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Detection of cyclic carbon clusters. I. Isotopic study of the $\nu_4(e')$ mode of cyclic C_6 in solid Ar

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The cyclic C_6 cluster has been identified for the first time in Fourier transform infrared spectra of the products from the laser evaporation of graphite rods trapped in Ar at ~ 10 K. Measurements on spectra produced using both ^{12}C- and ^{13}C-enriched rods combined with the results of new density functional theory calculations performed in the present work as well as previous calculations by Martin and Taylor, have resulted in the assignment of the most intense infrared active mode, $\nu_4(e') = 1694.9\ \mathrm{cm}^{-1}$ of the cyclic C_6 isomer with D_{3h} symmetry. This assignment is based on excellent agreement of the frequency, ^{13}C isotopic shifts, and relative intensities with the theoretical predictions. [S0021-9606(97)02540-3]

I. INTRODUCTION

Although carbon clusters have long been the subject of extensive theoretical and experimental studies (see Refs. 1 and 2 for reviews), activity in this area of research has now reached an unprecedented level of intensity with the ongoing development of fullerene chemistry. Linear C_6 with a $D_{\infty h}$ cumulenic form has been identified and its fundamental vibrations have been assigned.[3–8] Similarly, vibrational fundamentals have been firmly established by matrix and gas phase measurements for all the other small linear carbon clusters up to C_9, with the possible exception of C_8. More recently laser diode spectroscopic measurement of a mode of linear C_{13} has also been reported.[9] No identification of vibrational modes of cyclic carbon clusters has been reported, however, despite the predictions of extensive *ab initio* calculations that cyclic geometries are generally preferred as the lowest energy structures for small carbon clusters with an even number of atoms ($n \leqslant 8$) and for all larger clusters ($n \geqslant 10$).

In the case of C_6 (and C_4), because of an apparently small difference in energy between the linear and cyclic isomers, some uncertainty surrounds the lowest energy structure. A cyclic C_6 isomer with a D_{3h} symmetry, which is essentially a distorted benzene ring in which alternate atoms of the hexagon have moved radially in or out, was first predicted to be the most stable form by Raghavachari and co-workers.[10,11] They optimized geometries at the Hartree–Fock (HF) level using a 6-31G* basis set and found that beyond second-order many-body perturbation theory the D_{3h} structure was energetically favored. The frequencies of the infrared-active carbon stretching modes were calculated as 1726 and $1365\ \mathrm{cm}^{-1}$ by the same group. These results were later challenged, by Parasuk and Almlöf[12] who predicted on the basis of multireference configuration interaction (MRCI) calculations with complete active space self-consistent field (CASSCF) optimized geometries that the linear form was the most stable and that the cyclic isomer lay 37.2 kcal/mol higher in energy. These results were in turn challenged by Hutter and co-workers'[13,14] higher level density functional theory (DFT) calculations at the BP86/$4s3p1d$ level and coupled cluster calculations with single, double, and triple excitations [CCSD(T)/TZ2P]. They found that the linear and cyclic forms of C_6 were very close in energy and concluded that both structures might be experimentally observable.

In experimental work, Szczepanski and Vala[15] reported that the intensity of an infrared band located at $1695\ \mathrm{cm}^{-1}$, which was first assigned to a pure carbon molecule in an Ar matrix in Weltner's classic study,[3] grew dramatically upon annealing and speculated that it belonged to a cyclic cluster containing six or more carbons. In this laboratory, comparison of the results of density functional theory (DFT) calculations[16] at the BVWN5 level (Becke–Vosko–Wilk–Nusair functionals) using a standard 6-31G* basis set, with preliminary data obtained from the laser evaporation of graphite suggested that the $1694.9\ \mathrm{cm}^{-1}$ band, also seen in earlier thermal evaporation experiments,[17] was a potential candidate for the cyclic C_6 isomer.

