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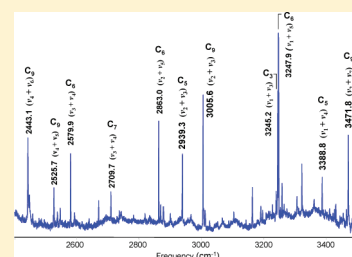
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Isotopic Study of New Fundamentals and Combination Bands of Linear C₅, C₇, and C₉ in Solid Ar

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ABSTRACT: A high yield of carbon chains has been produced by the laser ablation of carbon rods having ¹³C enrichment. FTIR spectroscopy of these molecules trapped in solid Ar has resulted in the identification of two new combination bands for linear C₅ and C₉. The ($\nu_1 + \nu_4$) combination band of linear C₅ has been observed at 3388.8 cm⁻¹, and comparison of ¹³C isotopic shift measurements with the predictions of density functional theory calculations (DFT) at the B3LYP/cc-pVDZ level makes possible the assignment of the $\nu_1(\sigma_g^+)$ stretching fundamental at 1946 cm⁻¹. Similarly, the observation of the ($\nu_2 + \nu_7$) combination band of linear C₉ at 3471.8 cm⁻¹ enables the assignment of the $\nu_2(\sigma_g^+)$ stretching fundamental at 1871 cm⁻¹. The third and weakest of the infrared stretching fundamentals of linear C₇, the $\nu_6(\sigma_u^+)$ fundamental at 1100.1 cm⁻¹, has also been assigned.



1. INTRODUCTION

C_n carbon clusters have been of spectroscopic interest for many years, particularly because of their roles in the chemistry of the interstellar medium and circumstellar shells. Understanding their structures and how they bond has been a challenge for theorists and experimentalists alike. In the first systematic experimental investigation Weltner and McLeod¹ reported infrared fundamentals for C_n species formed by trapping the products of graphite evaporation in Ne matrices. Later, the discovery of C₆₀ fullerene² stimulated renewed interest in carbon chains, rings, and clusters. Despite considerable work by many investigators focused on small C_n species ($n \leq 12$), the frequencies of many vibrational fundamentals remain unmeasured.

Linear C₅ has been extensively studied with several spectroscopic techniques both in the gas phase and in matrices.^{1,3–16} All the fundamentals have been assigned except for the $\nu_1(\sigma_g^+)$ symmetric stretch. In the present work FTIR (Fourier transform infrared) measurements of frequencies and ¹³C isotopic shifts coupled with DFT (density functional theory) calculations have enabled the assignment of the ($\nu_1 + \nu_4$) combination band of linear C₅. Since the $\nu_4(\sigma_u^+)$ fundamental has been previously observed in an Ar matrix,¹⁵ it has now been possible to obtain a frequency for the $\nu_1(\sigma_g^+)$ fundamental.

Linear C₉ has similarly been the subject of many spectroscopic studies,^{1,3,11,14,17–24} but of the eight stretching fundamentals, the three symmetric modes, $\nu_1(\sigma_g^+)$, $\nu_2(\sigma_g^+)$, and $\nu_8(\sigma_g^+)$, have yet to be observed. In the present study, the ($\nu_2 + \nu_7$) combination band has been measured, and using the frequency of the $\nu_7(\sigma_u^+)$ mode reported earlier in an Ar matrix,²⁴ a frequency for the $\nu_2(\sigma_g^+)$ fundamental has been obtained. Earlier isotopic studies of carbon clusters trapped in Ar by Vala and co-workers have included measurements of combination bands of C₃ (ref 25) and C_n ($n = 5, 6, 7, 9$).^{26,27} The present work, with the observation of new combination bands of C₅ and C₉, complements those studies.

Extensive studies of linear C₇ in both the gas phase and in matrices,^{28,29,26,30–38} have resulted in the assignment of all the

infrared active, asymmetric stretching modes with the exception of $\nu_6(\sigma_u^+)$, which is predicted to be very weak. The FTIR measurements and DFT calculations performed as part of the present study have enabled the assignment of this fundamental.

2. THEORY

DFT calculations were performed using the *Gaussian 03* suite³⁹ with the B3LYP^{40–42} functional (Becke type 3 exchange and the correlation functional of Lee, Yang, and Parr) and cc-pVDZ basis set. Currently, this program suite does not include calculations of the anharmonic corrections to the fundamentals, combination bands, or overtones of molecules having a point group with degenerate irreducible representations. Since this is the case for linear molecules, in the present study of combination bands of C₅ and C₉ the chains have been slightly bent to give a distorted structure of C_{2v} symmetry. The global minima for the distorted structures are shifted respectively, only 2×10^{-3} and 4×10^{-4} kcal/mol from those of the linear structures, and the frequencies of the stretching modes of the distorted isomers differ by only ~ 0.1 cm⁻¹ from their linear counterparts. Using the C_{2v} structures, however, has permitted the calculation of anharmonic corrections for the fundamentals, combination bands, and overtones of vibrational transitions including stretching modes only.

