Isotopic Infrared Absorption Study of C_5^-, C_7^-, and C_9^- Carbon Cluster Anions in Ar Matrices

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The carbon cluster anions C_5^-, C_7^-, and C_9^- have been formed via a dual laser beam technique, trapped in Ar matrixes, and studied by infrared spectroscopy. ^{13}C-Isotopic substitution combined with density functional (B3LYP/6-31G*) calculations of vibrational frequencies and intensities has led to the assignment of asymmetric stretching modes in the three anionic clusters. From the excellent fit of the calculated and experimental singly ^{13}C-substituted cluster bands, a linear geometry for all three clusters has been determined.

I. Introduction

The chemistry and physics of small carbon clusters and their ions have been the focus of much research activity over the past several years.[1−4] In addition to their astrophysical significance, carbon clusters and their ions appear to play an important role in such diverse areas as combustion chemistry, catalysis, and materials science.

Through a very fruitful collaboration of vapor-phase spectroscopy, matrix isolation spectroscopy, and theoretical computations, a number of linear and cyclic carbon clusters have been discovered and characterized.[1−12] However, despite this effort, much work remains to be done.

The first observation of the asymmetrical stretching frequencies of the C_n^- carbon cluster anions ($n = 3-7, 9$) in Ar matrixes was reported recently.[13,14] Later, using a mass selection/matrix isolation approach, Freivogel et al.[15] reported some of the IR absorption bands for a series of C_n^- anions ($n = 5-10, 12$). We have recently reported on the IR spectra of the isotopically labeled ($^{12}C/^{13}C$) anionic clusters C_3^-, C_4^-, and C_6^-.[16−18] Using comparisons to ab initio and density functional theory calculations, these results support our earlier IR band assignments.[14] In addition, resonance Raman spectra of isotopically labeled C_6^- were shown to fit well with the calculated isotopic frequency shift patterns for a linear cluster geometry.[18]

In this paper, we present the vibrational absorption spectra of isotopically mixed C_5^-, C_7^-, and C_9^- carbon cluster anions trapped in Ar matrixes at 12 K. Carbon cluster anions were generated by attaching electrons to preformed vapor-phase neutral clusters.[16,17] These clusters are known to possess high electron affinities, ranging from 1.995 (C_3) to 4.8 eV (C_8).[19] The isotopomeric vibrational frequencies observed here have been compared to calculated frequencies (B3LYP/6-31G* level) for optimized structures of C_5^-, C_7^-, and C_9^-. Based on these comparisons, the geometries of the above clusters have been deduced.

II. Experimental Section

As in previous work, a dual laser beam method was employed.[16,18] This is a very effective approach for carbon cluster anion production. Shida and co-workers recently reported on a similar dual laser beam technique that has also been employed in the production of C_n^- clusters.[20] Briefly, the beam from a Nd:YAG laser (Spectra Physics/Quanta Ray) was split using a quartz plate aligned at ca. 80° angle of incidence. At this angle, the intensities of the reflected and transmitted beams were almost identical, as described by the well-known Fresnel formula. One beam, focused on a pressed pellet of a mixture of $^{12}C/^{13}C$ isotopes, vaporized the carbon material, and the other beam, focused on an yttrium chip, generated a blue Ar/Y plasma, which acted as the source of the added electrons. Both beam targets were located side-by-side inside the cryostat deposition chamber held at 10^{-7} Torr. Isotopically mixed samples with $[^{12}C]/[^{13}C]$ concentration ratios $\cong 5$ were used exclusively. Because the ^{13}C isotope powder is highly noncohesive, vaporization of samples with the inverse isotopic ratio yielded low-quality matrices which exhibited poor signal-to-noise ratios. Electrons produced in the plasma region, located 2−3 mm from the carbon vaporization region, were trapped by the carbon clusters.[16] At a laser repetition rate of 10 Hz, the electron current (20−40 μA) was collected by an O-ring electrode (held at +60 V) located 3 cm from the plasma region. The energy of the first laser beam was ca. 5 mJ/pulse and was focused to a spot 2−3 mm in diameter, while the intensity of the second beam was partially reduced by a shutter and focused to a spot less than 1 mm in diameter. The vapor containing both C_n and C_n^- clusters was trapped with Ar on a CsI cryostat window at 12 K. The sample/matrix was scanned for infrared absorption using a Fourier transform IR spectrometer (Nicolet, Magna 560) with 0.25 cm^{-1} resolution.