Martin and Taylor[18] showed on the basis of calculations at the CCSD(T)/cc-pVTZ level, that the cyclic form of C_6 is slightly favored energetically over the linear form. Earlier, Martin and co-workers[19] predicted a frequency for the most intense band of this cyclic structure using the B3LYP (Becke 3-parameter-Lee–Yang–Parr) functionals which suggested an assignment in the 1700–1800 cm^{-1} region. Specifically, they proposed two absorptions observed at 1695 and $1715\ \mathrm{cm}^{-1}$ in Ar matrices,[15,20] as leading contenders and provided a complete set of ^{13}C isotopic shifts[18] for comparison with future experimental studies.

In the present paper, with the support of detailed ^{13}C isotopic measurements, we assign the $1694.9\ \mathrm{cm}^{-1}$ band to $\nu_4(e')$, the most intense mode of cyclic C_6 with D_{3h} symmetry. Extensive ^{13}C isotopic data are in very good agreement with present B3LYP/cc-pVTZ DFT calculations as well as with Martin and Taylor's predictions at the B3LYP/cc-pVDZ level.[18]

II. THEORETICAL CALCULATIONS

Recently, in conjunction with the presentation of their new coupled cluster calculations, Martin and Taylor[18] summarized the history of theoretical calculations of the C_6 cluster. In the pioneering work of Raghavachari *et al.*[10,11] a best estimate of 13.9 kcal/mol was obtained for the energy separation between the linear and cyclic isomers. This value was derived from a single-point coupled cluster doubles (CCD) calculation with partial inclusion of fourth-order effects [CCD+ST(CCD)/6-31G*] at HF/6-31G* geometries. This energy ordering has subsequently been confirmed by most higher level calculations. Martin and Taylor's[18] range of values of 11–15 kcal/mol for the energy separation was based on their extensive CCSD(T)/cc-pVTZ calculations at optimized geometries. These coupled cluster calculations include single and double excitations as well as a quasiperturbative inclusion of connected triple excitations. Given that ten years has passed since the work of Raghavachari and co-workers[10,11] it may seem that little progress has been made. This is, however, not true since the evolution of hardware, software, and new theoretical techniques has led to the possibility of including electron correlation effects to high orders when optimizing geometries as well as when calculating vibrational frequencies. With regards to the identification of new carbon clusters in the laboratory this development has been crucial.

Based on the theoretical energy separation between the cyclic and linear isomers Slanina *et al.*[21] have shown that thermodynamical considerations make the linear isomer dominate strongly in the high-temperature production of C_6. This explains the experimental situation where linear C_6 can be readily produced by various means whereas the cyclic structure has been more elusive.

In our matrix Fourier transform infrared (FTIR) experiments identifications of new molecular species rely heavily on the method of isotopic substitution. In the case of shorter carbon chains a majority of the isotopomers can be identified, and by comparison with theoretical predictions a particular absorption band can be assigned with a high level of confidence. As longer carbon chains are considered the large number of isotopomers gives rise to an increasing number of overlapping bands and the identification of a subset of isotopomers (primarily the singly substituted ones) can give sufficient support for a new identification. An additional complication originates from the increasing density of high-frequency stretching modes which can lead to strong interactions between modes as the symmetry of the molecule is broken upon isotopic substitution. This provides a further challenge to the theorist in that it may require a delicate ''fine-tuning'' of the full force constant matrix in order to obtain isotopic shifts accurate enough to be useful to the experimentalist. Recently we have investigated this situation in studies of linear C_7 and C_9 (Refs. 22 and 23) as well as for the linear SiC_2H cluster.[24]

In an attempt to quantify the behavior described above we defined an ''isotopic sensitivity index'' as the ratio of higher order to first-order effects:

$$\boldsymbol{\iota}_s=\left|\frac{\Delta_2+\Delta_3+\cdots}{\Delta_1}\right|=\left|1-\frac{\Delta\omega_\infty}{\Delta_1}\right|.$$

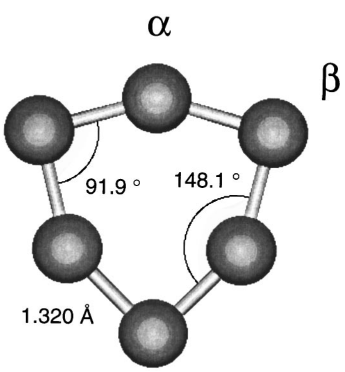

FIG. 1. Optimized geometry parameter for cyclic C_6 obtained at the DFT-B3LYP/cc-pVTZ level.

