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C_3^- Carbon Cluster Anion: Structure and Asymmetric Stretching Mode Frequency

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Carbon cluster anions have been formed by a combination laser ablation/plasma generation method and then deposited in argon matrices and studied via Fourier transform infrared spectroscopy. In this paper a full isotopic study of the C_3^- anionic cluster is reported. All six isotopomeric bands of the ν_3 antisymmetric stretching mode at 1721.8 cm^{-1} (all ^{12}C isotopomer) have been observed and used together with a normal coordinate calculation to deduce that C_3^- in Ar matrices is linear. This is in agreement with previous high-level ab initio calculations and with new density functional theory (DFT) and ab initio (MP2) results. Frequency shifts for all six C_3^- isotopomers calculated by DFT and MP2 approaches match the observed shifts very well. Finally, evidence is presented that the C_3^- anionic clusters are formed by electron capture and not by fragment aggregation.

I. Introduction

Interest in the spectroscopic properties of the anions of small carbon clusters has been increasing in the past few years.[1−6] Recently, we showed that small anionic carbon clusters could be easily formed by mixing low-energy electrons with graphite-ablated carbon clusters and depositing the resulting species in a rare gas matrix.[1] New infrared absorption bands were observed and assigned to the asymmetric stretching modes of a number of small linear carbon cluster anions, C_n^- ($n = 3$, 5, 6, 7, and 9).[1] Of particular interest for the present work was the observation of a band at 1721.8 cm^{-1} (Ar matrix) which was tentatively assigned to the asymmetric stretch mode of the C_3^- ion. This assignment was based on (1) a photosensitive energy threshold for bleaching at 2.79 eV, which is reasonably close to the 1.995 eV electron photodetachment energy threshold of gaseous C_3^-;[2] (2) a similar annealing behavior of the 1721.8 cm^{-1} band to the annealing behavior found for neutral C_3, and (3) good agreement between the observed 1721.8 cm^{-1} band and the 1772 cm^{-1} calculated frequency for the asymmetric stretch of linear C_3^-.

Several previous theoretical studies on C_3^- have been reported. Using high-level QCISD(T)/6-31G* calculations, Raghavachari[3] determined that C_3^- in its $^2\Pi_g$ electronic ground state is linear and that C_3^- harmonic vibrational frequencies should appear at 1754 (σ_u), 1175 cm^{-1} (σ_g) and 251, 399 cm^{-1} (π_u). A linear ground state structure was also found in an earlier theoretical study by Sunil et al.[4] and in later studies by Adamowicz[5] and Watts and Bartlett.[6] The latter authors[5,6] also determined the electron affinity of C_3 and the possible energetic and fragmentation channels of C_3^-.

Experimental work on C_3^- has been reported by Neumark and co-workers, who used photoelectron spectroscopy to determine the electron affinity (E_A) of C_3 and the symmetric stretching mode frequency of C_3^- (1075 ± 100 cm^{-1}).[2] From the trends in the E_A values for a series of small negative carbon clusters, Arnold et al.[2] as well as Yang et al.[7] suggested that these species are probably linear.

In this paper we present an experimental and theoretical study of C_3^-. Our twofold goal is the proof of its structure (bent vs linear) and the assignment of its infrared asymmetric stretching (σ_u) band. Fourier transform infrared spectra of all six possible ^{13}C/^{12}C isotopomers of C_3^- isolated in Ar matrices are presented. These results are complemented by ab initio, density functional theory (DFT), and **GF** matrix method calculations.

II. Experimental Procedures

Small linear neutral carbon clusters, C_n ($n < 10$), have been easily formed by vaporization of graphite using a laser beam (of several millijoules energy) focused to a diameter of ca. 1 mm. To form negatively charged carbon clusters, either an electron beam or a plasma as a source of electrons needs to be added. Trapping of electrons by neutral carbon clusters is expected since the cluster electron affinities are known to range from 1.995 (C_3) to 4.379 eV (C_8).[2]

