

The Cologne Carbon Cluster Experiment: ro-vibrational spectroscopy on C₈ and other small carbon clusters

P. Neubauer-Guenther*, T.F. Giesen, U. Berndt, G. Fuchs, G. Winnewisser

I. Physikalisches Institut, Universität zu Köln, Zùlpicher Str. 77, D-50937 Köln, Germany

Abstract

We report on our ongoing efforts in obtaining the IR-spectra of the linear carbon cluster molecules C_n with $n = 8-13$. So far C₈, C₉, C₁₀, and C₁₃ have been recorded at Cologne. With the exception of C₈ all assignments have been secured. For C₈ a tentative assignment could be derived with the bandcenter of the σ_u antisymmetric stretching mode located at $\nu_0 = 2067.9779 \text{ cm}^{-1}$ and a preliminary rotational constant in the vibrational ground state of $B'' = 0.02068 \text{ cm}^{-1}$. The measured signal to noise ratio of the ro-vibrational band is fairly weak and thus the lower J ro-vibrational transitions can not be assigned with certainty. As a consequence the band center remains uncertain by 4 J or 0.17 cm^{-1} . For a more reliable assignment the sensitivity of the system has to be increased by at least one order of magnitude. The envisaged sensitivity increase of our experiment will be discussed along with the intention to perform terahertz observations of the low energetic bending ro-vibrational spectra. These sub-mm wave measurements will be carried out simultaneously with the IR measurements.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: C₈; Carbon clusters; Tunable diode laser; Infrared

1. Introduction

The main architectural theme of interstellar chemistry is that of the carbon bond. Despite the harsh conditions of interstellar space the four valencies of the C-atom remain unaffected, lending atomic carbon the capability to form chains, rings and branched molecules. With a total of more than 125 entries in the list of interstellar molecules, the ‘organic’ or carbon containing material dominates the ‘inorganic’ molecules by a ratio of 3:1. Carbon

containing interstellar molecules form linear chains and rings, leading to a rich organic interstellar chemistry. Linear carbon chain molecules are important interstellar trace gases. They are highly abundant, and widely distributed.

Small pure carbon clusters have been found as constituents in a variety of extrasolar sources, such as the tails of comets, shells of late type stars and in star forming regions of interstellar clouds. On the other hand, the nuclei of interstellar dust grains are believed to consist of huge conglomerates of carbon and silicon.

Pure carbon chain molecules, i.e. carbon clusters of the type C_n with $n > 2$, are linear and non-polar, and thus they display no rotational spec-

* Corresponding author

E-mail address: neubauer@ph1.uni-koeln.de (P. Neubauer-Guenther).

trum. They can, however, be detected by their IR-active modes, two of which can principally supply the spectroscopic information via ro-vibrational spectra. These two types are:

- 1) the asymmetric stretching modes, which for the pure carbon chains cover a portion of the IR region, i.e. the region from about 1700 to 2400 cm^{-1} in inverse wavelengths, and
- 2) the low bending modes, which occur in the far IR region from about 10 to 150 cm^{-1} .

By infrared tunable diode laser spectroscopy, IR–TDLs, the asymmetric stretching transitions can be recorded. But combination bands of both types of vibrational modes are infrared active and their measurement will support the search for the low bending modes. In order to detect these bending modes, which are predicted to occur in the terahertz or submm-wave region, we plan to use other approaches, e.g. ‘microwave-related’ techniques, as will be discussed later in this paper.

In what follows, we will give a short overview of our recent spectroscopic results including new detections and then we will discuss certain aspects of the technical effort we have expended in using very high resolution IR spectroscopy on carbon cluster molecules. In particular, an external cavity has been introduced into the spectrometer to increase the sensitivity. We will close the paper by mentioning our next experimental goal: it calls for combining two techniques, tunable diode laser spectroscopy with terahertz spectroscopy, to detect the ro-vibrational spectra of the low energy bending vibrations of the different carbon chain species. Hopefully we will break the deadlock between our imprecise knowledge of the location of the ro-vibrational spectra and the difficult generation of reliable abundances of the appropriate carbon chain molecule in studying for the first time simultaneously the asymmetric stretching and the low bending modes of carbon clusters.

2. IR measurements of carbon clusters

In the last decade, the combination of infrared and visible spectroscopy of mass-selected matrix

isolated clusters [1] and high resolution infrared gas phase absorption spectroscopy [2,3] has made crucial contributions in characterizing the structure and dynamics of small carbon clusters. High level ab initio calculations have been applied to this new class of molecules, leading to a better prediction of their chemical and physical properties (see e.g. [4,5]), including their ro-vibrational spectra.

In the following we present a brief overview of our previous measurements on carbon clusters. Figs. 1–4 show the asymmetric stretching mode infrared absorption spectra of the linear carbon clusters C_8 , C_9 , C_{10} and the R-branch of C_{13} , which were recorded with the Cologne TDL spectrometer. These spectroscopic data partially supplement already existing data sets for C_9 and C_{13} . The spectra of the two clusters C_8 and C_{10} presented here represent first detections in the gas phase.

Odd numbered clusters like C_9 possess a $^1\Sigma$ electronic ground state. Therefore the spectrum of C_9 is divided into a clearly discernible P- and R-branch. On the contrary, Clusters with an even number of carbon atoms have a $^3\Sigma$ electronic ground state, which leads to a more complicated P- and R-branch pattern in the spectra of C_8 and C_{10} due to the superimposed triplet structure.