III. Results

A. C_5^- Anion. In Figure 1 are shown portions of the IR spectra obtained for a vaporized sample with a $^{12}C/^{13}C$ concentration ratio $\cong 5$. The lower spectrum was recorded after 10 h of photolysis (100-W Hg medium-pressure lamp with full spectral output). All bands due to anionic species decline in intensity due to photodissociation and electron photodetachment.

It is of interest to estimate the relative concentration of anionic and neutral species in the matrix. From DFT B3LYP/6-31G* level calculations, we have found that the intensities of the most intense asymmetric stretching modes for neutral C_6 and anionic C_6^- are very similar.[18] Assuming that these intensities are correct, the upper spectrum in Figure 1 shows a ca. 1:1 ratio

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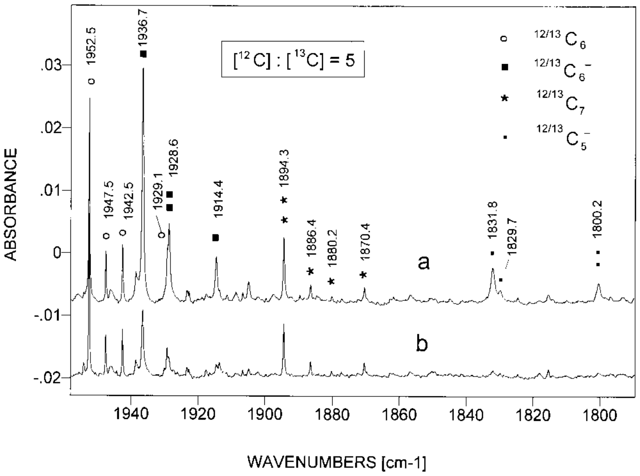

Figure 1. Part of IR absorption spectrum of $^{12/13}C_n$/$^{12/13}C_n^-$ carbon clusters isolated in Ar matrix at 12 K with an isotope ratio of [^{12}C]/[^{13}C] ≈ 5. Only the bands due to all-^{12}C and singly ^{13}C-substituted isotopomers are marked. (a) Spectrum recorded before matrix photolysis. (b) Spectrum recorded after 10 h of photolysis using a 100-W medium-pressure Hg lamp with full spectral output.

for the [C_6^-]:[C_6] concentrations. We have used this ratio as a measure of production efficiency for carbon cluster anions in our experiments.

With a 5-fold greater ^{12}C concentration (with respect to ^{13}C), it is expected that the isotopomers formed will contain either only ^{12}C atoms or, at most, one ^{13}C atom. In fact, a comparison of band energies observed in the known isotopomeric spectra of $^{12/13}C_6$,[7] $^{12/13}C_6^-$,[18] and $^{12/13}C_7$[7] shows that all of the most intense bands marked in Figure 1 are due to either all-^{12}C or singly ^{13}C-substituted clusters. Consequently, we expect a similar intensity band distribution for the unknown isotopomeric band pattern of $^{12/13}C_5^-$. As shown previously and confirmed below, the isotopomeric band pattern for a specific cluster size and geometry is unique. Therefore, the comparison of experimental to calculated band frequencies is a powerful method for the identification of a carbon molecular species and a determination of its structure.

