Terahertz Spectroscopy of Linear Triatomic CCC: High Precision Laboratory Measurement and Analysis of the Ro-Vibrational Bending Transitions

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We report concise measurements of the bending vibration transition $(0,1^1,0) \leftarrow (0,0^0,0)$ near 63.416529(40) cm^{-1} of the carbon cluster CCC in the electronic ground state $(X^1\Sigma_g^+)$. The ν_2 vibration-rotation spectrum consists of P-, Q-, and R-branch transitions. A total of ten ro-vibrational transitions have been measured with the Cologne Sideband Spectrometer for Terahertz Applications, COSSTA. It is essentially a Backward Wave Oscillator (BWO) based, and frequency stabilized sideband spectrometer. The essential feature of COSSTA is the absolute frequency accuracy of the measurements. Absolute frequency calibration is better than 5 kHz at 2 THz, i. e. COSSTA reaches microwave accuracy.

The band centre frequency was determined to be 1.901181506(162) THz: The derived molecular parameters are: $(\mathbf{0},\mathbf{0^0},\mathbf{0})$: B = 12908.242(142) MHz; D = 44.30(40) kHz; H = 4.068(184) Hz; $(\mathbf{0},\mathbf{1^1},\mathbf{0})$: B = 13262.946(109) MHz; D = 70.33(39) kHz; H = 7.71(38).

Key words: Far Infrared Spectra; Interstellar: Molecules; Laboratory Spectra; Line Identification; Rotational-Vibrational Transitions.

1. Introduction

In recent years, the scientific investigation of the diverse properties of pure carbon clusters by experimental and theoretical means has assumed prominence. Pure carbon clusters display a large variety of structures, which include bare linear carbon chains, e.g. C_3, C_4, C_5, …, rings, planar structures such as sheets, cylindrical arrangements known as nano-pipes, and spheroidal fullerenes, notably C_{60}.

In astrophysics, smaller carbon clusters, with a total of about 2 to 13 carbon atoms, have gained importance due to interesting properties: first to mention is their apparently ubiquitous interstellar spatial distribution, their likely participation in the formation of long carbon chain molecules, and their involvement in possible photo-fragmentation processes. Of particular interest is the sputtering process of carbonaceous materials, such as might happen with interstellar dust grains, forming a likely source for the high abundance of carbon in its various forms detected in the interstellar medium.

Last but not least, it is widely believed and has been suggested by Douglas in 1977 [1] that carbon chain species could be key substances for the long sought-after assignments of the Diffuse Interstellar Bands, known as the DIBs (Herbig 1975 and 1995) [2]. DIBs are found in absorption between 4400 Å and about 8000 Å towards reddened stars. The full widths at half intensity of the DIBs range from about 1Å to about 20 Å. They seem to be of interstellar origin. The source of the DIBs has remained a mystery since their discovery about 100 years ago. Since that time many suggestions have been made concerning the possible carriers of the DIBs, none of which has been proven nor any secure assignment has been found [3]. This statement includes also the latest suggestion by John Maier's group, namely that the negative molecular ion C_7^- could be at least a partial carrier deluding an almost perfect match between the appropriate DIBs and the five strongest transitions of the gas-phase laboratory spectrum of the $A\,^2\Pi_u - X\,^2\Pi_g$ band system of the molecular negative ion C_7^- (M. Tuley et al. 1998 [4]). Very recently, newly recorded, highly precise astronomical as well as laboratory measurements refuted the hope of finally establishing the first firm assignment. (B. J. McCall and Oka (2001) [5, 6]).

Thus, the problem of the DIBs remains to be solved as a future task. None of the molecules which have been recorded in the laboratory can be assigned with confidence to any one of the DIBs. However, it seems highly likely that at least a partial resolution of the assignment problem must rest with the carbon chain problematic. The DIBs ubiquitous occurrence suggests that fairly simple and widely spread molecules, probably carbon chain molecules, free radicals, and ions should account for at least some of the strongest "lines" in the diffuse spectrum. An intense effort to help unravel the molecular spectra of potential candidates, such as the bare carbon chains, remains a prerequisite for understanding the DIBs.

Our effort in Cologne is directed to provide precise laboratory spectroscopic information of carbon chain clusters to be used for astrophysical searches. We investigate the relevant spectra with scrutiny, commencing in the microwave region up to and through the terahertz region, as high as 2 THz, and in special cases the region of 2.3 THz can be included. In addition we measure and analyse those parts of their IR spectra which are considered fundamentally important towards understanding and predicting their spectra especially in the terahertz region. These are notably the ro-vibrational spectra displayed by the low bending vibrations of bare carbon chain clusters.

This paper reports on highly precise (microwave accuracy) laboratory spectra near 2 THz of the ν_2 bending vibration of C_3. The interstellar detection of C_3 and a sample of the present high-precision measurements have been presented earlier [7, 8, 9] (Van Orden et al. (1995) and Giesen et al. (2001)). More recently, C_3 has been discovered in dense interstellar clouds [9, 10] by a large variety of many different rovibrational transitions of the ν_2 bending vibration by Cernicharo et al. [10]. Very recently, C_3 has been detected in very translucent, diffuse interstellar clouds via their electronic spectra by the Basel group of John Maier [11].