Here $\Delta\omega_\infty$ denotes the infinite order calculated shift from an *ab initio* calculation and the first-order singly substituted isotopic shift (for nondegenerate modes) of the mode with frequency ω is obtained from

$$\Delta_1=\frac{\omega}{2}\left(1-\frac{m_i}{m_f}\right)|\mathbf{u}|^2,$$

where m_i and m_f are the initial and final isotopic masses, respectively, and $\mathbf{u}$ is the mass weighted normal-mode vector for the isotopically substituted nucleus. Since first-order effects should dominate for small values of $|m_i-m_f|$ and interactions with the remaining vibrational modes occur at higher order, this index should provide us with a feel for the importance of describing the full vibrational spectrum accurately.

To investigate the behavior of calculated isotopic shifts of cyclic C_6 as well as to aid in the experimental identification of this cluster we performed a series of calculations at various levels of theory. All calculations were made on an IBM RS/6000-370 workstation using the GAUSSIAN 94[25] program package using standard basis sets. For comparison with our experimental data (see Sec. IV) we initially performed a DFT calculation with the standard B3LYP functionals and cc-pVTZ basis set available in GAUSSIAN 94.[25] Figure 1 gives the DFT-B3LYP/cc-pVTZ optimized geometry parameters and Table I gives the harmonic frequencies and infrared intensities obtained at this geometry. These results are in line with previous calculations (see Refs. 18 and 19).

TABLE I. Harmonic frequencies calculated at the DFT-B3LYP/cc-pVTZ level of cyclic C_6.

Vibrational mode	Frequency (cm^{-1})	Infrared intensity (km/mol)
$\nu_1(a_1')$	1220.9	0
$\nu_2(a_1')$	650.4	0
$\nu_3(a_2')$	1408.5	0
$\nu_4(e')$	1758.5	435×2
$\nu_5(e')$	1228.1	0.7×2
$\nu_6(e')$	644.9	22×2
$\nu_1(a_2'')$	438.1	6.2
$\nu_8(e'')$	538.7	0

TABLE II. Isotopic sensitivity index calculated at the DFT-B3LYP/cc-pVTZ level for the $\nu_4(e')$ mode of cyclic C_6.

Isotopomer C_α-C_β-C_α-C_β-C_α-C_β	Δ_1	$\Delta\omega_\infty$	ι_s
13-12-12-12-12-12	0.03	0.04	~ 0
	30.55	29.82	0.025
12-13-12-12-12-12	5.09	4.87	0.045
	9.55	9.29	0.027

Subsequently, we used the normal-mode coordinates from the B3LYP/cc-pVTZ calculation to calculate the isotopic sensitivity index for the $\nu_4(e')$ mode for single ^{13}C substitutions. Since this is a degenerate mode, the first-order shift must be obtained from the diagonalization of the first-order matrix Δ_1 with matrix elements given by

$$[\Delta_1]_{rs} = \frac{\omega}{2}\left(1 - \frac{m_i}{m_f}\right)\mathbf{u}_r \cdot \mathbf{u}_s .$$

