Master Dissertation

Formation and Characteristics of Heteroatom-containing Carbon Clusters

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Contents

Chapter 5 **Theoretical Studies of XC$_n$X (X=O, S, Se; *n*=1~8): Structures, Spectroscopic Properties, and Dissociation Energies**

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ROHF　B3LYP　　　　　　　　，

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2、　ROHF、DFT、MP2　QCISD　　　　　　C_nSe　　，

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6-311G　6-311G*　　　　　。

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。　　　C_nO、C_nS　C_nSe　　　，

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。　，　　　，　　C_nSe^-

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3、　B3LYP/6-311G*　　　　　　　　、

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，　　C_nX_2　ΔE_n　　　　　ΔE_n　，

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C_nO_2、C_nS_2、C_nSe_2 。 ，

， CX 。

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Abstract

Recently, Cluster Science has undergone an explosive growth in activity. Stimulated by the astrophysical interest and the special properties for the carbon clusters doped by heteroatoms, several series of heteroatom-containing carbon clusters have been studied both experimentally and theoretically. Main results and conclusion could be summarized in the three parts.

1. Polycarbon selenides C_nSe^- were produced by laser ablation recorded by TOFMS. Only the cluster with even n could be produced in the experiment. Experiments of collision-induced dissociation (CID) verified molecular formulas of the C_nSe^- clusters and found that they tend to lose a Se atom (for smaller size) or a CSe unit (for larger size). To examine their unique characteristic, the cluster ions were further investigated by ab initio calculations at ROHF and B3LYP levels, and the theoretical results matched well with the mass spectrometric observation. Furthermore, the structural difference between opposite parties of C_nSe^- is found to reduce following the growth of the chain. The theoretical investigation also shows that electron correlation has to be considered in the calculation and the result obtained by the DFT method is sufficient to describe the structural features of C_nSe^- clusters. Besides, dissociation energies of six dissociation channels, losing C, C_2, C_3, CSe, C_2Se or Se fragment, were calculated for C_nSe^- anions and the results also exhibit the parity effect and match well with the CID experimental observation.

2. Theoretical studies of the C_nSe (n=1 to 9) clusters have been performed by employing ROHF, DFT, MP2 and QCISD theories combined with various basis sets. The computation determines that the linear C_nSe clusters are more stable than those with bending structure in their ground states and their structural difference is very insignificant. Based on the comparison, it could be concluded that the (DFT) method can sufficiently predict the characteristics of the clusters at 6-311G or 6-311G* level. Relative stabilities and the structural parameters of the C_nSe clusters exhibit drastic odd/even alternation, but this effect

reduces with the increase of the carbon atoms. Comparison shows that C_nO, C_nS and C_nSe clusters possess the similar structural characteristics such as the parity and the size effect. The theoretical studies, especially the comparisons, describe the effect of the heteroatom to the carbon chain, that is, the influence of the heteroatom on the carbon chain decreases along the chain. Moreover, because of the addition of the negative charge, for C_nSe^- anions, the alternation effect still exists but its parity is reversed.

3. The structural parameters, energies and vibrational frequencies of XC_nX (n=1~8; X=O, S, Se) clusters were computed at B3LYP/6-311G* level. The theoretical results show that C_nO_2, C_nS_2 and C_nSe_2 clusters, especially the latter two species, exhibit the similar symmetric structure and the same parity. For example, energies differences ΔE_n of C_nX_2 with odd n is lower than that of even-numbered ones, indicating that the former is more stable. Interestingly, their parity effect reduces with the growth of the carbon chain, indicating that influence of heteroatoms on the carbon chain decreases along with the chain's elongation. Furthermore, this alternation effect is also weakened following the sequence: C_nO_2>C_nS_2>C_nSe_2. Finally, the fragment energies of XC_nX also show the parity effect and these molecules are in favor of losing CX unit.

Keywords: Heteroatom-containing Clusters, Structure, Spectroscopic Properties, Dissociation Energies

Chapter 1　Introduction

§1.1 Progress of Cluster Science

It is useful to begin the discussion by providing some definition of a cluster. Clusters are aggregates of atoms or molecules ranging in size from two to tens of thousands of monomer units. Clusters are distinct from bulk materials because they are dominated by surface species, and consequently, clusters have structures and properties that often differ from anything that can be observed in the bulk.[1] The upper size limit to what we may call a cluster has something to do with the onset of bulk behavior, and the cluster size at which bulk properties appear depends on the particular physical property chosen for study. We should emphasize here that we are concerned with the physical transformation from finite to bulk behavior, not with the mathematical transition. Clusters are not to be viewed as some finite representation of a bulk material forced to take on bulk structure with the imposition of periodic boundary conditions. The dependence of many physical properties on the size of such constrained system is well understood using scaling relations. For true finite systems, the change in physical properties with cluster size can be erratic.

