

High resolution infrared spectra of the linear carbon cluster C₇: The ν_4 stretching fundamental band and associated hot bands

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High resolution infrared spectra of the ν_4 fundamental antisymmetric stretching mode and associated hot bands of the linear carbon cluster C₇ were recorded using a tunable diode laser spectrometer in the frequency range of 2135–2141 cm⁻¹. Spectra of the ν_4 fundamental, $\nu_4 + \nu_{11} - \nu_{11}$, $\nu_4 + 2\nu_{11} - 2\nu_{11}$, and $\nu_4 + \nu_8 - \nu_8$ bands have been analyzed and are compared to recent experimental results and high level *ab initio* calculations. In particular, the presented results give experimental evidence for the rigidity of C₇ and confirm theoretical predictions of a rather regular chain molecule, similar to the cases of C₄, C₅, and C₉. For the two energetically low-lying bending modes, ν_8 and ν_{11} , the rotational constants differ by less than 0.2%, from the ground state value, $B_0 = 0.030\,624\,4(28)$ cm⁻¹, in good agreement with the recent calculations by Botschwina [Chem. Phys. Lett. **354**, 148 (2002)]. From the hot band analysis and the ℓ -type doubling constant q , experimental values for the band origins of the ν_8 and ν_{11} fundamentals have been derived. © 2007 American Institute of Physics. [DOI: 10.1063/1.2749520]

I. INTRODUCTION

Small carbon molecules are believed to play a dominant role in interstellar chemistry. Even some bare carbon clusters have been identified in diverse sources ranging from comets and stellar objects to diffuse interstellar clouds. The linear species C₂ (e.g., Ref. 2), C₃ (e.g., Refs. 3–7), and C₅ (Ref. 8) have been detected so far either through their rovibrational mid- to far-infrared or rovibronic optical spectra.

Apart from the mere astrophysical relevance, pure carbon clusters are still of great interest for molecular spectroscopists even after many years of research on their structures, infrared frequencies, and electronic properties. Thanks to rotationally resolved infrared spectra of C₃–C₁₀ and C₁₃,^{9–11} it is now commonly accepted that small carbon clusters appear as linear chains, although some important aspects, e.g., their bending dynamics, are still not well understood.

Ab initio calculations on various levels predict the lowest bending modes for the C_n chains with $n=3$ –10 between 0.5 and 5 THz (e.g., Refs. 9, 12, and 13). So far, C₃ is the only pure carbon chain for which direct measurements on a bending mode have been performed.^{14,15} The lack of suitable radiation sources in the relevant frequency range is the main reason for the sparse number of data. However, infrared measurements of hot band transitions arising from the lowest bending modes can be used to obtain molecular parameters on the pure bending modes, such as rotational ℓ -type doubling and centrifugal distortion constants. Over the last two decades, measurements of hot band transitions have been performed for the linear chains C₃, C₄, C₅, C₇, and C₉.^{9,16} C₃ is known to be a quasilinear molecule with an extraordinary shallow bending potential. Both experimental and theoretical investigations point at a remarkable floppiness of the chain

(e.g., Refs. 17–19). On the other hand, the longer chain molecules C₄, C₅, and C₉ appear to be quite rigid, a finding which is confirmed by quantum mechanical calculations.⁹

In 1990, Heath *et al.*²⁰ reported on the first detection of C₇ in the gas phase. This pioneering work was followed by a hot band analysis of C₇ by the same group. Heath *et al.*²¹ measured transitions of the ν_4 stretching mode and hot bands associated with the ν_{11} lowest bending mode. The derived rotational constant for the lowest bending mode differs by roughly 9% from their ground state value $B_0 = 0.030\,615(15)$ cm⁻¹, which the authors explained by large amplitude bending motion of an extremely floppy carbon chain. Furthermore, the unusually large and negative distortion constant for the ground state was supposed to arise from Coriolis interactions between the ground state and excited levels of the ν_{11} mode.

On the contrary, high level coupled-cluster calculations performed by Botschwina¹ showed no evidence of floppiness for the C₇ chain. Neither the negative large D constant nor the dramatic change in the rotational constant due to the excitation of the first bending level could be confirmed in these calculations.

The large discrepancy of theory and experiment showed that further measurements were on strong demand. It is the purpose of this work to study the rigidity of the C₇ chain and to prove or disprove the hypothesis of its unusual floppiness by means of high resolution spectroscopy.