In comparison to the other spectra, the C_8 pattern has a significantly worse signal-to-noise ratio which hampers a secure assignment process. Despite this shortcoming, the spectrum can be assigned to consist of a P- and R-branch. The $^3\Sigma$ structure of each ro-vibrational transition can be recognized in the strongest parts of the P- and R-branch. From the $^3\Sigma$ splitting, observed in each ro-vibrational transition, with a sufficiently good signal to noise ratio, the spin–spin coupling constant λ can be derived (Table 1). This value of λ seems to be consistent with the matrix derived ESR value [7]. We note that the uncertainty of the matrix value is not given. To improve the precision of our data it is still necessary to enhance the experimental sensitivity. For reasons of completeness we summarize the spectroscopic parameters for the carbon clusters C_3 up to C_{13} in the Tables 1 and 2.

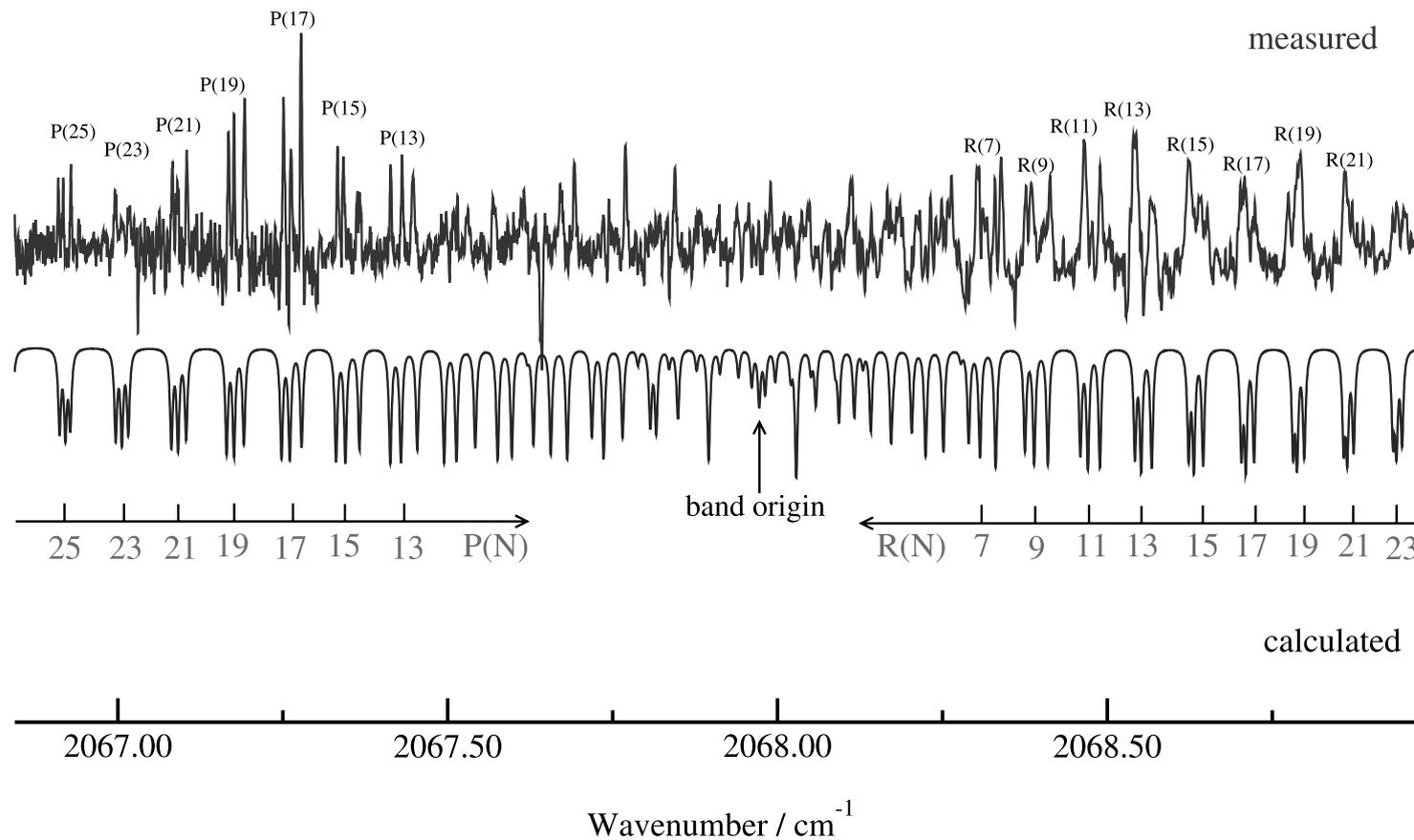
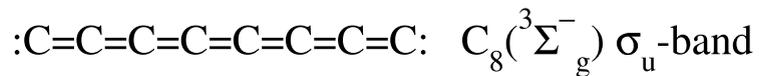
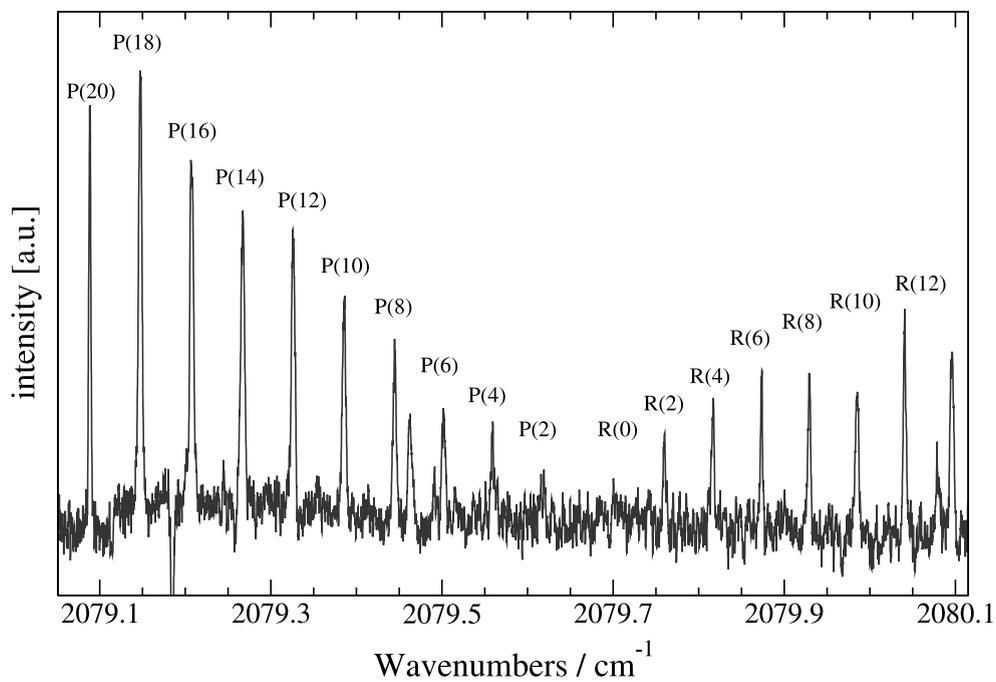
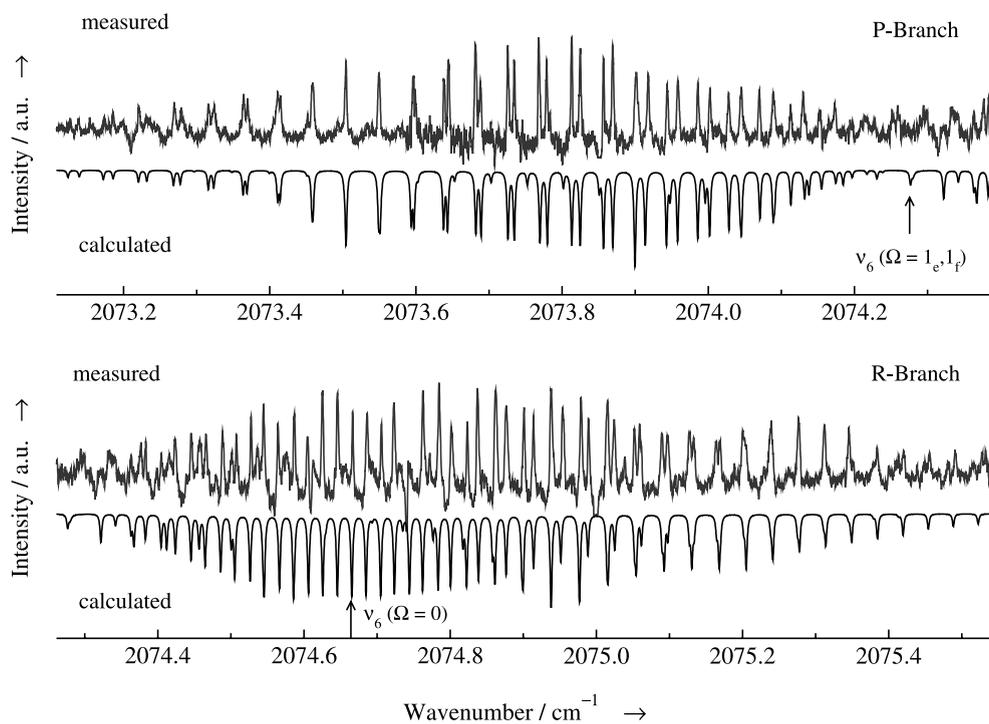


