Infrared Spectroscopy of the C_4 Anion: Reassignment of the 1699.8 cm^{-1} Band

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Using a newly developed dual beam laser plasma method, the C_4^- anion cluster has been formed and deposited in an argon matrix and studied via Fourier transform infrared spectroscopy. An infrared band at 1699.8 cm^{-1}, previously assigned to a combination mode of the neutral C_4 cluster, is shown to be due to the asymmetric stretching fundamental of the C_4^- anion. This attribution is based on the different behavior of the known 1543.4 cm^{-1} neutral C_4 asymmetric stretching mode and the 1699.8 cm^{-1} band under action of annealing, photolysis, and addition of the electron trap, CCl_4, to the plasma gas. Density functional theory and ab initio theory calculations predict a stable, linear C_4 anionic cluster that should possess a moderately strong IR band close to this position. Previous isotopic ($^{12}C/^{13}C$) splitting patterns are reinterpreted and shown to match very well with the theoretically predicted splitting patterns for C_4^-. An electron photodetachment energy of 4.51 eV is found and compares well with the gas-phase value when account is taken of the matrix stabilization energy of 0.63 eV. It is proposed that anions are formed via electron capture by preformed neutral C_4 clusters and that a steady state of neutral and anionic C_4 clusters is established in the matrix.

I. Introduction

Carbon clusters are of intense current interest because of their involvement in soot formation, fullerene and nanotube production, and astrochemistry.[1−3] Although most recent work has concentrated on the carbon fullerenes and nanostructures, a combination of gas-phase, matrix-phase, and theoretical work has focused on the smaller clusters C_n, where $n = 1$ to ∼10. Most of this small cluster work has probed the structure and spectroscopy of neutral species.

Recently, however, a number of experimental articles have appeared on the structure and spectroscopy of the ions of the smaller clusters.[4−12] Several high-level theoretical calculations have also been reported on the carbon cluster ions.[13−17] We have just reported on a new plasma/matrix isolation method for the production of small carbon cluster anions and suggested the assignment of a number of new infrared bands to the species C_3^-−C_9^-.[18]

In the present paper we focus on the C_4^- anion and show that an IR band at 1699.8 cm^{-1} (in Ar), previously assigned[19] to a combination mode of neutral C_4, is, in fact, due to a fundamental mode of its anion. In the previous experiments, matrices were prepared by photolyzing a mixture of argon and diacetylene (C_4H_2) or butadiene (C_4H_6) using vacuum ultraviolet radiation. Isotopic studies using C_4D_2 or various ^{13}C-substituted and deuterated C_4H_6 isotopomers were used. A completely different approach was employed in the present experiments. Graphite or mixtures of $^{12}C/^{13}C$ graphite were laser-ablated in the presence of an argon plasma and the resultant species deposited in argon matrices. Neutral and anionic C_4 clusters are produced in both approaches, but the present method is more efficient for the production of anionic species.

II. Experimental Procedures

Small anionic carbon clusters have been produced by Nd:YAG pulsed laser ablation of graphite (using the 532 nm beam) in the presence of a plasma generated by focusing part of the 1064 nm beam on a small piece of yttrium positioned adjacent to the graphite.[18] The bright blue plasma pulse produced acts as a rich source of electrons, photons, and ions of Ar and Y. X-ray photons are also known to be generated in such a plasma.[20] Electron attachment to the neutral C_4 carbon cluster is expected, since its electron affinity is large, 3.882 eV.[7] The anions are attracted by a positive potential on an O-ring electrode placed just in front of the matrix deposition window. The matrix window (BaF_2) was maintained at 10−12 K by a closed-cycle helium cryostat (APD). An average current of 10−30 μA was observed on the electrode (held at +60 V) during deposition using a 10 Hz laser pulse repetition rate. Absorption spectra were recorded on a MIDAC Fourier transform infrared (FTIR) spectrometer (0.7 cm^{-1} resolution).