II. EXPERIMENTAL PROCEDURE

The spectra presented here were recorded with the Cologne Carbon Cluster Experiment, which consists of a high resolution infrared tunable diode laser spectrometer com-

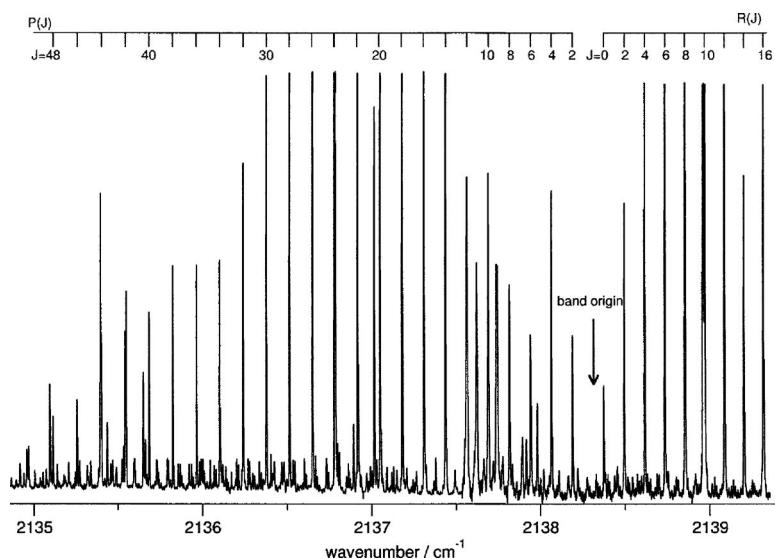


FIG. 1. The infrared spectrum of C_7 near 2138 cm^{-1} observed in the present study is reproduced; the strong series of lines with $\sim 4B$ spacing belongs to the fundamental ν_4 band.

bined with an UV laser ablation source. Carbon clusters are produced when a pulsed excimer laser beam at 248 nm is focused onto a rotating graphite rod. The ablated carbon is diluted in a pulse of helium gas at a backing pressure of 10–20 bars forming small carbon clusters in an adiabatically expanding supersonic jet. The background pressure in the vacuum chamber is kept below 0.1 mbar by a two stage root pump. The jet is probed 10 mm downstream by the light of a tunable IR diode laser cooled by liquid N_2 . The sensitivity of the spectrometer is enhanced by multipass optics using a Herriott-type cell with 48 passes through the jet. The probing beam is focused onto a liquid N_2 cooled InSb detector, and the signal is amplified by a fast ac-coupled amplifier, which allows the time resolved detection of the weak signals employing a pair of gated boxcar integrators. Part of the IR laser beam is used for frequency calibration; the spectrum of N_2O and the fringe spectrum of a germanium étalon ($FSR \approx 0.016\text{ cm}^{-1}$) were recorded simultaneously. For all measurements, the calibration accuracy is better than 0.002 cm^{-1} .

To cover the spectral range from 2134.9 to 2139.3 cm^{-1} and from 2141.1 to 2141.7 cm^{-1} , two high power, single mode diode lasers (Laser Components) were used and most of the P branch, the band origin, and part of the R branch of the ν_4 fundamental mode of C_7 were recorded.

III. SPECTRA AND ANALYSIS

Figure 1 shows the P -branch and the low J R -branch transitions of the ν_4 antisymmetric stretching mode of C_7 .

A number of weaker lines belong to hot bands of the ν_4 mode associated with low-lying bending vibrations. Furthermore, two strong transitions of the $2\nu_2 + \nu_3$ combination band of C_3 and some lines of unknown origin appear in the presented frequency region.

In the following, the analysis of the ν_4 fundamental and three associated hot bands of ν_8 ($\nu_8=1$) and ν_{11} ($\nu_{11}=1, 2$) is described in detail.

A. The ν_4 fundamental band

The ν_4 vibrational transition consists of well resolved P and R branches with a clearly visible center gap, which indicates the band origin. Due to the nuclear spin statistics of a Σ_g^+ centrosymmetric molecule ($D_{\infty h}$) with identical nuclei of spin zero, all odd numbered J levels of the ground state are missing. Thus, adjacent lines of the fundamental ν_4 stretching mode show a spacing of four times the rotational constant B and a $6B$ spacing of the lowest P - and R -branch transitions, $P(2)$ and $R(0)$.

P -branch transitions up to $J=50$ and R -branch transitions up to $J=62$ have been recorded. In total, 41 lines have been assigned and the data set has been supplemented with data of Heath *et al.*²¹ for those spectral regions where frequency coverage of our diodes was incomplete. Among them, 34 lines were measured in both studies and their line positions agree within experimental errors.

The data were fitted to a standard Hamiltonian for $^1\Sigma$ ground state molecules, employing a least squares fit program LINX for linear molecules.²² For transitions measured in this work, the calibration accuracy allows for a frequency uncertainty of 0.001 cm^{-1} in most cases, and data taken from Heath *et al.* have uncertainties of 0.002 cm^{-1} .

Observed frequencies and deviations from calculated values are given in Table I. The standard deviation of the fit was found to be 0.0012 cm^{-1} . The obtained molecular parameters are given in Table II. The band origin and the rotational constants B'' and B' agree very well with the values given by Heath *et al.*, although no quartic or sextic centrifugal distortion parameters were needed to fit all measured lines within 1σ error bars. When D'' and D' are included they have positive sign and are one order of magnitude smaller than those given by Heath *et al.*

In Table II the predicted B'' and B' constants are also listed for comparison, which were derived from the equilibrium value B_e and vibration rotation coupling constants α_v , given in Ref. 1 using $B_v = B_e - \sum_i \alpha_i (v_i + \frac{d_i}{2})$.

