Resonance-Enhanced Multiphoton Electron Detachment (REMPED) Study of Carbon Anions up to C_{21}^-

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The electronic spectra of C_{2n}^- ($n = 6-8$) and C_{2n+1}^- ($n = 6-10$) were measured in the gas phase for the first time using the REMPED technique. The spectra show common features in their electronic transitions, which characterize these species as chain-form anions. This spectroscopic data confirmed that a considerable number of chain-form carbon cluster anions are formed in a laser vaporization cluster beam with sizes up to C_{21}^-, but their abundance decreases with increasing size. The results also strongly suggest that the ratio of chain and ring forms produced is significantly dependent on the laser fluence conditions for the laser vaporization of graphite. In contrast to the smaller ring-form anions already reported, the species in the size range studied here (i.e., C_n^- with $11 < n < 22$) appear to be "silent" with respect to REMPED spectroscopy.

Introduction

Carbon clusters have been a subject of extensive experimental and theoretical investigation in the last decade because of their importance in fullerene network formation, and also as possible absorbers in interstellar clouds, hydrocarbon flames, and so on.[1,2] The presence of negatively charged carbon clusters was established in an early mass spectroscopic study, in the 1950s.[3] The anionic species of every size of carbon cluster are stable in a vacuum, since their electron affinities are all positive and relatively large. These anions play an important role in various plasmas, and possible industrial uses have been suggested.[4] The presence of interstellar anionic species is also suggested from high-resolution electronic spectra of C_7^-.[5] The study of these cluster anions is also significant because of their close correlation with neutral clusters. For example, the size distribution of neutral clusters produced with a conventional laser vaporization source is very similar to that of the anions. These facts strongly suggest that both cluster formation processes share a common mechanism.[6]

Aside from fullerenes, study of the morphology of small- and medium-sized carbon cluster anions (smaller than C_{60}^-) was initiated by the pioneering work of Yang et al. in 1988.[7] They measured ultraviolet photoelectron spectra (UPS) of anions using a laser vaporization source and claimed that the chain-form anions are the dominant species for sizes smaller than C_{10}^-, while the ring-form anions are mainly produced for the larger cluster sizes. In 1991, in a simple photodetachment experiment using fixed photon energy,[8] we reported that the long chain anions are produced under specific laser vaporization conditions.

Gotts et al. systematically examined the relative abundance of linear chain anions in a laser vaporization source using an ion chromatography (IC) technique.[9] They stated that considerable amounts of chain-form anions are formed up to C_{32}^-. The chain forms are minor products for anions larger than C_9^-, consistent with the aforementioned UPS studies. They reported that the abundance of the linear chain generally decreases from about 20% for C_{11}^- to about 5% for C_{29}^-. There are exceptions, the chain forms of C_{13}^- and C_{14}^- are relatively abundant, about 40% for each case, while those of C_{10}^- and C_{18}^- are extremely rare. Long chain-form anions up to C_{50}^- have also been detected using a modified IC technique.[10] Their drift time spectra contained huge peaks caused by chain-form anions; however, they did not conclude that these chains were the dominant species in the nascent laser vaporization source because of the complexity arising from structure-dependent electron attachment/detachment.

Although these IC experiments provide unique information on ring/chain abundance, how the source conditions govern the ratio has not been examined. In fact, the abundance of the chain- and ring-form anions is sensitive to the source condition, especially the laser fluence for vaporization. This was verified for anions up to C_{16}^- by measuring UPS under various source conditions.[11] The photoelectron peaks assigned to the chain-form anions are greatly enhanced under high laser fluence conditions but are not observed under low fluence conditions. Since higher fluence tends to enhance the magic numbers 5, 8, and 11 in the anion mass spectra, when these magic numbers appear to be enhanced, considerable numbers of chain-form anions are formed. Using this empirical rule, we identified resonance enhanced multiphoton electron detachment (REMPED) signals of the ring- and chain-form anions for C_{10}^- and C_{11}^- from the fact that the REMPED spectra vary as a function of the laser fluence.[12]

So far, the photoelectron signals of chains larger than C_{16}^- have not been found despite carefully adjusting the laser vaporization conditions.[11] Only the peaks of ring-form anions were identified, as first pointed out in 1988. The peaks of the chain-form anions are probably missing due to the scarcity of chain-form anions. In UPS, the signal intensity is generally thought to be insensitive to the properties of target molecules if the anions are detached directly by a single photon. Therefore, the signals of the chain-form anions might be hidden by the intense signals of the ring-form anions.