Fig. 1. Spectrum of linear C_8 with a tentative assignment of the ro-vibrational lines.

Fig. 2. Spectrum of linear C_9 .Fig. 3. Spectrum of linear C_{10} .

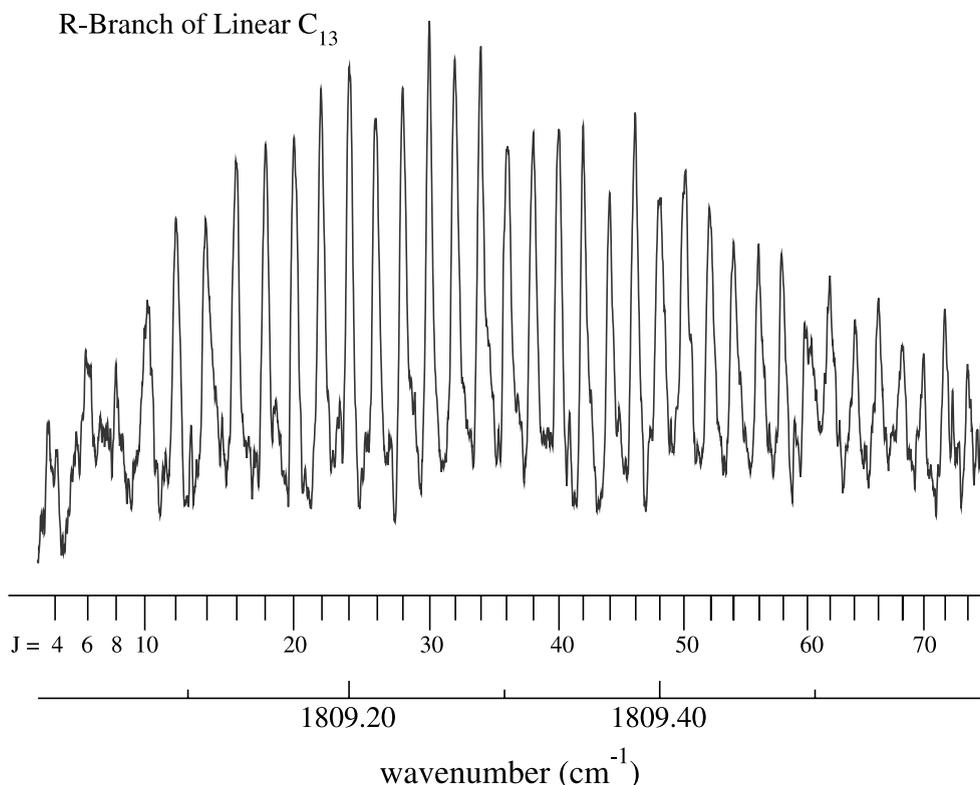
Fig. 4. R-branch of linear C₁₃.

