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Electronic Absorption Spectra of Carbon Chain Anions C_{2n+1}^- ($n = 2-5$) in Neon Matrices

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Absorption spectra showing transitions to several excited electronic states of C_{2n+1}^- ($n = 2-5$) chains were observed. The spectra were recorded after codeposition of mass-selected anions with neon to form a matrix at 5 K. The assignment follows from mass-selection, the monotonic dependence of the wavelength of the electronic origin band on the number of carbon atoms, photobleaching changes, and spectroscopic considerations. The absorption band systems can be attributed to $^2\Pi \leftarrow X\ ^2\Pi$ transitions. For C_5^- two transitions are observed, for C_7^- three, and for C_9^- and C_{11}^- four.

Introduction

The spectroscopy of neutral and charged carbon molecules contributes to the understanding of combustion processes, soot formation, and extraterrestrial environments.[1,2] Whereas most anions do not possess bound excited electronic states, those of carbon species are unusual because they have sufficiently high electron detachment thresholds (2.8−3.9 eV for C_{2n+1}^- ($n = 2-5$)[3−5]) so that several excited electronic states can be bound.

However, only recently information on electronic spectroscopy of carbon anions C_n^- ($n > 3$) has been obtained. The even-numbered C_{2n}^- ($n = 2-10$) chains were spectroscopically characterized in neon matrices using mass-selected codeposition.[6] This led to the identification of their C $^2\Pi \leftarrow X\ ^2\Pi$ transitions. On the basis of these data, it proved possible to observe the same transitions in the gas phase for C_4^-, C_6^-, and C_8^- by means of a one- or two-photon detachment approach.[7,8] Prior to this the first gas phase electronic spectrum of a polyatomic carbon anion, C_5^-, was reported using such a technique.[9] The present results show a rather unique situation: transitions to several bound excited electronic states of the C_{2n+1}^- ($n = 2-5$) anions.

Experiment

The technique used combines mass-selection and matrix isolation.[10] Anions are produced in a cesium sputter source and extracted by electrostatic lenses to form a continuous ion beam.[11,12] A quadrupole mass-selects the ions, which are then codeposited on a cryogenic surface with excess of neon over a period of 2 h. The substrate is a rhodium-coated sapphire plate held at 5 K by a closed cycle helium cryostat. The metal surface is grounded via an ammeter. The attainable ion currents decrease with size from 40 (C_5^-) to 0.8 nA (C_{11}^-). Deposition energies are nominally 50 eV. However, this impact energy is compensated by space charge effects, as no absorption band broadening is observed when the spectrum of, for example, mass-selected $Cl-C{\equiv}C-Cl^+$ is compared with the one obtained after a traditional deposition.[13] Although some fragment species (e.g. C_2, C_2^-) can be observed, the assignment of new spectral features is not prevented.[14]

The absorption spectra of the translucent neon matrices are recorded with a standard set of light sources, monochromator and detectors in a waveguide manner.[15] The range covered is 220−1000 nm. In order to distinguish absorption bands of charged and neutral species, the neon matrix is exposed to the unfiltered light of a medium-pressure mercury lamp. The UV radiation with a maximum energy of ∼5.4 eV liberates electrons from the anions. The electrons migrate in the neon lattice and neutralize cations. This photobleaching process leads to an intensity decrease of bands due to ions, while those of the neutral species remain unchanged or grow somewhat.

Results and Discussion

A. Size and Charge of the Species. Mass-selected C_{2n+1}^- anions ($n = 2-5$) are trapped in a neon matrix at 5 K. A number of new electronic absorption systems appear that are specific to the mass-selected species (Figure 1). The strongest of the new bands are marked with ●, ◆, ▲, and ■ in the Figure and can be attributed to the origins of the electronic transitions of the indicated anions (*vide infra*). These origin bands show a regular shift to longer wavelengths with size of the carbon species. This trend is seen clearly in Figure 2, where the wavelengths of the marked bands are plotted against the number of carbon atoms. The almost linear dependence suggests the attribution of the new bands to electronic transitions within a homologous series, consistent with the mass-selection.