Table 1 lists the harmonic fundamentals calculated for linear C₅ and the anharmonic fundamentals for the structure slightly distorted from the linear isomer. The anharmonic bending mode frequencies are not shown; a singularity occurs because of pairs of close lying energy levels, which result from the distorted structure. Table 2 gives similar results calculated for the stretching fundamentals of C₉. The isotopic shifts for the combination bands ($\nu_1 + \nu_4$) of C₅ and ($\nu_2 + \nu_7$) of C₉, which are presented in Tables 3 and 4, were computed using the distorted structures.

Received: December 16, 2010

Revised: February 6, 2011

Published: March 08, 2011

Table 1. Observed and DFT-B3LYP/cc-pVDZ Predicted Vibrational Frequencies, Combination Bands (cm^{-1}), and Band Intensities for Linear and Slightly Distorted Structures of C_5

IR active fundamentals and combination bands	obsd (cm^{-1})		frequency linear structure	anharmonic frequency distorted structure	expected frequency using eq 2	IR intensity (km/mol)
	Ar	gas				
$\nu_1(\sigma_g^+)$	1946 ^a		2046	2015	1938	0
$\nu_2(\sigma_g^+)$	776 ^b	779 ± 10	800	799	811	0
$\nu_3(\sigma_u^+)$	2163.8 ^c	2169.441 ^d	2270	2228	2174	2539
$\nu_4(\sigma_u^+)$	1446.6 ^e		1499	1481	1443	122
$\nu_5(\tau_g)$		218 ± 13 ^f	280			0
$\nu_6(\tau_u)$		535 ± 10 ^g	676			3
$\nu_7(\tau_u)$		118 ± 3 ^h	138			14
$(\nu_1 + \nu_3)$			4316	4230	4112	
$(\nu_1 + \nu_4)$	3388.8 ^a		3545	3486	3381	
$(\nu_2 + \nu_3)$	2939.9 ^b		3070	3018	2985	
$(\nu_2 + \nu_4)$			2299	2282	2254	

^a This work. ^b References 26 and 27. ^c Reference 13. ^d References 5–8. ^e Reference 15. ^f References 3, 4, and 8. ^g References 3 and 4. ^h References 3, 4, 8, and 16.

Table 2. Observed and DFT-B3LYP/cc-pVDZ Predicted Vibrational Frequencies, Combination Bands (cm^{-1}), and Band Intensities for Linear and Distorted Structures of C_9

IR active fundamentals and combination bands	obsd (cm^{-1})		frequency linear structure	anharmonic frequency distorted structure	expected frequency using eq 2	IR intensity (km/mol)
	Ar	gas				
$\nu_1(\sigma_g^+)$			2276	2237	2144	0
$\nu_2(\sigma_g^+)$	1871 ^a		1970	1943	1870	0
$\nu_3(\sigma_g^+)$		1258 ± 50 ^b	1294	1327	1300	0
$\nu_4(\sigma_g^+)$	448 ^c	484 ± 48 ^b	464	492	526	0
$\nu_5(\sigma_u^+)$	2078.1 ^c	2079.67 ^d	2217	2184	2095	4074
$\nu_6(\sigma_u^+)$	1998.0 ^e		2132	2095	2011	6526
$\nu_7(\sigma_u^+)$	1601.0 ^f		1670	1652	1602	393
$\nu_8(\sigma_u^+)$			895	894	899	0.2
$(\nu_1 + \nu_{5/6/7})$			4493/4408/3946	4415/4321/38831	4239	
$(\nu_2 + \nu_{5/6})$			4187/4102	4121/4030	3965	
$(\nu_2 + \nu_7)$	3471 ^a		3640	3587	3472	
$(\nu_3 + \nu_{5/6/7})$			3511/3426/2964	3508/3415/2977	3395	
$(\nu_4 + \nu_5)$	2525.7 ^g		2681	2675	2621	
$(\nu_4 + \nu_6)$	2443.0 ^g		2596	2587	2537	
$(\nu_4 + \nu_7)$			2134	2145	2128	

^a This work. ^b Reference 3. ^c Reference 26. ^d Reference 17. ^e Reference 22. ^f Reference 24. ^g References 26 and 27.

