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Determination of carbon cluster ionization potentials via charge transfer reactions

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Ionization potentials (IPs) for carbon clusters containing 6–24 atoms have been determined from charge transfer reactions of carbon cluster ions with compounds of known ionization potential in a Fourier transform ion cyclotron resonance mass spectrometer. Cluster IPs generally decrease with increasing cluster size, but the IPs for clusters containing $4n + 3$ atoms ($n = 1$–5) are found to be ~0.5 eV lower than those of neighboring clusters. The relationship between cluster IP and structure is discussed.

I. INTRODUCTION

There has been much recent interest in transition metal[1] and semiconductor[2] clusters. These molecules present possible applications in areas such as catalysis, where they could be used as prototypes for specific catalytic compounds, and materials science, where their electronic structures could play a role in the design of microelectronic circuits and semiconductor lasers. Moreover, reactions of clusters, particularly those of increasing size, can serve as models for surface chemistry.[3,4]

In the study of clusters both physical and chemical properties are of interest, and they are often intimately linked. Some early chemical studies have focused on cluster reactivities, including chemisorption of CO, O_2, H_2, and other species.[2,5–9] The presence of isomeric forms of a particular cluster species can occasionally be deduced from its reactivity (or lack of it). However, the most direct method of structural determination to date has been matrix isolation coupled with a relevant spectroscopic probe.[1]

Fourier transform ion cyclotron resonance (FTICR) mass spectrometry[10] is an ideal method for studying the reactivity and perhaps the structure of cluster ions. These ions can either be formed externally and injected into the FTICR analyzer cell,[6] or formed directly in the cell by laser desorption from suitable solids.[5,9,11–13] Once the ionic cluster of interest is trapped in the analyzer cell, a neutral reactant can be introduced into the system and the formation of ion/molecule reaction products can be monitored as a function of time.

Reactivities of cluster ions have been studied in FTICR mass spectrometers by a number of groups. For example, the reactions of small carbon cluster cations with D_2 and O_2,[5] niobium cluster cations with H_2,[6] as well as silicon cluster cations with various reactants[9] have all been reported. In these studies, structural differences could be inferred from the observation of reactive and non-reactive populations or from the determination of several different rate coefficients for the same ion mass.

Following initial investigations of carbon,[11] gold,[12,13] silver and copper[13] cluster ions, we have continued our FTICR studies of cluster ions by examining *charge transfer reactions* of carbon cluster cations. From these experiments, one can determine the ionization potentials of *neutral* carbon clusters. Carbon is an ideal candidate for this type of study because of the wealth of data available from previous investigations of its neutral and ionic clusters,[14] the ease with which the element can be vaporized, and the reproducibility of the cluster ion distribution for each shot of the vaporization laser.

The ionization potential of a molecule is one of its most important fundamental properties and can be strongly influenced by the species' structure. Ionization potentials for clusters of many elements have as yet not been determined with high accuracy or precision. In addition to providing fundamental physical information, an accurate determination of the ionization potential (IPs) of carbon clusters may lead to a better understanding of the isomeric forms of these species and may help indicate the cluster size at which the proposed[15] transition from a linear to a cyclic structure occurs. Previous multiphoton ionization experiments by Kaldor and co-workers[16,17] indicated that IPs are in the range 12.84 to 9.98 eV for carbon atoms, dimers, and clusters containing from 3 to 7 atoms, and between 12.84 and 6.42 eV for clusters containing from 8 to 30 atoms.