In the present experiments the second harmonic (532 nm) of a pulsed Nd:YAG laser was dispersed from its fundamental beam (1064 nm) and focused on the carbon sample (pressed powder of ^{12}C and ^{13}C isotopic mixture) while a portion of the 1064 nm beam was focused on a chip of yttrium located inside the sample holder cup (Figure 1). The 1064 nm beam generated a bright blue plasma which acted as a rich source of electrons, photons (visible, UV, and soft X-rays[8]), and Y/Ar ions. The ^{12}C/^{13}C sample was located 2 cm from the cryostat window and 3.5 cm from the window axis. The sample holder (7 mm diameter cup), mounted on the thermal shield of the cryostat, was cooled to reduce impurities (such as CO and CO_2). The charged species, partially extracted from the vaporization region by an electrical field created by +30−60 V applied to an O-ring electrode, were trapped with Ar matrix gas on a BaF_2 cryostat window (12 K) cooled by a closed-cycle helium cryostat. A 10−30 μA average current was collected by the O-ring electrode during matrix deposition using a 10 Hz laser pulse repetition rate. Absorption spectra were recorded using a Fourier transform infrared (FT-IR) MIDAC spectrometer with 0.7 cm^{-1} resolution.

III. Results

A. Experimental Results. Figure 2 shows infrared spectra recorded for two sample matrices: the lower spectrum is for an all-^{12}C isotopic cluster sample while the upper spectrum is for an all-^{13}C sample. For former spectrum, the assignment of the negative ion carbon cluster bands is based on our earlier work where a tentative attribution of the 1721.8 cm^{-1} band to $^{12}C_3^-$ was made.[1] For the ^{13}C run a pattern of bands similar to, but red-shifted from, the ^{12}C run is observed. The proposed band assignments and frequency attributions of the $^{13}C_n$ carbon

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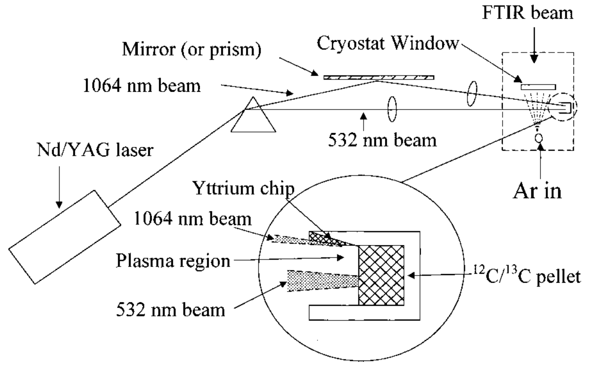

Figure 1. Schematic of experimental apparatus used for the preparation of the $^{12/13}C_n^-$/Ar matrix. Part of 1064 nm laser beam is dispersed from the second harmonic beam (532 nm) and focused on the yttrium surface to generate a plasma. The ^{12}C/^{13}C isotopic mixed pellet is ablated by the 532 nm beam forming $^{12/13}C_n$ carbon clusters. The latter capture electrons in the plasma region and, after extraction by the electrical field via the +60 V O-ring electrode, are trapped on the cryostat cold window together with the matrix gas.

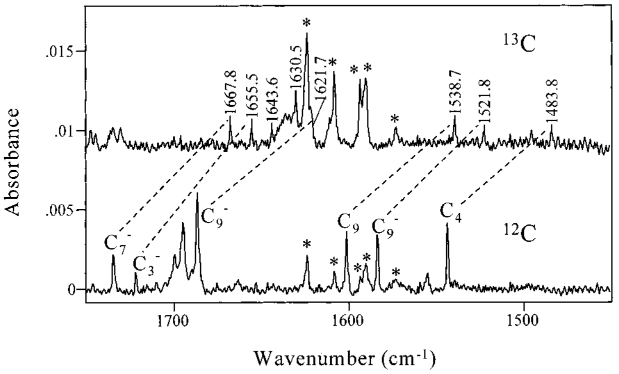

Figure 2. Part of the IR absorption spectra in the asymmetric stretching region for linear C_n^- ($3 < n < 9$) clusters isolated in an Ar matrix: upper spectrum recorded for the ^{13}C isotope and the lower spectrum for the ^{12}C isotope. The band positions in the lower spectrum are 1734.8 cm^{-1} ($\nu_5(\sigma_u)$, C_7^-); 1721.8 cm^{-1} ($\nu_3(\sigma_u)$,C_3^-); 1710.5 cm^{-1}($\nu_6(\sigma_u)$, C_8), unmarked band; 1700 cm^{-1} ($C_n + C_4^-$), unmarked band; 1695 cm^{-1} (C_n), unmarked band; 1686.7 cm^{-1} ($\nu_6(\sigma_u)$, C_9^-);1601.0 cm^{-1} ($\nu_7(\sigma_u)$, C_9);[9] 1583.3 cm^{-1} ($\nu_7(\sigma_u)$, C_9^-); and 1543.4 cm^{-1} ($\nu_3(\sigma_u)$, C_4).[11] H_2O bands are marked by asterisks.