In previous work, the experimental 1831.8-cm^{-1} band observed in Ar matrices (cf. Figure 1) was tentatively assigned to the most intense asymmetric vibration ($\nu_3(\sigma_u)$) of the $^{12}C_5^-$ carbon cluster.[13,14] Later, Freivogel et al.,[15] using mass selection and deposition of $^{12}C_5^-$ in a Ne matrix, reported an absorption at 1822.3 cm^{-1}. They also correlated the intensity of this band to the C_5^- electronic absorption band intensity. However, as mentioned earlier by this group, the assignment of species based on the correlation of IR and UV (or visible) band intensities, when one IR or UV (or visible) band is known, may be problematic.[21] The almost 10-cm^{-1} blue shift in going from Ne to Ar matrixes is very unusual. In all other known anionic carbon clusters, the energy shift is toward the red in going from Ne to Ar matrices.

As reported earlier, the optimized geometry and harmonic frequencies for the C_n^- ($n = 3-9$) clusters calculated at the B3LYP/6-31G* level support a linear structure for these clusters.[18] The bond lengths of 1.305 and 1.289 Å calculated at the B3LYP/6-31G* level for linear C_5^- are in good agreement with the 1.2996 and 1.2855 Å values found by Schmatz and Botshwina from higher level RCCSD(T)/204c GTO calculations.[11]

The band calculated to be the most intense in the linear C_n^- ($n = 3-9$) series and to lie closest to the observed 1831.8-cm^{-1} frequency is the intense $\nu_3(\sigma_u)$ asymmetric vibration of C_5^- (calculated intensity of 855 km/mol). Using the geometry and force constants from the $^{12}C_5^-$/B3LYP/6-31G* calculation, a determination of the harmonic frequencies for the $^{12/13}C_5^-$ isotopomers was carried out at the same theoretical level using the GAUSSIAN program package.[22] The calculated frequencies, listed in the Table 1, are only for either all-^{12}C or singly ^{13}C-substituted isotopomers of $^{12/13}C_5^-$. It can be seen that they fit the experimental band positions in the $^{12/13}C_5^-$ region rather well. The intensity of the 1800.2-cm^{-1} band (Figure 1), which is twice as intense as the 1829.7-cm^{-1} (**13**-12-12-12-12) band, results from the overlapping of the two (12-**13**-12-12-12) and (12-12-**13**-12-12) isotopomer bands (cf. Table 1).

In summary, the excellent match between the theoretical predictions and the observed energy and intensity band pattern has led to the assignment of these photosensitive bands to linear $^{12/13}C_5^-$ isotopomeric clusters.

B. C_7^- Anion. Figure 2 shows a slightly lower energy region for the same sample/matrix as shown in Figure 1. The 1734.8-cm^{-1} band has been tentatively assigned to the linear C_7^- cluster.[13,14] From the top spectrum (a), recorded before photolysis, a number of bands can be seen to lower energy of the 1734.8-cm^{-1} band. If these bands are the singly ^{13}C-substituted isotopomer bands of C_7^-, their positions should be well-predicted using DFT B3LYP/6-31G* theory, as found above for the C_5^- species. Table 1 shows the predicted band positions for the all-^{12}C, singly ^{13}C-substituted, and all-^{13}C-substituted isotopomers of C_7^-. To obtain these values, a full geometry optimization was first performed at the B3LYP/6-31G* level (yielding a linear geometry), after which the cluster's harmonic vibrational frequencies were determined. The most intense asymmetric stretching mode was found at 1835.7 cm^{-1} (with an intensity of 2331 km/mol). This value, when scaled by the recommended factor of 0.95, gives 1743.9 cm^{-1}. This close match with the observed peak at 1734.8 cm^{-1} was the basis for our previous assignment to C_7^-. The calculated equilibrium bond lengths of 1.284, 1.311, and 1.282 Å agree reasonably well with the 1.279, 1.307, and 1.279 Å values reported by Schmatz and Botschwina,[12] who used a large-scale coupled cluster RCCSD(T)/238 cGTO calculation.

The calculated harmonic frequencies of the C_7^- isotopomers, all scaled uniformly to the 1734.8-cm^{-1} band, are compared to the observed pattern of frequencies in Table 1. While all possible isotopomer frequencies were calculated, only those exhibiting the best fit are included in Table 1. It can be seen that the best fit was obtained with isotopomers containing only singly ^{13}C-substituted species, as expected from our experimental conditions.