Table 1

Spectroscopic parameters for even numbered carbon clusters $^3\Sigma$: the gas phase data of C₁₀ are taken from Giesen et al. [6]

	Mode	Gas phase	Ne-matrix[1]	B_0	λ	$ \lambda _{\text{ESR}}[7]$
C ₄	ν_3 (σ_u)	1548.6128 [2]	1547.2	0.166111 [2]		0.128
C ₆	ν_4 (σ_u)	1959.8585 [2]	1958.7	0.048479 [2]	(–)0.1875	0.182
C ₈	(σ_u)	2067.9779	2067.8	0.02068	(–)0.7047	0.392
C ₁₀	ν_6 (σ_u)	2074.4109	2074.5	0.010476	–1.787	
C ₁₂	(σ_u)		2003.9			

All units in cm^{-1} .

It is our goal to provide new spectroscopic data on longer chains ($n > 13$), combination bands of asymmetric stretching and bending modes. In addition we are interested in those clusters, whose cyclic form have been indicated by matrix isolation methods, such as C₆ and C₈ [8,9]. For this purpose it is also essential to increase the sensitivity by at least one order of magnitude.

We attempted to detect linear C₁₁ and C₁₂. Regarding the matrix measurements concerning the linear C₁₁ molecule one expects it to exhibit strong ro-vibrational transitions [1]. Despite a wide scanning range, we could not identify either C₁₁ or C₁₂ in the gas phase up to now. This is another indication, that the spectral sensitivity of the Cologne Carbon Cluster experiment has to be improved.

Table 2
Spectroscopic parameters for odd numbered carbon clusters $^{1}\Sigma$

	Mode	Gas phase [2]	Ne-matrix [1]	B_0 [2]
C_3	$\nu_3 (\sigma_u)$	2040.019	2036.4	0.43057
C_5	$\nu_3 (\sigma_u)$	2169.441	2166.4	0.08531
C_7	$\nu_4 (\sigma_u)$	2138.315	2134.6	0.03060
	$\nu_5 (\sigma_u)$	1898.375	1897.5	
C_9	$\nu_5 (\sigma_u)$	2079.673	2081.1	0.01432
	$\nu_6 (\sigma_u)$	2014.278	2010.0	
C_{11}	$\nu_7 (\sigma_u)$		1938.6	0.00473
	$\nu_8 (\sigma_u)$		1853.4	
C_{13}	(σ_u)	1809.964 [3]		

All units in cm^{-1} .

3. Experiment

It is the purpose of this paper, to outline the experiments carried out in the Cologne laboratories to record the laboratory IR ro-vibrational spectra of different carbon clusters. The difficulties in trying to measure spectra of transient molecular species in the gas phase at high spectral resolution are usually threefold: (1) the generation of the transient molecular cluster in sufficiently high abundance, (2) the availability of sensitive detec-

tion methods to record the ro-vibrational spectra with the appropriate sensitivity and spectral resolution, and (3) high quality predictions for the energy levels, which permit a precise prediction of the location of the spectra and their transition dipole moments. The transient species are produced by laser ablation with time-of-flight measurements for selecting different mass species. This method will be discussed in the next section. Finally, for the strength of the transition moments we rely on quantum theoretical calculations.

The Cologne Carbon Cluster experiment combines a high resolution tunable IR diode laser spectrometer with an UV laser ablation source to record the rotationally resolved spectra of asymmetric stretching modes of small carbon clusters. The experimental arrangements are shown in Fig. 5. The IR laser beam probes the carbon cluster supersonic jet roughly 10 mm downstream from the nozzle. An increase of the sensitivity is achieved by employing a multipass Herriott cell with 30 passes through the jet. After traversing the cell the IR laser beam is focused on a HgCdTe photo-conductive detector. A fast ac-coupled amplifier allows time resolved detection of the weak absorption signal on a pair of gated box car

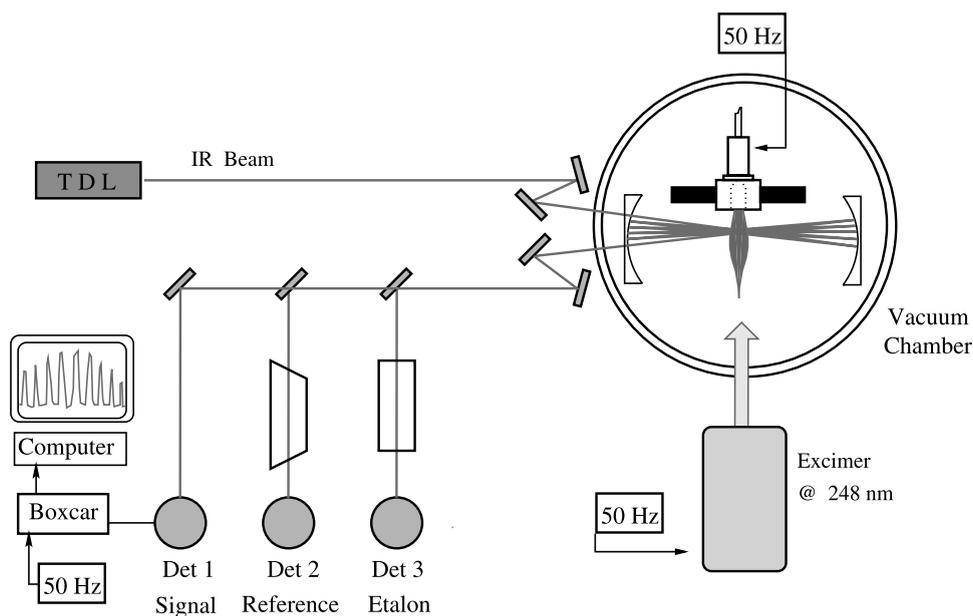


Fig. 5. Tunable IR diode laser spectrometer and ablation source.