TABLE 1: Experimental (Ar Matrix) and Calculated (Scaled) Frequencies (cm^{-1}) of Absorption Bands for $^{12}C_n^-$ and $^{13}C_n^-$ Carbon Cluster Ions

	Ar matrix			B3LYP/6-31G*[b]		
cluster, mode	$\nu_{^{12}C}$	$\nu_{^{13}C}$	$\Delta\nu_{exp}$	$\nu_{^{12}C}$	$\nu_{^{13}C}$	$\Delta\nu_{calc}$
C_3^-, $\nu_3(\sigma_u)$	1721.8	1655.5	66.3	1721.8	1654.2	67.6
C_5^-, $\nu_3(\sigma_u)$[a]	1831.5	1760.9	70.6	1831.5	1759.7	71.8
C_6^-, $\nu_4(\sigma_u)$	1936.7	1861.7	75.0	1936.7	1860.5	76.2
C_7^-, $\nu_5(\sigma_u)$[a]	1734.8	1667.8	67.0	1734.8	1666.7	68.1
C_9^-, $\nu_6(\sigma_u)$[a]	1686.7	1621.7	65.0	1686.7	1620.6	66.1
C_9^-, $\nu_7(\sigma_u)$[a]	1583.3	1521.8	61.5	1583.3	1521.2	62.1

[a] Tentative assignment (in Ar) was proposed in ref 1. For C_6^- the above assignment was recently confirmed via an $^{12/13}$C isotopic study.[18] [b] Frequencies scaled by 0.97189, 0.96268, 0.95095, 0.94503, and 0.92957, 0.95138 for C_3^-, C_5^-, C_6^-, C_7^-, and C_9^-, respectively.

neutral and ionic clusters are marked in the figure and given in Table 1. The results of density functional calculations (vide infra) for both ^{12}C and ^{13}C species and the predicted frequency shifts are also given in Table 1. The 1538.7 cm^{-1} frequency for the $\nu_7(\sigma_u)$ mode of the $^{13}C_9$ neutral cluster was reported earlier.[9] The 1643.6 cm^{-1} band probably is the $\nu_6(\sigma_u)$ mode of linear $^{13}C_8$ carbon clusters, analogous to the 1710.5 cm^{-1} (unmarked band in lower spectrum) assigned as the $\nu_6(\sigma_u)$ mode of $^{12}C_8$.[10] The 1483.8 cm^{-1} band is here ascribed to neutral $^{13}C_4$. This band has not been observed previously.[11]

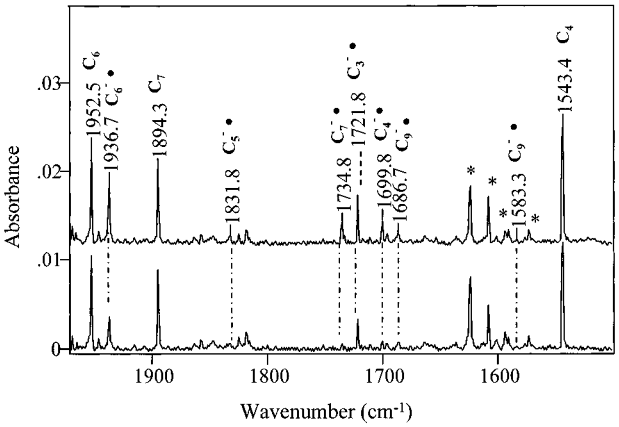

Figure 3. Effect of photolysis on carbon cluster anions. Photolysis was by the full output of a 100 W Hg lamp for 20 min on a C_n^-/C_n/Ar matrix (lower spectrum, photolyzed). The C_n^- clusters anions are marked by dots in the upper, unphotolyzed spectrum. Note the very strong 1543.4 cm^{-1} (C_4) band, formed by the high flux 532 nm beam ablating graphite.