Apart from the new bands, known transitions of C_2^+, C_2^-, C_3, C_5, and C_7[16] were also apparent after C_5^- and C_7^- depositions. These are present due to neutralization and fragmentation processes that accompany deposition with large quantities of ions. Some of the additional absorption systems obscure the region near 300 nm. Thus the bands attributed to C_7^- in this region were only discernible in a spectrum that was recorded after deposition with a lower C_7^- ion current (inset of Figure 1).

The intensities of the previously identified $^1\Sigma_u^+ \leftarrow X\ ^1\Sigma_g^+$ electronic transitions of C_{2n+1} ($n = 2-5$)[16] increase while the new bands diminish on UV irradiation. Wavelength cutoff filters were used to determine the electron detachment threshold of the trapped species. No change in band intensities of C_9^- was observed after irradiation by a medium-pressure mercury lamp using a cutoff filter with 10% transmission at 295 nm (4.2 eV) (Figure 3, upper trace). Bands due to C_9 appeared, while those of C_9^- diminished after additional irradiation with the unfiltered light of this source (Figure 3, lower). Therefore, the electron detachment threshold of the trapped C_9^- lies in the range 4.2−5.4 eV. This is larger than in the gas phase (3.68 eV)[3,5] by ∼1 eV because ionic states are stabilized in neon.

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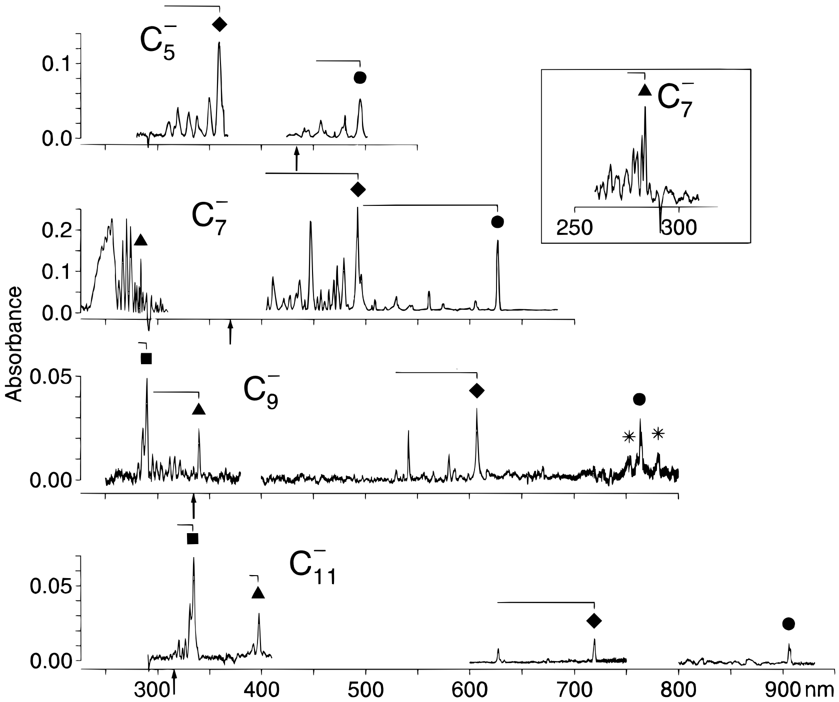

Figure 1. Electronic absorption spectra of C_{2n+1}^- ($n = 2-5$) recorded after mass-selected anions were codeposited with excess neon on a substrate to form a matrix at 5 K. The origin bands of the transitions from the X $^2\Pi$ to the A $^2\Pi$, B $^2\Pi$, C $^2\Pi$, and D $^2\Pi$ states are marked by ●, ◆, ▲, and ■ respectively. The location of the electron detachment thresholds in the gas phase[3−5] are shown by the arrows. The inset is a C_7^- spectrum recorded under conditions such that absorption bands of C_7 were less intense. (The bands in the C_9^- spectrum marked with ∗ are not real.)