The small change in the rotational constant upon excitation of the ν_4 fundamental and the small upper value for the

TABLE I. Observed line positions in cm⁻¹ for the ν_4 antisymmetric stretching fundamental band of C₇. (Lines marked with an asterisk are taken from Ref. 21. The value in parentheses is a calculated one.)

J	$R(J)$	Obs.-Calc. ($\times 10^{-3}$)	$P(J)$	Obs.-Calc. ($\times 10^{-3}$)
0	2138.375 56	0.01		
2	2138.496 71	-0.19	2138.191 13	-0.68
4	2138.617 23	-0.09	2138.067 03	-1.13
6	2138.736 32	-0.50	2137.944 70	1.12
8	2138.854 73	-0.67	2137.818 19	0.10
10	2138.972 09	-0.96	2137.692 26	0.59
12	2139.088 96	-0.82	2137.565 50	1.17
14	2139.204 76	-0.83	2137.437 30	1.24
16	2139.319 45	-1.03	2137.307 66	0.78
18	2139.435 80*	1.36	2137.178 24	1.47
20	2139.546 90*	-0.59	2137.046 66	0.92
22	2139.660 20*	0.60	2136.913 65	-0.13
24	2139.771 80*	1.00	2136.778 59	-2.32
26	(2139.881 08)	calc.	2136.646 10	-1.01
28	2139.992 20*	1.77	2136.511 92	-0.47
30	2140.098 90*	0.04	2136.378 00	1.26
32	2140.211 00*	4.64	2136.240 18	0.00
34	2140.313 70*	0.75	2136.102 47	-0.22
36	2140.421 60*	2.99	2135.963 61	-0.67
38	2140.527 80*	4.45	2135.824 60	-0.34
40	2140.631 30*	4.14	2135.684 17	-0.52
42	2140.732 00*	1.94	2135.544 73	1.22
44	2140.832 50*	0.47	2135.402 50	1.09
46	2140.934 20*	1.12	2135.258 12	-0.26
48	2141.032 70*	-0.50	2135.114 18	-0.25
50	2141.131 18	-1.23	2134.968 25	-1.32
52	2141.229 95	-0.74	2134.822 90*	-0.87
54	2141.327 13	-0.92	2134.677 60*	0.54
56	2141.423 00	-1.48	2134.528 80*	-0.62
58	2141.517 72	-2.27	2134.380 40*	-0.46
60	2141.612 99	-1.60	2134.233 70*	2.32
62	2141.706 62	-1.63	2134.084 40*	3.42
64			2133.929 30*	-0.35

centrifugal distortion constant D clearly point to a more rigid than floppy C₇ molecule. This finding was confirmed in the hot band analysis.

B. Hot band analysis

Several hot band transitions have been assigned to weak lines in the spectral range of the ν_4 fundamental. Part of the hot bands is shown in Fig. 2. Three groups of transitions with half the spacing of lines in the fundamental band are shown, which most likely arise from the lowest and the second lowest bending modes of C₇, denoted ν_{11} and ν_8 . Figure 3 gives an overview of the energy levels involved and illustrates possible hot band transitions.

The ℓ -type interaction splits the energy levels of bending modes with $\ell=1, 2, \dots$ into two components of e and f symmetries. For the $\nu_{11}=1$ state of C₇, which is of Π_u symmetry, only odd J levels are allowed for the e component and even J levels for the f component, due to the nuclear spin statistics for Bosons. On the contrary, for the $\nu_8=1(\Pi_g)$ and $\nu_{11}=2(\Delta_g)$ states, even J levels are allowed for the e component and odd J levels for the f component. Adjacent lines in

TABLE II. Molecular constants in cm⁻¹ for the ν_4 antisymmetric stretching fundamental of C₇ in comparison with the experimental results by Heath *et al.* (Ref. 21) and the predicted values by Botschwina (Ref. 1). [The values for B'' and B' predicted by *ab initio* calculations are derived from B_e and α_i values (Ref. 1), and D'' is assumed to be equal to D_e .]

Parameter	This work	Heath <i>et al.</i> (Ref. 21)	<i>Ab initio</i> (Ref. 1)
ν_4	2138.314 42(20)	2138.315 2(5)	2203.8
B''	0.030 624 4(28)	0.030 615(15)	0.030 65
D'' ($\times 10^{-8}$)		-2.4(9)	0.033 7
H'' ($\times 10^{-12}$)		-5.6(15)	
B'	0.030 509 1(27)	0.030 497(16)	0.030 54
D' ($\times 10^{-8}$)		-2.6(10)	
H' ($\times 10^{-12}$)		-6.1(17)	

the P - and R -branch spectra are thus of alternating e/f symmetry with slightly staggered $2B$ spacings. The staggering is most prominent for $\ell=1$ states, which has been used for assignment of bands.

1. The $\nu_4 + \nu_{11} - \nu_{11}$, $\ell=1$ hot band

A total of 52 lines has been assigned to the $\nu_4 + \nu_{11} - \nu_{11}$ band. Adjacent lines occur in a $2B$ distance with a notable staggering. Since this band exhibits the most pronounced staggering, it must arise from the $\nu_{11}=1$ vibration, which is lowest in energy.