The relationship between the chain/ring abundance of C_n^- ($n > 16$) and the source conditions is not clear. In this study, we employed the REMPED technique to deduce the structure of medium-sized carbon cluster anions up to C_{21}^-. The REMPED spectra of C_{2n}^- ($n = 6-8$) and C_{2n+1}^- ($n = 6-10$) were measured in the gas phase for the first time, and peaks were attributed to several excited states of linear chain carbon

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anions. For C_{12}^-, C_{13}^-, and C_{14}^-, spectra were recorded under different source conditions, to identify signals due to large ring-form anions.

Experimental Section

Carbon cluster anions were generated by the laser vaporization method in a helium gas flow. Anions accelerated to 2 keV by a pulsed high voltage were separated according to their mass-to-charge ratio. The anion bunch was then exposed to a tightly focused laser beam from a tunable laser. In this study, we used the idler light of the optical parametric oscillator in the 731−1838 nm region. The wavelength of the laser light was carefully calibrated by measuring the REMPI spectrum of NO. In our REMPED series, the spectral resolution is probably lowered due to the high power laser used and the high temperature of the anions. Consequently, we used a relatively large scan step: 20−40 cm^{-1}. A secondary electron multiplier detected neutral clusters generated via the REMPED process. The remaining parent ions were reflected by a reflector (4 kV) and detected by a microchannel plate. Observed signals of the neutral clusters were normalized to both the number of parent ions and the detachment laser power. REMPED spectra accumulated for several scans of the wavelengths are presented in this paper. The experimental procedure is also described in previous reports.[12−14]

Results and Discussion

The spectra of C_{12}^-−C_{17}^-, C_{19}^-, and C_{21}^- can be divided into two groups according to the parity of the cluster size. As will be shown, the overall features of the spectra are similar within the same parity group, but those associated with the other parity are quite different. Therefore, the REMPED spectra of C_{2n}^- (n = 6−8) and C_{2n+1}^- (n = 6−10) are discussed separately, in sections A and B, respectively. Since the gas-phase electronic spectra of these anions have not been reported, we first examined whether the peaks observed in the REMPED spectra can be assigned to chain- or ring-form anions.

The assignment is aided by spectroscopic studies of long chain anions trapped in a cold matrix and previous REMPED studies of smaller chain-form anions. The matrix studies for the carbon cluster anions, C_{2n}^- (n = 2−10) and C_{2n+1}^- (n = 2−5), reported by Maier and co-workers,[15−17] are used for this purpose. The REMPED spectra of C_{2n+1}^- (n = 2−5) are a good guide for assigning larger odd-numbered species, because whole features of the REMPED spectrum change systematically as a function of the cluster size.[12−14]

A. Even-Numbered Series: C_{2n}^- (n = 6−8). REMPED spectra of C_{2n}^- (n = 6−8) are shown in Figure 1. Several common spectral features can be seen. The main band consists of a prominent peak, marked by "●", followed by smaller peaks. The peak positions systematically shift to lower energy as the cluster size increases from C_{12}^- to C_{16}^-. In the wavelength region surveyed in this study, all the distinct peaks can be reasonably assigned to chain-form anions as follows.