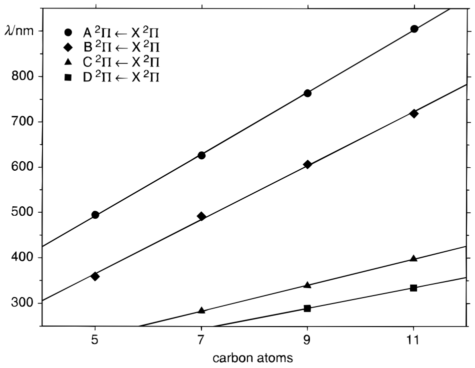

Figure 2. Plot of the wavelength of the 0_0^0 band of the observed electronic transitions of the C_{2n+1}^- series *versus* size. Linear least square fits indicate the trends.

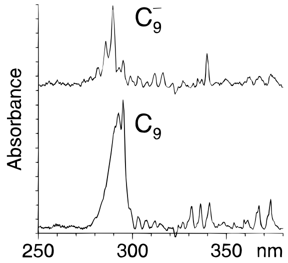

Figure 3. Absorption spectra recorded after mass-selected C_9^- co-deposition with neon on a cryogenic surface. The electronic transitions observed before (upper trace) and after (lower) medium-pressure mercury lamp irradiation are almost purely due to C_9^- and C_9, respectively.

The new band systems in Figure 1 are attributed to electronic transitions of the C_{2n+1}^- species ($n = 2-5$) because of the photobleaching behavior and the fact that they are relatively strong after deposition of anions with low kinetic energies. This excludes that the carriers of these new absorption bands are neutral or cationic species.

B. Electronic States. The acetylene and cyanoacetylene chains $HC_{2n+1}H^+$,[17,18] $HC_{2n}N^+$, and $NC_{2n-1}N^+$ [14] are isoelectronic with the C_{2n+1}^- species. The cations were isolated in neon matrices and show absorption band systems that were attributed to $^2\Pi \leftarrow X\ ^2\Pi$ transitions on the basis of spectroscopic considerations. The origin bands of these isoelectronic series lie close to those of the long wavelength transitions of the C_{2n+1}^- anions, but have a slightly smaller slope in the plot of the wavelength *versus* size. This similarity leads to the conclusion that the spectra observed for the carbon anions with an odd number of atoms also arise from $^2\Pi \leftarrow X\ ^2\Pi$ transitions.

On the basis of calculations[19] and molecular orbital considerations a $...\pi_g^4\pi_u^1$ X $^2\Pi_u$ ground electronic state can be deduced for C_5^- and C_9^- and $...\pi_u^4\pi_g^1$ X $^2\Pi_g$ for C_7^- and C_{11}^-. The observed transitions then probably correspond to $\pi-\pi$ electron excitation in line with the plots shown in Figure 2. In addition, the electronic transitions observed for each of the C_{2n+1}^- species have comparable intensities. This excludes that some of the new bands are due to $\Sigma \leftarrow \Pi$ transitions, which would have smaller intensities. On the basis of these considerations all the observed electronic transitions are attributed to $^2\Pi \leftarrow X\ ^2\Pi$ transitions of the C_{2n+1}^- anions.

C. Electronic Transitions. Each spectrum shows the presence of several electronic band systems. This is evident from the Franck−Condon intensity distribution of the bands and the spacing between them. The differences between two neighboring bands marked in Figure 1 are on the average 5000 cm^{-1} and at least 2800 cm^{-1}, which is too large even for the strongest C−C bonds. Therefore the peaks marked in Figure 1 with ●, ◆, ▲, and ■ can be assigned to 0_0^0 bands of different $^2\Pi \leftarrow X\ ^2\Pi$ electronic transitions of the C_{2n+1}^- anions, which we label as A ← X, B ← X, C ← X, and D ← X.