A binary combination band is related to the fundamentals and the anharmonicity constant χ_{ij} via⁴³

$$(\nu_i + \nu_j) = \nu_i(\sigma_g) + \nu_j(\sigma_u) - 2\chi_{ij} \quad (1)$$

If the observed combination band involves an observed asymmetric stretching fundamental, the symmetric and infrared inactive $\nu_i(\sigma_g)$ fundamental can be calculated using eq 1, giving a frequency within a few wave numbers of the actual value.

Tables 1 and 2 present in the sixth column the frequencies expected to be observed that have been calculated in units of cm^{-1} using the relation

$$\nu_{\text{observed}} = 0.92673\nu_{\text{anharmonic-B3LYP/cc-pVDZ}} + 70.3(\text{cm}^{-1}) \quad (2)$$

which was derived⁴⁴ from a linear fit of the experimental frequencies for C_{2n+1} ($n = 1-4$) linear carbon chains versus

the calculated B3LYP-cc-PVDZ anharmonic results. Equation 2 predicts the frequencies expected to be observed to within a few cm^{-1} of those actually measured. This relation can also provide valuable information for high resolution gas phase laser spectroscopy studies because it predicts the expected frequencies of odd carbon chains to within a few cm^{-1} . For example, the fundamentals $\nu_1(\sigma_g^+)$, and $\nu_8(\sigma_u^+)$ modes of C_9 have not been observed, but the frequency of the $\nu_3(\sigma_g^+)$ fundamental has been measured at $1258 \pm 50 \text{ cm}^{-1}$ in a photoelectron spectroscopy experiment.⁴⁵ As shown in Table 2, eq 2 predicts the frequencies of these modes to be respectively 2144, 899, and 1300 cm^{-1} .

4. EXPERIMENTAL PROCEDURE

Carbon clusters were formed by the ablation of carbon rods using the pulsed beam of a Nd:YAG laser (Spectra Physics)

Table 3. Comparison of Observed Vibrational Frequencies (cm^{-1}) of the $(\nu_1 + \nu_4)$ Combination Band for Single ^{13}C -Substituted Isotopomers of Linear C_5 with the Predictions of B3LYP/cc-pVDZ Level Calculations

			B3LYP/cc-pVDZ	B3LYP/cc-pVDZ	B3LYP/cc-pVDZ	
			harmonic	anharmonic	anharmonic	difference
isotopomer C—C—C—C—C		obsd ($\nu_1 + \nu_4$) (cm ^{−1})	linear C ₅	distorted C ₅	scaled ^a	obsd − scaled
12−12−12−12−12	A	3388.8	3544.8	3486.7		
13−12−12−12−12	B	3364.6	3519.0	3461.8	3364.6	0.0
12−13−12−12−12	C	3355.4	3510.0	3452.6	3355.7	−0.4
12−12−13−12−12	D	3368.0	3521.3	3464.5	3367.2	0.8

^a Results of the DFT-B3LYP/cc-pVDZ calculation scaled by a factor of 3388.8/3486.7.**Table 4. Comparison of Observed Vibrational Frequencies (cm^{-1}) of the $(\nu_2 + \nu_7)$ Combination Band for Single ^{13}C -Substituted Isotopomers of Linear C_9 with the Predictions of B3LYP/cc-pVDZ Level Calculations**

			B3LYP/cc-pVDZ	B3LYP/cc-pVDZ	B3LYP/cc-pVDZ	
			harmonic	anharmonic	anharmonic	difference
isotopomer C—C—C—C—C...		obsd (cm ^{−1}) (ν ₂ + ν ₇)	linear C ₉	distorted C ₉	scaled ^a	obsd − scaled
12−12−12−12−12−...	A	3471.8	3640.7	3587.8		
13−12−12−12−12−...	B	3457.0	3625.3	3573.1	3457.6	−0.6
12−13−12−12−12−...	C	3445.8	3616.4	3563.9	3448.7	−2.9
12−12−13−12−12−...	D	3460.1	3628.4	3575.9	3460.3	−0.2
12−12−12−13−12−...	E	3455.2	3623.9	3571.3	3455.8	−0.6
12−12−12−12−13−...	F	3455.2	3624.0	3571.7	3456.2	−1.0

^a Results of the DFT-B3LYP/cc-pVDZ calculation scaled by a factor of 3471.8/3587.8.

operating at 1064 nm with a power of ~ 2.8 W, and loosely focused on an area of ~ 25 mm². The evaporated products were condensed in solid Ar (Matheson, 99.9995% purity) on a gold surfaced mirror cooled to ~ 10 K by a closed refrigeration system (ARS, Displex) and enclosed in a vacuum chamber maintained at a pressure of $\sim 10^{-8}$ Torr. During the deposition, the Ar flow rate entering the chamber was ~ 1 mmol/h for depositions lasting 1.5 h. The measurement of ^{13}C isotopic shifts has enabled the determination of the structure and the assignment of vibrational fundamentals and combination bands. For this purpose carbon rods were made with mixtures of ^{12}C (Alfa Aesar, 99.9995% purity) and ^{13}C (Isotec, 99.3% purity).