In the present work the ionization potentials of carbon clusters containing from 6 to 24 atoms have been determined with an uncertainty of a few tenths of an eV by observing the occurrence or nonoccurrence of charge transfer reactions with neutral molecules of known ionization potential. Charge transfer reactions have previously been utilized to determine ionization potentials of moderate-size organic molecules via ion/molecule reaction equilibria.[18,19]

The ionization potentials reported here are adiabatic rather than vertical.[20] The long lifetimes of charge transfer ion/molecule collisions allow for geometry changes from the most stable ionic cluster structure to the most stable neutral structure. Multiphoton ionization and photoelectron spectroscopic studies will generally determine vertical ionization potentials, since the transitions involved are quite rapid and do not allow time for possible structural rearrangement. The adiabatic ionization energy allows for possible changes in geometry, is rigorously correct at 0 K and is the generally reported[20] value for the ionization potential.

II. EXPERIMENTAL

Charge transfer reactions were carried out using a Nicolet[21] FTMS-1000 FTICR mass spectrometer equipped with a 3 T superconducting magnet and a 2.5 cm cubic stainless steel cell. The carbon clusters were produced by focusing the output of a Lumonics CO_2[22] laser through a 7.6 cm focal length ZnSe lens across the FTICR analyzer cell and onto a graphite plug mounted on the end of a solids insertion probe. The instrumental arrangement has been described elsewhere in detail.[23] A trapping potential of 2.0 V was used for all experiments. The charge transfer compounds (Table I) were leaked into the vacuum system via the gas/liquid inlet valves on the instrument, usually at a pressure of $1-2 \times 10^{-8}$ Torr above the background pressure (0.3×10^{-8} Torr). Because clusters produced by the laser undoubtedly have excess kinetic and internal energy, the use of a pulsed value to introduce a burst of unreactive argon (Airco, 99.95%) and later SF_6 (Matheson, 99.9%) collision gas (at about 7.5×10^{-7} Torr peak pressure) to remove excess translational and/or internal energy in the cluster ions proved quite useful.

The pulse sequence used for these experiments is shown in Fig. 1. Following a 1.5 s quench pulse which removed all ions from the cell and allowed for complete pump out of any remaining collision gas, the laser was triggered (firing 44.1 ms later) and the pulsed valve (General Valve Corp. Model 9-181-900) was opened for 135 μs with about 10 psi backing pressure. Next a series of ejection sweeps were used to eject[24] all cluster cations except the one of interest from the cell. A "thermalizing" delay then allowed time for ion/neutral collisions to occur. This delay period also provided time for the thermalizing gas to be pumped out of the vacuum chamber (the approximate pressure profile of the thermalizing gas is also shown in Fig. 1). A second set of ejection sweeps was used to eject any charge transfer products formed during the thermalizing delay period. Cluster cations differing by one carbon from the cation under study were ejected using a fixed frequency ejection of a duration sufficiently long (10 ms) to minimize the translational energy imparted to the ion of interest by the ejection pulse. This procedure is especially critical at higher masses (lower frequencies), where the frequency separation between mass units becomes smaller. Next a variable delay time permitted charge transfer reactions to occur. This reaction period was routinely varied from 0.003 to 3 s in length, although at times it was extended up to 10 s to follow slow reactions.

For each of the chosen reaction delay times, a broad band (10 kHz to 2.66 MHz) time domain signal consisting of 32 K data points was collected and averaged for 20 repetitions. This (averaged) time domain data set was apodized using a three term Blackman–Harris window function[25] and zero filled once prior to Fourier transformation.

Ionization potentials of the clusters were determined using a bracketing technique. Each of the cluster cations was allowed to interact with a particular neutral to determine the occurrence or nonoccurrence of charge transfer. Intensity measurements (integrated peak intensity[26]) for all major ions were obtained at 10 to 20 different delay times of approximately equal spacing during each experiment. Plots of these intensities vs reaction time were then made to assess whether or not charge transfer was occurring. This process was repeated for all of the charge transfer agents listed in Table I.