(a) C_5^-. C_5^- shows two electronic band systems, one with an origin at 495.1 nm and the other at 359.1 nm (Figure 4). The former, the A ← X band system, has already been detected in the gas phase at 495 nm and tentatively assigned to a $^2\Pi_g \leftarrow X\ ^2\Pi_u$ transition.[9] A vibrational frequency, 718 cm^{-1}, was derived and associated with the ν_2 mode in the electronically

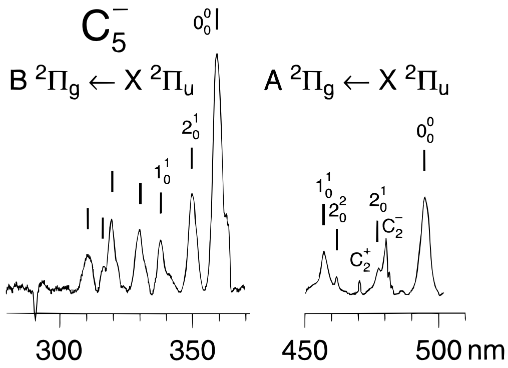

Figure 4. A $^2\Pi_g \leftarrow$ X $^2\Pi_u$ and B $^2\Pi_g \leftarrow$ X $^2\Pi_u$ band systems of C_5^- observed after mass-selected codeposition with neon to form a matrix at 5 K. The vertical lines mark the bands listed in Table 5.

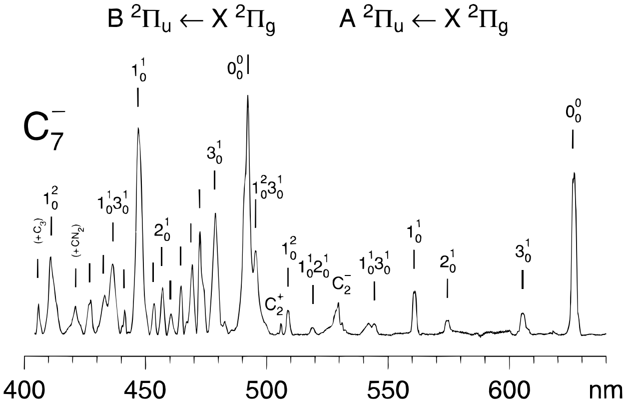

Figure 5. A $^2\Pi_u \leftarrow$ X $^2\Pi_g$ and B $^2\Pi_u \leftarrow$ X $^2\Pi_g$ transitions of C_7^-, recorded after these anions were mass-selected and subsequently trapped in neon at 5 K. The vertical lines mark the bands listed in Table 5.

TABLE 1: Observed Bands (Maxima ±0.2 nm) of the $^2\Pi_g \leftarrow X\ ^2\Pi_u$ Electronic Transitions of C_5^- in 5 K Neon Matrices

λ (nm)	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	assignment
495.1	20 200	0	A $^2\Pi_g \leftarrow$ X $^2\Pi_u$ 0_0^0
477.6	20 936	737	2_0^1 (+ C_2^-)
461.9	21 652	1452	2_0^2
457.1	21 878	1679	1_0^1
359.1	27 847	0	B $^2\Pi_g \leftarrow$ X $^2\Pi_u$ 0_0^0
350.0	28 571	724	2_0^1
337.8	29 603	1756	1_0^1
330.2	30 285	2437	
319.1	31 338	3491	
316.0	31 646	3798	
311.1	32 144	4297	

TABLE 2: Observed Bands (Maxima ±0.2 nm) of the $^2\Pi_u \leftarrow X\ ^2\Pi_g$ Electronic Transitions of C_7^- in 5 K Neon Matrices

λ (nm)	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	assignment
626.8	15 954	0	A $^2\Pi_u \leftarrow$ X $^2\Pi_g$ 0_0^0
605.5	16 516	562	3_0^1
574.4	17 410	1457	2_0^1
560.8	17 831	1877	1_0^1
544.4	18 369	2416	$1_0^1 3_0^1$
519.0	19 267	3314	$1_0^1 2_0^1$
508.9	19 651	3697	1_0^2
495.3	20 190	4236	$1_0^2 3_0^1$
492.3	20 314	0	B $^2\Pi_u \leftarrow$ X $^2\Pi_g$ 0_0^0
478.7	20 890	575	3_0^1
472.3	21 172	858	
469.2	21 312	997	
464.5	21 527	1212	
460.2	21 728	1413	
457.0	21 883	1569	2_0^1
453.5	22 051	1736	
447.0	22 372	2058	1_0^1
441.5	22 652	2338	
436.3	22 918	2603	$1_0^1 3_0^1$
433.2	23 083	2769	
427.5	23 392	3078	
421.2	23 745	3430	(+ CN$_2$)
411.0	24 331	4016	1_0^2
406.3	24 614	4300	(+ C$_3$)
401.9	24 879	4565	$1_0^2 3_0^1$
380.1	26 308	5994	1_0^3
283.8	35 231	0	C $^2\Pi_u \leftarrow$ X $^2\Pi_g$ 0_0^0
282.3	35 428	197	8_0^2
279.9	35 722	491	3_0^1
278.4	35 921	690	$3_0^1 8_0^2$