integrators before collecting the data by a computer. Part of the IR laser beam is used for frequency calibration by simultaneously recording the spectrum of a reference gas and a fringe spectrum of a germanium etalon.

To produce the carbon clusters, a pulsed excimer laser beam at 248 nm is focused onto a rotating graphite rod. Thereby single carbon atoms are ablated and carried out by pulses of Helium gas at a pressure of 10 bar. Small carbon clusters form in the dense plasma within the slit source, before adiabatically expanding into the vacuum chamber. The background pressure in the vacuum chamber is kept below 10^{-1} mbar. With every single laser pulse a total amount of roughly 10^{13} – 10^{14} clusters of different sizes are produced. Due to their mass the clusters leave the source at different times, so that the time window set by the boxcar allows a kind of mass–velocity selection of the clusters.

Carbon clusters seeded in a buffer gas flow usually separate readily down stream probably because of their different times of formation. So far only linear carbon chains have been detected in our spectrometer, their time dependence is shown in Fig. 6. As can be seen, after the excimer pulse it takes the carbon clusters roughly 6–20 μ s to reach the multipass optics, in which they have another ~ 3 μ s to absorb the IR laser radiation. It is thus possible to clearly distinguish between clusters of different sizes in the time domain e.g. by using boxcar integrators, which enables us to pick out the frequency spectra of certain clusters with little or no interference by other species.

4. Envisaged sensitivity increase

The sensitivity of a spectrometer can principally be increased by optimizing the length of the absorption path and by reducing the noise of the receiving equipment to the theoretical limit. Because of the very narrow region in front of the slit nozzle, only a limited number of passes in a Herriott type multipass optics can cover the region where clusters are present. Thus the maximum number of passes is limited to 20–30. To overcome these constraints, optical resonators can be used

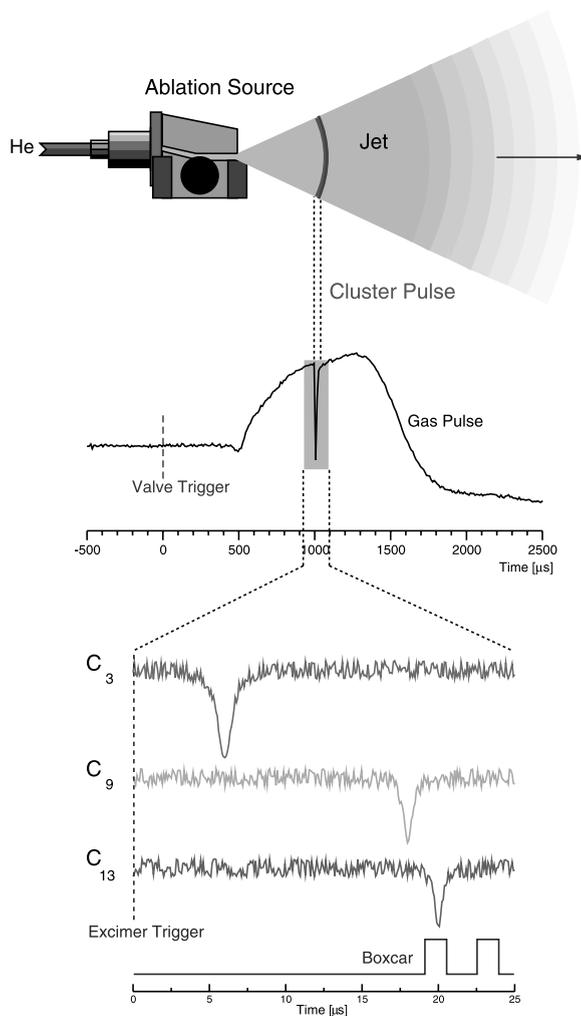


Fig. 6. Scheme to illustrate the time scale of our measurements.

instead of multipass optics, and this has been successfully demonstrated for laser diode spectrometers in the visible frequency range (see e.g. [10,11]). Moreover an external cavity can serve as an optical feedback element to lock the diode laser frequency to a resonance frequency of the external cavity and thus decreasing the spectral laser line width while keeping the laser emission always at the peak of the cavity resonance. This provides the opportunity not only to gain sensitivity of the cluster spectrometer but at the same time to stabilize the TDL frequency.

We have already introduced these cavity techniques to the mid-infrared region by constructing a test alignment consisting of a 2000 cm^{-1} lead-salt diode laser, a confocal resonator and a HgCdTe-detector. Two dielectrical spherical mirrors with a radius of curvature of 150 mm and a reflectivity better than 98% have been used in a confocal arrangement. Frequency tunability of the cavity locked diode laser can be achieved by mounting one of the mirrors on a piezo-electrical element allowing continuous tuning of the optical path length.