The sources of the compounds used as charge transfer agents were as follows: N, N-dimethyl-p-toluidine, azulene, durene, hexamethylbenzene, and hexafluorobenzene (Aldrich); 1, 2, 4-trichlorobenzene, p-chlorotoluene, m-cresol, and m-toluidine (Chem Service); benzene, toluene, m-xylene, and aniline (Fisher Scientific); m-dichlorobenzene, p-dichlorobenzene, p-bromotoluene, p-xylene, and p-cresol (Kodak); xenon (Cryogenic Rare Gas Laboratories, Inc.); and tetrachloroethylene (Mallinckrodt). Liquids were purified by several freeze–pump–thaw cycles before use, and solids were pumped on for several minutes before use. Purity was verified by broad band FTICR mass analysis.

TABLE I. Charge transfer compounds.

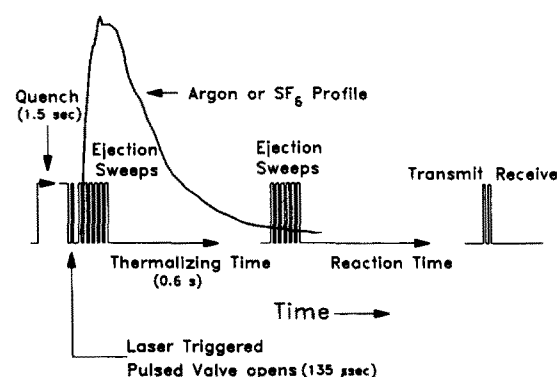| Compounds	IP (eV)[a]
Xenon	12.13
Hexafluorobenzene	9.91
Tetrachloroethylene	9.32
Benzene	9.25
m-Dichlorobenzene	9.11
1,2,4-Trichlorobenzene	9.04
p-Dichlorobenzene	8.89
Toluene	8.82
p-Chlorotoluene	8.69
m-Xylene	8.56
p-Xylene	8.44
m-Cresol	8.29
p-Cresol	8.13
Durene	8.04
Hexamethylbenzene	7.85
Aniline	7.72
m-Toluidine	7.50
Azulene	7.41
N,N-Dimethyl-p-toluidine	6.93

[a] From Ref. 20.

FIG. 1. FTICR pulse sequence employed for the charge transfer reactions. An approximate profile of the thermalizing gas pressure is also shown.
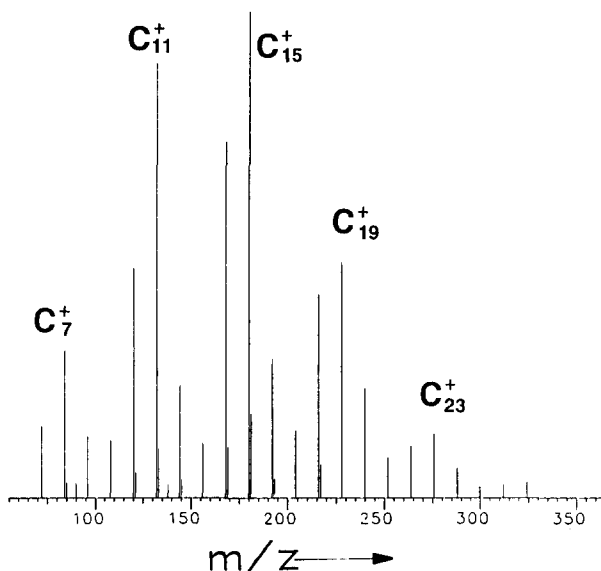
FIG. 2. Typical mass spectrum of carbon cations observed with laser vaporization from a graphite plug by a pulsed CO_2 laser.

III. RESULTS

A typical mass spectrum of carbon cluster cations formed by CO_2 laser desorption is shown in Fig. 2. Each of the cations from C_6^+ to C_{24}^+ was isolated as described above and its charge transfer reactions followed. Results for various combinations of cluster sizes and charge transfer compounds are given in Table II. The ionization potential of a particular size cluster is taken to lie in the range of energy between the IPs of the neutrals for which no charge transfer was observed and the IPs of the neutrals where it was observed. The uncertainty in the ionization potential of the carbon cluster determined in this way is obviously dependent on the magnitude of the energy range (i.e., on the existence of compounds which do not undergo charge transfer or which transfer an electron cleanly and have closely spaced IPs).