TABLE 3: Observed Bands (Maxima ±0.2 nm) of the $^2\Pi_g \leftarrow X\ ^2\Pi_u$ Electronic Transitions of C_9^- in 5 K Neon Matrices

λ (nm)	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	assignment
764.4	13 082		A $^2\Pi_g \leftarrow$ X $^2\Pi_u$ 0_0^0
607.3	16 468	0	B $^2\Pi_g \leftarrow$ X $^2\Pi_u$ 0_0^0
599.1	16 693	225	11_0^2
586.3	17 057	589	
580.5	17 226	759	
565.4	17 686	1219	
541.5	18 469	2001	1_0^1
528.5	18 922	2455	
339.6	29 446	0	C $^2\Pi_g \leftarrow$ X $^2\Pi_u$ 0_0^0
336.9	29 680	233	
334.7	29 881	435	4_0^1
332.3	30 091	644	
326.7	30 609	1163	
324.3	30 839	1393	
321.4	31 112	1666	2_0^1
316.2	31 624	2177	1_0^1
311.8	32 073	2626	
307.8	32 487	3040	
303.0	32 999	3553	
298.9	33 456	4010	
295.1	33 888	4442	
289.6	34 536	0	D $^2\Pi_g \leftarrow$ X $^2\Pi_u$ 0_0^0
285.6	35 010	474	4_0^1
281.5	35 519	983	3_0^1

excited state. Whereas the bands in the gas phase spectrum are broad (~7 nm), these are well-defined (~0.2 nm) in the neon matrix spectrum at 5 K. The latter shows the excitation of the ν_1 and ν_2 symmetric stretching modes with frequencies of 1679(9) and 737(8) cm^{-1} in the A $^2\Pi_g$ state (Table 1).

The second band system is assumed also to be of $^2\Pi_g \leftarrow X\ ^2\Pi_u$ symmetry on the basis of its intensity. The origin and the 2_0^1 and 1_0^1 transitions can be assigned; however, the pattern of other bands in the 300−330 nm region cannot be simply explained. This band system lies at energies above the gas phase electron detachment threshold (at 434 nm). The threshold is expected to be ~1 eV larger in solid neon, at ~326 nm, near the region where the vibrational pattern becomes anomalous.

(b) C_7^-. The absorption spectrum of C_7^- in a neon matrix reveals three electronic transitions (Figure 1). The first two, A $\leftarrow$ X and B $\leftarrow$ X, are shown in more detail in Figure 5, with the vibrational assignments. Whereas the pattern is simple for the A $^2\Pi_u \leftarrow$ X $^2\Pi_g$ transition, the B $^2\Pi_u \leftarrow$ X $^2\Pi_g$ one shows

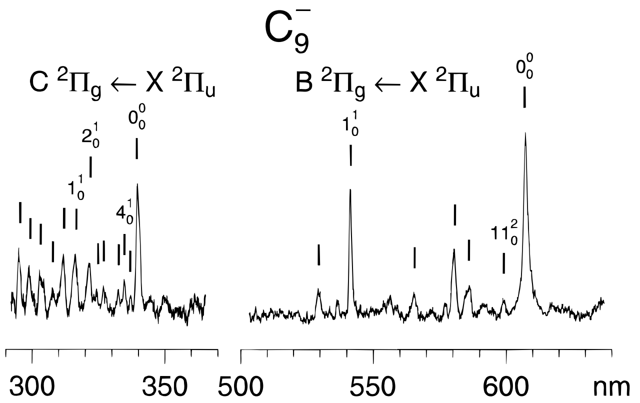

Figure 6. B $^2\Pi_g \leftarrow$ X $^2\Pi_u$ and C $^2\Pi_g \leftarrow$ X $^2\Pi_u$ transitions of C_9^- in a 5 K neon matrix. The bands around 300 nm are partially overlapped by the $^1\Sigma_u^+ \leftarrow$ X $^1\Sigma_g^+$ band system of C_9.[16] The vertical lines mark the bands listed in Table 5.