In refs 16 and 17, it was demonstrated that the $^{12/13}C_3^-$ and $^{12/13}C_4^-$ cluster bands have the same isotopomeric intensity pattern as their corresponding neutral $^{12/13}C_3$ and $^{12/13}C_4$ parents. The same results are seen here for C_7 and C_7^-. Note in Figures 1 and 2 that the three nonoverlapped isotopomeric bands due to C_7 at 1886.4 (**13**-12-12-12-12-12-12), 1880.2 (12-12-12-**13**-12-12-12), and 1870.4 cm^{-1} (12-**13**-12-12-12-12-12) yield an intensity pattern similar to that of the C_7^- bands at 1730.0, 1731.2, and 1715.5 cm^{-1}, respectively. Unfortunately, the 1730.0- and 1731.2-cm^{-1} bands are partially overlapped, but a ratio of the sum of the 1730.0- and 1731.2-cm^{-1} band intensities to the 1715.5-cm^{-1} band is similar to the ratio of the sum of the 1886.4- and 1880.2-cm^{-1} band intensities to the 1870.2-cm^{-1} band. In the experiment, the source of electrons (i.e., the plasma region) is separate from the source of neutral carbon clusters (i.e., the vaporization region). Since the intensity distribution in the $^{12/13}C_7^-$ spectrum is very similar to the pattern

TABLE 1: Comparison of All-^{12}C, Singly ^{13}C-Substituted, and All-^{13}C-Substituted Isotopomer Frequencies (cm^{-1}) Observed (Ar Matrix, 12 K) and Calculated at the B3LYP/6-31G* Level for $^{12/13}C_5^-$, $^{12/13}C_7^-$, and $^{12/13}C_9^-$ Carbon Cluster Anions[a]

isotopomer	obsd	Δ obsd	B3LYP[b]	ΔB3LYP	obsd-B3LYP
		$^{12/13}C_5^-$, ν_3			
12-12-12-12-12	1831.8	0.0	1831.8	0.0	0.0
13-12-12-12-12	1829.7	2.1	1829.2	2.6	0.5
12-**13**-12-12-12	1800.2	31.6	1799.2	32.6	1.0
12-12-**13**-12-12	1800.2	31.6	1799.6	32.2	0.6
13-13-13-13-13	1760.9[c]	70.9	1760.0	71.8	0.9
		$^{12/13}C_7^-$, ν_5			
12-12-12-12-12-12-12	1734.8	0.0	1734.8	0.0	0.0
13-12-12-12-12-12-12	1730.0	4.8	1729.5	5.3	0.5
12-**13**-12-12-12-12-12	1715.5	19.3	1713.8	21.0	1.7
12-12-**13**-12-12-12-12	1726.2	8.6	1726.8	8.0	−0.6
12-12-12-**13**-12-12-12	1731.2	3.6	1732.1	2.7	−0.9
13-13-13-13-13-13-13	1667.8[c]	67.0	1666.7	68.1	1.1
		$^{12/13}C_9^-$, ν_6			
12-12-12-12-12-12-12-12-12	1686.7	0.0	1686.7	0.0	0.0
13-12-12-12-12-12-12-12-12	1686.5	0.2	1686.7	0.0	−0.2
12-**13**-12-12-12-12-12-12-12	1681.8	4.9	1682.9	3.8	−1.1
12-12-**13**-12-12-12-12-12-12	1671.3	15.4	1670.1	16.6	1.2
12-12-12-**13**-12-12-12-12-12	1675.2	11.5	1673.7	13.0	1.5
12-12-12-12-**13**-12-12-12-12	1684.9	1.8	1683.6	3.1	1.3
13-13-13-13-13-13-13-13-13	1621.5[c]	65.2	1620.5	66.2	1.0
		$^{12/13}C_9^-$, ν_7			
12-12-12-12-12-12-12-12-12	1583.3	0.0	1583.3	0.0	0.0
13-12-12-12-12-12-12-12-12	1574.5	8.8	1575.3	8.0	−0.8
12-**13**-12-12-12-12-12-12-12	1575.7	7.6	1576.6	6.7	−0.9
12-12-**13**-12-12-12-12-12-12	1575.3	8.0	1576.3	7.0	−1.0
12-12-12-**13**-12-12-12-12-12	1583.3	0.0	1583.3	0.0	0.0
12-12-12-12-**13**-12-12-12-12	1558.9	24.4	1559.8	23.5	−0.9
13-13-13-13-13-13-13-13-13	1521.8[c]	61.5	1521.2	62.1	0.6