The main absorption system is assigned to the (1) $^2\Pi \leftarrow X\ ^2\Pi$ electronic transition of the chain-form anions, since the wavenumber of the band origin (marked by "●") for each species is very close to the previously reported value determined in the neon matrix.[15] In each spectrum shown in Figure 1, subsequent peaks are observed on the higher energy side of the band origin. According to the matrix study for the even-numbered series C_4^-−C_{20}^-, the symmetric stretching mode with the lowest frequency is observed mainly in the absorption spectra. The prominent progression in the REMPED spectra is consistent with the prediction that the symmetric stretching mode for C_{2n}^- (n = 7, 8) would also be active in the gas phase. The structures for C_{12}^- seem to be more complicated in comparison with the other species. The spacing is irregular; therefore the progressions are not easily assigned to a specific signal mode. Nevertheless, these structures are most likely due to vibrational excitation, because the transition (1) $^2\Pi \leftarrow X\ ^2\Pi$ of even-numbered chain-form anions examined so far has always been accompanied by vibrational excitation.

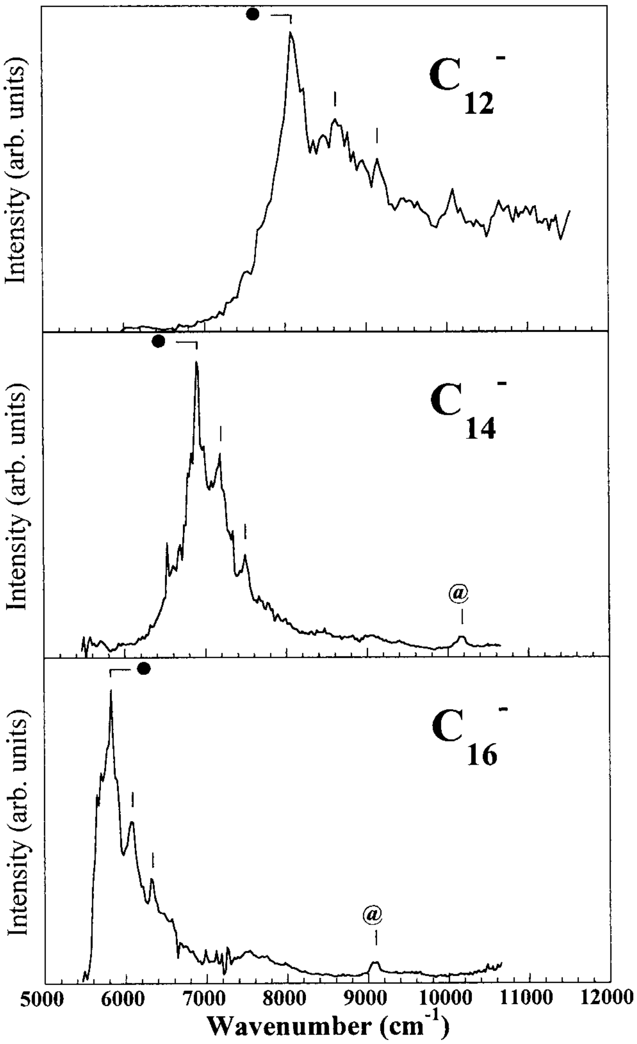

Figure 1. REMPED spectra of C_{2n}^- (n = 6−8). The mark "●" indicates the band origin for the (1) $^2\Pi \leftarrow X\ ^2\Pi$ electronic transition. The mark "@" in the spectra of C_{14}^- and C_{16}^- indicates the peak for the electronic transition to the (2) $^2\Pi$ state. The vertical lines indicate the other distinguishable peaks.

The weak peaks marked by "@" observed for C_{14}^- and C_{16}^- can also be assigned to the excitation of chain-form anions. These peaks are likely due to the transition to higher excited states, because the peak positions are very close to those measured in the matrix.[16] All the peaks observed in this study are attributed to chain-form anions and there is no evidence for the presence of ring-form anions. The REMPED signals of the ring-form anions will be discussed in section C.

The peak positions for the even numbered series are summarized in Table 1 together with the suggested assignments. When the exact assignment to a specific vibronic state is not clear, the positions of the peaks indicated by vertical lines in Figure 1 are merely listed in Table 1 with the tentative assignments of the vibrational modes.