A least squares fit analysis routine (LINX) was used to simultaneously fit transitions of e and f symmetries to energy levels expressed by

$$E = \left(v + \frac{1}{2}\right)\nu + B_v[J(J+1) - \ell^2] - D_v[J(J+1) - \ell^2]^2 \pm \frac{1}{2}q_v J(J+1). \quad (1)$$

Although blurred by a couple of other lines, the band origin could be determined due to the significant shape of the beginning R branch (see Fig. 4).

All 52 lines of the $\nu_{11}=1$ hot band and their assignment to quantum numbers J are listed in Table III along with their residuals. Molecular parameters resulting from the fit are given in Table IV. Including centrifugal distortion constants did not improve the quality of the fit. The standard deviation of the fit was 0.702×10^{-3} cm⁻¹.

The band origin at 2137.738 56(16) cm⁻¹ is shifted against the fundamental band by roughly 0.58 cm⁻¹ toward lower frequencies. The derived B_{11} value of 0.030 675 9(38) cm⁻¹ is only 0.16% larger than the ground state value B_0 and 0.11% smaller than the calculated value for B_{11} derived from B_e and the corresponding vibrational correction terms α_i given in Ref. 1.

2. The $\nu_4 + \nu_8 - \nu_8$, $\ell=1$ hot band

A second band with slightly lower intensity was found presenting clearly staggered $2B$ spacing. The transitions stem from an $\ell=1$ bending mode and were assigned to the hot band arising from the $\nu_8=1$ vibration.

A total of 49 lines has been assigned to the $\nu_4 + \nu_8 - \nu_8$ band. In this case, the band origin could not be identified and the J assignment of lines remained uncertain by a few inte-

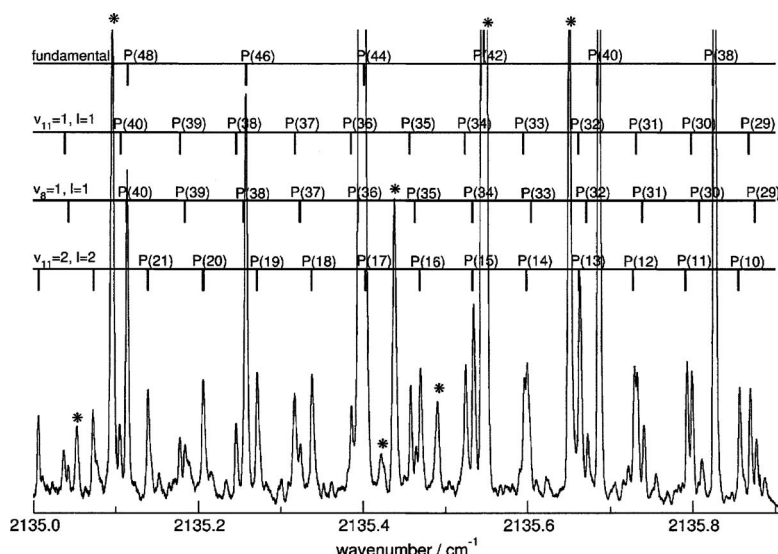


FIG. 2. A part of the spectrum of C_7 is displayed in an expanded scale; the assignments made in the present study for the ν_4 fundamental and the three identified hot bands are indicated. Lines labeled with asterisks are unidentified ones.

gers. For final assignment, we followed the approach of Moazzen-Ahmadi *et al.* which was applied in the analysis of hot bands of linear C_4 and C_5 .^{23,24} Here, the J assignment leading to the smallest deviation of the rotational constants from the ground state value was chosen, which is based on the assumption of a nearly rigid rotor. Given the results on the $\nu_{11}=1$ hot band, this assumption is justified.

Observed line positions and their residuals are given in Table V. The fit was performed using Eq. (1), which led to the molecular constants listed in Table VI. The standard deviation of the fit was $0.768 \times 10^{-3} \text{ cm}^{-1}$. Again, D'' and D' proved to be not significant as expected in the case of a rigid molecule.

Compared to constants for the $\nu_{11}=1$ hot band, the value for the rotational constant B_8 of $0.030\,669\,7(36) \text{ cm}^{-1}$ is slightly smaller than B_{11} but still larger (0.14%) than the ground state value B_0 . This finding is in good agreement with the calculated B_8 value.¹ The experimental value for B_8 is only 0.13% smaller than the calculated one.

The band center at $2137.749\,32(18) \text{ cm}^{-1}$ is shifted compared to the fundamental band by 0.56 cm^{-1} to lower frequencies, which is quite close to the origin of the $\nu_{11}=1$ hot band. A similar behavior was reported by Moazzen-Ahmadi

*et al.*²⁶ for hot bands of C_4 , where the band centers of the hot bands originating from the two lowest bendings are shifted by 0.64 and 0.6 cm^{-1} , respectively.

3. The $\nu_4+2\nu_{11}-2\nu_{11}$, $\ell=2$ hot band

Another hot band with a $2B$ distance of adjacent lines has been extracted from the measurements. The band intensity is weaker than that found for the $\nu_{11}=1$ hot band but comparable to the $\nu_8=1$ hot band, which lies energetically close to the $\nu_{11}=2$ state (see Fig. 3). A staggering of lines is not observable. Both the band intensity and the absence of line staggering indicate that these lines belong to a hot band arising from a $\nu=2$ state, i.e., $\nu_4+2\nu_{11}-2\nu_{11}$, $\ell=2$ band.