2. Spectra of Pure Carbon Chain Clusters

The linear pure carbon chain clusters, C_n, are nonpolar and thus they are entirely lacking any rotational spectra. However, carbon molecules can be observed by their various infrared-active modes. In the region of the asymmetric stretching mode, rotationally resolved IR spectra can be obtained and have been recorded. A second very promising method is furnished by recording the far-infrared bending ro-vibrational spectrum in Doppler-resolution. It is this latter avenue we are trying to explore in the Cologne laboratories.

2a) Asymmetric Stretching Vibration

Detection of carbon chain clusters in space or in the laboratory, and their spectroscopic characterisation in the optical, IR and microwave region constitutes presently a very active and fast moving and highly competitive field of research [12] (Van Orden et al. 1998). Very recently the carbon chain molecule C_{10} has been detected by its laboratory spectrum [13], which displays a beautiful, but fairly complicated $^3\Sigma$ band structure. The bandcenter of the asymmetric stretching mode is located near 2074 cm^{-1}.The precise value of the band center could be extracted from a rather tedious and time consuming analysis of the experimental data by Giesen et al. [13]. These data should help to hopefully find its bending vibrational spectra.

2b) Low Energy Bending Vibrations

It remains surprising that the ro-vibrational spectra of the energetically low lying bending vibrations ($\sim$ 30 to $\sim$ 150 cm^{-1}) of carbon chains, such as C_3, C_4, C_5, … etc. do still today represent a spectroscopic void, despite tremendous efforts on the part of the various spectroscopy laboratories world wide. These low bending vibrations have to a large extent eluded any systematic, detailed investigation. The reasons for this shortcoming are to be seen in a variety of serious obstacles. Partly to blame are experimental difficulties, which are associated with the intrinsic part of the electromagnetic spectrum in the terahertz region. All bending vibrations display measurable ro-vibrational transitions in the far infrared or the terahertz region, i. e. between $\sim$ 1 to $\sim$ 5 THz. This part of the electromagnetic spectrum is a notoriously difficult region to experimentally work with. Consequently, this part of the spectrum has remained for high resolution spectroscopy almost a "terra incognita". In addition to the experimental difficulties other problems exist. These concern with the production of the appropriate carbon cluster. In addition, the not very precisely known dipole transition-moments pose further difficulties. But it is expected that precise quantum chemical *ab-initio* calculations will be of help to elucidate the situation.

There have been in the recent past considerable experimental efforts towards opening the terahertz region for high resolution Doppler limited spectroscopy [14]. The Cologne Sideband Spectrometer for Terahertz Application, COSSTA, has been specifically designed in filling in the region around 2 THz. As a first application, we observed and measured the ro-vibrational transitions of C_3 with “microwave” accuracy [9]. Part of these spectra was first observed in the laboratory by Schmuttenmaer et al. [7]. The detection of the rovibrational spectra of the ν_2 bending vibration of C_3 with the band center at 63.42 cm^{-1} or 1.901 THz serves as the first example towards the ambitious aim of observing the low lying bending vibrations of many other carbon chain clusters. The linear carbon chain clusters, such as C_n with $n > 3$, form a special subset.

The present paper aims to reports on the complete measurements and on the full spectroscopic analysis of C_3. Some further details on the experimental procedures, particularly the newly designed discharge cell for use at low temperatures, will briefly be discussed.

3. Experimental Techniques

The main problems encountered in measuring in the terahertz region ro-vibrational spectra are basically threefold.

(i) On the experimental side the principle requirement rests in the availability of a monochromatic source with sufficient output power. In Cologne we have chosen to employ backward wave oscillators, BWOs, in the frequency range of about 100 to 1000 GHz to provide the basic power requirements for the spectrometer. The Cologne sideband spectrometer builds on the use of a BWO delivering the power for sideband generation and for wide frequency tunability [15, 16].

(ii) For detecting ro-vibrational transitions of carbon clusters it remains a major problem to establish a reliable source for their efficient and selective generation with high chemical abundances. In this experiment we have chosen two methods for producing the clusters: laser ablation and microwave discharge arrangement.

(iii) Thirdly we have to rely on quantum chemical *ab initio* calculations to predict and evaluate the appropriate transition moments. These methods have been discussed at many different instances to which the reader is referred to [17].

We will in turn discuss the essentials of the two former requirements: (i) the use of phase stabilized BWOs and (ii) the generation mechanism for carbon clusters of specified chain length.

3a) Frequency Stabilized Sideband Spectrometer: the Cologne Sideband Spectrometer for Terahertz Applications, COSSTA

The newly developed side band spectrometer for broad band high resolution Doppler limited spectroscopy near 2 THz consists of the following components as shown schematically displayed according to Fig. 1, where we have arranged the outlay according to the two paths of the two radiation sources, the power of which are being mixed and added on a corner cube Schottky diode. The output power of the high precision broadband tunable THz source used for spectroscopy, consists two superimposed signals:

(1) the signal of a frequency locked FIR ring laser, presently tuned to a frequency of 1.626 THz, running on a difluromethane (CH_2F_2) laser line, and

(ii) the output power of a phase locked tunable submillimeter wave backward wave oscillator (BWO).

These two signals are brought together on and a whisker contacted Schottky barrier sideband mixer, mounted inside an evacuated chamber.