TABLE 4: Observed Bands (Maxima ±0.2 nm) of the $^2\Pi_u \leftarrow$ X $^2\Pi_g$ Electronic Transitions of C_{11}^- in 5 K Neon Matrices

λ (nm)	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})	assignment
905.6	11 042		A $^2\Pi_u \leftarrow$ X $^2\Pi_g$ 0_0^0
719.1	13 906	0	B $^2\Pi_u \leftarrow$ X $^2\Pi_g$ 0_0^0
633.4	15 788	1882	2_0^1
627.5	15 938	2032	1_0^1
397.6	25 151	0	C $^2\Pi_u \leftarrow$ X $^2\Pi_g$ 0_0^0
392.1	25 506	355	5_0^1
334.6	29 884	0	D $^2\Pi_u \leftarrow$ X $^2\Pi_g$ 0_0^0
330.8	30 228	344	5_0^1
326.3	30 649	765	4_0^1
323.7	30 897	1013	
320.0	31 253	1369	

TABLE 5: Inferred Vibrational Frequencies (cm^{-1}) of the σ_g^+ Stretching Modes of the C_{2n+1}^- Anion Chains in the Respective Electronic States[a]

C_5^-	A $^2\Pi_g$	B $^2\Pi_g$			C_5 X $^1\Sigma_g^+$
ν_1	1679(9)	1756(17)			2046
ν_2	737(8)	724(16)			800
C_7^-	A $^2\Pi_u$	B $^2\Pi_u$	C $^2\Pi_u$		C_7 X $^1\Sigma_g^+$
ν_1	1877(6)	2058(10)			2221
ν_2	1457(5)	1569(9)			1609
ν_3	562(5)	575(8)	491(25)		589
C_9^-	A $^2\Pi_g$	B $^2\Pi_g$	C $^2\Pi_g$	D $^2\Pi_g$	C_9 X $^1\Sigma_g^+$
ν_1		2001(6)	2177(19)		2209
ν_2			1666(19)		1903
ν_3				983(25)	1247
ν_4			435(17)	474(24)	458
C_{11}^-	A $^2\Pi_u$	B $^2\Pi_u$	C $^2\Pi_u$	D $^2\Pi_u$	C_{11} X $^1\Sigma_g^+$
ν_1		2032(5)			2276
ν_2		1882(4)			2114
ν_3					1710
ν_4				765(18)	1085
ν_5			355(13)	344(18)	382

[a] The assignment is based on spectroscopic evidence and comparison with calculated ground state frequencies of linear C_n.[20,21] Infrared bands (σ_u^+ modes) for C_5^-, C_7^-, and C_9^- trapped in neon matrices have also been observed at 1822.3, 1736.4, and 1692.6 cm^{-1}, respectively.[22]

too many bands for a simple explanation. The ν_1, ν_2, and ν_3 totally symmetric stretching modes are clearly apparent. The third electronic transition, C $^2\Pi_u \leftarrow$ X $^2\Pi_g$, with origin at 283.8 nm, lies above the gas phase electron detachment threshold (∼370 nm). It overlaps with the previously identified $^1\Sigma_u^+ \leftarrow$ X $^1\Sigma_g^+$ transition of C_7 (Figure 1). Only the excitation of the ν_3 mode is discernible. All the observed bands are compiled in Table 2.

(c) C_9^-. In case of C_9^- four $^2\Pi_g \leftarrow$ X $^2\Pi_u$ electronic transitions are detected. For the A $^2\Pi_g \leftarrow$ X $^2\Pi_u$ system only the origin band at 764.4 nm is seen (the peaks nearby marked with $*$ are an experimental artifact). The first three systems are below the gas phase electron detachment threshold, whereas the last, the D $^2\Pi_g \leftarrow$ X $^2\Pi_u$ system (origin 289.6 nm), is within the 1 eV stabilization due to solvation in the neon environment.