The results are presented in Table II. Since there are two sets of three equivalent carbon atoms (labeled α and β in Fig. 1), there are only two distinct singly substituted isotopomers. The lifting of the degeneracy of the e' mode gives rise to four singly substituted isotopic shifts. From our previous experience with linear carbon clusters[22,23] a sensitivity index of less than 0.1, i.e., a contribution from higher orders of less than 10% of that from first order, usually indicates that the calculated shift will be relatively stable with respect to a change of method or basis set, provided post-HF methods are considered. For cases where $\iota_s > 0.1$, care has to be taken when trying to compare theoretical shifts with those from experiment. A modest change in the calculation may give rise to a dramatic change in the shift. To illustrate the situation for cyclic C_6, we simulated isotopic spectra for the $\nu_4(e')$ mode at three levels of theory, HF, second-order many-body perturbation theory [MBPT(2)], and DFT-B3LYP, using the same 6-31G* basis set. These spectra assume a ratio of concentrations between ^{13}C and ^{12}C isotopes $^{13}C{:}^{12}C \equiv c = 1/9$, and have been scaled so that the main band corresponds to the experimental value obtained in this work. From Table II we find that we should expect three strong bands corresponding to the singly substituted species, with the fourth overlapping the main band. Each singly substituted band should have an intensity of $3 \times c \times I$ where $2 \times I$ is the intensity of the (degenerate) main band. The relative intensity of a singly substituted species and the main band is thus

$$\frac{3 \times c \times I}{2 \times I \times 3 \times c \times I} = 1/[(2/3c) + 1].$$

As can be seen in Fig. 2, one of the singly substituted bands is persistently stronger than the others in all three calculations. This is due to an overlap with one of the components of the doubly substituted isotopomer containing diametrically positioned ^{13}C atoms, i.e., combining the 9 cm^{-1} β-site shift with the ~ 0 cm^{-1} α-site shift. This should be an observable effect for large enough concentrations of ^{13}C.

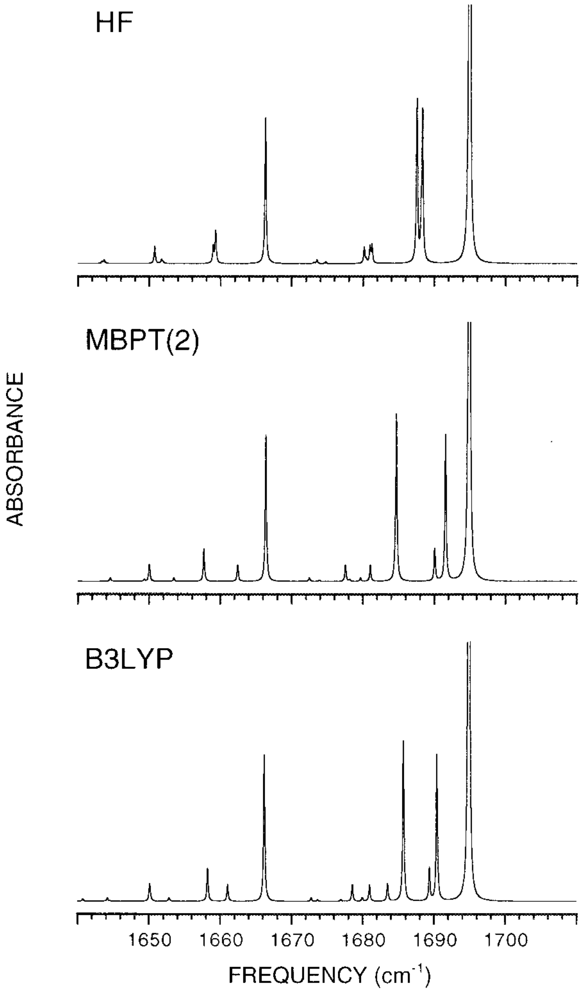

FIG. 2. Simulated spectra for the $\nu_4(e')$ mode of cyclic C_6 at three different levels of theory using a 6-31G* basis set.

Furthermore, we note that the simulated spectra are relatively stable as we go beyond the HF level as anticipated from the behavior of the sensitivity index in Table II and the discussion above. The isotopic spectrum of C_6 is thus expected to be relatively well described by theory with a distinct position and intensity pattern for the singly substituted isomers.