Typical growth and decay curves for the reactions of C_{18}^+, C_{19}^+, and C_{20}^+ with aniline are shown in Fig. 3. The positive clusters with 18 and 20 carbon atoms readily undergo charge transfer with aniline [Figs. 3(a) and 3(c)], while C_{19}^+ [Fig. 3(b)] forms an adduct ($m/z = 321$), and shows no appreciable charge transfer. Adduct formation will be discussed more fully in a subsequent paper.[27] Given errors in ion intensity, we have reported charge transfer only if more than 20% of the total ion signal observed at the end of a 3–10 s reaction period could be assigned to the parent ion of the charge transfer agent.

The curves in Fig. 3 suggest that only one form of each cluster ion is being observed, because the ions react completely with the exponentially decaying intensity expected for a pseudofirst order reaction with only one rate constant. (C_{19}^+ has been followed to longer reaction times than those shown in Fig. 3, and is also observed to react completely.) This behavior has been observed for all of the clusters studied in this work. None of the charge transfer results indicates the presence of multiple isomeric forms of any of the carbon clusters containing 6 to 24 atoms.

The experimental results summarized in Table II are presented in a more quantitative form in Fig. 4. For each
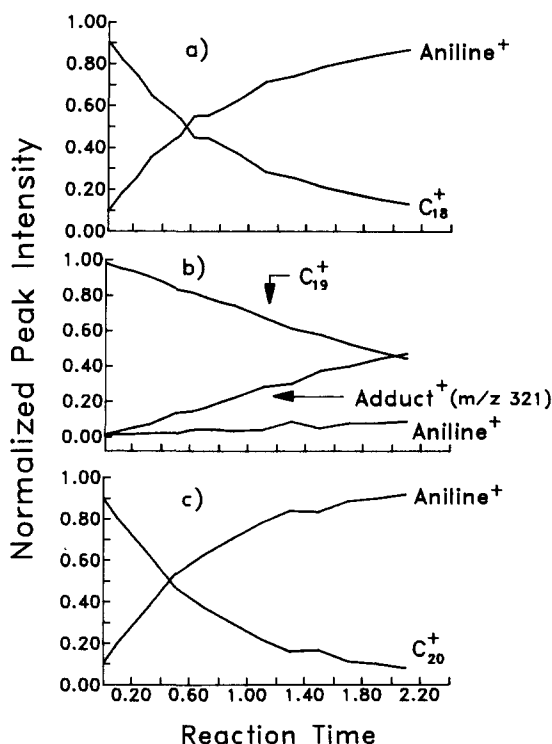
TABLE II. Results of charge transfer reactions between carbon cluster cations and various neutrals.[a]

Neutral	Carbon cluster cation size																		
	1														2				
	6	7	8	9	0	1	2	3	4	5	6	7	8	9	0	1	2	3	4
Hexafluorobenzene	N	N	N	N	N														
Tetrachloroethylene	Y																		
Benzene	Y	N	N	N	N														
m-Dichlorobenzene			N		N														
1,2,4-Trichlorobenzene			N	N	Y														
p-Dichlorobenzene	Y	N	N	N	Y	N		N											
Toluene	N	N	N	Y	N	N	N	N	N	N		N							
p-Chlorotoluene	N	Y	Y	Y															
p-Bromotoluene			Y	N			N	N	N										
m-Xylene	N	Y	Y	Y	N	N	N	N	N	N	N	N	N		N	N	N		
p-Xylene	N		Y	N	Y	N	Y	N	N	N	N	N	N						
m-Cresol	N		Y	N	Y	N	Y	N	N	N	N	N	N	N					
p-Cresol	N			N	Y	N	Y	N	N	N	N								
Durene	Y			N	Y	Y	Y	N	Y	Y	Y	Y	N	Y	Y	Y	N	N	
Hexamethylbenzene						N													
Aniline	Y					N			Y	N	Y	Y	Y	Y	N	Y	Y	Y	N
m-Toluidine						N			N	Y		N	Y		Y	N	Y		
Azulene			Y	Y		Y	N		Y	Y		Y	N	Y					
N,N-Dimethyl-p-toluidine			Y	Y		Y	Y		Y	Y		Y	Y						