In Figure 6 the B $^2\Pi_g \leftarrow$ X $^2\Pi_u$ and C $^2\Pi_g \leftarrow$ X $^2\Pi_u$ band systems are shown. The B $^2\Pi_g \leftarrow$ X $^2\Pi_u$ structure is simple, whereas the C $^2\Pi_g \leftarrow$ X $^2\Pi_u$ pattern is again too complex both from frequency spacings and intensities, and an interpretation will require a theoretical treatment. All observed bands are listed in Table 3 together with proposed vibrational assignments.

(d) C_{11}^-. Four electronic band systems are observed, which all lie below the gas phase detachment threshold (Figure 1). The vibrational structure apparent is limited, and the suggested assignments are summarized in Table 4.

D. Conclusion. Transitions from the ground to several bound electronic states of the C_{2n+1}^- (n = 2−5) carbon chain anions have been observed. With this spectroscopic information in hand studies in the gas phase should follow. A summary of the inferred vibrational fundamentals is given in Table 5. As no calculated values are available, a comparison with their neutral counterparts is given for these anions. For a more detailed assignment of the transitions and the vibrational structure quantum chemical calculations are desirable.

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References and Notes

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

(2) Kroto, H. W. *Int. J. Mass Spectrom. Ion Processes* **1994**, *138*, 1.

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

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

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

(6) Freivogel, P.; Fulara, J.; Jakobi, M.; Forney, D.; Maier, J. P. *J. Chem. Phys.* **1995**, *103*, 54.

(7) Zhao, Y.; de Beer, E.; Neumark, D. M. *J. Chem. Phys.* **1996**, *105*, 2575.

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

(9) Ohara, M.; Shiromaru, H.; Achiba, Y.; Aoki, K.; Hashimoto, K.; Ikuta, S. *J. Chem. Phys.* **1995**, *103*, 10393.

(10) Maier, J. P. *Mass Spectrom. Rev.* **1992**, *11*, 119.

(11) Middleton, R.; Adams, C. T. *Nucl. Instrum. Methods* **1974**, *118*, 329.

(12) Middleton, R.; *Nucl. Instrum. Methods* **1983**, *214*, 139.

(13) It was claimed that deposition of mass-selected ions with high energy leads to spectral band broadening: Smith, A. M.; Agreiter, J.; Härtle, M.; Engel, C.; Bondybey, V. E. *Chem. Phys.* **1994**, *189*, 315. However, this difference arises because absorption and laser excitation spectra were compared. Thus, diacetylene cation for example shows practically an identical absorption spectrum after mass-selection or after vacuum-UV irradiation of diacetylene embedded in the matrix.

(14) Forney, D.; Freivogel, P.; Fulara, J.; Maier, J. P. *J. Chem. Phys.* **1995**, *102*, 1510.

(15) Rossetti, R.; Brus, L. E. *Rev. Sci. Instrum.* **1980**, *51*, 467.

(16) Forney, D.; Freivogel, P.; Grutter, M.; Maier, J. P. *J. Chem. Phys.* **1996**, *104*, 4954.

(17) Fulara, J.; Freivogel, P.; Forney, D.; Maier, J. P. *J. Chem. Phys.* **1995**, *103*, 8805.

(18) Freivogel, P.; Fulara, J.; Lessen, D.; Forney, D.; Maier, J. P. *Chem. Phys.* **1994**, *189*, 335.

(19) Fan, Q.; Pfeiffer, G. V. *Chem. Phys. Lett.* **1989**, *162*, 472.

(20) Martin, J. M. L.; El-Yazal, J.; François, J. P. *Chem. Phys. Lett.* **1995**, *242*, 570.

(21) Martin, J. M. L.; El-Yazal, J.; François, J. P. *Chem. Phys. Lett.* **1996**, *252*, 9.

(22) Freivogel, P.; Grutter, M.; Forney, D.; Maier, J. P. *Chem. Phys.* **1997**, *216*, 401.