III. Theoretical Methods

Calculations of the optimized molecular geometry and harmonic vibrational frequencies and intensities for C_4^- were carried out using the GAUSSIAN 94 program package.[21] Density functional theory (DFT) calculations were performed using a B3LYP functional with 6-31G* and 6-31+G* basis sets.[22−24] The latter incorporates diffuse functions that are thought to provide a more accurate description of anionic species. Ab initio Hartree−Fock calculations with a 6-31G* basis set were also run for comparison. All three approaches gave comparable results (vide infra). Calculations using the B3LYP/6-31G* approach were also performed for the C_4^+ species.

IV. Results

Nd:YAG laser ablation of graphite at 532 nm with a low photon flux ensures formation of small clusters. To produce cluster anions, plasma generation was activated by focusing the 1064 nm beam either on a piece of graphite or on an yttrium chip. The respective IR spectra shown in Figures 1 and 2 were observed. In Figure 1, the 1543 cm^{-1} peak due to C_4 is

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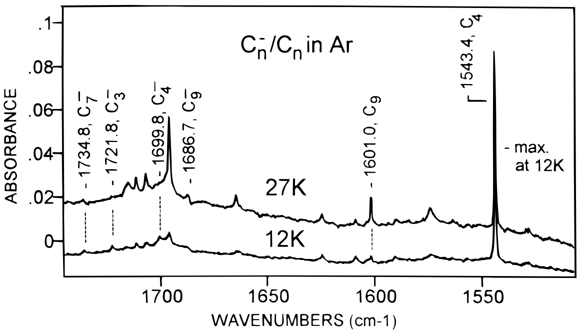

Figure 1. Portion of the infrared absorption spectrum of C_n^-/C_n carbon clusters isolated in an Ar matrix at 12 K (lower spectrum) and after annealing to 27 K and recooling to 12 K (upper spectrum). Matrix was deposited during ablation of graphite using the 1064 and 532 nm Nd:YAG laser beams with total energy of ca. 30 mJ/pulse focused to a spot ca. 1.0 mm in diameter.

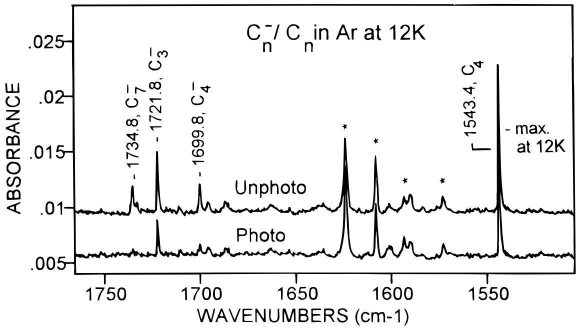

Figure 2. Portion of the infrared absorption spectrum of C_n^-/C_n carbon clusters isolated in an Ar matrix at 12 K. Matrix was prepared using a dual-laser beam deposition method in which the 1064 nm Nd:YAG laser beam is focused on a yttrium metal surface while the 532 nm ablates carbon from a nearby (2 mm) graphite piece. The effect of photolysis (20 min, 100 W Hg lamp, full spectral output) on the unphotolyzed sample/matrix (upper spectrum) is shown in the lower spectrum. Starred bands are due to isolated H_2O bands.

TABLE 1: Linear C_4^- Carbon Cluster Anion Vibrational Frequencies (Unscaled, cm^{-1}), Intensities (in Brackets, km/mol), Geometries (Bond Lengths (R), Å, and Rotational Constants (B, GHz) Calculated at Different Levels of Theory

parameter	HF/6-31G*	B3LYP/6-31G*[a]	B3LYP/6-31+G*
ν_1 (σ_g)	2384.0 [0]	2112.7 [0]	2193.2 [0]
ν_2 (σ_g)	870.3 [0]	926.4 [0]	923.6 [0]
ν_3 (σ_u)	1742.8 [1162]	1785.2 [87]	1775.2 [115]
ν_4 (π_g)	651.5 [0]	605.4 [0]	595.2 [0]
		533.1 [0]	547.2 [0]
ν_5 (π_u)	281.6 [13.2]	265.5 [27]	248.8 [14]
		241.5 [50]	233.7 [41]
R_1 (Å)[b]	1.2156	1.281	1.2803 (1.2773)[c]
R_2 (Å)	1.4125	1.341	1.3409 (1.3357)[c]
B (GHz)	5.022 650	4.946 407	4.948 948