FTIR absorption spectra of the products condensed in the Ar matrix were recorded over the range 500–5000 cm^{-1} , at a resolution of 0.2 cm^{-1} using a Bomem DA3.16 Fourier transform spectrometer equipped with a liquid nitrogen cooled Hg—Cd—Te (MCT) detector, KBr beamsplitter, and Globar source. For the combination bands the spectra were also recorded in the 1800–5000 cm^{-1} region using a liquid nitrogen cooled InSb detector, which improved the signal-to-noise ratio by a factor of 7. This enhancement was indispensable to the observation of isotopic frequency shifts for the new combination bands identified in the present work since they are ~ 100 times weaker in intensity than the most intense fundamentals. Details of the optical system and experimental apparatus have been reported previously.⁴⁶

5. RESULTS AND DISCUSSION

Figure 1 shows a section of the survey spectrum recorded in the 500–5000 cm^{-1} range using the MCT detector. The combination bands appeared after 45 min of deposition. Although the InSb detector gives a better signal-to-noise ratio than the MCT, it is limited to the region above ~ 2000 cm^{-1} where there is only the $\nu_3(\sigma_u^+)$ fundamental of linear C_5 , and no fundamentals of

either linear C_9 or C_7 . The spectrum recorded with the MCT detector was thus necessary for correlating combination bands with fundamentals using the observed intensity ratios, which should remain constant for absorptions by the same molecule. From the intensity ratios measured in several experiments producing different yields of carbon clusters, it was found that the absorption at 3388.8 cm^{-1} , labeled A in Figure 2a, is correlated to both the $\nu_3(\sigma_u^+)$ and $\nu_4(\sigma_u^+)$ fundamentals of linear C_5 .¹⁵ Similarly, the absorption at 3471.8 cm^{-1} , labeled A in Figure 3a, is correlated to both the $\nu_6(\sigma_u^+)$ and $\nu_7(\sigma_u^+)$ fundamentals of linear C_9 .²⁴ Tables 1 and 2 list the DFT calculated values for the harmonic and anharmonic fundamentals of linear C_5 and C_9 , respectively. These predictions suggest that the observed 3388.8 and 3471.8 cm^{-1} absorptions are the $(\nu_1 + \nu_4)$ and $(\nu_2 + \nu_7)$ combination bands of linear C_5 and C_9 , respectively. By itself, this argument is not conclusive since the yields of different carbon chain species can be correlated; many fundamentals for different clusters lie close together; and traces of H_2O , CO , and CO_2 could bond to carbon chains and produce additional absorptions. Thus it is necessary to have isotopic shift measurements for unambiguous assignment of the combination bands.

Figure 2a shows a region to the low frequency side of the 3388.8 cm^{-1} , absorption where new bands emerge when a carbon rod with 10% ^{13}C enrichment is used. For comparison, Figure 2b shows the identical region recorded with no ^{13}C enrichment. Three new absorptions appear in Figure 2a, labeled B, C, and D, which have intensity ratios with respect to the 3388.8 cm^{-1} band of ~ 20 , 20, and 10%, respectively. This is what would be expected for the isotopic frequency shift profile of linear C_5 when 10% ^{13}C enrichment is used. A detailed comparison of these shift bands with the theoretical predictions for linear C_5 is presented in Table 3. As expected, the absorptions labeled B and C correspond to the 13—12—12—12—12 and 12—13—12—12—12