The relative frequency stability of the sideband signal is about 1 – 2 kHz and the absolute frequency calibration is better than 5 kHz. These values on the achievable frequency accuracy have been derived from a very detailed study of the rotational spectra of CO and its various stable isotopomers [18, 19].

The actual available frequency range is 1750 – 2000 GHz, determined by the two high power BWOs and the optical design employed to superimpose the two beams. The laser lock is achieved by beating the 1.626 THz laser line with the 15th harmonic of a phase locked Gunn oscillator at 108.4 GHz on a specially Cologne developed harmonic mixer. The intermediate frequency IF is processed in an analog f/U (frequency/voltage) converter and the resulting frequency error signal is superimposed to the piezo voltage of the CO_2 laser cavity actuator to control the FIR laser frequency.

3b) Cryogenic Discharge Cell

The production of small carbon clusters proceeds with relative ease in any discharge arrangement. Accordingly, a wide variety of production schemes have been reported in the literature. Among them are techniques such as excimer laser ablation of a carbon rod, photolysis of hydrocarbons, flames which provide soot, combustion experiments with soot as fallout, and gas phase discharges (Haberland 1995 [20]). These different methods for generating carbon chain molecules address different levels of technical sophistication, whereby laser ablation is probably the most complex, but certainly the most expensive. We use it for the generation of the longer carbon chains, i. e. C_n

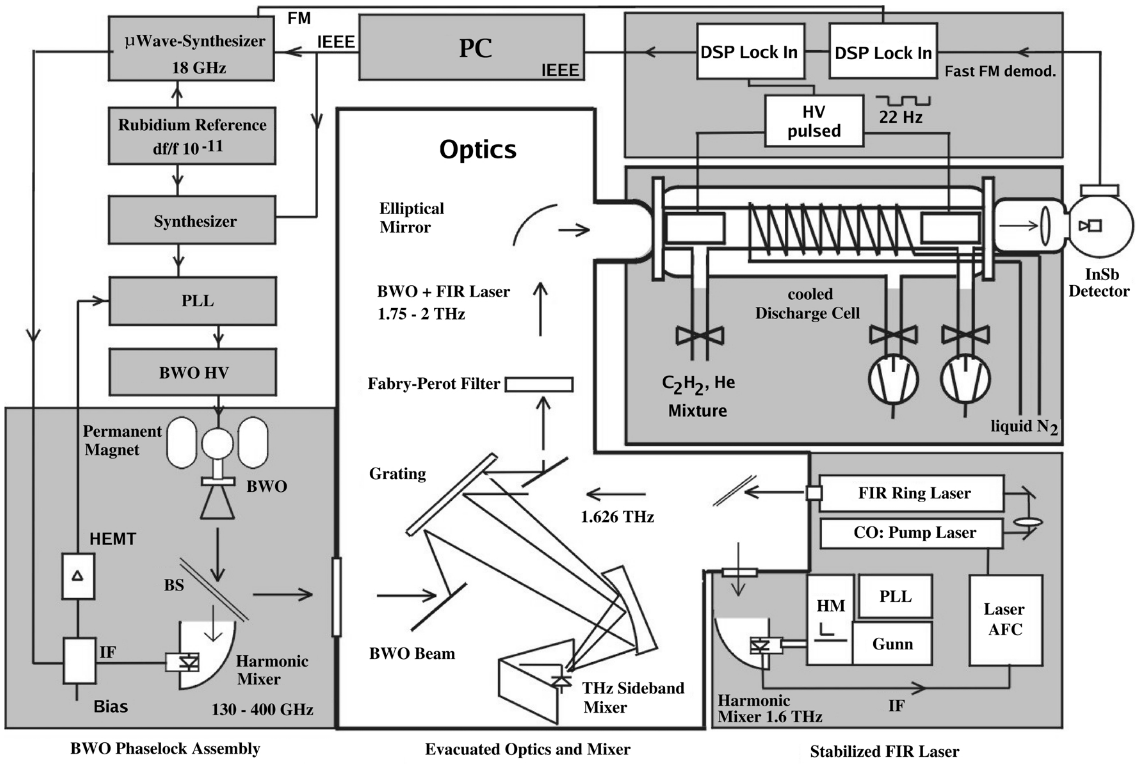

Fig. 1. Schematic display of the **Co**logne **S**ideband-laser **S**pectrometer for **T**erahertz **A**pplication, COSSTA. The outlay is arranged for quick recognition of COSSTA's three major electronic sub-units. These are specifically designated according to their function: (*i*) the BWO phaselock assembly, (*ii*) the frequency stabilized FIR Laser sub-unit, and (*iii*) the evacuated optics and mixer beam combining compartment. The gas handling and discharge arrangements are depicted in the upper right corner. The cell-outlay has been optimized for radical production.

