	5	29	773.4673	-0.0009
34	6	28	33	5	28	772.1643	0.0012
34	6	28	34	5	30	755.7378	-0.0009
35	6	30	34	5	30	773.9992	0.0003
35	6	29	34	5	29	772.4636	0.0008
35	6	29	35	5	31	755.8902	-0.0017
36	6	30	36	5	32	756.0902	0.0004
37	6	31	37	5	33	756.3417	0.0010
37	6	31	36	5	31	773.0947	-0.0010
38	6	32	37	5	32	773.4418	-0.0007
39	6	33	38	5	33	773.8214	-0.0006
40	6	34	39	5	34	774.2401	-0.0007
9	7	2	8	6	2	762.5152	-0.0014
10	7	3	9	6	3	763.0309	-0.0017
13	7	6	12	6	6	764.5665	-0.0021
14	7	7	13	6	7	765.0745	-0.0022
19	7	13	18	6	13	767.5776	0.0005
19	7	12	18	6	12	767.5776	0.0003
20	7	13	19	6	13	768.0691	0.0020
20	7	14	19	6	14	768.0705	0.0012
21	7	15	20	6	14	768.5617	-0.0004
28	7	21	27	6	21	771.8776	0.0000
28	7	22	27	6	22	771.9087	-0.0002
28	7	22	28	6	22	756.8988	0.0016
29	7	23	29	6	23	756.7999	0.0015
29	7	23	28	6	23	772.3727	0.0011
29	7	22	28	6	22	772.3269	0.0007
29	7	22	29	6	24	756.8807	0.0022
30	7	24	30	6	24	756.6886	0.0012
30	7	24	29	8	22	753.4254	0.0002
30	7	23	30	6	25	756.8071	0.0020
30	7	24	29	6	24	772.8356	0.0010
31	7	24	30	6	24	773.2005	-0.0014
31	7	24	31	6	26	756.7340	0.0010
31	7	25	31	6	25	756.5629	0.0005
32	7	26	32	6	26	756.4178	0.0013
32	7	26	31	6	26	773.7565	-0.0001
32	7	25	31	6	25	773.6182	-0.0009
32	7	25	32	6	27	756.6611	0.0010
33	7	26	33	6	28	756.5924	-0.0001
33	7	27	33	6	27	756.2518	0.0019
33	7	26	32	8	24	755.0054	-0.0017
33	7	27	32	6	27	774.2157	-0.0007
33	7	26	32	6	26	774.0214	-0.0003
34	7	27	34	6	29	756.5272	0.0009
34	7	28	34	6	28	756.0625	0.0014
35	7	28	35	6	30	756.4719	0.0006
36	7	30	36	6	30	755.5968	-0.0002
36	7	30	35	8	28	756.5321	0.0016
36	7	29	36	6	31	756.4275	0.0014
37	7	30	37	6	32	756.3996	0.0020
39	7	32	39	6	34	756.4154	0.0002
40	7	33	40	6	35	756.4671	0.0011
41	7	34	41	6	36	756.5583	0.0010
10	8	2	9	7	2	764.4679	-0.0025
11	8	3	10	7	3	764.9814	-0.0021
12	8	4	11	7	4	765.4936	-0.0021
16	8	8	15	7	8	767.5233	-0.0011
17	8	9	16	7	9	768.0236	0.0014
18	8	10	17	7	10	768.5249	0.0008
29	8	21	28	7	21	773.8617	0.0002
29	8	22	28	7	22	773.8649	0.0001
30	8	22	29	7	22	774.3267	0.0002
30	8	23	29	7	23	774.3320	-0.0001
33	8	26	32	9	24	753.4661	0.0017
9	9	0	8	8	0	765.3899	-0.0015
13	9	4	12	8	4	767.4402	0.0011
14	9	5	13	8	5	767.9497	0.0007
15	9	6	14	8	6	768.4566	0.0011
22	9	13	21	8	13	771.9549	0.0003
23	9	14	22	8	14	772.4459	0.0006
24	9	15	23	8	15	772.9349	0.0005
25	9	16	24	8	16	773.4234	-0.0016
26	9	17	25	8	17	773.9066	-0.0008
35	9	27	34	10	25	753.0020	-0.0016
36	9	28	35	10	26	753.4989	0.0007
10	10	0	9	9	0	767.3454	0.0001
11	10	2	11	9	2	762.0172	0.0010
11	10	1	10	9	1	767.8582	0.0015
12	10	3	11	9	2	768.3705	0.0018
13	10	4	13	9	4	761.9787	0.0001
14	10	5	14	9	5	761.9560	0.0004
15	10	6	15	9	6	761.9326	-0.0003
16	10	7	16	9	7	761.9060	0.0003
17	10	8	17	9	8	761.8779	0.0005
19	10	10	19	9	10	761.8161	0.0007
19	10	9	18	9	9	771.9120	0.0010
20	10	10	19	9	10	772.4105	0.0011
20	10	11	20	9	11	761.7825	0.0005
21	10	12	21	9	12	761.7455	0.0015
21	10	11	20	9	11	772.9070	0.0013
22	10	13	22	9	13	761.7083	0.0006
22	10	12	21	9	12	773.4038	-0.0007
23	10	13	22	9	13	773.8961	-0.0003
23	10	14	23	9	14	761.6683	0.0003
24	10	15	24	9	15	761.6251	0.0009
25	10	16	25	9	16	761.5796	0.0015