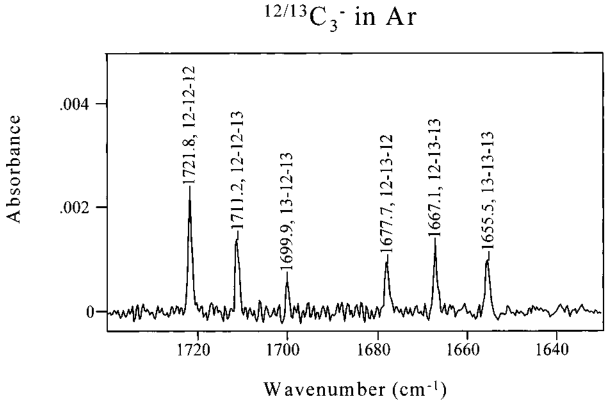

Figure 4. IR absorption spectrum of $^{12/13}C_3^-$ carbon cluster ions isolated in Ar matrix at 12 K.

To confirm the attribution of the IR bands to negatively-charged carbon clusters (marked as C_n^- in Figure 2), experiments with the electron acceptor, CCl_4 (and its plasma products CCl_3, CCl_3^+, Cl), mixed with the Ar matrix gas (0.5%) were carried out. The carbon tetrachloride species compete for electrons with the neutral C_n carbon clusters, so the intensities of the anion peaks would be expected to decrease compared to the neutral cluster peaks when CCl_4 is added. In these experiments, the [C_n^-]/[C_n] concentration ratios were found to be smaller than the similar ratios with no CCl_4 added.

The effect of photolysis on the anion bands was also determined. As Figure 3 shows, all bands assigned to C_n^- species were bleached (i.e., decreased in intensity) during full Hg lamp photolysis, whereas there was no (or little) effect on the neutral cluster band intensities.

Laser ablation of a 1:1 isotopic mixture of ^{12}C/^{13}C with plasma generation yields a series of bands in the 1700 cm^{-1} region (cf. Figure 4) and, during the same run, the well-known series of bands of the $^{12/13}C_3$ isotopomers in the 2040 cm^{-1} region (cf. Figure 5). The intensity distribution of the bands in the1700 cm^{-1} region is very similar to the distribution in the 2040 cm^{-1} region.[12] A substantially lower ablating laser flux was used here compared to the flux used for the spectra shown in Figure 2 in order to reduce the yield of clusters larger than C_3. As evidence of a reduced yield of larger clusters, Figure 5 shows that the 1952.5 cm^{-1} (C_6) band is not seen. The similar spectral band intensity distributions in Figures 4 and 5 suggest that the mechanism of $^{12/13}C_3^-$ formation is predominantly an

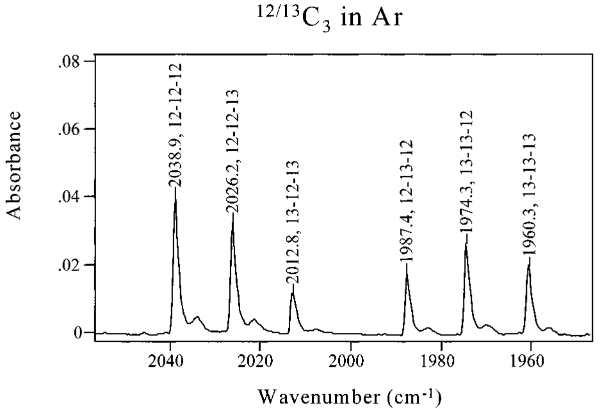

Figure 5. Asymmetric stretching mode IR absorption spectrum of the neutral $^{12/13}C_3$ carbon cluster recorded during the same run as Figure 3. Note the similarity in the band intensity distributions for both spectra.