The $\nu_{11}=2$ bending level splits into a Σ_g and a Δ_g component corresponding to $\ell=0$ and $\ell=2$ vibrational angular momenta. The Δ state consists of an e and an f sublevel with either even or odd J quantum states, while transitions arising from an $\ell=0$ level have only even-numbered J levels with a $4B$ spacing of successive lines.

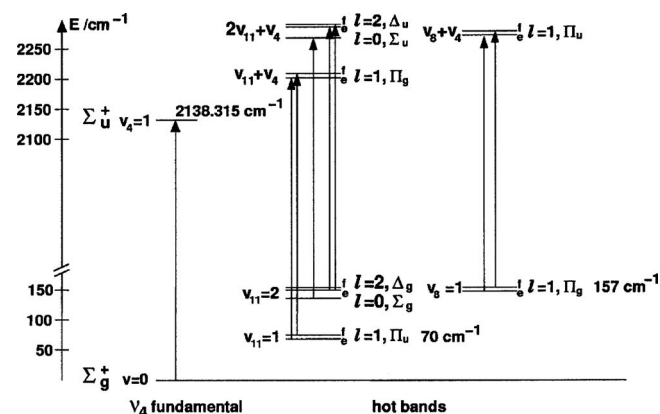


FIG. 3. The energy level diagram for the C_7 is schematically illustrated for the low energy region. The energies of levels, for which energy term values are indicated, are predicted by the *ab initio* calculation (Ref. 1).

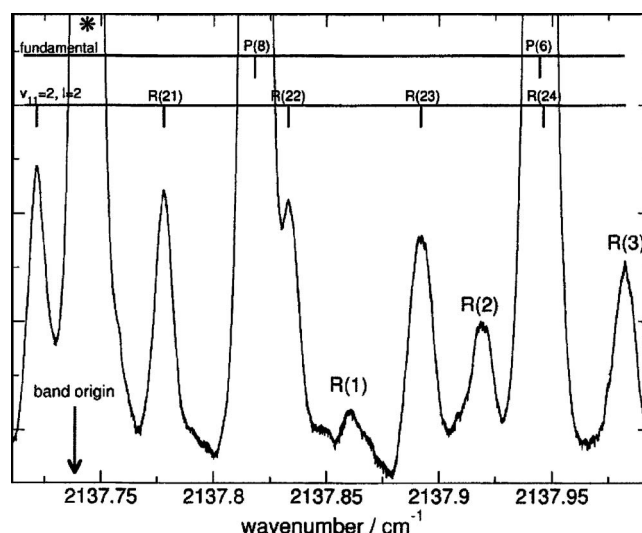


FIG. 4. A part of the observed spectrum is reproduced for the head of the R branch of the $\nu_4+\nu_{11}-\nu_{11}$ band. The observed spectrum indicates a typical pattern expected near the band origin.

TABLE III. Observed line positions in cm⁻¹ for the $\nu_4 + \nu_{11} - \nu_{11}$ hot band of C₇. (Values in parentheses are calculated ones.)

<i>J</i>	<i>R</i> (<i>J</i>)	Obs.-Calc. (×10 ⁻³)	<i>P</i> (<i>J</i>)	Obs.-Calc. (×10 ⁻³)
1	2137.860 51	-0.11		
2	2137.919 15	-2.33	(2137.615 67)	^a
3	2137.982 29	0.64	(2137.554 05)	^a
4	(2138.042 21)	^a	2137.493 53	1.78
5	(2138.101 78)	^a	(2137.429 82)	^a
6	(2138.162 03)	^a	2137.367 40	0.47
7	2138.220 92	-0.07	(2137.304 68)	^a
8	2138.280 61	-0.34	2137.241 64	0.44
9	2138.339 51	0.22	(2137.178 64)	^a
10	2138.399 01	0.06	2137.112 90	-1.66
11	2138.454 09	-2.59	2137.052 21	0.53
12	2138.515 86	-0.19	2136.986 94	-0.07
13	2138.573 45	0.30	2136.923 21	-0.59
14	2138.632 52	0.28	2136.858 74	0.19
15	2138.689 27	0.55	2136.794 50	-0.52
16	2138.747 91	0.39	2136.728 68	-0.50
17	2138.802 07	-1.30	2136.664 75	-0.58
18	(2138.861 89)	^a	2136.599 15	0.25
19	2138.916 08	-1.03	2136.532 13	-2.59
20	(2138.975 35)	^a	2136.467 62	-0.10
21	2139.030 36	0.42	2136.404 26	1.06
22	(2139.087 90)	^a	2136.336 26	0.64
23	2139.141 98	0.12	2136.270 33	-0.45
24	(2139.199 54)	^a	2136.202 36	-0.26
25	2139.253 39	0.52	2136.136 60	-0.84
26	(2139.310 28)	^a	2136.069 50	0.79
27			2136.003 02	-0.16
28			2135.933 31	-0.58
29			2135.867 73	-0.29
30			2135.797 32	-0.84
31			2135.732 73	0.79
32			2135.661 31	-0.21
33			2135.596 27	1.31
34			2135.524 81	0.84
35			2135.457 95	0.89
36			2135.386 35	0.84
37			2135.317 55	-0.70
38			2135.246 02	-0.12
39			2135.177 73	-0.80
40			2135.105 10	-0.77