38	10	28	37	11	26	753.0294	0.0002
16	11	5	15	10	5	771.8501	0.0012
17	11	6	16	10	6	772.3540	0.0018
18	11	7	17	10	7	772.8567	0.0018
19	11	8	18	10	8	773.3597	-0.0002
20	11	9	19	10	9	773.8588	-0.0001
21	11	10	20	10	10	774.3558	0.0003
25	11	15	25	10	15	763.0388	0.0003
26	11	16	26	10	16	762.9936	0.0005
27	11	17	27	10	17	762.9464	0.0003
28	11	18	28	10	18	762.8969	0.0002
29	11	19	29	10	19	762.8448	0.0004
30	11	20	30	10	20	762.7906	0.0002
31	11	21	31	10	21	762.7336	0.0003
32	11	22	32	10	22	762.6740	0.0005
33	11	23	33	10	23	762.6121	0.0004
36	11	26	36	10	26	762.4089	0.0009
12	12	1	12	11	1	764.8907	0.0014
13	12	1	12	11	1	771.7741	0.0015
13	12	2	13	11	2	764.8717	0.0003
14	12	2	13	11	2	772.2833	0.0019
14	12	3	14	11	3	764.8500	0.0003
15	12	3	14	11	3	772.7917	0.0015
15	12	4	15	11	4	764.8265	0.0005
16	12	5	16	11	5	764.8011	0.0008
17	12	6	17	11	6	764.7749	0.0003
17	12	5	16	11	5	773.8037	0.0005
18	12	7	18	11	7	764.7470	-0.0003
18	12	6	17	11	6	774.3071	0.0001
19	12	8	19	11	8	764.7166	-0.0002
20	12	9	20	11	9	764.6841	0.0003
21	12	10	22	11	11	762.9621	0.0012
21	12	10	21	11	10	764.6511	-0.0006
22	12	11	22	11	11	764.6147	0.0001
23	12	12	23	11	12	764.5786	-0.0015
24	12	13	24	11	13	764.5383	-0.0007
25	12	14	25	11	14	764.4967	-0.0006
26	12	15	26	11	15	764.4529	-0.0004
27	12	16	27	11	16	764.4079	-0.0009
28	12	17	28	11	17	764.3602	-0.0009
29	12	18	29	11	18	764.3104	-0.0009
30	12	19	30	11	19	764.2587	-0.0012
13	13	0	12	12	0	773.2278	-0.0010
15	13	2	14	12	2	774.2456	-0.0010
23	13	10	24	12	12	753.2830	0.0013
34	13	22	34	12	22	765.5013	-0.0013
35	13	23	35	12	23	765.4399	-0.0008
36	13	24	36	12	24	765.3764	-0.0006
37	13	25	37	12	25	765.3100	0.0003
38	13	26	38	12	26	765.2426	-0.0002
39	13	27	39	12	27	765.1725	-0.0004
40	13	28	40	12	28	765.0994	0.0000
42	13	30	42	12	30	764.9463	0.0000
43	13	31	43	12	31	764.8659	0.0000
47	13	35	47	12	35	764.5166	0.0000
48	13	36	48	12	36	764.4226	-0.0005
49	13	37	49	12	37	764.3254	-0.0009
50	13	38	50	12	38	764.2239	-0.0001
14	14	1	14	13	1	767.7557	0.0009
15	14	2	15	13	2	767.7332	0.0005
16	14	3	16	13	3	767.7101	-0.0010
17	14	4	17	13	4	767.6864	-0.0014
18	14	5	18	13	5	767.6558	-0.0006
19	14	6	19	13	6	767.6276	-0.0019
20	14	7	20	13	7	767.5960	-0.0014
21	14	8	21	13	8	767.5633	-0.0015
22	14	9	22	13	9	767.5292	-0.0019
23	14	10	23	13	10	767.4936	-0.0026
24	14	11	24	13	11	767.4545	-0.0015
25	14	12	25	13	12	767.4146	-0.0014

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^r representation in the A reduction was used [20].

The rovibrational parameters obtained in this way, together with the corresponding ground-state constants [5] wich 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 Δ_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 ± 0.0004) 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 ${}^RQ_8$, the lowest complete one on the left is ${}^PQ_9$. 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 $\varkappa = -0.98$ 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 ($\varkappa = -0.847$) 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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