TABLE 1: Peak Positions for the REMPED Spectra of C_{2n}^- (n = 6−8)

ν (10^4 cm^{-1})		assignment	
0.810	C_{12}^-	(1) $^2\Pi_u \leftarrow X\ ^2\Pi_g\ 0_0^0$	●
0.860		6_1^0	
0.910		6_0^2	
0.690	C_{14}^-	(1) $^2\Pi_g \leftarrow X\ ^2\Pi_u\ 0_0^0$	●
0.720		7_0^1	
0.750		7_0^2	
1.020		(2) $^2\Pi_g \leftarrow X\ ^2\Pi_u\ 0_0^0$ @	
0.580	C_{16}^-	(1) $^2\Pi_u \leftarrow X\ ^2\Pi_g\ 0_0^0$	●
0.610		8_0^1	
0.630		8_0^2	
0.910		(2) $^2\Pi_u \leftarrow X\ ^2\Pi_g\ 0_0^0$	@

B. Odd-Numbered Series: C_{2n+1}^- (n = 6 - 10). REMPED spectra of C_{2n+1}^- (n = 6−10) are shown in Figure 2. The general trend in the spectral features of the first three bands (denoted by ●, ◆, and ▲) is similar to those reported previously for smaller odd-numbered clusters, C_7^-−C_{11}^-.[14] As shown below, all the distinct peaks can be identified as chain-form anions.

The plot of the wavelength of the peak "●" versus the cluster size is shown in Figure 3. There is a linear relationship for the wavelengths of the peaks determined in this study; this connects with the line for the A $^2\Pi \leftarrow$ X $^2\Pi$ transitions of the smaller clusters, C_{2n+1}^- (n = 2−5).[17] Consequently, these bands can be assigned to the A $^2\Pi \leftarrow$ $^2\Pi$ transition of the chain form of C_{2n+1}^- (n = 6−10), in which the peak marked by "●" is the band origin. This assignment is also consistent with absorption spectra measured in a matrix without mass selection.[18] A progression of peaks following peak "●" is discernible in the spectra of C_{2n+1}^- (n = 6−10). These peaks, indicated by the vertical lines in Figure 2, are likely due to the excitation of one of the vibrational states in the A $^2\Pi$ states.

Several peaks or humps are seen in the lower energy region of the first band "●", particularly for C_{13}^- and C_{15}^-. These bands might be caused by vibrationally hot anions. Prominent hot bands were observed for C_{15}^- and their peak separations were 280 and 250 cm^{-1}. Previously, we roughly estimated the internal temperature of the C_5^- formed by our laser vaporization source to be about 1000 K or less. These results indicate that the larger chain-form anions are also hot, and the internal temperature is estimated to be similar.

The characteristic peaks "◆" are also commonly observed for C_{2n+1}^- (n = 6−10). The spectral features of these peaks are similar to those for n = 3−5 reported previously.[12,14] The plot of the wavelength of these peaks against cluster size for n = 6−10 (C_{13}^-−C_{21}^-) is also shown in Figure 3, together with those of the corresponding peaks for n = 3−5. As, demonstrated in the figure, the plots "-◆-" can be connected smoothly from n = 3 to n = 1.0. For n = 3−5, the peaks "◆" have been assigned to the band origins of the B $^2\Pi \leftarrow$ X $^2\Pi$ transition. Consequently, it is natural to assign those peaks observed for n = 6−10 to the band origins of the B $^2\Pi \leftarrow$ X $^2\Pi$ electronic transition.

As in the case of even-numbered cluster anions, all the distinct peaks appearing in the REMPED spectra are described by the presence of only one isomer, the chain- form anions. The peak positions are summarized in Table 2, together with the suggested assignments.