Fig. 7 shows a schematic arrangement. We chose a V-type path for the laser traversing the resonator to eliminate reflections from the entrance mirror into the diode laser. The intensity on the detector without an absorbing probe gas is given by the Airy-function of a cavity with four traversals:

$$I = I_0 \frac{t^2 r^2}{(1 - r^2)^2 + 4r^2 \sin^2(2kd)} \quad (1)$$

where I_0 is the laser intensity, t and r represent the coefficients of transmissivity and reflectivity, k is the norm of the wave vector, and d signifies the distance of the mirrors. Since the resonator is confocal, the mirror distance is equal to the radius of curvature. The free spectral range is defined as

$$\text{FSR} = \frac{c}{4d} \quad (2)$$

with c as speed of light, and the finesse F^* as:

$$F^* = \frac{\pi\sqrt{r^2}}{1 - r^2} \quad (3)$$

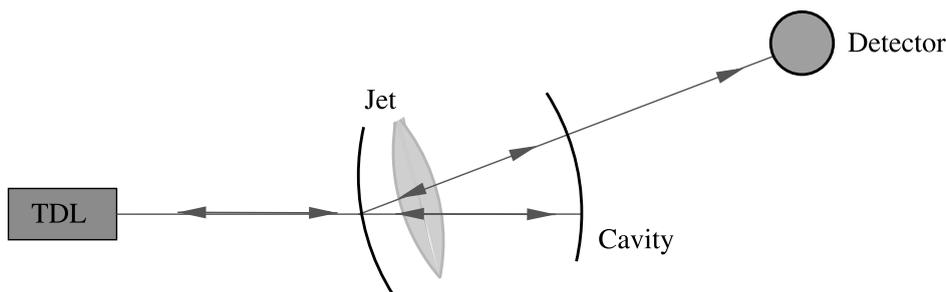


Fig. 7. V-shaped optical path to lock the frequency to a cavity resonance [13].

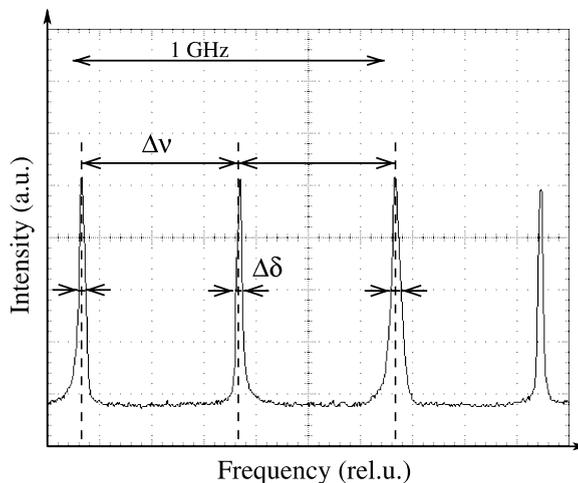


Fig. 8. Cavity response to the unlocked TDL.

The distance between the two mirrors in our experiment is 150 mm which corresponds to a free spectral range of 500 MHz. Fig. 8 shows the transmitted intensity through the resonator. With a reflectivity of $r = 0.98$ the finesse F^* is 78 and the expected transmission peak width is 6.4 MHz. From Fig. 8 we have determined the peak width to be 25 MHz ($\equiv F^* = 20$). This discrepancy is caused by fast frequency fluctuations of the tunable diode laser, which are typically in the same order, as has been shown in our recent paper [12], while the cavity acts as a sharp band gap filter, transmitting only radiation within a 6.4 MHz window. To avoid losses in the transmitted laser intensity it is thus necessary to reduce the laser line width below this limit. Dahmani et al. have demonstrated that the spectral line width of a GaAlAs diode laser at 850 nm can be reduced to

Table 3
Characteristic parameters for cavities with different reflectivities

r	F^*	$\Delta\delta$ (MHz)	I_{cav}/I_1
0.934	23	22.7	30
0.98	78	6.4	99
0.99	156	3.2	197
0.999	1570	0.3	1736

20 kHz by using optical feedback of an external cavity [13]. Comparable results seem to be possible for IR-diode lasers [14]. It is thus possible to use cavities with even higher finesse. In Table 3 we have listed the finesse F^* and the width of the cavity transmission curve $\Delta\delta$ for different reflection coefficients of the mirrors. Introducing an absorber into the cavity causes an absorption signal of intensity I_α on the detector which is given by:

$$I_\alpha = I_0 \frac{t^2 r^2 e^{-3\alpha d}}{(1 - r^2 e^{-2\alpha d})^2 + 4r^2 e^{-2\alpha d} \sin^2(2kdn(k))} \quad (4)$$

Where α is the absorption coefficient and d the absorption path length. The index of refraction $n(k)$ needs to also be considered, since anomalous dispersion is always present together with molecular absorption. Table 3 also shows the relative peak absorption I_{cav} of a weak absorber with $\alpha d = 10^{-4}$, in comparison to the single path absorption I_1 . To compare the cavity system with the Herriott cell that value for the reflectivity is needed, where the single path absorption increases by a factor of 30. It can be seen that even for rather poor mirrors with a low reflectivity of 0.934 the systems become competitive. Mirrors with a reflectivity of 0.98 amplify the single path absorption by two orders of magnitude and are thus a factor of 3 more efficient than a multi-reflection cell with 30 passes.

Mirrors with a reflectivity of 0.999–0.9999 are now commercially available. In using high reflectivity cavities in the near future we expect at least a gain of two orders of magnitude in sensitivity.