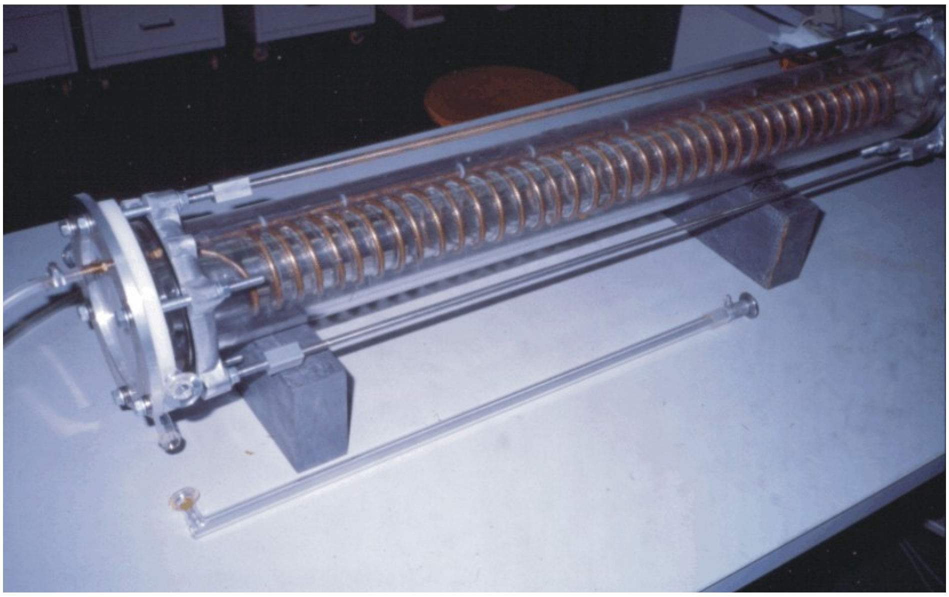

Fig. 2. Photography of the cryogenic gas phase discharge cell with 1 m absorption length. The inner tubing contains the two ring-like electrodes (see for example Fig. 1 upper right corner) for introducing a pulsed high voltage which causes the burning of the discharge.

with *n* ranging between $\sim$ 8 to 13. Pure dc or ac discharge arrangements are comparatively simple and they have been used for producing C_3 in the present work. The principal design characteristics are of the cryogenic discharge cell are depicted in Figure 2.

We developed a new cryogenic discharge cell with the aim to optimize the production of C_3. The cryogenic capability ensured an increase of the population of the lower energy levels by a more favorable partition function. The C_3 species was produced with acceptable abundance.

The new cell consists of a 50 mm diameter Pyrex tube mounted inside a 100 mm diameter glass tube. The inner cell is enclosed by a copper cooling coil, where liquid nitrogen is flown through. The coil can also be used to apply a magnetic field for Zeeman modulation in case of paramagnetic species. The volume between the two cells is evacuated to reduce thermal heat load and freezing up of the cell. Inside of the inner cell are two hollow cathodes inserted. The optimum production conditions were found for a flow discharge of 300 mA pulsed (50 % duty cycle at 22 Hz) by pure C_2H_2 with 2 mbar pressure. LN_2 cooling was essential. For the measurement of C_3 a double modulation scheme was used. Source modulation (7 kHz) together with a low frequency production modulation (22 Hz), which essentially prevent high and low frequency noise from degrading the achievable sensitivity by reducing e. g. baseline effects.

4. Laboratory Spectra of Bare Carbon Clusters

In 1990, the Berkeley group suggested the possibility of detecting pure carbon chain molecules in dense and cold interstellar clouds via far-infrared bending ro-vibrational transitions [8] (Van Orden et al. 1995). One of the prime aims was the interstellar detection of C_3. After some ro-vibrational transitions had been measured in the laboratory for the first time by the Berkeley group [7] (Schmuttenmaer et al. 1990) the remainder of the spectrum was predicted. Recently, these 7 ro-vibrational lines were refined and extended by the Cologne laboratories. The feasibility of this approach was demonstrated by the first observation of the R(2) bending ro-vibrational transition of C_3 in absorption towards Sgr B2 [8] (Van Orden et al. 1995). Unfortunately, this first discovery could not be confirmed at that time by a second independent observation. However, by the combined laboratory and interstellar measurements on C_3, a firm route has been established to the general study of pure carbon chains (and indeed, many other non-polar molecules) in space. The advent of a new airplane-borne 3m telescope by the year 2004 with the SOFIA mission, sponsered by the USA and Germany, will greatly expand the possibilities for new observations, so far completely impossible.

With SOFIA operating a new and wider look at the interstellar carbon problematic will become reality. One of the main tasks in unraveling the riddles associated with the abundance, architecture, and the excitation mechanisms of interstellar carbon and the carbon clusters seem now not to be a mere dream. It appears now that the main problem in settling the interstellar carbon question consists in the availability of appropriately accurate rest frequencies of the ro- vibrational transitions of the different carbon chain molecules. This is a big order for any spectroscopic laboratory, but in cooperation it might be possible to shed new light on this important but pending issue.

5. Results

5a) *Ro-Vibrational Spectrum of C_3*

A total of 10 ro-vibrational transitions of the C_3 bending mode were measured with microwave accuracy, i. e. with an absolute frequency accuracy of ±5 kHz. In Table 1 these 10 new Cologne measurements are collected together with the 7 transitions reported by the Berkeley group [7] (Schmuttenmaer et al.). Two transitions out of these 17 lines, i.e. Q(4) and Q(6), are the only common ones measured independently in both laboratories. The agreement between the two measurements, i.e. Q(4) and Q(6), their absolute line position determined in either laboratory is surprisingly good. In fact, their differences range well within the respectively quoted experimental error limits from the two laboratories. The line center positions of the two Q branch lines determined at Berkeley, i. e. Q(4) and Q(6), differ from our measurements by 582 kHz and 366 kHz, respectively. We believe that our measurements have the edge in accuracy.