III. EXPERIMENT

Matrix samples were prepared by vaporizing the surface of carbon rods using a slightly focused Nd:YAG (DCR-11, Spectra-Physics) pulsed laser operating at 532 nm. The evaporated species were condensed in solid Ar (99.999% pure) on a gold plated surface cooled to ~ 10 K by a closed cycle refrigerator (APD Cryogenics, Displex) in a vacuum of 10^{-7} Torr or better during the experiment.

The carbon rods were fabricated by mixing carbon-12 (Alfa, 99.9999% purity) and carbon-13 (Isotec, 99.3% purity) powder in various ratios and then pressing the mixtures into rods. A degassing procedure was used to remove any gas trapped in the rods by heating them to ~ 200 °C under vacuum for 24 h.

During evaporation, the carbon rod was continuously rotated and translated to provide a fresh target surface for the laser beam. A filter was used to prevent unvaporized large particles sputtered off the rod surface from reaching the deposition site. After the evaporation, controlled, thermally induced diffusion in the matrix was used to enable the growth of large clusters by warming the matrix to a specific temperature and maintaining it there for ~10 min before cooling back to ~10 K.

FTIR absorption spectra of the matrix samples were recorded in the region of 550–3900 cm^{-1} at a resolution of 0.2 cm^{-1} using a Bomem DA 3.16 Fourier transform spectrometer equipped with a liquid-nitrogen-cooled MCT (Hg–Cd–Te) detector and KBr beamsplitter. Details of the optical system have been reported previously.[26] All frequencies reported were measured to $\pm 0.1\ \text{cm}^{-1}$.

IV. RESULTS AND DISCUSSION

The most intense infrared band for the cyclic C_6 structure with D_{3h} symmetry is predicted to be the doubly degenerate $\nu_4(e')$ mode with frequency in the region of 1700 cm^{-1}.[18,19] Four isotopomer bands are possible on single ^{13}C-substitution with one of them predicted to have zero shift and therefore, to underlie the absorption for the unsubstituted isotopomer. As discussed earlier (see Sec. II), the intensity of each of the three observable singly substituted ^{13}C isotopomer absorptions relative to the main absorption should then be $1/[(2/3c)+1]$, where c is the ^{13}C:^{12}C isotopic ratio for the sample used. This result differs from the situation for linear carbon clusters where the relative intensity of the singly substituted ^{13}C isotopomers is $2c$ for clusters with an even number of atoms, and $2c$ or c for the ''odd number'' clusters. For example, if the ^{13}C originates with the 1% natural abundance of the ^{13}C isotope, the relative intensity of singly substituted bands for cyclic C_6 will be ~1.5%, and increasing the ^{13}C abundance to ~7% through enrichment of the carbon rod will lead to ~10% relative intensity, a readily observed difference from the intensities expected for a linear chain.

In our experiments, all absorptions observed in the 1600–1900 cm^{-1} region have been considered as potential candidates for the $\nu_4(e')$ vibration. Each band has been thoroughly investigated by comparing its observed frequency, and the frequencies and relative intensities of its isotopic shift bands with the predictions of the available DFT calculations.

Instead of relying on the nominal ^{13}C:^{12}C ratio in the mixture used to fabricate the rod, the relative intensities for the singly substituted ^{13}C isotopomer bands of cyclic C_6 are based on the actual ^{13}C:^{12}C ratio in the product species as determined from the intensities of the well-known isotopomer bands of linear C_3 and C_6.[5] The reason for this procedure is that the actual ^{13}C:^{12}C ratio in the molecular clusters formed in the matrix can differ significantly from the nominal ratio in the rod, especially when a relatively high ^{13}C:^{12}C ratio is used. For ^{13}C:^{12}C ratios of less than 15%, however, the effect is found not to be significant. The discrepancy is believed to originate with the different laser evaporation characteristics for the ^{13}C and ^{12}C powders owing to differences in average particle size.