[a] Reference 18. [b] Bond lengths are numbered from the outer to the central C−C bond. [c] RCCSD/all + (T)/val calculation with basis set of 256 cGTOs (ref 32).

prominent, while the 1699.8 cm^{-1} band is considerably smaller (compared to its intensity in Figure 2). Two observations suggest that the 1543.4 and 1699.8 cm^{-1} bands do not arise from the same species. First, although previous work[19] reported that the ratio I (1543.4 cm^{-1})/I (1699.8 cm^{-1}) was ~20, in the present experiments this ratio is closer to 60, as the upper spectrum in Figure 1 shows. If the bands originate from the same species, the ratio should be independent of the method of preparation. Second, as the upper panel in Figure 1 also shows, the 1543.4 cm^{-1} peak increases slightly after annealing (to 27 K) at the same time that the 1699.8 cm^{-1} band decreases. This behavior is not consistent with a common carrier for these bands. These findings shed serious doubt on the common origin of the 1543.4 and 1699.8 cm^{-1} bands.

The effect of photolysis on these two peaks is shown in Figure 2. The upper (unphotolyzed) spectrum shows that the band intensity ratio I (1543.4 cm^{-1})/I(1699.8 cm^{-1}) $\approx$ 5. Upon photolysis (full output, Hg arc, 20 min) the ratio grew to ca. 11, primarily because of a 350% decrease in the 1699.8 cm^{-1} band (although the 1543.4 cm^{-1} band increased about 15%). Thus, annealing and photolysis lead to opposite behaviors for these two bands, which leads to the conclusion that these two bands do not arise from the same species.

If the bands do not belong to the same species, the question then becomes which of the bands is misassigned. The assignment of the 1543 cm^{-1} to C_4 is solid.[25] Based on a detailed isotopic study of seven isotopomers (of the 10 possible), in conjunction with ab initio calculations, this band is clearly the fundamental antisymmetric C=C stretching mode of chainlike C_4. The attribution of the 1699.8 cm^{-1} band is thus in question. The first problem is its charge state: is it ionic or neutral? Its behavior upon UV photolysis mirrors that of other anions[18] such as C_3^- (cf. Figures 1 and 2). Furthermore, the addition of CCl_4 (0.5%) to the Ar gas results in a substantial decrease in the intensity of the 1699.8 cm^{-1} band, as has been observed previously for other C_n^- cluster bands. This effect is the result of competitive electron capture between C_4 (or other C_n species) and the plasma products of CCl_4, viz.,Cl, Cl_2, CCl_3, CCl_3^+, etc. Thus, based on the experimental observations, we conclude that the species giving rise to the 1699.8 cm^{-1} band is an anion.

The atomic composition of this species is most probably pure carbon. Hydrogen is not present in the molecule, since no C−H stretching vibrations have been observed, except for a small band due to C_2H_2 probably produced in the multistep photoreaction of $C_3{\cdot}H_2O$.[26] It has been reported previously[19] that complete deuteration of the butadiene precursor resulted in no shift of the 1699.8 cm^{-1} band. Other small carbon chain anions have been reported previously, and none of their known frequencies correspond to the present one. In a recent study of C_3 and other anions, the 1699.8 cm^{-1} band was tentatively assigned to the linear C_4 anion.[18] This attribution rested chiefly on its good match with DFT calculational results. Table 1 presents these results plus a new ab initio calculation for the linear C_4 anion. The approaches and basis sets used were (a) ab initio Hartree−Fock with a 6-31G* basis set and (b) B3LYP density functional with 6-31G* and (c) 6-31+G* basis sets. Harmonic frequencies, bond lengths, and rotational constants are given. All three approaches predict an infrared-allowed band at 1742.8 (HF/6-31G*), 1785.2 (B3LYP/6-31G*), and 1775.2 cm^{-1} (B3LYP/6-31+G*), all unscaled. Scaling using the reasonable factors of 0.9752 and 0.9528 for the HF/6-31G* and B3LYP/6-31G* approaches, respectively, yields exact matches with the experimental frequency. Comparison of the bond lengths calculated by the B3LYP/6-31+G*and higher level ab initio calculations by Schmatz and Botschwina[32] (cf. Table 1) shows very good agreement, with the central bond longer than the two end bonds.