Table 2 shows the molecular constants obtained from a least squares fit alalysis of the data (see Section 5b).

The ν_2 bending vibration of C_3 displays a perpendicular ro-vibrational spectrum, since the change of the electric dipole moment vector with respect to the bending normal coordinate takes place perpendicular to the molecular a-axis. It produces a ro-vibrational spectrum

Table 1. Measured far-IR rovibrational transitions of C_3; the ν_2 bending mode $(0, 1^1, 0) \leftarrow (0, 0^0, 0)$.

Transition	ν_{Cologne} [MHz]	obs. − calc. [MHz]	ν_{Berkeley} [MHz]
P(6)		−8.669[a]	1741 122.646(6895)
P(4)		−5.554[a]	1787 890.569(6895)
P(2)		−4.768[a]	1836 821.195(6895)
Q(2)	1890 558.063(250)	−0.213	
Q(4)	1896 706.555(250)	−0.108	1896 707.137(899)
Q(6)	1906 337.903(250)	0.328	1906 338.269(899)
R(0)	1914 274.133(400)	0.314	
Q(8)	1919 410.760(200)	0.429	
Q(10)	1935 870.177(150)	−0.073	
Q(12)	1955 648.963(200)	−0.423	
R(2)	1968 595.391(200)	−0.023	
Q(14)	1978 667.579(150)	0.122	
Q(16)	2004 835.934(3000)[b]	2.968[b]	
R(4)		−0.891[a]	2025 051.586(899)
R(6)		0.649[a]	2038 626.535(899)

[a] obs. − calc. values are based on the observed transitions in [7].
[b] weak line, possibly blended.

Table 2. Molecular constants of the ν_2 bending mode $(0, 1^1, 0) \leftarrow (0, 0^0, 0)$ of C_3.

State	Constant	Value[a]	Value[b]
$(0, 0^0, 0)$	B [MHz]	12 908.242 (142)	12 908.23 (17)
	D [kHz]	44.30 (40)	44.13 (39)
	H [Hz]	4.068 (184)	3.996 (177)
$(0, 1^1, 0)$	ν_0 [MHz]	1901 181.506 (162)	1901 179.7 (12)
	B [MHz]	13 262.946 (109)	13 263.02 (16)
	D [kHz]	70.33 (39)	70.78 (48)
	H [Hz]	7.71 (38)	8.00 (36)
	q_l [MHz]	170.686 (74)	170.699 (63)
	q_D [kHz]	−26.36 (90)	−26.05 (48)
	q_H [Hz]	1.20 (78)	0.81 (69)

a) This work. b) Schmuttenmaer et al. [7] (values are converted with 29.9792458 GHz = 1 cm^{-1}).

Table 3. Predicted transitions for the ν_2 bending mode $(0, 1^1, 0) \leftarrow (0, 0^0, 0)$ of C_3.

Transition	Frequency [MHz]	Transition	Frequency [MHz]
P(14)	1575602.3057	P(12)	1613777.9232
P(10)	1654081.6601	P(8)	1696528.9245
P(6)	1741131.3158	P(4)	1787896.1229
Q(2)	1890558.2764	Q(4)	1896706.6634
Q(6)	1906337.5755	R(0)	1914273.8195
Q(8)	1919410.3313	Q(10)	1935870.2503
Q(12)	1955649.3865	R(2)	1968595.4137
Q(14)	1978667.4569	Q(16)	2004832.9662
R(4)	2025052.4771	Q(18)	2034044.5259
Q(20)	2066192.3709	R(6)	2083625.8857
Q(22)	2101160.0691	Q(24)	2138826.4290
R(8)	2144292.3590	Q(26)	2179067.6009
R(10)	2207025.0093	Q(28)	2221759.3749
Q(30)	2266779.6736	R(12)	2271794.0300

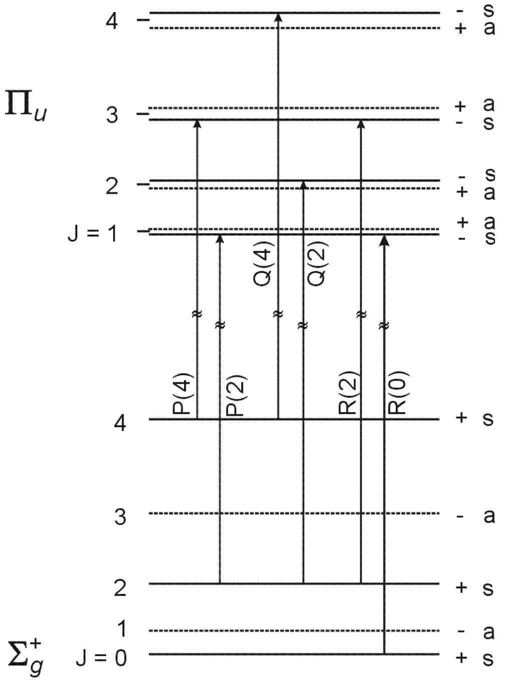

Fig. 3. Energy level diagram of the ν_2 bending vibration of C_3, depicting the ground state and the first excited doubly degenerate bending state. The degeneracy and the effects of the nuclear spin statistics are indicated by the occurrence of dashed energy levels. In consequence of the nuclear spin statistics, only half of the levels appear. The symmetry of the total wavefunction and the parity of the levels are depicted on the right hand side.