[a] Charge transfer agents are listed from highest to lowest ionization potential. Y–Charge transfer did occur. N–Charge transfer did not occur.

FIG. 3. Typical growth and decay curves observed in the charge transfer reactions of (a) C_{18}^+, (b) C_{19}^+, and (c) C_{20}^+ with aniline.
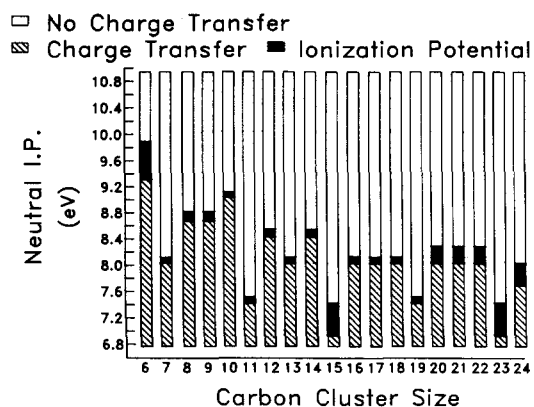
FIG. 4. Estimates of ionization potentials (black boxes) of carbon clusters containing from 6 to 24 atoms as obtained from charge transfer bracketing reactions.

FIG. 5. Reaction of D_2 with C_7^+. (a) pulse sequence of Fig. 1; (b) modified pulse sequence (see the text). (The peak at $m/z = 101$ results from reaction of C_7^+ with water present in the background).

cluster the white area shows the IPs of neutral compounds which did not transfer an electron to the cluster. The lower limit of this range must correspond to the upper limit of the cluster's IP. Likewise, the IPs of neutrals for which charge transfer was observed are indicated by the hashed bar, the upper limit of which corresponds to the lower limit of the cluster's IP. The black area indicates the range of energy in which the cluster's IP must lie. A general decrease of the carbon cluster ionization potential with increasing number of atoms in the cluster is seen, but pronounced differences from one cluster to the next are also apparent. Table III lists the ionization potentials of carbon clusters containing from 6 to 24 atoms and their associated errors as determined in these investigations.

As mentioned above, evidence was found for only one isomeric form of each carbon cluster cation. Because other
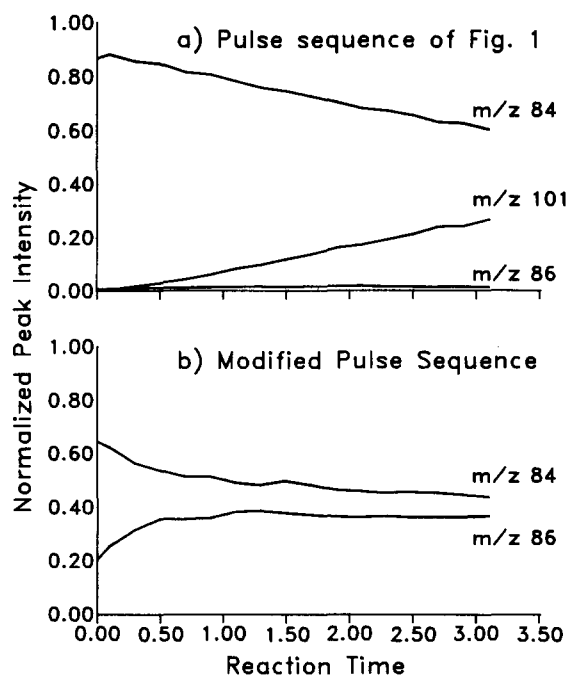
workers[5] have reported multiple forms of some cluster cations (specifically C_7^+), the reactivity of C_7^+ with D_2 was examined using CO_2 laser cluster ion formation and the methodology discussed above for following charge transfer reactions. The results obtained using the pulse sequence of Fig. 1 are shown in Fig. 5(a). There was no evidence of formation of C_7D^+ (m/z 86), the reported[5] product of the reaction with D_2. The pulse sequence was then modified, so that any products formed during the thermalization and pump down period would not be ejected, and their intensities were followed during this period as well as the usual reaction delay time. Using this pulse sequence, a reactive and unreactive form of the C_7^+ cluster were observed [Fig. 5(b)]. This indicates that none of the reactive form of C_7^+ remained by the time the usual charge transfer reaction phase of our experiments began. Thus the ionization potential determined in our investigations of C_7^+ was for the unreactive form only.