In previous work[18] a stable nonlinear isomer of the C_4^- cluster was found. Its structure, a carbon atom attached to a three-membered ring, displayed the lowest total energy of a family of nonlinear structures, but its energy was still 37.7 kcal/mol higher than the linear anionic structure. Since its most intense calculated band lies at 1683.9 cm^{-1} [1901 km/mol] (not scaled, B3LYP/6-31G* level), which is close to the observed 1699.8 cm^{-1} peak, it was investigated further. The frequency shifts for all the possible isotopomers of this nonlinear structure show the following pattern: 0, 0.2, 12.7, 12.9, 21.8, 23.0, 33.3, 35.0,

TABLE 2: Comparison of Observed (Ar Matrix) and Calculated (6-31G* Basis Set) ν_3 Asymmetric Stretching Mode Frequencies (cm^{-1}) for All Isotopomers of Linear $^{12/13}C_4^-$ Carbon Cluster Anion[e]

isotopomer	ν_{HF}[a]	$\Delta\nu_{HF}$	ν_{B3LYP}[b]	$\Delta\nu_{B3LYP}$	ν_{Exp}[c]	$\Delta\nu_{Exp}$	$\nu_{Exp} - \nu_{B3LYP}$
12-12-12-12	1699.8	0	1699.8	0	1699.8[d]	0	0
12-12-12-13	1683.1	16.7	1683.2	16.6	1683.4	16.4	0.2
12-12-13-12	1682.5	17.3	1681.6	18.2	1681.8	18.0	0.2
12-13-12-13	1667.1	32.7	1666.8	33.0	1667.2	32.6	0.4
12-13-13-12	1666.8	33.0	1666.8	33.0	1667.2	32.6	0.4
13-12-12-13	1666.8	33.0	1666.8	33.0	1667.2	32.6	0.4
12-12-13-13	1664.1	35.7	1662.7	37.1	1663.2	36.6	0.5
12-13-13-13	1649.8	50.0	1649.8	50.0			
13-12-13-13	1649.2	50.6	1648.3	51.5			
13-13-13-13	1633.2	66.6	1633.2	66.6			

[a] Scaled by 0.9752 factor. [b] Scaled by 0.9528 factor. [c] From ref 19. [d] This work. [e] Isotopic shifts (cm^{-1}) are collected in the Δ columns.

66.5, 66.7 cm^{-1}. This is very different from the pattern observed (cf. Table 2, column 7) and leads to the exclusion of this species as the carrier of the 1699.8 cm^{-1} band.

Although the C_n/CCl_4/Ar experiments indicated that the 1699.8 cm^{-1} arises from an anionic species, the possibility of the C_4^+ cluster as the carrier was also explored. DFT calculations determined that the most stable geometry is a double deltoid structure (C_{2v}) with a doublet ground state. The bond lengths and angles found are $R(1,2) = R(1,4) = 1.395$ Å, $R(2,3) = R(3,4) = 1.481$ Å, $\angle(4,1,2) = 72.3°$ and $\angle(1,2,3) = \angle(1,4,3) = 110.1°$. The calculated harmonic frequencies for this structure (intensities in brackets) are 1289.7 [76], 1198.0 [0], 980.8 [25], 580 [57], 325.3 [224], and 187.8 cm^{-1} [17 km/mol]. These values are sufficiently far from the observed 1699.8 cm^{-1} band to discount this species as the carrier.

No convergence in the geometry optimization (B3LYP/6-31G*) could be achieved for any doublet linear C_4^+ isomer. However, two stable quartet electronic ground-state structures were found. One was linear and the other rhombic with energies 0.9 and 7.6 kcal/mol higher than the doublet deltoid structure, respectively. Their most intense IR frequencies, 1916.6 cm^{-1} [5261 km/mol] for the linear and 1399.9 cm^{-1} [47 km/mol] for the rhombic structures, should be treated with caution, however, because of the strong spin contamination ($\langle S^2 \rangle = 3.75$) of both high-spin systems. In summary, the attribution of the 1699.8 cm^{-1} band to a C_4^+ species is not supported by theory, whereas the linear C_4 anion is supported by both experimental and theoretical results.