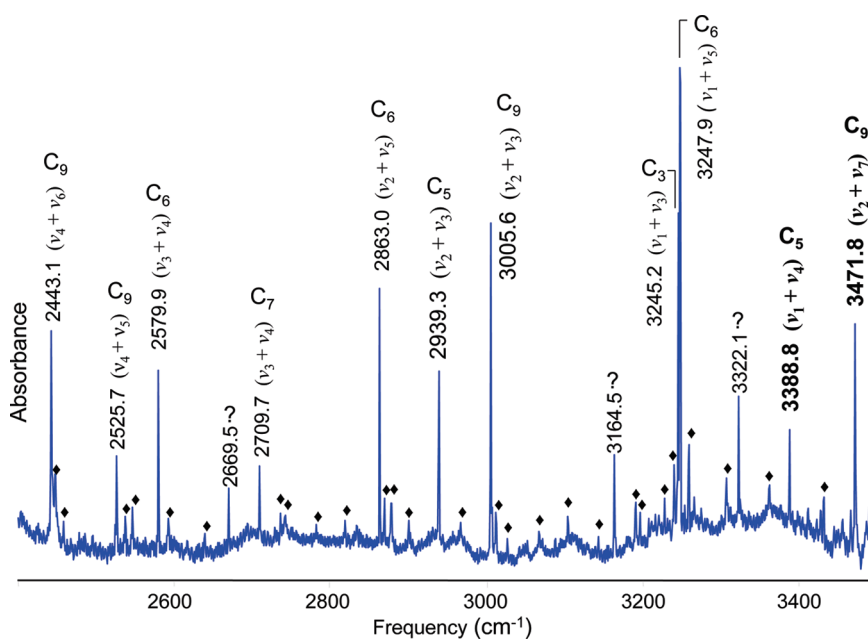


Figure 1. FTIR spectrum produced by the products of the laser ablation of a ^{12}C rod. The weak absorptions labeled with a diamond (♦) could be triple or quadruple ^{13}C -substituted combination bands. The newly observed combination bands of linear C_5 and C_9 are in boldface; the other combination bands have been observed in refs 26 and 27.

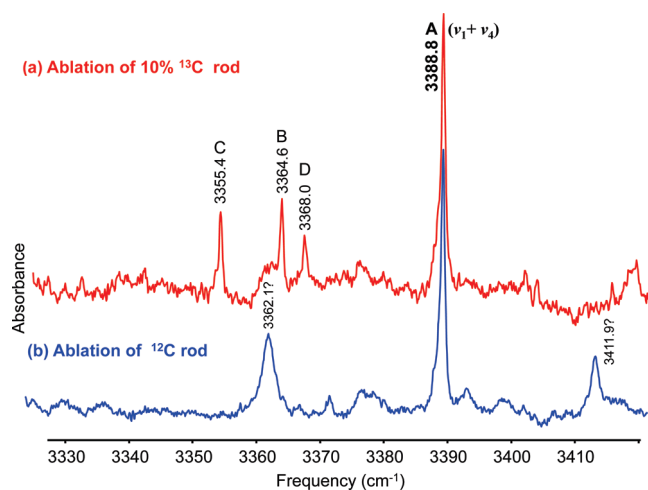


Figure 2. $(\nu_1 + \nu_4)$ combination band of linear C_5 . FTIR spectra produced by the laser ablation of (a) a carbon rod having a 10% ^{13}C enrichment and (b) a ^{12}C rod. Letters correspond to the single ^{13}C -substituted isotopomers listed in Table 3.

isotopomers, each with two equivalent sites, and D is the absorption of the 12–12–13–12–12 isotopomer with the unique central site. As seen in Table 3, the agreement between the measured isotopic shift bands and the DFT predicted frequencies is good, confirming the assignment of the $(\nu_1 + \nu_4)$ combination band of linear C_5 at 3388.8 cm^{-1} . Using the frequency of the previously assigned¹⁵ $\nu_4(\sigma_u^+)$ fundamental at 1446.6 cm^{-1} in eq 1 gives a frequency of 1946 cm^{-1} for the symmetric stretching mode $\nu_1(\sigma_g^+)$ of linear C_5 .

Figure 3a shows the spectrum to the low frequency side of the absorption at 3471.8 cm^{-1} obtained using a carbon rod with 10% ^{13}C enrichment. For comparison, Figure 3b shows the identical region of the spectrum obtained using a ^{12}C rod. The new