which consists of the typical P- and R-branch lines and a somewhat more narrowly spaced Q-branch. Due to the nuclear spin statistics only every other energy level carries population (see the energy level diagram in Figure 3). The calculated spectrum is displayed in the top trace of Fig. 4 and has been summarized in Table 3 to support future astrophysical searches. The displayed spectrum has been calculated using the molecular constants quoted in Table 2. The lower two traces of Fig. 4 reproduce all 10 recorded transitions, separated in eight Q branch transitions i.e. Q(2) through Q(16) and two R branch lines R(0) and R(2).The intensity distribution of the measured Q branch lines allows a rough estimate of the rotational gas temperature in the discharge cell. It is determined to about 300 K.

5b) Fitting Procedure

Introducing the new Cologne data set into the already existing data basis the model Hamiltonian

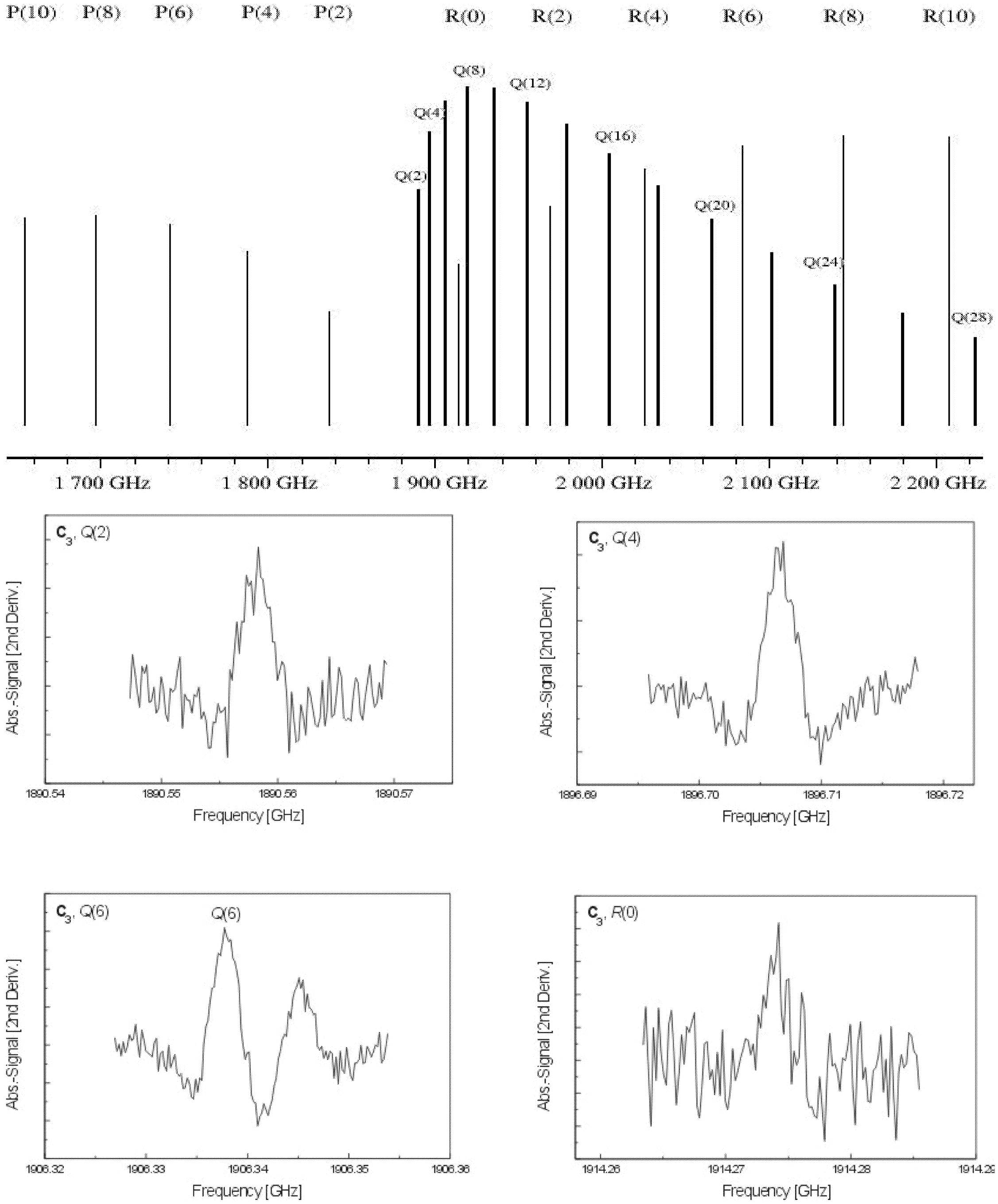

Fig. 4. Full display of the ν_2 bending-vibrational spectrum of C_3 at 2 THz in Doppler limited resolution. a) The observed transitions, their derived intensity, and calculated frequency positions of the bending vibration of C_3 are presented in the top trace as stick diagram. b) The recordings of the vibrational rotational transitions taken with the COSSTA. It is to be noted that the intensities displayed by the individual lines are *not* intensity calibrated! Their true intensity can not be judged from the recorded signal to noise level.