Further strong support for this assignment is based on a reinterpretation of the isotopic results of Shen, Withey, and Graham (SWG).[19] These authors prepared matrices containing C_4 by photolyzing a mixture of acetylene or 1,3-butadiene with argon (and various deuterated and ^{13}C-substituted isotopomers). Vacuum ultraviolet photolysis (at 121 nm) during deposition was effected by a microwave-discharged flowing mixture of hydrogen and helium gases. Seven different $^{12}C/^{13}C$ C_4 isotopomers were obtained from singly and doubly substituted ^{13}C butadienes. C_4 isotopomers containing three or four ^{13}C atoms were not produced. The experimental frequencies obtained by SWG are given in Table 2 together with the frequency shifts from the all-^{12}C isotopomer frequency. Interestingly, three different isotopomers yield the same frequency (and were so assigned by SWG), and this is predicted by both the HF and DFT results. In addition, shifts calculated via HF/6-31G* and B3LYP/6-31G* methods are also presented in the table. Both theoretical approaches give shifts that agree well with each other and with the experimental shifts. The worst match between the theoretical results is off by 1.4 cm^{-1}, while between experiment and theory the worst match is off by only 0.5 cm^{-1}. It should be noted that only one scaling factor was used here for all isotopomers. An alternative procedure has been suggested recently in which a sliding scaling factor is used for different isotopomers.[27] If such a scheme were used here, the match would, of course, be almost exact. Theoretical calculations of the vibrational frequency and isotopic frequency shifts fully support the attribution of the 1699.8 cm^{-1} band to the C_4 anion.

V. Discussion

In an earlier paper, the 1699.8 cm^{-1} band was assigned to neutral C_4.[19] Several lines of evidence for this attribution were presented. The band was unshifted when C_4D_2 was photolyzed, indicating that it was not hydrogen-bearing. A variation in concentration ratios of the precursor C_4H_2 in Ar revealed that the intensity ratio of the 1534.4 and 1699.8 cm^{-1} bands remained constant. Furthermore, the isotopic ($^{12}C/^{13}C$) splitting patterns of the 1534.4 and 1699.8 cm^{-1} bands were remarkably similar. These observations led to the reasonable conclusion that the two bands arise from a common carrier, C_4. Other possibilities, such as rhombic C_4, and other carbon chain species such as C_5, C_6, C_7, C_8, or C_{10} were considered and eliminated.

The assignment of the 1699.8 cm^{-1} band to a particular mode or modes of C_4 proved, however, to be more problematic. Recent ab initio theoretical calculations cited predicted that the only fundamental vibration near the new band was the ν_2 C=C stretching frequency already assigned to the 1534.4 cm^{-1} band. As a result, it was deduced that the 1699.8 cm^{-1} band had to be a combination band, most probably involving ν_2 and a bending mode. Simple subtraction yielded a bending mode at ca. 156 cm^{-1}. But theoretical calculations predicted that the ν_4 (π_g) mode should lie in the 385−454 cm^{-1} range and the ν_5 (π_u) mode in the 175−214 cm^{-1} range. Although the 175 cm^{-1} prediction would yield a ν_3 (σ_u) + ν_5 (π_u) combination band at ∼1718 cm^{-1} (= 1543 + 175 cm^{-1}), close to the observed value, this combination of two ungerade bands is infrared forbidden.