[a] Isotopic shifts (cm^{-1}) are given in the Δ columns. [b] Scaled by 0.9628 ($^{12/13}C_5^-$), 0.945 ($^{12/13}C_7^-$), 0.9294 ($^{12/13}C_9^-$, ν_6), and 0.9515 ($^{12/13}C_9^-$, ν_7) factors. [c] From ref 16.

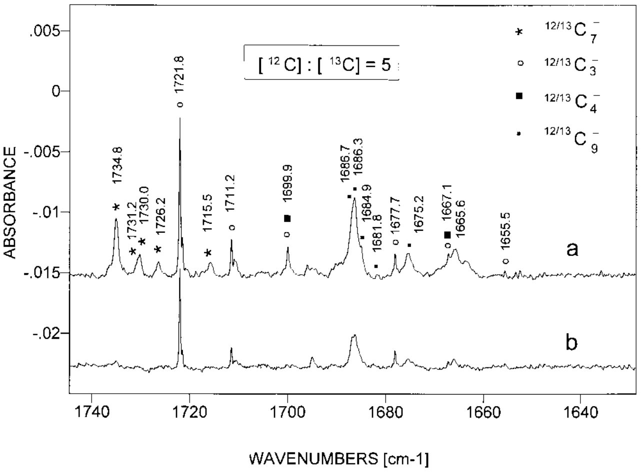

Figure 2. Infrared absorption spectrum of asymmetric stretching region of the carbon cluster anions, C_n^- (n = 3, 4, 7, and 9) trapped in Ar matrix before photolysis (spectrum a) and after 10 h of photolysis (spectrum b). The all-^{12}C and singly ^{13}C-substituted isotopomers are marked, except for C_3^-, for which all six ^{12}C/^{13}C isotopomeric bands, and C_4^-, for which three doubly ^{12}C-substituted isotopomeric bands, which are overlapped at 1667.1 cm^{-1}, are indicated.

of the $^{12/13}C_7$ bands, we conclude, as previously, that the process of C_7^- formation is predominantly electron capture by the neutral C_7 species, rather than an ion−neutral reaction.

C. C_9^- Anion. The attribution of new IR bands to specific anionic (or other) carbon clusters is greatly aided by the calculation of the harmonic vibration frequencies (and intensities) for a geometry-optimized contender. Geometry optimization (B3LYP/6-31G* level) of the C_9^- anion yielded a linear structure with two strong asymmetric stretching vibrations at 1724.2 (4201 km/mol) and 1580.8 cm^{-1} (728 km/mol). Both frequencies have been scaled by 0.95. The appearance of two IR bands (which are photosensitive and, therefore, due to an anionic species) in this vicinity (at 1686.7 and 1583.3 cm^{-1}) led to our previous assignment of these bands to the $\nu_6(\sigma_u)$ and $\nu_7(\sigma_u)$ modes of linear C_9^-. Freivogel et al. recently reported the results of a mass selection/Ne matrix isolation experiment on C_9^-, in which one absorption band at 1692.6 cm^{-1} was found.[15] The +5.9-cm^{-1} red shift (from Ne to Ar) is reasonable for this cluster, compared to the +12.0-cm^{-1} shift noted earlier for a similar mode of neutral C_9.[25]