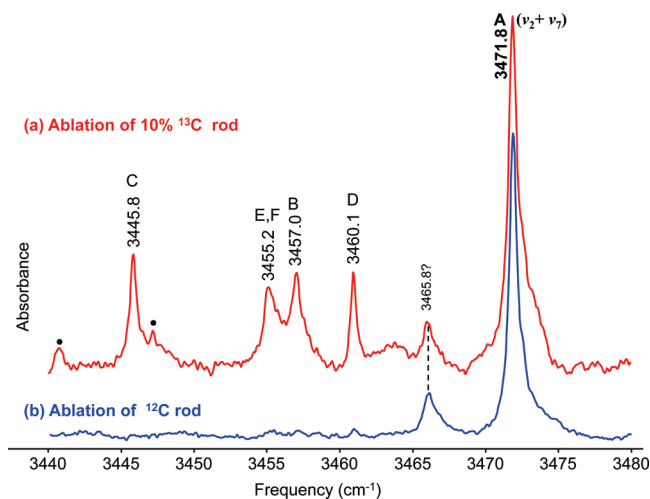


Figure 3. $(\nu_2 + \nu_7)$ combination band of linear C_9 . FTIR spectra produced by the laser ablation of (a) a carbon rod having a 10% ^{13}C enrichment and (b) a ^{12}C rod. Judging from the intensity of the weak absorptions (labeled ♦) with respect to the main band A, they could be ^{13}C double substitutions. Letters correspond to the single ^{13}C -substituted isotopomers listed in Table 4.

absorptions shown in Figure 3a, labeled B, C, D, and E,F, have intensity ratios with respect to the main 3471.8 cm^{-1} band of ~20, 20, 20, and 30%, respectively. The intensities of B, C, and D are what would be expected for single substitutions at three different pairs of equivalent sites in linear C_9 when there is 10% ^{13}C enrichment. The intensity of the fourth (E,F) band can then be explained as the overlap of an equivalent site absorption contributing 20% and the absorption corresponding to substitution at the unique, central site contributing 10%. As shown in Table 4, the bands of the 12–12–12–13–12–... and 12–12–12–12–13–... isotopomers

are theoretically predicted to be separated by only 0.4 cm^{-1} , consistent with this interpretation. Table 4 shows good agreement between the predicted and observed bands and confirms the identification of the $(\nu_1 + \nu_4)$ combination band of linear C_9 at 3471.8 cm^{-1} . Using the previously assigned²⁴ $\nu_7(\sigma_u^+)$ = 1601.0 cm^{-1} fundamental of linear C_9 , the frequency of the symmetric stretching mode $\nu_2(\sigma_g^+)$ of linear C_9 is calculated as 1871 cm^{-1} .

It is also worth noting in Tables 1 and 2 that eq 2 predicts from the anharmonic DFT calculation that the $\nu_1(\sigma_g^+)$ fundamental for linear C_5 should be observed in the gas phase at 1938 cm^{-1} and the $\nu_2(\sigma_g^+)$ fundamental for C_9 at 1870 cm^{-1} . These values are very close to the frequencies $\nu_1(\sigma_g^+) = 1946\text{ cm}^{-1}$ for linear C_5 and $\nu_2(\sigma_g^+) = 1871\text{ cm}^{-1}$ linear C_9 derived from the measurement of combination bands in the present work.

Figure 4 shows the $1050\text{--}1250\text{ cm}^{-1}$ region in which the $\nu_5(\sigma_u^+) = 1197.3\text{ cm}^{-1}$ fundamental of C_6 appears and in addition, a new, unidentified absorption at 1100.1 cm^{-1} . The DFT calculation for linear C_7 , presented in Table 5, predicts that the so far unobserved $\nu_6(\sigma_u^+)$ fundamental should lie at 1118 cm^{-1} , which suggests that the unidentified absorption could be a candidate. The 1100.1 cm^{-1} absorption only appears under conditions that produce a high yield of the C_7 molecule, as indicated by

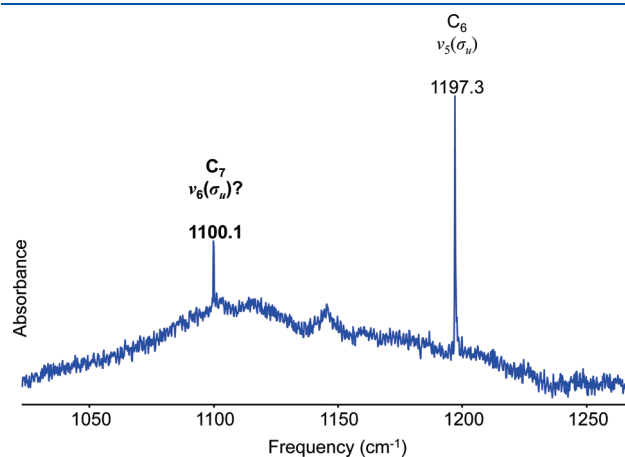


Figure 4. FTIR spectrum in the $1050\text{--}1250\text{ cm}^{-1}$ region produced by the laser ablation of a carbon rod.