Consideration was next given to a nonlinear geometry for C_4. An earlier EPR study had found evidence for a slight departure from linearity, with a ∼2.5° angle at both ends.[28] An optimized force constant fit to the isotopic peaks of the ν_2 C=C stretching mode (1543.4 cm^{-1}) showed no preference for a linear, trans-bent or cis-bent structure. Such a calculation, however, also yielded values for the bending modes at 496 (ν_4 (π_g)) and 212 cm^{-1}(ν_5 (π_u)) for linear C_4. The combination mode comprised of ν_2 (σ_u) + ν_5 (π_u) is in the right range but is forbidden. This is true also for the trans-bent species. However, for the cis-bent species the lower bending frequency is predicted at ∼170 cm^{-1} (ν_3 (a_1)), close to the ab initio values. This mode combined with the ν_5 (b_2) C=C stretching fundamental would produce an IR-allowed combination mode at 1713 cm^{-1}. Thus, the 1699.8 cm^{-1} band was assigned to the ν_3 (a_1) + ν_5 (b_2) combination mode of cis-bent C_4 chain trapped in an Ar matrix.

The question then arises: was there evidence in the previous study that suggested the presence of anions in the sample with the neutral C_4 clusters? There are several observations that point to their presence. First, a weak band at 903.7 cm^{-1} was observed. Known to be due to HAr_2^+ cations, the appearance of this band implies the existence of counteranions. Second, vacuum ultraviolet irradiation of matrices containing carbon clusters has been reported to lead to the formation of other ionic species such as C_2^- ions.[29,30] Finally, as shown above, the isotopic splitting pattern of the 1699.8 cm^{-1} band fits very well with the predicted theoretical pattern for a fundamental mode in the C_4 anion. Thus, the presence of C_4 anions in the previous study is indicated. Presumably, during the vacuum UV photolysis of the precursor butadiene molecules, sufficient quantities of mobile electrons were photodetached in the matrix and were trapped out on the already-formed C_4 clusters. This supposition is bolstered by photolysis experiments in matrices containing neutral and ionic carbon clusters. During a 1 h photolysis with a 100 W Hg lamp (full spectral output), the C_n^- bands (including C_4^-) decreased initially but then no further, indicating that a saturation or quasi-steady-state had been reached. Irradiation of the matrix with vacuum ultraviolet radiation may set up a steady state between electron photodetachment processes involving the anion and electron capture processes involving the neutral C_4 cluster. In matrices, electrons may be liberated via the $X + h\nu \rightarrow X^+ + e^-$ process or the $Y^- + h\nu \rightarrow Y + e^-$ process, where X and Y are Ar, carbon or yttrium clusters, or impurities (such as water). Because of their high electron affinities, carbon clusters may act as electron traps in the matrix. If the ionization conditions are kept the same during matrix deposition, the 1699.8 cm^{-1} band is observed to grow in parallel with the 1543.4 cm^{-1} neutral C_4 band. This is why the former band was not observed in our earlier C_n^-/C_n/Ar matrix experiments when the conditions employed yielded low C_4 production.[18]

The C_n^-/C_n/Ar matrix photolysis was performed using a 100 W Hg lamp with a set of filters whose $\lambda_{\text{cut on}}$ varied (2 h irradiation/filter). No effect on the 1699.8 cm^{-1} band intensity was noted with longer wavelength filters until one with $\lambda_{\text{cut on}}$ =275 nm (4.51 eV) was used. This filter, with a transmission of 10% at 283 nm (4.38 eV), reduced the initial intensity of the 1699.8 cm^{-1} band by 15%. This energy can be connected to the 3.882 eV electron photodetachment energy for C_4^- reported from gas-phase studies.[7] Generally, electron photodetachment energies are higher in rare gas matrices than in the gas phase. They have now been reported for a number of anionic species, and the departure from the gas-phase value represents the stabilization energy of the ion in the matrix. The closest gas-phase electron detachment energies to 4.0 eV for the C_n^- ($3 < n < 9$) linear carbon cluster anions are due to C_9^- (3.684 eV), C_6^- (4.185 eV), and C_8^- (4.379 eV).[7] The 1699.8 cm^{-1} band can be excluded as either C_9^- or C_8^- bands because of the very small band intensities of the C_9 and C_8 parent clusters in this experiment. For the C_6^-/Ar matrix, a 4.67 eV energy onset of the electron photodetachment was reported,[18] which is higher than the photobleaching threshold energy found here for the 1699.8 cm^{-1} band. The 1699.8 cm^{-1} band cannot result from C_9^-, C_8^-, or C_6^-, based on the calculated energy disagreement of the 1699.8 cm^{-1} frequency with the asymmetric stretching modes frequencies of these clusters.[18] In conclusion, the UV photolysis with filters supports the assignment of the 1699.8 cm^{-1} band to the asymmetric stretching mode of the C_4^- anion.