Finally, we compared the relative intensities of the REMPED spectra with those obtained in the matrix study. In our gas-

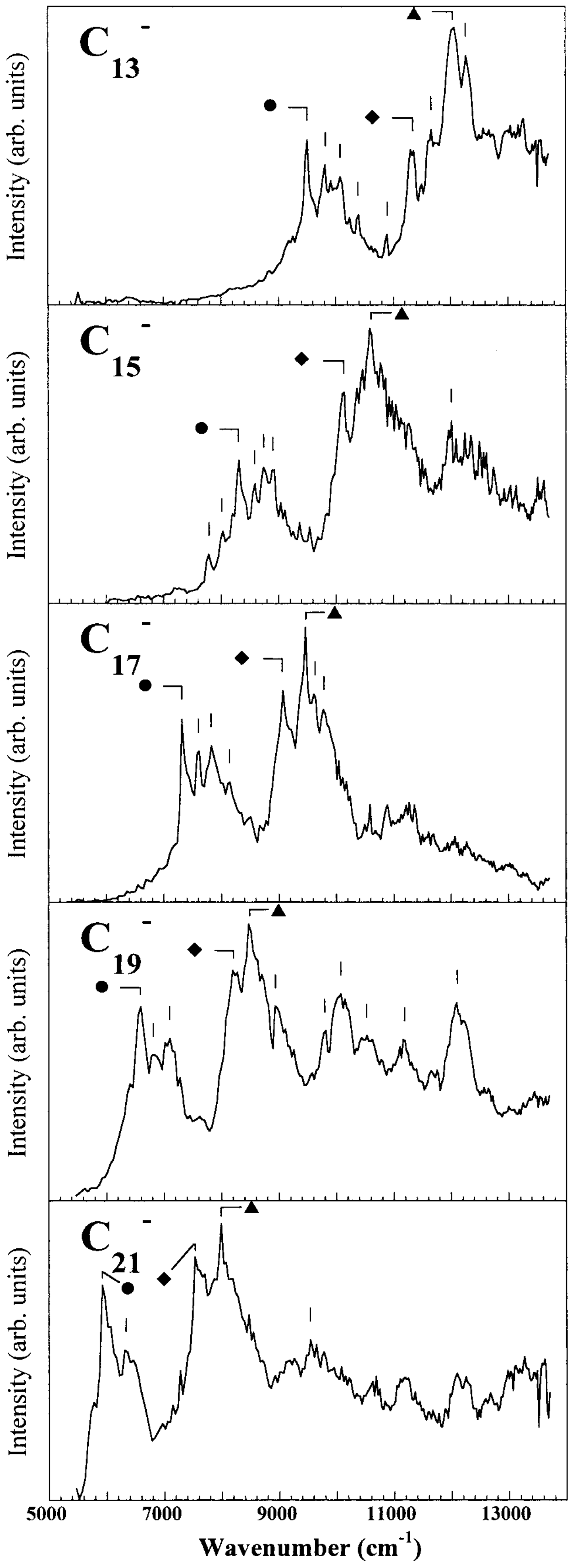

Figure 2. REMPED spectra of C_{2n+1}^- (n = 6−10). The marks "●" and "◆" indicate the band origins for the A $^2\Pi \leftarrow$ X $^2\Pi$ and the B $^2\Pi \leftarrow$ X $^2\Pi$ electronic transition, respectively. The prominent peaks indicated by "▲" are not assigned. The vertical lines indicate the other distinguishable peaks.

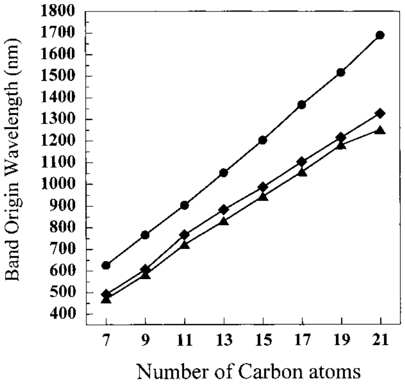

Figure 3. Plots of the wavelength of band origins for several electronic transitions, (●) $A\,^2\Pi \leftarrow X\,^2\Pi$, (◆) $B\,^2\Pi \leftarrow X\,^2\Pi$, and (▲) against cluster size, for odd-numbered chain-form clusters, C_{2n+1}^- ($n = 2-10$).