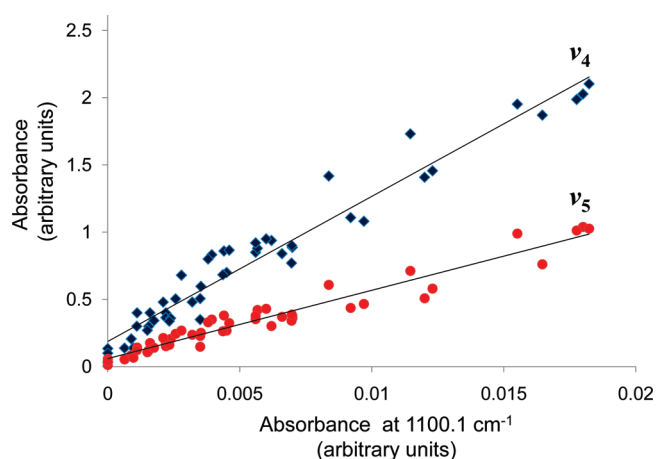


Figure 5. Intensity correlation plot of the $\nu_4(\sigma_u^+)$ and $\nu_5(\sigma_u^+)$ absorbances vs the absorbance at 1100.1 cm^{-1} . The integrated intensities are in arbitrary units.

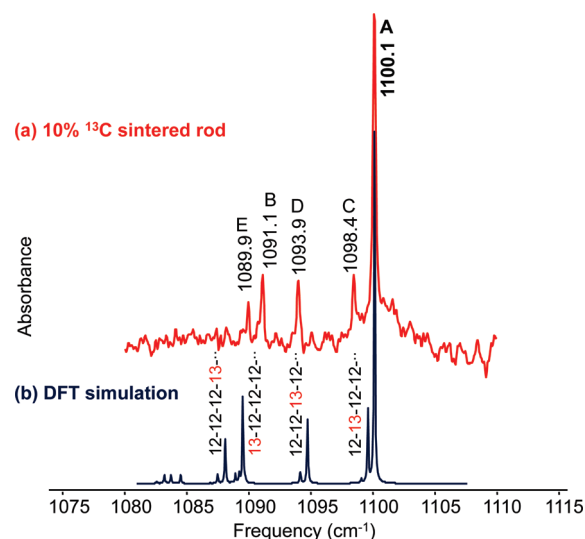


Figure 6. (a) FTIR spectra produced by the ablation of a carbon rod with $10\%\text{ }^{13}\text{C}$ enrichment and (b) a DFT simulation using the B3LYP/cc-pVDZ level of theory for the $\nu_6(\sigma_u^+)$ fundamental of linear C_7 .

Table 5. Observed and DFT-B3LYP/cc-pVDZ Predicted Vibrational Frequencies and Band Intensities for Linear C_7

vibrational mode	observed (cm^{-1})			calculated harmonic frequency	IR intensity (km/mol)
	Ar	Ne	gas		
$\nu_1(\sigma_g^+)$				2221.4	0
$\nu_2(\sigma_g^+)$				1609.5	0
$\nu_3(\sigma_g^+)$	582 ^a		548 ± 90 ^b	588.8	0
$\nu_4(\sigma_u^+)$	2127.8 ^c	2134.6 ^d	2138.315 ^e	2258.2	4656
$\nu_5(\sigma_u^+)$	1894.3 ^f		1898.376 ^g	1988.4	1303
$\nu_6(\sigma_u^+)$	1100.1 ^h			1118.8	16
$\nu_7(\pi_g)$			496 ± 110 ^b	574.4	0
$\nu_8(\pi_g)$				190.2	0
$\nu_9(\pi_u)$				708.0	(6.1)2
$\nu_{10}(\pi_u)$				293.1	(6.2)2
$\nu_{11}(\pi_u)$				80.1	(9.9)2

^a Reference 26. ^b Reference 45. ^c Reference 28. ^d References 33 and 34. ^e References 30–32. ^f Reference 47. ^g Reference 30. ^h This work.

Table 6. Comparison of Observed and Predicted Harmonic DFT (B3LYP/cc-pVDZ) Frequencies for Single ^{13}C -Substituted Isotopomers of the ν_6 Mode of Linear C_7

isotopomer		obsd (cm^{-1})	B3LYP/cc-pVDZ		difference obsd – scaled
			harmonic	scaled ^a	
12–12–12–12–12–12...	A	1100.1	1118.8	1100.1	
13–12–12–12–12–12...	B	1091.1	1106.6	1089.5	1.6
12–13–12–12–12–12...	C	1098.4	1118.3	1099.6	−1.2
12–12–13–12–12–12...	D	1093.9	1113.3	1094.7	−0.8
12–12–12–13–12–12...	E	1089.9	1108.0	1088.1	1.8