The process envisaged for the formation of the C_4 anion is the electron capture by the preformed neutral C_4 cluster and not a reaction of carbon fragments such as $C_2 + C_2^-$, $C_3 + C^-$, or $C_3^- + C$. This conclusion is based on two observations. First, the intensity distribution of the isotopomeric bands in the 1699.8 cm^{-1} region mirrors exactly the pattern seen in the 1543.4 cm^{-1} region for neutral C_4. If anionic C_4 had been produced by an aggregation of smaller clusters, this similarity in intensity distributions would not be expected. If, however, a portion of the neutral C_4 clusters formed in the vapor phase attract an electron and form C_4 anions, such a pattern would be anticipated. Furthermore, with aggregation of clusters occurring during matrix annealing, the isotopomeric band intensity patterns of neutral $^{12/13}C_n$ and anionic $^{12/13}C_n$ clusters were observed to be dramatically different. And second, from the spectrum in Figure 2 (upper), it is possible to roughly estimate the yield of C_4^- produced in our dual-beam ionization experiment. When calculated (B3LYP/6-31G*) values for the vibrational intensities of the linear C_4 and C_4^- clusters[18] are used, the yield can be expressed as the ratio of concentrations $[C_4^-]/([C_4] + [C_4^-])$. This is found to be 34%, which places the yield of C_4^- in third place behind C_8^-(46%) and C_6^- (44%). This order is consistent with the order of electron affinities reported for small neutral carbon clusters C_n ($3 < n < 9$) (the highest EA is for C_8).[7] The above consistency also supports the concept of C_n^- formation by electron capture rather than via ion-neutral reactions. Such a simple "whole cluster electron capture" mechanism has been proposed previously to explain the similar intensity patterns in the isotopomeric bands of neutral and anionic C_3.[31]

The fact that the I (1699.8 cm^{-1})/I (1543.4 cm^{-1}) intensity ratios was found to be constant in the former study was taken as evidence for the common origin of the two bands. However, with the introduction of the more efficient ion production technique in the present work, the intensity ratio was found to differ and to depend on the photolysis, annealing history, or ionization technique employed. This is further support for the steady-state proposition discussed above. If a nonsteady-state mixture of anions and neutrals is present in the matrix, photolysis or annealing will act to increase one at the expense of the other and their bands will grow or shrink. Once steady state is reached, annealing or photolysis affects both species equally and their intensity ratio remains unchanged.

VI. Conclusions

In this paper it has been shown that the formation of an electron-rich plasma in the vicinity of carbon clusters results in the production of carbon cluster anions, including C_4^-. The 1699.8 cm^{-1} infrared band is reassigned to the ν_3 asymmetric stretching mode of the C_4 anion on the basis of (1) annealing and photolysis behavior in argon matrices, (2) the isotopic splitting pattern and isotopic shifts, and (3) theoretical calculations. From a comparison of the theoretical calculations and the present experimental results, the ground-state structure of the C_4 anion is found to be linear.

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References and Notes

(1) Weltner, W., Jr.; Van Zee, R. J. *Chem. Rev.* **1989**, *89*, 1713.

(2) Herbig, G. H. *Annu. Rev. Astrophys.* **1995**, *33*, 19, and references therein.

(3) Rinzler, A. G.; Hafner, J.; Nikolaev, P.; Lou, L.; Kim, S. G.; Tomanek, D.; Nordlander, P.; Colbert, D. T.; Smalley, R. E. *Science* **1995**, *269*, 1550 and references therein.

(4) Forney, D.; Freivogel, P.; Jacobi, M.; Lessen, D.; Maier, J. P. *J. Chem. Phys.* **1995**, *103*, 43. Freivogel, P.; Fulara, J.; Jacobi, M.; Forney, D.; Maier, J. P. *J. Chem. Phys.* **1995**, *103*, 54.