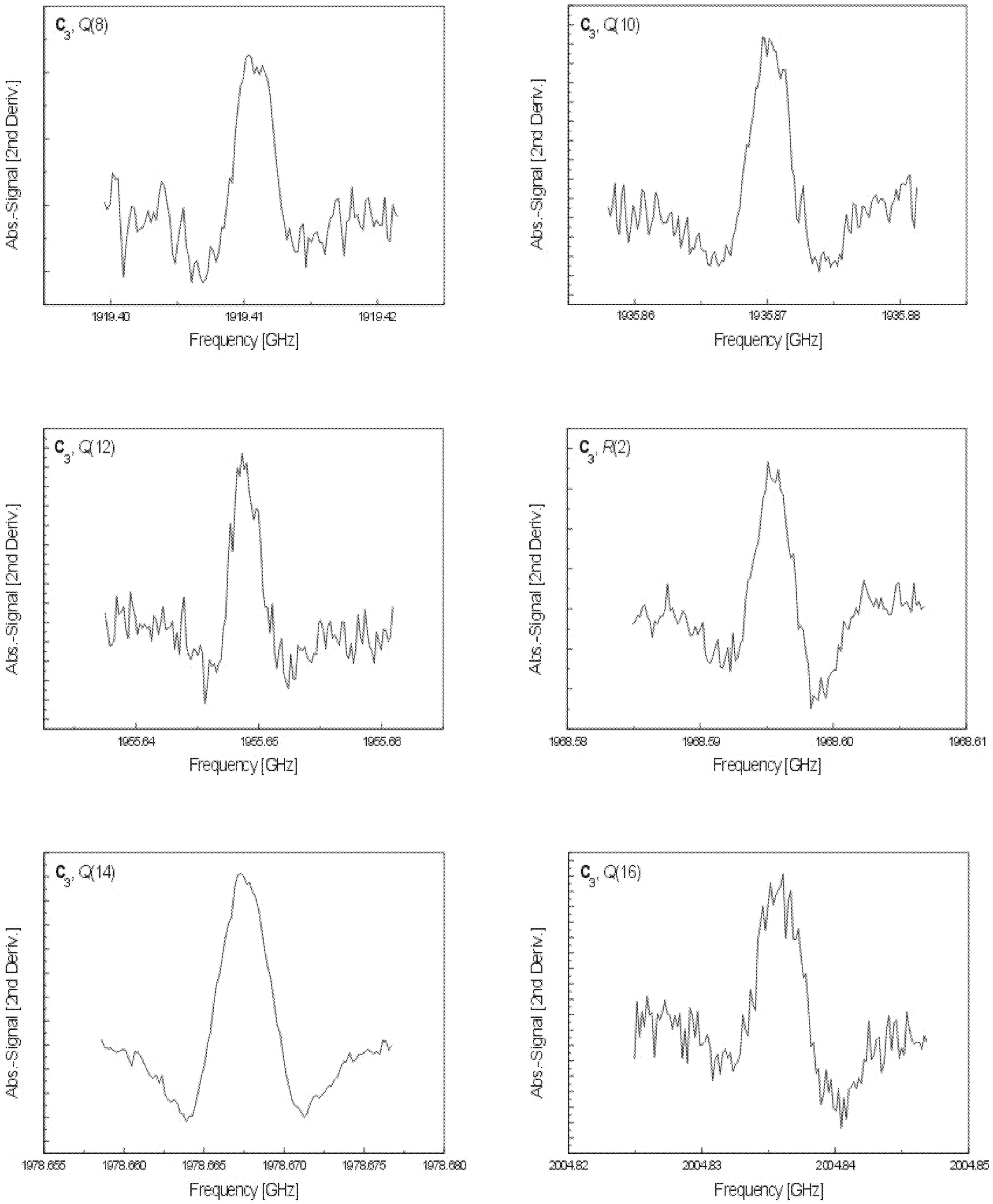

Fig. 4b (continued).

employed by the Berkeley group can be used without any additional terms.

The linear triatomic C_3 has a $^1\Sigma_g^+$ electronic ground state and thus the energy for the ground state rotational levels (00^00) is