Experiments were undertaken to compare the effect of using sulfur hexafluoride rather than argon as a thermalizing gas prior to the charge transfer reactions. As would be expected, SF_6 appeared to be more efficient than argon in "cooling" the carbon clusters. For example, when durene was used as a charge transfer compound less charge transfer and more adduct formation was observed following SF_6 cooling of C_{10}^+–C_{20}^+. In no case, however, did the use of SF_6 cause the experimentally determined IP to be moved to the next lower "gap" between the IPs of two charge transfer neutrals. Thus we estimate that SF cooling removed no more than an additional 0.05 eV from the cluster ions. Similar trends were seen when comparing the effect of argon cooling to the use of no thermalizing gas at all.

TABLE III. Ionization potentials of carbon clusters determined in this work.

Cluster	IP (eV)
C_6	9.6 ± 0.3
C_7	8.09 ± 0.1
C_8	8.76 ± 0.1
C_9	8.76 ± 0.1
C_{10}	9.08 ± 0.1
C_{11}	7.45 ± 0.1
C_{12}	8.50 ± 0.1
C_{13}	8.09 ± 0.1
C_{14}	8.50 ± 0.1
C_{15}	7.2 ± 0.3
C_{16}	8.09 ± 0.1
C_{17}	8.09 ± 0.1
C_{18}	8.09 ± 0.1
C_{19}	7.45 ± 0.1
C_{20}	8.17 ± 0.2
C_{21}	8.17 ± 0.2
C_{22}	8.17 ± 0.2
C_{23}	7.2 ± 0.3
C_{24}	7.9 ± 0.2

Many other charge transfer compounds in addition to those given in Table I were screened. Unfortunately, the majority of those investigated did not react with the carbon clusters via charge transfer, but rather fragmented or transferred some functional group. A major problem to date in determining the IP of C_5 (not reported here) is its preference for forming C_5H^+, probably because of a reaction of C_5^+ with background hydrogen and/or water.

TABLE IV. Comparison of experimental and theoretical ionization potentials of C_6 through C_9.

Carbon cluster	Experiment[a]	Theory[b]
C_6	9.6 ± 0.3	9.8^c
C_7	8.09 ± 0.1	10.0^d
C_8	8.76 ± 0.1	9.2^c
C_9	8.76 ± 0.1	9.4^d

[a] Present work.
[b] Reference 31.
[c] IP's calculated using a linear form for the ion.
[d] Evaluated from the orbital energies using Koopman's theorem.