(5) Schafer, M.; Grutter, M.; Fulara, J.; Forney, D.; Freivogel, P.; Maier, J.P. *Chem. Phys. Lett.* **1996**, *260*, 406.

(6) Yang, S.; Taylor, K. J.; Craycraft, M. J.; Conceicao, J.; Pettiette, C. L.; Cheshnovsky, O.; Smalley, R. E. *Chem. Phys. Lett.* **1988**, *144*, 431.

(7) Arnold, D. W.; Bradforth, S. E.; Kitsopoulos, T. N.; Neumark, D. M. *J. Chem. Phys.* **1991**, *95*, 8753.

(8) Handshuh, H.; Gantefor, G.; Kessler, B.; Bechthold, P. S.; Eberhardt, W. *Phys. Rev. Lett.* **1995**, *77*, 1095.

(9) Kitopoulos, T. N.; Chick, C. J.; Zhao, Y.; Neumark, D. M. *J. Chem. Phys.* **1991**, *95*, 5479.

(10) Arnold, C. C.; Zhao, Y.; Kitopoulos, T. N.; Neumark, D. M. *J. Chem. Phys.* **1992**, *97*, 6121.

(11) Helden, G.; Gotts, N. G.; Bowers, M. T. *Nature* **1993**, *363*, 60.

(12) Zhao, Y.; deBeer, E.; Xu, C.; Taylor, T.; Neumark, D. M. *J. Chem. Phys.* **1996**, *105*, 4905.

(13) Raghavachari, K. *Z. Phys. D*. **1989**, *12*, 61.

(14) Raghavachari, K. *Chem. Phys. Lett*. **1990**, *171*, 249.

(15) Watts, J. D.; Bartlett, R. J. *J. Chem. Phys*. **1992**, *97*, 3445.

(16) Adamowicz, L. *Chem. Phys. Lett*. **1991**, *182*, 45.

(17) Schmatz, S.; Botschwina, P. *Chem. Phys. Lett*. **1995**, *235*, 8. Schmatz, S.; Botschwina, P. *Chem. Phys. Lett*. **1995**, *245*, 136. Schmatz, S.; Botschwina, P. *Int*. *J*. *Mass Spectrom*. *Ion Processes* **1995**, *149*/*150*, 621.

(18) Szczepanski, J.; Ekern, S.; Vala, M. *J. Phys. Chem.* **1997**, *101*, 1841

(19) Shen, L. N.; Withey, P. N.; Graham, W. R. M. *J. Chem. Phys*. **1991**, *94*, 2395.

(20) Wellegehausen, B.; Hube, M.; Jin, F. *Appl*. *Phys*. **1989**, *B49*, 173.

(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94*, Revision B.2; Gausssian, Inc.: Pittsburgh, 1995.

(22) Lee, C.; Yang, W.; Parr, R. Phys. Rev. B, **1988**, *37*, 785.

(23) Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648.

(24) Becke, A. D. *J. Chem. Phys*. **1988**, *88*, 1053.

(25) Shen, L. N.; Graham, W. R. M. *J. Chem. Phys*. **1989**, *91*, 5115.

(26) Ekern, S.; Szczepanski, J.; Vala, M. *J. Phys. Chem.* **1996**, *100*, 16109.

(27) Kranze, R. H.;Rittby, C. M. L.; Graham, W. R. M. *J. Chem. Phys*. **1992**, *96*, 2517. Kranze, R. H.; Rittby, C. M. L.; Graham, W. R. M. *J. Chem. Phys*. **1993**, *98*, 71.

(28) Cheung, H. M.; Graham, W. R. M. *J. Chem. Phys*. **1989**, *91*, 6664.

(29) Milligan, D. E.; Jacox, M. E.; Abouaf-Marguin, L. *J. Chem. Phys*. **1967**, *46*, 4562.

(30) Milligan, D.; Jacox, M. E. *J. Chem. Phys*. **1969**, *51*, 1952.

(31) Szczepanski, J.; Wehlburg, C.; Vala, M. *J. Phys. Chem*. *A* **1997**, *101*, 7039.

(32) Schmatz, S.; Botschwina, P. *Int. J. Mass Spectrom. Ion Phys*. **1995**, *149*/*150*, 621.