$$E_{\rm rot} = BJ(J+1) - D[J(J+1)]^2 + H[J(J+1)]^3 \pm \ldots,$$

whereas for the 1st excited bending state (01^10) the

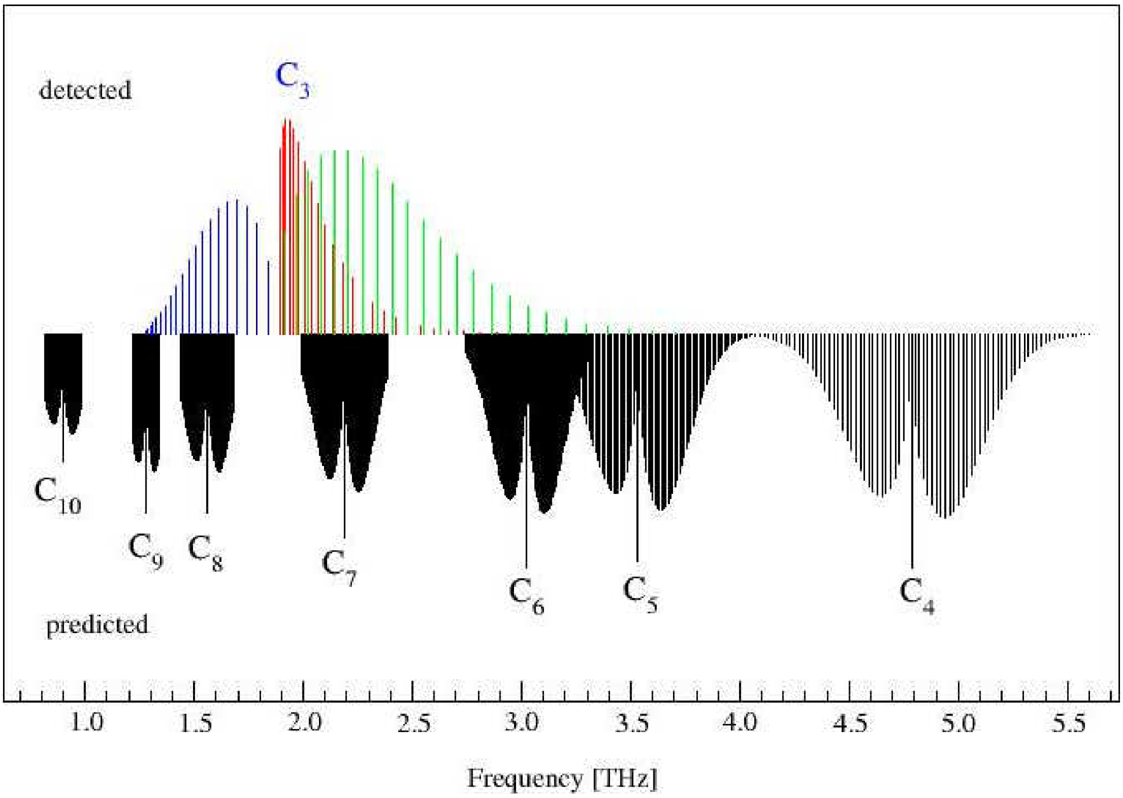

Fig. 5. Predictions of the frequency positions of low energy bending modes of the linear carbon clusters CCC, C_4, C_5, . . . up to C_{10}. The predictions cover the frequency region from 0.7 THz to about 5.3 THz.

ℓ-type doubling terms have to be included and the band center ν_0 has to be added. With these alterations, the known energy expression reads

$$E_\pm = \nu_0 + B[J(J+1)-\ell^2] - D[J(J+1)-\ell^2]^2 + H[J(J+1)-\ell^2]^3 \pm \frac{1}{2}\Big\{q_\ell J(J+1) + q_D[J(J+1)]^2 + q_H[J(J+1)]^3 + \ldots\Big\}$$

with B, D, and H are the rotational constants, the centrifugal distortion constants of second and third-order, respectively. The three constants q i.e. q_ℓ, q_D, and q_H take care of the associated ℓ-type doubling contributions. The $+$ and $(-)$ signs refer to states with even and (odd) J.

The highly precise data set from the Cologne laboratories together with the Berkeley measurements and the infrared data provided by Matsumura et al. [21] were used to derive a new set of molecular constants which are collected in Table 2. They agree very well with the ones quoted by the Berkeley group. The Pickett program [22] was used to fit the new data set together with the FIR data from Schmuttenmaer et al. and the IR combination differences from Matsumara et al.

The predicted rest frequencies of C_3 in the frequency range from 1600 to 2200 GHz are compiled together with calculations of the line strength. This information is accessible via our online Cologne Database for Molecular Spectroscopy (CDMS) 'www.cdms.de' or see our homepage 'www.ph1.uni-koeln.de'. The line intensities can be calculated online for gas temperatures ranging from 10 to 300 K.

6. Conclusions

Triatomic carbon, C_3, continues to play an important role in astrophysics. Since its first detection by means of the 4050 Å electronic band system in comets Swings (1942), it has recently been detected by its low frequency bending vibration in the dense interstellar cloud Sgr B2 (Cernicharo et al. 2000, Giesen et al. 2001) and the circumstellar envelope of IRC+10216. Most recently Maier et al. (2001) report the detection of C_3 in dilute interstellar clouds such as ζ Ophiuci and ζ Persei via electronic transitions of the band near 4052 Å.

The interstellar ubiquity of the C_3 bare carbon chain molecule provides a powerful incentive for continued laboratory study of the ro-vibronic as well as electronic transitions of the longer bare carbon chain clusters and other carbon containing molecular species with the ultimate aim of direct comparison with the DIBs via electronic spectra. The ro-vibronic laboratory spectra serve as a scrutinizing characterization of the molecular properties and a subsequent search in interstellar space. The ro-vibrational transitions may become observable in absorption towards bright background sources or possibly in emission towards hot and dense protostellar objects.

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