phase spectra, in addition to the "●" and "◆" peaks, relatively strong peaks, "▲", commonly appear on the higher energy side of the "◆" peaks. Peaks corresponding to the "▲" peaks were also commonly seen in the REMPED spectra for smaller chain-form anions, C_7^- to C_{11}^-. (It should be noted that ring-form anions are not found for C_7^-.) Comparing our REMPED spectra for $n = 3$, 4 with those recently reported by Forney et al.[17] suggests that peak "▲" ($n = 3$, 4) might be due to unassigned vibronic bands, and not due to impurities or the presence of the second isomer.

C. REMPED Signals of the Ring-Form Clusters. In the previous section, we identified REMPED signals of the chain-form anions up to C_{21}^-. However, the ring form is considered the major isomer of anions of these sizes, as has widely been reported. Thus, it is worthwhile considering why REMPED signals corresponding to a ring form are not detected. Recently, we reported UPS evidence for the coexistence of the ring- and chain-form isomers up to C_{16}^-. For anions larger than C_{16}^-, the photoelectron signals of chain-form anions were very small in comparison with those of the ring form. Furthermore, to detect chain-form anions with a good signal to noise ratio in the UPS measurements, it was necessary to use a relatively high-fluence laser light for vaporization. Under low fluence conditions, all the UPS signals were due to ring-form clusters. These UPS results clearly show that the ring-form clusters are actually the most abundant isomer for anions larger than C_{10}.

To identify the REMPED signals due to ring-form anions, we carried out REMPED measurements of C_{12}^-, C_{13}^-, and C_{14}^- under different conditions, including conditions favorable and unfavorable for the formation of the chain-form anions. If the ring-form anions made a significant contribution to the REMPED spectrum, a change in the spectral shape would be observed, as demonstrated in detecting the C_{10}^- ring form by REMPED.[12] The results for C_{14}^- are shown in Figure 4. Clearly, the experimental evidence is entirely different from the expectation that signals of the ring form coexist with those of the chain form. That is, the observed spectra were essentially the same, except that the intensity of the REMPED spectra was two or three times lower when we used laser fluence conditions unfavorable for chain-forming. The same was true for C_{12}^- and C_{13}^-. All this evidence strongly suggests that monocyclic ring-form clusters are formed in the beam but are "silent" species for REMPED detection in the wavelength region covered in this study.

In principle, REMPED consists of a resonant process. Thus, the detachment efficiency is affected by the lifetime of the intermediate resonant state. If the lifetime of the resonant level were too short, the detachment efficiency would decrease markedly. Therefore, one plausible explanation for the absence of REMPED signals is as follows. For these ring-form anions, the internal conversion of the excited state is so fast that the electronic excited states tend to be relaxed before the next photon is absorbed. This trend may be more prominent for the larger monocyclic rings because the number of vibrational modes increases. The smallest rings, C_{10}^- and C_{11}^-, are an exception in which REMPED spectra associated with both the chain- and ring-form clusters are detected under appropriate conditions.

TABLE 2: Peak Positions for the REMPED Spectra of C_{2n+1}^- ($n = 6-10$)