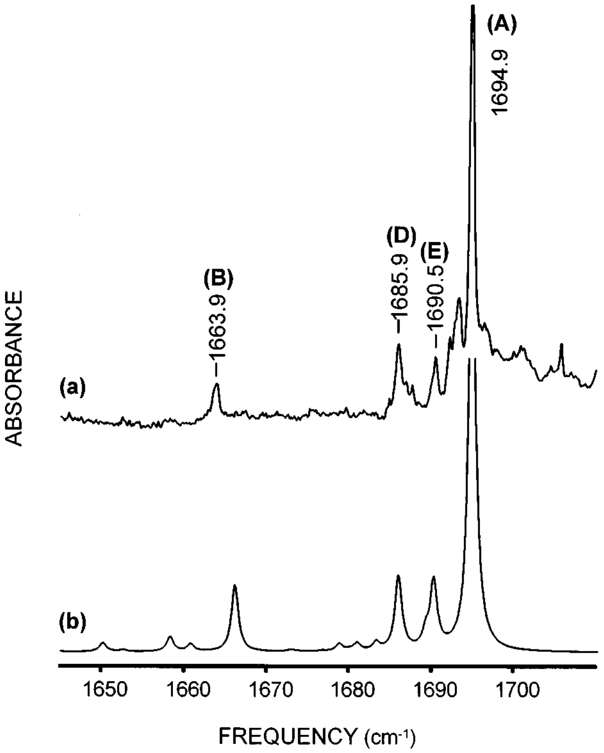

FIG. 3. (a) FTIR spectrum showing singly substituted isotopomer absorptions of cyclic C_6 produced by the laser evaporation of a ^{13}C-enriched rod with measured ^{13}C:$^{12}\text{C}=7.5\%$ in the products. (b) A simulated spectrum based on the predictions of the B3LYP/cc-pVTZ DFT calculations from the present study.

The only absorption found in our experiments which is consistent with the predicted behavior of the $\nu_4(e')$ mode is the absorption located at 1694.9 cm^{-1} and shown in Fig. 3(a). This band appears strongly in spectra recorded for samples prepared using rods with only ~1% natural ^{13}C abundance, although the intensities of the three single ^{13}C isotopomer bands are too weak for accurate measurements. The situation was drastically improved by the addition of 7% to 8% ^{13}C in the rods during fabrication. The assignment of the 1694.9 cm^{-1} band to the $\nu_4(e')$ mode is based on very good agreement between the experimental values and the DFT calculated values for the ν_4 mode's frequency, ^{13}C isotopic shift frequencies, and relative intensities. A second e' mode is predicted at 645 cm^{-1}; however, its low calculated intensity and the decline in the MCT detector's sensitivity in this region made a definite identification impossible.

Figures 3(a) and 4 show the absorption at 1694.9 cm^{-1} and other bands in the immediate vicinity. The spectra were produced by the evaporation of a $^{12}\text{C}/^{13}\text{C}$ rod for 15 and 20 min, respectively, with measured ^{13}C:^{12}C ratio in the products of 7.5%. The difference between the two spectra can be attributed in part to different evaporation times but perhaps more importantly, to the greater compactness or rigidity of the rod used to produce the spectrum in Fig. 4, owing to improvements in the rod fabrication technique.

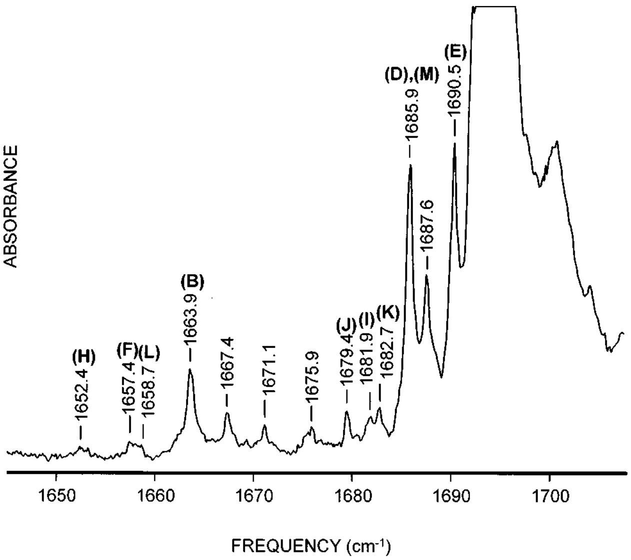

FIG. 4. FTIR spectrum showing both single and double substituted isotopomer absorptions of cyclic C_6 produced by the laser evaporation of a ^{13}C-enriched rod with measured 7.5% enrichment in the products.