While this close correspondence is highly suggestive that the attribution of these bands to the C_9^- cluster is correct, proof via isotopic substitution is preferable. In Figure 2 is shown the isotopomeric absorption spectrum for the ν_6 mode and, in Figure 3, a similar spectrum for the ν_7 mode. The top panel in both figures shows the spectra before photolysis (a) and the bottom panel, after photolysis (b). The comparison of these bands to the calculated isotopomeric frequencies (B3LYP/6-31G* level) is collected in Table 1. As Figures 1 and 2 show for the $^{12/13}C_6$, $^{12/13}C_6^-$, $^{12/13}C_3^-$, $^{12/13}C_7$, and $^{12/13}C_7^-$ isotopomers, the most intense bands for $^{12/13}C_9^-$ are expected to be due to all-^{12}C and singly ^{13}C-substituted isotopomers. All photosensitive bands (marked in Figures 2 and 3 as $^{12/13}C_9^-$) fit reasonably well with the calculated frequencies listed in Table 1. Of particular interest is the photosensitive 1558.9 cm^{-1} band (isolated from the others) with an isotopic shift of 23.4 cm^{-1}, which matches well the prediction for the ν_7 mode of the (12-12-**13**-12-12-12-12-12-12) anion.

Because the total number of ^{12}/$^{13}C_9^-$ isotopomers is very large for the linear C_9^- cluster (272), with bands expected to be spread over rather small intervals (65.2 cm^{-1} for ν_6 and 61.5 cm^{-1} for ν_7), some isotopomeric bands may overlap, even using only

TABLE 2: Summary of Fundamental Vibration Frequencies (in cm^{-1}) of Linear C_n^- ($n = 3-9$) Carbon Cluster Anions in the Electronic Ground State, Observed in Gas and Matrix ($T \leq 12$ K) Phases

cluster	mode	gas phase	Ne matrix	Ar matrix	B3LYP[d]
$C_3^-(X^2\Pi_g)$	$\nu_1(\sigma_g)$	~1075 [19][a]			1167.7
	$\nu_3(\sigma_u)$			1721.8 [16]	1721.8
$C_4^-(X^2\Pi_g)$	$\nu_1(\sigma_g)$		2047(20) [27]		2011.6
	$\nu_2(\sigma_g)$		936(20) [27]		882.1
	$\nu_3(\sigma_u)$			1699.8 [17]	1699.8
	$\nu_4(\sigma_g)$		396(20) [27]		576.3,507.5
$C_5^-(X^2\Pi_u)$	$\nu_3(\sigma_u)$		1822.3 [15]	1831.8[b]	1831.8
	$\nu_7(\sigma_u)$	~200 [23]			164.5, 161.5
$C_6^-(X^2\Pi_u)$	$\nu_1(\sigma_g)$			2086 [18]	2085.6
	$\nu_2(\sigma_g)$			1775 [18]	1773.9
	$\nu_3(\sigma_g)$	564 [2]		634 [18]	625.6
	$\nu_4(\sigma_u)$		1938.5 [15]	1936.7 [18]	1936.7
	$\nu_7(\sigma_g)$	~220 [2]			526.3, 491.3
	$\nu_8(\sigma_g)$	201 [2]		~233 [18]	279.0, 271.0
	$\nu_9(\sigma_u)$	~111 [24]			126.3, 121.2
$C_7^-(X^2\Pi_g)$	$\nu_4(\sigma_u)$		1736.4 [15]	1734.8[b]	1734.8
$C_8^-(X^2\Pi_g)$	$\nu_5(\sigma_u)$		2067.8[b,c]	2064 [18]	2064.0
	$\nu_6(\sigma_u)$		1796.0 [15]		1786.1
$C_9^-(X^2\Pi_u)$	$\nu_6(\sigma_u)$		1692.6 [15]	1686.7[b]	1726.9
	$\nu_7(\sigma_u)$			1583.3[b]	1583.3

[a] ±100 cm^{-1}. [b] This work. [c] Tentative assignment based on the spectrum of Figure 1 in ref 15 (see text). [d] Frequencies scaled by 0.9716 (C_3^-), 0.952 (C_4^-), 0.9628 (C_5^-), 0.9509 (C_6^-), 0.945 (C_7^-), 0.949 (C_8^-), and 0.9515 (C_9^-) factors. Calculated frequencies not explicitly given here may be found in ref 14.