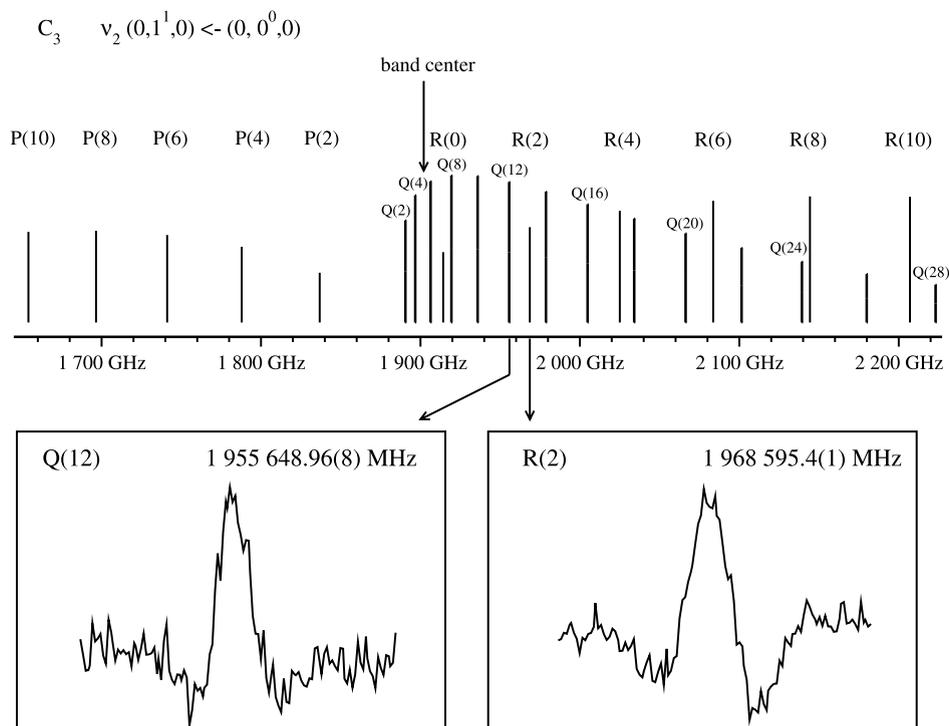


Fig. 9. Ro-vibrational spectrum of the ν_2 bending vibration of C_3 near 2 THz recorded by ‘microwave’ techniques by Giesen et al. [15].

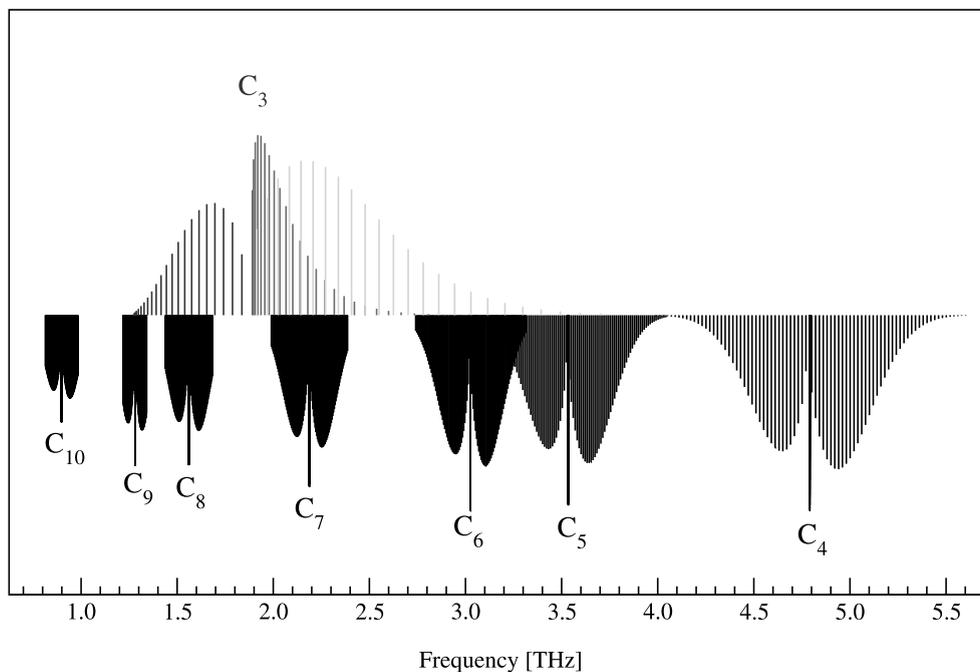


Fig. 10. Predicted spectra of the lowest bending modes of linear carbon clusters. Band center frequencies from ab initio calculations [16].