Prior to recording the spectra shown in Figs. 3(a) and 4 the matrix samples were subjected to successive annealing cycles of warming and quenching to ~10 K. The spectrum in Fig. 3(a), was observed after the sample had been annealed in cycles to 20, 25, 30, 33, and 37 K with 10 min spent at each of the successively higher temperatures; however, the spectrum in Fig. 4 resulted from only one annealing cycle to 20 K. Usually, annealing increases the intensity and sharpness of bands for large carbon clusters. Furthermore, these effects are enhanced by increasing the number of annealing cycles at temperatures lower than ~40 K and the length of time spent at each temperature. Indeed, the main absorption at 1694.9 cm^{-1} in Fig. 3(a), which was originally weak and broad (~10 cm^{-1}) before annealing, increased in intensity by a factor $\geqslant 5$ and narrowed to less than 3 cm^{-1} after multiple annealing cycles. The band in Fig. 4, although originally strong, was very broad, but grew in intensity and sharpened after only one cycle at the relatively low, 20 K annealing temperature.

In Figs. 3(a) and 4, additional bands to the low-frequency side of the main band at 1694.9 cm^{-1} can also be clearly seen. While some of these bands are related to the main band and are enhanced by ^{13}C enrichment, others are not. The most prominent of the secondary bands, those located at 1663.9, 1685.9, and 1690.5 cm^{-1} [See Fig. 3(a)], which show the same behavior during annealing and for experiments with different ^{13}C:^{12}C ratios, are clearly related. Their shifts of 31.0, 9.0, and 4.4 cm^{-1}, respectively, enable them to be easily assigned to the three, singly substituted, ^{13}C isotopomers (B), (D), and (E), which as shown in Table III, have predicted shifts of 28.8, 9.0, and 4.7 cm^{-1}, respectively. (The labeling scheme identifying the isotopomers of cyclic C_6 is explained in Table III.) The intensities of the three bands relative to the 1694.9 cm^{-1} absorption are also consistent with this assignment, averaging 9.5% compared to 10% predicted by the formula $1/[(2/3c)+1]$, discussed earlier. Moreover, as predicted earlier (see Sec. II), the (D) isotopomer band is consistently observed to be slightly stronger. The very good agreement between the observed spectrum and the results of the DFT calculations is further illustrated by Fig. 3(b) which shows a simulated spectrum generated from the B3LYP/cc-pVTZ calculation assuming ^{13}C:^{12}C $=1:9$. Comparison of the observed spectrum in Fig. 3(a)

TABLE III. Comparison between isotopic shifts (cm^{-1}) observed for the ν_4 mode of (D_{3h}) cyclic C_6 and those predicted by DFT calculations.

Isotopomer		Observed		B3LYP/ cc-pVDZ[a]	B3LYP/ cc-pVTZ[b]
C_α-C_β-C_α-C_β-C_α-C_β		Freq.	Shift	Scaled shift	Scaled shift
12-12-12-12-12-12	(A)	1694.9	--	--	--
13-12-12-12-12-12	(B)	1663.9	31.0	28.7	28.8
	(C)	--	--	0.0	0.0
12-13-12-12-12-12	(D)	1685.9[c]	9.0	9.1	9.0
	(E)	1690.5	4.4	4.5	4.7
13-13-12-12-12-12	(F)	1657.4	37.5	36.6	36.6
	(G)	overlapped[d]	overlapped	5.5	5.7
13-12-13-12-12-12	(H)	1652.4	42.5	44.8	44.7
	(I)	1681.9	13.0	13.9	14.0
12-13-12-13-12-12	(J)	1679.4	15.5	16.2	16.2
	(K)	1682.7	12.2	11.4	11.7
13-12-12-13-12-12	(L)	1658.7	36.2	34.0	35.4
	(M)	overlapped[c]	overlapped	9.1	9.0

[a] Values scaled by a factor=0.9583 obtained from the ratio of the measured and predicted frequencies at the B3LYP/cc-pVDZ level by Martin and Taylor (Ref. 18).