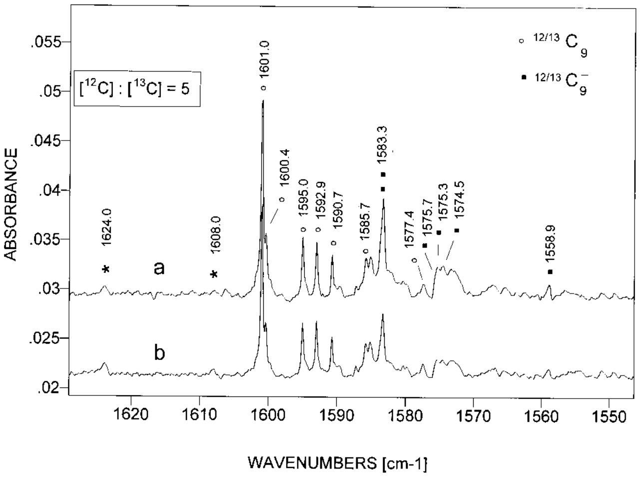

Figure 3. Infrared absorption spectrum of neutral C_9 and anionic C_9^- carbon clusters in the ν_7 mode region after matrix annealing (to 35 K) and recooling (to 12 K) (spectrum a) and after 8 h of photolysis (100-W Hg medium pressure lamp, full spectral output) (spectrum b). The starred bands are due to isolated H_2O. The all-^{12}C and singly ^{13}C-substituted isotopomers are marked, except for the 1577.4 cm^{-1} band, which is due to overlapped bands from the 12-12-13-13-12-12-12-12-12 and 12-13-12-13-12-12-12-12-12 isotopomers of neutral C_9.

preferentially formed singly substituted isotopomers. The 1665.6-cm^{-1} band in Figure 2 and the 1573.3-cm^{-1} band in Figure 3 (not marked) may be due to a group of bands of doubly ^{13}C-substituted isotopomers (or higher).

Finally, in Figure 3 we report three new bands at 1595.0, 1592.9, and 1590.7 cm^{-1} that can be assigned to the ν_6 mode of the (12-**13**-12-12-12-12-12-12-12), (**13**-12-12-12-12-12-12-12-12) and (12-12-**13**-12-12-12-12-12-12) singly ^{13}C-substituted isotopomers of the *neutral* linear C_9 cluster. The calculated (B3LYP/6-31G*) harmonic frequencies (scaled) for these clusters had previously been reported as 1595.3, 1593.1, and 1590.2 cm^{-1}, respectively.[7] The match is excellent.

IV. Discussion

Table 2 summarizes the current state of our knowledge of the fundamental ground-state vibrations for the linear carbon cluster anions, C_n^- ($n = 3-9$). Both vapor- and matrix- (Ne and Ar) phase results are presented. While there remain many holes in the table, significant progress has been made. For those bands observed in Ne and Ar matrices, the frequency shifts are seen to be relatively small. This table should prove useful in locating bands for high-resolution vapor-phase studies.