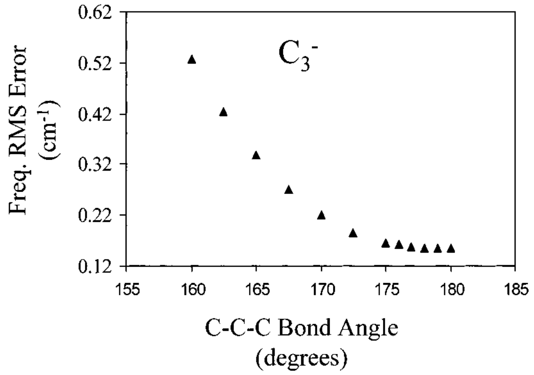

Figure 6. Plot of rms deviation of the calculated (**GF** matrix method, see text) and experimental isotopic shifts for the asymmetric stretching modes of $^{12}C^{13}C^{12}C$ and $^{13}C^{12}C^{13}C$ isotopomers of C_3^- clusters vs an assumed C−C−C bond angle, α. The curve minimum is located at α = 180°.

TABLE 2: Optimized Geometry, Harmonic Frequencies (cm^{-1}) and Intensities (km/mol, in Brackets) and Rotational Constants, *B* (in GHz), Calculated at Different Levels of Theory for the C_3^- Carbon Cluster Ion in Its Electronic Ground State

	B3LYP/6-31G*	MP2/6-31G*	QCISD(T)/6-31G*[a]
geometry:			
R (Å)	1.3119	1.3068	1.322
α (deg)	180.0	180.0	180.0
frequency:			
σ_u	1771.6 [152.4]	1705.1 [163.1]	1754
π_u	453.8 [27.9]	470.4 [28.8]	399
	319.8 [39.9]	314.1 [44.7]	251
σ_g	1201.3 [0]	1256.6 [0]	1175
rot. const *B*	12.235800	12.3307229	

[a] Reference 3.

TABLE 3: Calculated (B3LYP/6-31G* and MP2/6-31G* Level) and Observed (in Ar Matrices) Vibrational Frequencies (in cm^{-1}) of Asymmetric Stretching Mode for All $^{12}C/^{13}C$ Isotopomers of C_3^- Carbon Cluster Ion

	theory		exp	isotopic shift		
isotopomer	B3LYP[a]	MP2[b]	Ar at 12 K	$calc_{B3LYP}$	$calc_{MP2}$	exp_{Ar}
12−12−12	1721.8	1721.8	1721.8	0.0	0.0	0.0
12−12−13	1711.1	1711.2	1711.2	10.7	10.6	10.6
13−12−13	1699.5	1699.6	1699.9	22.3	22.2	21.9
12−13−12	1676.9	1677.1	1677.7	44.9	44.7	44.1
12−13−13	1665.9	1666.3	1667.1	55.9	55.5	54.7
13−13−13	1654.0	1654.4	1655.5	67.8	67.4	66.3

[a] Frequencies scaled by 0.9719 factor. [b] Frequencies scaled by 1.00979 factor.

electron capture by the parent $^{12/13}C_3$ clusters, rather than an aggregation of either $^{12/13}C_2^- + {}^{12/13}C$ or $^{12/13}C^- + {}^{12/13}C_2$. This "whole cluster electron capture" mechanism is expected by two experimental conditions. First, the formation region for the neutral carbon clusters, C_n ($n < 4$ mainly), is separated from the source of electrons (plasma region, Figure 1) so that clusters should be formed prior to their exposure to the excess electron environment. And, second, aggregation between the C_n and C_n^- carbon species in an effusive beam is unlikely due to the large mean free paths involved. However, once formed in the matrix, cluster aggregation such as $^{12/13}C_3^- + {}^{12/13}C_n$ may occur, since it is observed that the 1721.8 cm^{-1} (C_3^-) band intensity decreases during matrix annealing.

A tentative assignment of the 1699.8 cm^{-1} band to the asymmetric stretch of linear C_4^- is made here. This band was not observed in our earlier study of C_n^- ions because the concentration of neutral C_4 was too low. But here it is relatively large. During the process of matrix deposition, the high photon flux at 532 nm was used to ablate carbon from graphite, and this invariably led to a strong absorption signal at 238 nm due to C_2 (Mulliken system) as well as strong absorption at 1543.4 cm^{-1} due to C_4 (cf. Figure 3). The 1699.8 cm^{-1} assignment is in agreement with the theoretical 1785.2 cm^{-1} (σ_u, unscaled) value calculated at the B3LYP/6-31G* level[1] and the 1775.2 cm^{-1} (σ_u, unscaled) value calculated in this work using a diffuse function added to the 6-31G* basis set. Frequency scaling factors of 0.952 and 0.957 were used to fit the calculated frequencies to the 1699.8 cm^{-1} band frequency observed in Ar. Factors of this magnitude are recommended for use with B3LYP/6-31G* and B3LYP/6-31+G* levels of theory, respectively.