[b] Values scaled by a factor=0.9638 obtained from the ratio of the measured and predicted frequencies at the B3LYP/cc-pVTZ level in the present work.

[c] Absorptions of the (D) and (M) isotopomers overlap.

[d] Absorption (G) is overlapped by the 1687.6 cm^{-1} absorption.

with the simulated spectrum shows a good match for the dominant singly ^{13}C-substituted bands.

Additional, weaker features in the simulated spectrum in Fig. 3(b) belong to the doubly substituted isotopomers. Corresponding absorptions observed in the FTIR spectrum are clearly observable in the spectrum of Fig. 4 at 1652.4 (H), 1657.4 (F), 1658.7 (L), 1679.4 (J), 1681.9 (I), and 1682.7 cm^{-1} (K). Under a variety of conditions they also exhibit intensity behavior which is similar to that for the three singly substituted isotopomer bands. As shown in Table III, these weaker absorptions are readily assigned to isotopomers with double ^{13}C substitutions. The experimental frequency values are in reasonably good agreement with the DFT predicted values despite the fact that some of the isotopomer bands overlap. For example, a band was not assigned to the (M) isotopomer because it is overlapped by the singly substituted ^{13}C isotopomer (D) band. Similarly, an assignment for (G) was not made because it is overlapped by a band at 1687.6 cm^{-1}.

Additional bands appearing at 1667.4, 1671.1, 1675.9, and 1687.6 cm^{-1} in Fig. 4 are not, however, related to the 1694.9 cm^{-1} absorption. This conclusion is based both on the evidence of their different behavior during annealing and on the correlation of their intensities with other bands to the high-frequency side of the 1694.9 cm^{-1} absorption. The intensity of the band at 1687.6 cm^{-1} decreases slightly on annealing while the intensities of the 1694.9 cm^{-1} band and its associated isotopic shift bands all increase. Although apparently not a member of the 1694.9 cm^{-1} band group, the 1687.6 cm^{-1} band remains unidentified. The intensities of the bands at 1667.4, 1671.1, and 1675.9 cm^{-1} seem correlated to other moderately intense bands located to the high-frequency side of the 1694.9 cm^{-1} absorption (e.g., 1705.7, 1710.6, and 1714.2 cm^{-1}), but not shown in both Figs. 3(a) and 4, and may belong to unidentified carbon clusters trapped in the matrix.

Table III, comparing the observed frequencies and corresponding shifts with the values calculated at two different levels of DFT calculations, summarizes the proposed assignments. It can be seen that all of the single ^{13}C shifts and almost all of the doubly ^{13}C substituted isotopic shifts, except for one singly and two doubly substituted shifts which are overlapped by other bands, can be unambiguously assigned to isotopomers of cyclic C_6 (D_{3h}).

V. CONCLUSION

FTIR measurements in an Ar matrix combined with predictions from a new B3LYP/cc-pVTZ DFT calculation performed in the present work, and previous B3LYP/cc-pVDZ calculations by Martin and Taylor,[18] have resulted in the first spectroscopic identification of cyclic C_6. The most intense infrared active mode, $\nu_4(e')=1694.9\ \mathrm{cm}^{-1}$ of the cyclic C_6 structure with D_{3h} symmetry, has been assigned and measured for the first time based on the excellent agreement of the frequency, isotopic shifts, and their relative intensities with the predictions from DFT calculations. Cyclic C_6 is the first cyclic carbon cluster so far discovered spectroscopically.

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