IV. DISCUSSION

As mentioned in Sec. I, previously reported[16] ionization potentials for carbon clusters had large uncertainties for all cluster sizes. The results of this study certainly fall within previously determined IP ranges for clusters containing 8 to 24 carbon atoms, and the uncertainties have been reduced to a few tenths of an eV. Our result for the C_6 IP is slightly lower, and for the C_7 IP substantially lower (by 1.75 eV) than those reported earlier. Values given here are also consistent with IPs determined experimentally for C_1–C_4,[20] (11.26, 12.11, 12.1, and 12.6 eV, respectively) lying somewhat below the values for the smaller clusters. It is expected that cluster ionization potentials should decrease with increasing cluster size. Our IP value for C_{24}, however, is still significantly above the work function of bulk graphite, which ranges from 3.9 to 4.44 eV[28] depending on its form. A recent[29] experimental determination of 10.4 ± 1.0 eV for the C_6 IP agrees well with the value found in this work.

Dramatic differences in the ionization potentials as a function of carbon cluster size have been determined in this work (Fig. 4). It is tempting to seek some correlation between the observed IPs of the clusters and their geometric structures. Examination of the IPs of hydrocarbons[20] as their structures change from linear to cyclic to polycyclic and then to aromatic, reveals a reduction in IP by about 0.5 eV. For example, the ionization potential of hexane is 10.13 eV, cyclohexane is 9.86 eV, and benzene is 9.25 eV. However, this comparison may be confounded by the changing number of hydrogens (and thus carbon multiple bonding), which will not be the case with pure carbon clusters. Increasing the size of alkanes tends to decrease the ionization potential by about 0.1 eV per carbon atom, similar to the general decrease seen in this work.

Since the adiabatic ionization potential corresponds to a transition from the most stable neutral cluster to the most stable ionic cluster, it is difficult to deduce information about either of these structures from one experimentally determined IP. It should be noted that the ionic structures undergoing charge transfer in our experiments are not necessarily those which might be predicted by theory to have the lowest energy. Rather, they are the lowest energy forms produced by CO_2 laser ionization and stabilized by numerous ion/neutral collisions. While it is reasonable[30] for many cluster ion sizes that the strucutre undergoing charge transfer *is* the most stable form, this cannot be guaranteed.

As can be seen from Fig. 4, there is no clear break in the trend of IPs vs carbon number which might indicate a point where the structure of the clusters changes from linear to cyclic. The figure does show that clusters with 7, 11, 15, 19, and 23 ($4n + 3$) atoms have low IPs compared to their neighbors differing by one carbon atom. These species have also been observed in high abundance in this (Fig. 2) and previous[16] work. The results reported here support the suggestion[30] that the high intensities observed for these ions may be attributed to the relative ease of ionization of the neutral rather than to any special stability of particular size clusters. Our results also suggest that the larger ionic clusters are aromatic, since positive ions with $4n + 3$ carbon atoms will have $4n + 2$ pi electrons. The stability of ions with this number of pi electrons would result in lower IPs, as observed. A similar argument would suggest that clusters with $4n + 2$ atoms should have *higher* IPs, since the neutral should be stabilized with respect to its neighbors differing in size by one carbon atom, and this phenomenon is observed for at least the first members of the series (C_6, C_{10}, and C_{14}).

Raghavachari and Binkley[31] have estimated the ionization potentials of carbon clusters containing up to nine atoms based on the calculated lowest energy ground state structures. Their values are in reasonable agreement with our results for C_6, C_8, and C_9, although our experimental results differ by almost 2 eV from their estimate for C_7 (Table IV). The IP calculated for C_7 assumed a linear structure for both the neutral and the ion. Our charge transfer reactions were preformed on the isomeric form of C_7^+, which is unreactive toward D_2 and thus argued[5] to be cyclic. If the neutral produced in the charge transfer reaction is also cyclic, recent calculations[32] predict an IP of 8.4 eV for this structure, in reasonable agreement with our experimental results.

Additional studies which extend these measurements to smaller (specifically C_4^+ and C_5^+) and larger carbon clusters, and experiments which examine clusters formed by Nd:YAG laser ionization or electron ionization/fragmentation of suitable fluorocarbons[33] are in progress. Application of the methodology discussed here to other classes of cluster ions is also underway.

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