^a Results of the B3LYP/cc-pVDZ calculation scaled by a factor of $1100.1/1118.8 = 0.983285$.

strengths of the $\nu_4(\sigma_u^+)$ and $\nu_5(\sigma_u^+)$ absorptions of linear C_7 . The strong intensity correlation between the $\nu_4(\sigma_u^+)$ and $\nu_5(\sigma_u^+)$ bands and the 1100.1 cm^{-1} band is shown in Figure 5. This evidence is not conclusive, of course, because the yields of different species of carbon chains can be correlated; many vibrational fundamentals of different clusters lie in the same spectral regions, and spectra indicate H_2O , CO , and CO_2 that could react with carbon chains to produce additional absorptions. Isotopic shift measurements are necessary to unambiguously assign the fundamental. The best signal-to-noise ratio for the isotopic shift pattern was observed when sintered rods were ablated with 10% ^{13}C enrichment and is shown in Figure 6a. Five new absorptions appear in Figure 6a labeled B, C, D, and E, which have intensity ratios with respect to the 1100.1 cm^{-1} band of ~ 20 , 20, 20 and 10%, respectively. This is what would be expected for the isotopic pattern for linear C_7 when 10% ^{13}C enrichment is used. A detailed comparison of these shifts with the theoretical predictions for linear C_7 is presented in Table 6. As expected, the absorptions labeled B, C and D correspond to the 13–12–12–12–..., 12–13–12–12–..., and 12–12–13–12–... isotopomers, each with two equivalent sites, and E is the absorption of the 12–12–12–13–... isotopomer with the unique central site. The agreement between the measured isotopic shifts and the DFT predictions is very good, confirming the conclusion that the 1100.1 cm^{-1} absorption can be assigned to the $\nu_6(\sigma_u^+)$ fundamental of linear C_7 .

6. CONCLUSIONS

New combination bands of carbon chains have been observed, $(\nu_1 + \nu_4) = 3388.8\text{ cm}^{-1}$ of linear C_5 and $(\nu_2 + \nu_7) = 3471.8\text{ cm}^{-1}$ of linear C_9 . These assignments are based on very good agreement between measured isotopic shifts and DFT predictions at the B3LYP/cc-pVDZ level of theory and the correlation of the intensities of the combination bands with vibrational fundamentals of the same molecule. Since the asymmetric stretching modes involved in these absorptions have been measured previously,^{15,24} it has been possible to assign the infrared inactive symmetric stretching modes, the $\nu_1(\sigma_g^+)$ mode of linear C_5 at 1946 cm^{-1} and the $\nu_2(\sigma_g^+)$ mode of linear C_9 at 1871 cm^{-1} . The close agreement of the measured $\nu_1(\sigma_g^+)$ fundamental of linear C_5 and $\nu_2(\sigma_g^+)$ of linear C_9 with the frequencies predicted by eq 2 from the B3LYP anharmonic calculation gives further support to the identifications of the fundamentals and combination bands.

It has also been possible to measure for the first time the relatively weak $\nu_6(\sigma_u^+)$ fundamental of linear C_7 at 1100.1 cm^{-1} . This new assignment has been confirmed by the very good agreement between the predictions of DFT calculations and measured ^{13}C isotopic shifts.

In the course of this work isotopic data have also been acquired for the combination bands of linear C_5 , C_6 , and C_9 presented in refs 26 and 27: $(\nu_2 + \nu_3) = 2939.3\text{ cm}^{-1}$ for C_5 , $(\nu_1 + \nu_5) = 3247.9\text{ cm}^{-1}$, $(\nu_2 + \nu_5) = 2863.0\text{ cm}^{-1}$, and $(\nu_3 + \nu_4) = 2579.9\text{ cm}^{-1}$ for C_6 , and $(\nu_4 + \nu_5) = 2525.7\text{ cm}^{-1}$ and $(\nu_4 + \nu_6) = 2443.1\text{ cm}^{-1}$ for C_9 with only minor discrepancies in the last figure. Although we have a high yield of carbon clusters, there are no absorptions in the $4000\text{--}4400\text{ cm}^{-1}$ range, indicating that for carbon chains the intensities of infrared active combination bands of $\nu_1(\sigma_g^+)$ and the most intense asymmetric stretching modes are very weak. Surprisingly, in this region the first overtones reported in ref 1 have not been observed.

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ACKNOWLEDGMENT

Grants from the TCU Research and Creative Activities Fund and the W. M. Keck Foundation are gratefully acknowledged.

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