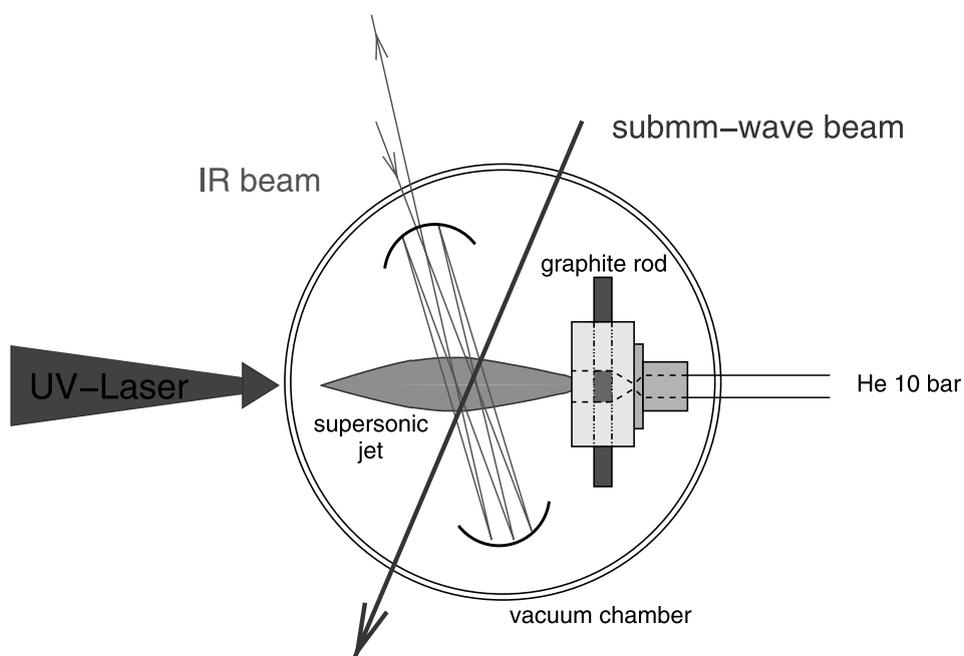


Fig. 11. Combination of sub-mm wave beam, IR-TDL beam and UV-laser ablation source. With this new spectrometer, using the THz Beam for recording, it is hoped that the low bending ro-vibrations of carbon chains will become detectable. The IR beam is intended to check the abundance of the C-clusters.

5. Low bending vibrations

Only very few of the low bending vibrational modes of carbon clusters have been observed to date, although the spectroscopic characteristics of these species are of highest interest, both in their own spectroscopic right, but also due to their possible discovery in space.

The CCC or C₃ cluster is presently the only pure carbon chain molecule, the IR and terahertz spectra of which have been observed in the laboratory and in space (Fig. 9) [15]. For recording the spectra in the 1.8–2.1 THz region, we have developed a highly sensitive frequency stabilized side band spectrometer operated with phase-stabilized backward wave oscillators, (BWOs), as side band source. The far IR laser is frequency stabilized. Thus the recorded line positions represent absolute frequencies [15].

In extending these measurements to low bending vibrations of other carbon clusters (Fig. 10), it is our intention to combine the two techniques, i.e. IR monitoring measurements and terahertz recording in a crossed-beam type of arrangement. This experiment will make use of a BWO as radiation source and the laser ablation technique for cluster production. Fig. 11 depicts the crossed-beam experiment. The tunable diode laser beam will allow both to monitor the production conditions, record the IR absorption spectra, and indicate optimal cluster production. These conditions are seen as a prerequisite for terahertz detection.

6. Conclusion

The Cologne Carbon Cluster experiment has provided highly accurate data on asymmetric stretching transitions of small linear carbon clusters. New challenges are seen in the detection of longer carbon chains, cyclic clusters, combination bands including low bending modes and the pure low bending transitions. This goal requires a substantial increase of the instrumental sensitivity. The necessary enhancement can be achieved by replacing the Herriott cell in the IR experiment with an external cavity. The combination of the two spectroscopic techniques, i.e. tunable diode

laser spectroscopy and the simultaneous use of a terahertz beam, is expected to lead to new spectra otherwise difficult to obtain, e.g. low bending vibrational transitions. These new data will be essential spectroscopic information for future missions, such as Stratospheric Observatory For Infrared Astronomy (SOFIA) and Herschel, a 3-m telescope space mission.

Acknowledgements

This work has been supported in part by the Deutsche Forschungsgemeinschaft (DFG) via grant SFB 494 and by the Ministry of Science of the Land NRW.

References

- [1] P. Freivogel, M. Grutter, D. Forney, J.P. Maier, *Chem. Phys.* 216 (1997) 401.
- [2] A. Van Orden, R.J. Saykally, *Chem. Rev.* 98 (1998) 2313.
- [3] T.F. Giesen, A. Van Orden, H.J. Hwang, R.S. Fellers, R.A. Provencal, R.J. Saykally, *Science* 265 (1994) 756.
- [4] J.M.L. Martin, P.R. Taylor, *J. Phys. Chem.* 100 (1996) 6047.
- [5] R.O. Jones, *J. Chem. Phys.* 110 (11) (1999) 5189.
- [6] T.F. Giesen, U. Berndt, K. Yamada, G. Fuchs, R. Schieder, G. Winnewisser, A. Provencal, F.N. Keutsch, A.O. Van Orden, R.J. Saykally, *Chem. Phys. Chem.* 4 (2001) 242.
- [7] R.J. Van Zee, R.F. Ferrante, K.J. Zeringue, W. Weltner, D.W. Ewing, *J. Chem. Phys.* 88 (1988) 3465.
- [8] S.L. Wang, C.M.L. Rittby, W.R.M. Graham, *J. Chem. Phys.* 107 (16) (1997) 6032.
- [9] S.L. Wang, C.M.L. Rittby, W.R.M. Graham, *J. Chem. Phys.* 112 (3) (2000) 1457.
- [10] B.A. Paldus, R.N. Zare, *Cavity ringdown Spectroscopy—An Ultratrace-Absorption Measurement Technique*, ACS Symposium Series 720, 1999 p. 49.
- [11] D. Romanini, *Cavity ringdown Spectroscopy—An Ultratrace-Absorption Measurement Technique*, ACS Symposium Series 720, 1999, p. 125.
- [12] G. Winnewisser, T. Drascher, T. Giesen, I. Pak, F. Schmülling, R. Schieder, *Spectrochimica Acta Part A* 55 (1999) 2121.
- [13] B. Dahmani, L. Hollberg, R. Drullinger, *Optics Lett.* 12 (11) (1987) 876.
- [14] M. Mürtz, M. Schaefer, M. Schneider, J.S. Wells, W. Urban, U. Schiessl, M. Tacke, *Optics Commun.* 94 (1992) 551.
- [15] T.F. Giesen, A.O. Van Orden, J.D. Cruzan, R.A. Provencal, R.J. Saykally, R. Gendriesch, F. Lewen, G. Winnewisser, *Astrophys. J.* 551 (2001) L181.
- [16] R.O. Jones, *Priv. commun.*