^aThese lines are blended with fundamental or unidentified transitions.TABLE IV. Molecular constant in cm⁻¹ for the $\nu_4 + \nu_{11} - \nu_{11}$ hot band of C₇ in comparison with some literature values. [*Ab initio* *B''* and *B'* are derived from *B_e* and α_i values calculated by Botschwina (Ref. 1). Constants reported by Heath *et al.* (Ref. 21) are given for comparison.]

Parameter	This work	Heath <i>et al.</i> (Ref. 21)	<i>Ab initio</i> (Ref. 1)
ν	2137.738 56(16)	2136.068 7(9)	
<i>B'</i>	0.030 675 9(38)	0.033 583(40)	0.030 72
<i>q''</i> (×10 ⁻⁵)	3.71(76)		2.68
<i>B''</i>	0.030 562 2(41)	0.033 490(33)	0.030 61
<i>q'</i> (×10 ⁻⁵)	3.74(80)		
<i>B''/B₀</i>	0.16%	9.3%	0.23%

TABLE V. Observed line positions in cm⁻¹ for the $\nu_4 + \nu_8 - \nu_8$ hot band of C₇. (Values in parentheses are calculated ones.)

<i>J</i>	<i>R</i> (<i>J</i>)	Obs.-Calc. (×10 ⁻³)	<i>R</i> (<i>J</i>)	Obs.-Calc. (×10 ⁻³)
1	(2137.871 64)	^a		
2	(2137.932 15)	^a	(2137.626 75)	^a
3	(2137.992 73)	^a	(2137.564 83)	^a
4	(2138.052 66)	^a	2137.504 11	1.34
5	2138.111 40	-1.33	(2137.440 48)	^a
6	(2138.172 23)	^a	2137.378 17	0.13
7	2138.231 82	-0.15	(2137.315 19)	^a
8	2138.291 12	0.37	2137.253 06	0.69
9	2138.350 25	-0.03	2137.189 01	0.23
10	2138.409 60	1.13	2137.124 90	-0.87
11	2138.467 11	-0.55	2137.062 05	0.42
12	2138.525 56	0.31	2136.999 16	0.93
13	2138.584 26	0.15	2136.933 70	0.15
14	2138.641 56	0.46	2136.868 03	-1.73
15	2138.700 88	1.25	2136.805 21	0.67
16	2138.756 06	0.04	2136.739 68	-0.68
17	2138.813 71	-0.50	2136.673 50	-1.10
18	2138.869 72	-0.28	2136.608 73	-1.28
19	2138.927 34	-0.53	2136.542 53	-1.20
20	2138.982 05	-1.00	(2136.478 70)	^a
21	2139.040 69	0.10	2136.413 59	1.66
22	(2139.094 98)	^a	2136.347 11	0.58
23	2139.151 80	-0.59	2136.279 10	-0.10
24	(2139.206 09)	^a	2136.213 03	-0.35
25	2139.263 95	0.70	2136.144 89	-0.65
26	(2139.316 27)	^a	2136.080 11	0.81
27			2136.011 99	1.04
28			2135.944 02	-0.26
29			2135.874 38	-1.05
30			2135.808 37	0.04
31			2135.739 00	0.03
32			2135.670 64	-0.81
33			(2135.601 63)	^a
34			2135.534 61	0.98
35			2135.464 11	0.83
36			(2135.394 30)	^a
37			2135.324 41	0.38
38			(2135.254 53)	^a
39			2135.183 90	0.04
40			(2135.113 81)	^a
41			2135.042 31	-0.44

^aThese lines are blended with fundamental or unidentified transitions.TABLE VI. Molecular constants in cm⁻¹ for the $\nu_4 + \nu_8 - \nu_8$ hot band of C₇ in comparison with predicted values. [*B''* and *B'* predicted by *ab initio* calculations are derived from *B_e* and α_i values of Botschwina (Ref. 1)].

Parameter	This work	<i>Ab initio</i> (Ref. 1)
ν	2137.749 32(18)	
<i>B''</i>	0.030 669 7(36)	0.030 71
<i>q''</i> (×10 ⁻⁵)	2.49(69)	1.23
<i>B'</i>	0.030 553 1(38)	0.030 60
<i>q'</i> (×10 ⁻⁵)	2.54(73)	
<i>B''/B₀</i>	0.14%	0.20%

TABLE VII. Observed line positions in cm^{-1} for the $\nu_4+2\nu_{11}-2\nu_{11}$ hot band of C_7 . (Values in parentheses are calculated ones.)