B. Theoretical Results. The geometry optimization and harmonic vibrational frequencies were calculated using the GAUSSIAN 94 program package.[13] For the density functional theory (DFT) calculations, a Becke three-parameter fitting to a Lee−Yang−Parr functional (B3LYP) was employed. In both the ab initio electron correlation Moller-Plesset perturbation theory (MP2) and the B3LYP method, a standard 6-31G* basis set was used. The molecular parameters found at the B3LYP and MP2 levels of theory are collected in Table 2, while a comparison of the calculated and experimental frequencies for all $^{12/13}C_3^-$ isotopomers is presented in Table 3.

The **GF** matrix method[15] was used to calculate the isotopic frequency shifts. From fitting of the experimental isotopic frequency shifts to the calculated ones, the magnitude of the C−C−C bond angle in C_3^- cluster could be determined. The bond angle was varied around 180° to explore the possible influence of matrix interactions on the linearity of the C_3^- cluster. (The C_3 cluster has been shown to be bent in Ar and Kr matrices.[14]) The root-mean-square (rms) deviation between calculated and experimental (Ar) isotopic frequency shifts versus angle (α) is plotted in Figure 6. The linear geometry is computed to be the most stable.

IV. Discussion

Table 1 compares the experimental isotopic frequency shifts of the all-^{12}C and all-^{13}C-substituted isotopomers of five different C_n^- clusters ($\Delta\nu_{exp} = \nu(^{12}C) - \nu(^{13}C)$) with the calculated isotopic shifts (B3LYP/6-31G* level). It can be seen that the match between the calculated and experimental isotopic frequency shifts is very good.

The isotopic shifts can, of course, be alternatively described by the well-known Teller−Redlich rule,

$$\Delta\nu_{calc} = \nu_{^{12}C}[1 - (m_{^{12}C}/m_{^{13}C})^{1/2}]$$

The experimental isotopic shifts are generally lower than the calculated shifts by 1.1−1.3 cm^{-1} for the highest energy antisymmetric modes. This probably reflects the fact that the calculated values do not include any anharmonicity effects. The experimental isotopic shift for the ν_7 mode of C_9^- is only 0.6 cm^{-1} lower than the calculated shift (cf. Table 1). This probably indicates a different anharmonicity for this mode than for the smaller cluster anion modes listed.

For the other isotopomers the calculated isotopic frequency shift is α (= C−C−C) bond angle dependent. For the $^{12}C^{13}C^{12}C$ and $^{13}C^{12}C^{13}C$ isotopomer anions, the calculated isotopic frequency shifts for the asymmetric stretching mode, using the **GF** matrix formalism (AB_2 type molecule[15]), are respectively

$$\Delta\nu_{\rm calc} = \nu_{^{12}\rm C}\,\{1 - [1 - [(1 - \cos\alpha)(1 - m_{^{12}\rm C}/m_{^{13}\rm C})/(2 - \cos\alpha)]]^{1/2}\} \quad (1)$$

$$\Delta\nu_{\rm calc} = \nu_{^{12}\rm C}\{1 - [1 - [(1 - m_{^{12}\rm C}/m_{^{13}\rm C})/(2 - \cos\alpha)]]^{1/2}\} \quad (2)$$

Because the calculated isotopic frequency shift for the $^{13}C^{13}C^{13}C$ anion is α-independent and because this shift is higher by 1.46 cm^{-1} than the experimental one, a correction factor[9] is introduced: $\Delta\nu_{\rm corr} = (1.46\ {\rm cm^{-1}}/67.76\ {\rm cm^{-1}})\Delta\nu_{\rm calc} = 0.02157\Delta\nu_{\rm calc}$ (where 67.76 cm^{-1} = $\Delta\nu_{^{13}\rm C}$). In the $^{12}C^{13}C^{12}C$ and $^{13}C^{12}C^{13}C$ anion cases, the calculated corrected isotopic shifts frequencies are $\Delta\nu_{\rm calc(corr)} = \Delta\nu_{\rm calc} - \Delta\nu_{\rm corr}$, where $\Delta\nu_{\rm calc}$ is given by eqs 1 and 2, respectively. The fitting curve of the $\Delta\nu_{\rm calc(corr)}$ isotopic frequency shift to the $\Delta\nu_{\rm exp}$ (in Ar) experimental isotopic frequency shifts versus α for both isotopomers is shown in Figure 6. The best fit is found for α = 180° with only a 0.15 cm^{-1} rms deviation.