Although Table 2 is largely self-explanatory, the entry for the $\nu_5(\sigma_u)$ mode of $^{12}C_8^-$ in a Ne matrix merits discussion. A value of 2067.8 cm^{-1} has been entered on the basis of a reinterpretation of spectra reported in ref 15. In Figure 1 of this paper, the IR spectra of C_8 and C_8^- in the 2100−1650-cm^{-1} region after deposition of C_8^- in a Ne matrix are reported. Both “before photolysis” (BP) and “after photolysis” (AP) runs are presented. Only neutral C_8 clusters remain after photolysis, since all anionic C_8^- clusters have been photodestroyed. Measuring the intensity ratio $I(2067.8\ cm^{-1})/I(1707.4\ cm^{-1})$ gives 2.9 in the AP run. A similar ratio for these two C_8 bands is thus expected in the BP spectrum. But this intensity ratio is found to be significantly greater, i.e., 5.8. This difference can be understood if the 2067.8-cm^{-1} absorption in the BP spectrum is due to an overlapping of the $\nu_5(\sigma_u)$ vibrational bands from C_8 *and* C_8^- clusters. The $\nu_5(\sigma_u)$ mode of C_8^- has already been assigned to the band at 2064 cm^{-1} in Ar matrices.[18] The assignment of the band in Ne matrixes to the same mode results in a reasonable Ar-to-Ne matrix shift. In addition, the 2067.8-cm^{-1} assignment is in agreement with calculations that characterize it as the most intense IR absorption (1563 km/mol) in C_8^-. The second $\nu_6(\sigma_u)$ mode of C_8^- is predicted at a frequency of 1786 cm^{-1} (Table 2), with an intensity predicted to be 3 times lower (512 km/mol). This is also in good agreement with the observed band at 1796.0 cm^{-1}.

It is interesting to note that, during the UV/visible photolysis of a $C_n/C_n^-/Ar$ matrix, the anionic carbon cluster bands decreased at different rates. Comparison of spectra a and b in Figures 1 and 2 shows that the $^{12/13}C_5^-$ and $^{12/13}C_7^-$ bands are the most photosensitive. Both species are effectively photodestroyed during photolysis. Curiously, not even a small increase in the intensity of the parent neutral $^{12/13}C_n$ cluster bands was observed. This leads us to surmise that the photodetachment process is not the only photodestruction mechanism for C_n^- clusters in matrices. Photodissociation may also occur.

An ion cyclotron resonance study by Pozniak and Dunbar on the electron photodetachment and photodissociation reactions of C_n^- ($4 < n < 13$) clusters is relevant.[26] These authors found an alteration in the cross sections for electron photodetachment with the cluster size. Higher cross sections were found for the odd-numbered clusters. For example, C_5^- and C_7^- clusters exhibited cross sections 30 times larger than that of C_6^-. Photodissociation processes were found to be dominant, showing mainly loss of C_3, for the C_8^- and C_9^- species, while for the smaller anionic clusters ($n < 8$), only photodetachment processes were observed. Clearly, these vapor-phase results point out that the processes occurring in matrices are more complicated than simple photodetachment. One alternative, photodissociation to infrared-silent species (e.g., C_2, C_2^-, C, or C^-), may occur, but more work is needed before any conclusions can be reached.

There are still a number of frequencies that remain unknown for the small anionic C_n^- carbon cluster series. It is, however, satisfying that the density functional B3LYP/6-31G* approach (with scaling) seems to predict the stretching mode frequencies of the linear anionic carbon clusters very well. It can, therefore, be used with some confidence as a guide for those stretching modes not yet observed. The bending mode frequencies are, however, a different matter. Relatively large differences between observed and calculated frequencies have been reported. Furthermore, the calculations predict a splitting of most of the bending mode frequencies (Table 2). Schmatz and Botschwina have studied this effect thoroughly for C_3^-, a Renner–Teller system.[12] Clearly, further work on the larger carbon cluster anions is needed for these lower frequency vibrations.

V. Conclusions

Asymmetric stretching frequencies have been determined for the anionic carbon clusters C_5^-, C_7^-, and C_9^- using a combination of isotopic substitution matrix isolation infrared spectroscopy and density functional calculations. The following frequencies were determined in Ar matrices: 1831.8 cm^{-1} for $\nu_3(\sigma_u)$ of C_5^-, 1734.8 cm^{-1} for $\nu_4(\sigma_u)$ of C_7^-, and 1686.7 cm^{-1} for $\nu_6(\sigma_u)$ and 1583.3 cm^{-1} for $\nu_7(\sigma_u)$ of C_9^-.

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