J	$R(J)$	Obs.–Calc. ($\times 10^{-3}$)	$P(J)$	Obs.–Calc. ($\times 10^{-3}$)
2	2136.664 75	–0.26		
3	2136.728 68	3.00	2136.295 94	–0.18
4	(2136.786 12)	^a	2136.234 01	0.18
5	2136.846 63	0.30	2136.170 63	–0.67
6	(2136.906 31)	^a	(2136.108 55)	^a
7	2136.965 78	–0.27	2136.045 05	–0.51
8	2137.026 75	1.19	2135.982 17	–0.17
9	2137.084 02	–0.82	2135.918 20	–0.69
10	2137.144 56	0.67	2135.854 79	–0.42
11	2137.203 65	0.94	2135.790 84	–0.45
12	2137.262 11	0.81	2135.727 27	0.12
13	2137.319 38	–0.27	2135.661 31	–1.46
14	2137.378 17	0.39	2135.599 66	1.50
15	(2137.435 67)	^a	2135.534 61	1.29
16	2137.493 53	0.20	2135.469 90	1.65
17	2137.551 71	0.96	(2135.402 94)	^a
18	2137.608 42	0.47	2135.338 52	1.11
19	2137.665 65	0.73	2135.271 84	0.20
20	2137.721 42	–0.23	2135.206 06	0.42
21	2137.777 88	–0.27	2135.139 41	0.00
22	2137.833 04	–1.38	2135.072 78	–0.17
23	2137.891 73	1.27	2135.005 81	–0.45
24	(2137.946 27)	^a	2134.938 80	–0.53
25	2138.000 84	–1.00		
26	(2138.057 18)	^a		
27	(2138.112 30)	^a		
28	2138.164 90	–2.28		
29	2138.220 92	–0.91		
30	2138.275 69	–0.55		
31	2138.329 68	–0.75		
32	2138.383 73	–0.65		
33	2138.437 87	–0.23		
34	(2138.491 59)	^a		
35	2138.545 29	0.44		
36	2138.597 47	–0.41		
37	2138.651 01	0.34		
38	2138.700 88	–2.36		
39	2138.756 06	0.49		
40	2138.807 28	–0.39		
41	(2138.859 54)	^a		
42	2138.910 50	–0.68		
43	(2138.962 58)	^a		
44	2139.015 27	1.51		
45	2139.065 02	0.44		
46	2139.115 68	0.27		
47	2139.165 96	0.07		
48	(2139.216 14)	^a		
49	(2139.266 15)	^a		

^aThese lines are blended with fundamental or unidentified transitions.

As there was barely a staggering to be seen, the lines were assigned to the Δ component of the $\nu_{11}=2$ state. A fit of all transitions to a hot band with ($\nu=2$, $\ell=2$) was performed and only the band origin ν and the rotational constants for lower and upper state, B'' and B' , were used in the final fit. Table VII contains the 57 observed transition frequencies and their deviations from the calculated values. The obtained molecular parameters are given in Table VIII. The standard

TABLE VIII. Molecular constants in cm^{-1} for the $\nu_4+2\nu_{11}-2\nu_{11}$, $\ell=2$ hot band of C_7 in comparison with some literature values. [*Ab initio* B'' and B' are derived from B_e and α_i values calculated by Botschwina (Ref. 1). Constants derived by Heath *et al.* (Ref. 21) for the $\ell=0$ band are given for comparison.]

Parameter	This work	Heath <i>et al.</i> ($\ell=0$) (Ref. 21)	<i>Ab initio</i> (Ref. 1)
ν	2136.481 14(14)	2133.802 0(29)	
B''	0.030 798 8(37)	0.037 48(30)	0.0307 8
B'	0.030 683 0(35)	0.037 36(28)	0.0307 3
B''/B_0	0.56%	22.0%	0.42%

deviation of the fit was $0.763 \times 10^{-3} \text{ cm}^{-1}$.

The lower state rotational constant $B'' = 0.030 798 8(37) \text{ cm}^{-1}$ differs from the calculated value by less than 0.1%. Including centrifugal distortion constants yielded D values of the order of 10^{-5} cm^{-1} with large uncertainties of more than 70%, which were thus omitted from the fit. The shift of the band origin amounts to 1.8 cm^{-1} , which is larger than expected and will be discussed in the following section.

It is interesting to note that transitions of the $\ell=0$ component of the $\nu_{11}=2$ hot band cannot be found in the spectra. An expected band with lines of $4B$ spacing and comparable intensity to the $\ell=2$ component is completely missing.

IV. DISCUSSION

In general, it is not easy to find the band origins of parallel bands of a linear molecule because of the lack of Q -branch transitions. In the present study the origin of the fundamental band is most secure by observing the band gap of $6B$ at the center. The origin of the $\nu_{11}=1$ hot band is supported by observing the R -branch transitions for the lowest J values. For the ($\nu_{11}=2$, $\ell=2$) hot band, we expect a very large band gap ($12B$) at the center, and therefore there is no other choice of assignment than the present one.