Optimizing the C_3^- geometry at both B3LYP/6-31G* and MP2/6-31G* levels yields a linear structure as the most stable (Table 2). This is in agreement with results by Raghavachari,[3] Watts and Bartlett,[6] and Adamowicz[5] at the HF/QCISD(T)/6-31G*, ROHF/DZP, and MBPT levels, respectively. In our earlier study at the B3LYP/6-31G* level, a stable C_{2v} cyclic structure for C_3^- was also found. However, its minimum energy was 14.4 kcal/mol higher than the linear structure and its most intense IR transition (53 km/mol) is predicted to occur in the 900 cm^{-1} frequency region, where none is observed.[1] The C_{2v} cyclic structure does not appear to have been formed.

The electron configuration of C_3 neutral clusters is $(\sigma_g)^2(\sigma_u)^2(\sigma_g)^2(\sigma_u)^2(\pi_u)^4$ in the $^1\Sigma_g^+$ ground state.[3] The π_g lowest unoccupied orbital is partly filled in the anion. Because the π_g orbital has nonbonding character, the bond length in C_3^- clusters is expected to be very similar to the bonding in neutral C_3 ($R_{\rm C-C}$ = 1.297Å[16]). This is shown to be so in Table 2, where the bond lengths of 1.3068, 1.3119, and 1.322 Å are predicted by MP2/6-31G*, B3LYP/6-31G*, and QCISD(T)/6-31G* approaches, respectively.

Scaling the calculated asymmetric stretch mode frequencies to the experimental 1721.8 cm^{-1} value and transferring these scaling factors to the symmetric mode yields a frequency value of 1167.5 cm^{-1} (B3LYP/6-31G*) or 1153.4 cm^{-1} (QCISD(T)/6-31G*). The ν_1 experimental frequency observed by Neumark and co-workers (1075 ± 100 cm^{-1}) is close to these values.

Two different bending modes frequencies of C_3^- were found at all levels of theory, one at ≈400 cm^{-1} and the other at ≈300 cm^{-1} (Table 2). This bending mode energy shift was explained by Schmatz and Botschwina[19] based on Walsh diagrams applied to C_3^-. Comparison of these values to the calculated doubly degenerate bending frequency of 66 cm^{-1} for C_3 [3] and to the experimental value of 63.416 529(40) cm^{-1} for gaseous C_3[17] shows that C_3^- is definitely a more rigid molecule than the floppy neutral C_3.

V. Conclusions

The following conclusions have been reached in this work.

(1) The calculated isotopic frequency shifts for the asymmetric stretching mode of all linear C_3^- isotopomers at the MP2/6-31G* and B3LYP/6-31G* levels of theory are in very good agreement with the experimental shifts (Table 3). The band at 1721.8 cm^{-1} is thus definitively assigned to the asymmetric stretching mode of C_3^-.

(2) From the fitting procedure of the isotopic frequency shifts calculated by the **GF** matrix method, it was found that a linear geometry for C_3^- is preferred. This is different from the bent geometry found for neutral C_3 *in matrices* and is consistent with the higher rigidity expected in the anion compared to the neutral C_3 cluster. It is of course well-known that C_3 in the vapor phase is linear. Matrix forces deform the structure of neutral C_3,[20] but are unable to do so for the more rigid C_3^-.

(3) From the similarities of the band intensity distributions for the six isotopomers of C_3 and C_3^-, it can be inferred that the mechanism of cluster anion formation for $^{12/13}C_3^-$ is predominantly an electron capture process.

(4) A tentative assignment of the 1699.8 cm^{-1} (Ar) to the $\nu_3(\sigma_u)$ asymmetric stretching mode of linear C_4^- anion is proposed here.

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