ν (10^4 cm^{-1})	assignment		
0.950	C_{13}^-	$A\,^2\Pi_g \leftarrow X\,^2\Pi_u\,0_0^0$	●
0.980		6_0^1	
1.010		6_0^2	
1.040		6_0^3	
1.090			
1.130		$B\,^2\Pi_g \leftarrow X\,^2\Pi_u\,0_0^0$	◆
1.170		6_0^1	
1.200			▲
1.230			
0.780		7_2^0	
0.800		7_1^0	
0.830	C_{15}^-	$A\,^2\Pi_u \leftarrow X\,^2\Pi_g\,0_0^0$	●
0.860		7_0^1	
0.870		7_0^2	
0.890		7_0^3	
1.010		$B\,^2\Pi_u \leftarrow X\,^2\Pi_g\,0_0^0$	◆
1.060			▲
1.200			
0.730	C_{17}^-	$A\,^2\Pi_g \leftarrow X\,^2\Pi_u\,0_0^0$	●
0.760		8_0^1	
0.780		8_0^2	
0.820		8_0^3	
0.910		$B\,^2\Pi_g \leftarrow X\,^2\Pi_u\,0_0^0$	◆
0.950			▲
0.960			
0.980			
0.660	C_{19}^-	$A\,^2\Pi_u \leftarrow X\,^2\Pi_g\,0_0^0$	●
0.680		9_0^1	
0.710		9_0^2	
0.820		$B\,^2\Pi_u \leftarrow X\,^2\Pi_g\,0_0^0$	◆
0.850			▲
0.890			
0.980			
1.010			
1.050			
1.120			
1.210			
0.590	C_{21}^-	$A\,^2\Pi_g \leftarrow X\,^2\Pi_u\,0_0^0$	●
0.630		10_0^1	
0.750		$B\,^2\Pi_g \leftarrow X\,^2\Pi_u\,0_0^0$	◆
0.800			▲
0.950			

As mentioned above, REMPED signals due to chain-form clusters up to C_{21}^- are clearly observed, although the intensity of the REMPED signals is weak for the larger clusters. In this manner, the apparent contradiction between UPS (signals of large chains were not observed), IC (signals of large chains were observed, occasionally they were very strong), and REMPED (signals of large chains were observed exclusively) studies can be explained reasonably by differences in their detection

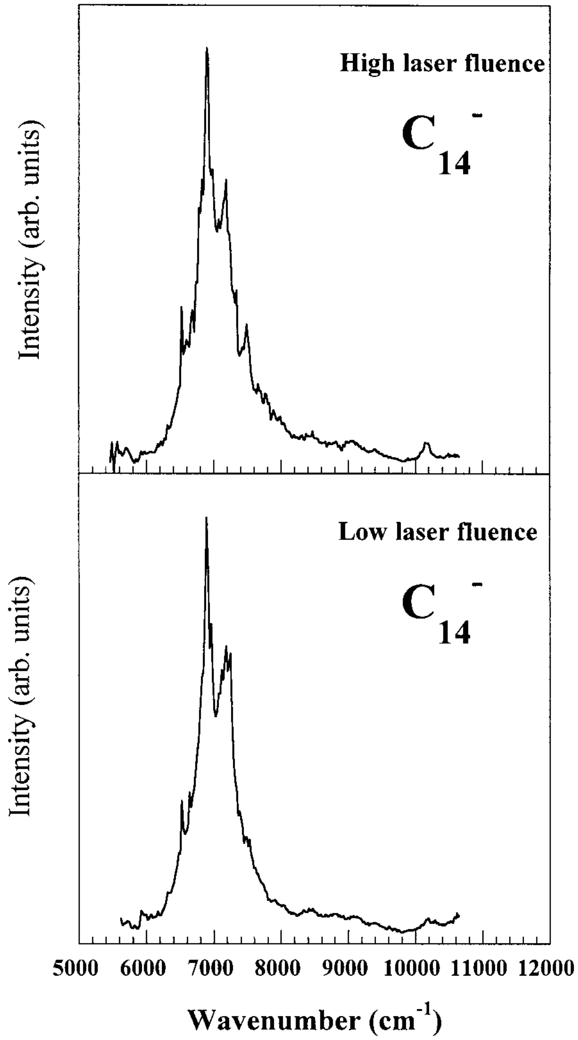

Figure 4. REMPED spectra of C_{14}^- measured under two sets of conditions: (upper) favorable for chain-form anions; (lower) unfavorable for chain-form anions.

abilities. In conclusion, REMPED measurement is very sensitive to the properties of the target anions. By virtue of this feature, the electronic spectra of large chain-form anions, which are still minor components after size selection, become measurable. Consequently, it was found that considerable numbers of long chain-form anions are always formed in a laser vaporization beam, but the abundance of the linear chain anions depends on the laser vaporization conditions and generally decreases with increasing size.

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