Contrarily, the band center of the $\nu_8=1$ hot band is not certain; the rotational assignment may be shifted at most by -4 and $+2$ in m , which is $J+1$ for R and $-J$ for P . If we shift the m assignments by n from the present one, the band origin and the lower state rotational constants are revised as given in Eqs. (3) and (6) in Ref. 27,

$$\nu_n = \nu_0 - (B' + B'')n + (B' - B'')n^2, \quad (2)$$

$$B''_n = B'' - (B' - B'')n, \quad (3)$$

where the parameters for the new assignment are indicated with subscript n . If $n < 0$, the B''_n value for the $\nu_8=1$ hot band is smaller than the ground state rotational constant, which is not realistic for a bending excited state. If $n > 0$, the B''_n value of this band is larger than the rotational constant of the lowest bending vibrational state, $\nu_{11}=1$, which is not reasonable. Thus, also for this hot band, the present assignment is the only one possible.

The constants obtained on the basis of the present assignments strongly support the results derived by Botschwina stating that the C_7 chain molecule is fairly rigid. Neither Coriolis interaction between the ground state and

excited ν_{11} levels nor large amplitude bending motion could be confirmed. All derived constants of both the fundamental and hot bands are by no means unusual and lie well within the scope of expectations. From the experimental point of view, it is desirable to obtain the quasilinearity parameter γ (Ref. 28) for a discussion on the rigidity of this molecule. In the present stage, however, we have not enough information of the energies for the ($\nu_{11}=2$, $\ell=0$) and ($\nu_{11}=2$, $\ell=2$) which is required to determine the γ value.

The rotational constants for the two energetically lowest bending modes, ν_{11} and ν_8 , differ by less than 0.2% from the ground state value, which is in good agreement to the comparable cases C₄, C₅, and C₉. For C₄, the analysis by Moazzen-Ahmadi *et al.* yielded a change in the rotational constant of 0.5% for the lowest bending and 0.4% for the second lowest bending with respect to the ground state value.²⁶ A similar value of 0.4% for both bending modes was derived by the same authors in the case of C₅.²⁴ Finally, for C₉, Van Orden *et al.*²⁵ derived 0.2% and 0.3% for the *e* and *f* bands of the hot band arising from the lowest bending vibration.

The band origin for the ($\nu_{11}=2$, $\ell=2$) hot band of C₇ is 1.22 cm⁻¹ below the origin of the $\nu_{11}=1$ hot band, which itself is 0.58 cm⁻¹ below the origin of the ν_4 fundamental. Thus, the shift increases nonlinearly. For C₄ and C₅, the frequency shifts between the band origins of the fundamental and the hot bands arising from the *n*th bending level grow quite linearly with *n* (*n*=1, 2).¹⁶ In both cases, the shifts for the hot bands including doubly excited bending levels amount to two times that of hot bands from the singly excited levels. For C₉, the shift increases more than linearly,²⁵ that is, with a factor of roughly 2.6 instead of 2. The corresponding factor for C₇ is comparably large and roughly 3.1. The identification of $\nu_{11}=2$ hot band is further confirmed by the band intensities. According to thermal population of energy levels (see Fig. 3), in general, comparable intensities were found for the $\nu_{11}=2$ and $\nu_8=1$ hot bands and significantly stronger lines for the $\nu_{11}=1$ band.

In the C₇ spectra presented here, no suitable features of the ($\nu_{11}=2$, $\ell=0$) hot band were found. The most likely explanation for the missing ($\nu_{11}=2$, $\ell=0$) band of C₇ would be that these transitions are blended by the strong fundamental ones of the same 4*B* pattern. An earlier detection of the $\ell=0$ band by Heath *et al.*,²¹ who assigned nine lines to the *R* branch of the ($\nu_{11}=2$, $\ell=0$) band, has not been confirmed.

The q values for the $\nu_{11}=1$ and $\nu_8=1$ hot bands allow for estimation of the wave numbers of the pure bending modes by using the approximation $\nu=f_q B_0^2/q$. Assuming that the bonding character for C₇ is comparable to other linear carbon molecules, f_q was chosen to be 2.15(5), which was derived from the analysis of C₃S₂ (Ref. 29) and has been used as reasonable value for C₅ (Ref. 24) and C₉.²⁵ The vibrational wave numbers were derived to be $\nu_{11}=54(11)$ cm⁻¹ and $\nu_8=81(23)$ cm⁻¹. Despite the rather large uncertainties, both results agree fairly well, considering discrepancies about three times the standard error, with the calculated values of 70 and 156 cm⁻¹ by Botschwina.¹ Of course, the values derived in the present study heavily depend on a proper choice for f_q , which, in turn, requires accurate knowledge of the

molecule itself. However, the more severe question concerns the quality of these predictions in terms of a laboratory or any astrophysical detection. The uncertainties for both band origins are presumably too large for selective laboratory measurements, because at present there is no source known to the authors allowing for a highly resolved 600 GHz scan around 1.6 THz to detect the lowest bending. Since the most significant contribution to the high uncertainties comes from the large inaccuracies of the q values, the precision of the band origins may be improved by observing *P*-branch transitions with higher *J* values to increase the accuracy for q .

Nevertheless, it is now possible to accurately predict the rotational structure of the ν_{11} fundamental which is composed of *P* and *R* branches and also a sharp *Q* branch. Especially the latter will be highly suited to enable an interstellar detection of C₇ in broadband scans of the PACS instrument on board the Herschel satellite.

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