Cluster Science has undergone an explosive growth in activity during the last few years, prompted both by the large number of basic problems to which studies of clusters may provide new insight, as well as the vast array of applied areas to which clusters relate. The field has developed along several lines, including intensive efforts devoted to carbon clusters, extensive investigations of metal and semiconductor systems, and a large number of studies devoted to rare gas and related van der Waals systems as well as those comprised of hydrogen-bonded molecules.[2-4] Elucidating the differences and similarities in the properties and reactivity of matter in the gaseous compared to the condensed state from a molecular point of view has been an overriding theme of many of investigations.

Among the branches of cluster science, carbon clusters have been extensively studied by use of both experiment and theory. This might be due to the discovery and preparation of C_{60}[5]. Starting in late 1985, Smalley's group at Rice University published a series of papers[5], which show that under special experimental conditions C_{60}^{+} can be the dominant ion signal when photoionizing neutral carbon clusters. To explain their observations, Kroto *et al.* Proposed that the 60 atom carbon cluster is an ultrastable cluster possessing the unique structure of a truncated icosohedron, a nearly spherical shell containing 20 six-membered rings and 12 five-membered rings and suggested the name Buckminsterfullerene.[5] The subsequent experiments were taken as strong support for this proposal. In addition it was proposed that all even atom C_n $n>40$ clusters are also spheroidal carbon shells,[6] and that the observation of C_nLa clusters containing only a single metal atom suggests that the lanthanum atom is surrounded by an aromatic shell of carbons arranged in networks of five- and six-membered rings.[7] Subsequently it

was demonstrated that the relative neutral and metal containing cluster ion signal are highly sensitive to the photoionization conditions.

In experiments using laser vaporization of stationary graphite targets in which large carbon cluster ions were injected and trapped in an ion cyclotron mass spectrometer, large cluster ions $n>32$ are not observed unless the axis of the laser drilled pit is parallel to the trapping magnetic field.[8] Enhanced abundance of C_{60}^+ again is observed with the overall mass spectrum being similar to that observed in laser vaporization/molecular beam/photoionization and laser vaporization/molecular beam/direct ion time of flight experiments. Recently both the laser-induced fragmentation and metastable decay of large C_n^+ have been extensively studied. It is found in both cases that C_{60}^+ and all other nearby even atom cluster ions fragment by elimination of C_2, producing the C_{n-2}^+ cluster ion, and that the odd atom cluster ions fragment by first eliminating C_1 which converts them to even atom cluster ions which subsequently lose only C_2's. Note that for the small $n<32$ carbon clusters C_3 is the major photofragment.[9] Moreover, the relative theoretical studies on clusters have proceeded with increasing vigor.

Stimulated by the in-depth studies on pure carbon clusters, in recent years there has been increasing interest in small carbon clusters mixed with heteroatoms. This effort toward understanding the basic principles governing these structures results from the fact that substitutions of heteroatms (N, Si, S...) into a pure carbon cluster is expected to induce significant changes on the electronic structure and the possibilities of new types of materials, with novel solid-state properties.[10-11] Furthermore, Heteroatom-doped carbon clusters have been also identified in space and the way carbon atoms organize into clusters with one or two heteroatoms is very important in interstellar chemistry.[12]

Recently, because of the instability of these carbon clusters, it is difficult to detect some floppy species through experimental means, so theoretical studies on these clusters has received more and more interest, and most of the calculations for carbon clusters were carried out by employing the Density Functional Theory.[13-15] For example, C_nS $(1 \leq n \leq 20)$ clusters have been investigated by means of the density functional theory.[15] As a general rule, when $1 \leq n \leq 17$ the energetically most favorable isomers are found to be the linear arrangement of nuclei ($C_{\infty v}$) with the sulphur atom at the very end of the carbon chain. The electronic ground state is alternately predicted to be $^1\Sigma^+$ for odd n or $^3\Sigma^-$ for even n with a conspicuous odd/even effect in the stability of these clusters.

Generally, following the double-quick development of cluster science, people

gradually recognize the importance of cluster research. Now, cluster science is not a pure science, it is studied under the combination with other sciences, such as, Astrophysics, Material Science. And it is not surprising that there has been considerable interest in cluster study, especially carbon clusters.

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Chapter 2 Experimental Instrument and Computational Methods

§2.1 Experimental Instrument

The experiments were performed on a homemade tandem time-of-flight (TOF) mass spectrometer[1] equipped with a pulsed laser, as shown schematically in Figure 2.1. The vacuum system consisted of six sections, the source chamber, collision chamber, two flight tubes (2 m in length for the first and 1 m for the second), which were perpendicular to each other, and two transition chambers which were just before and after the collision chamber respectively. The first three electrodes mounted in the source
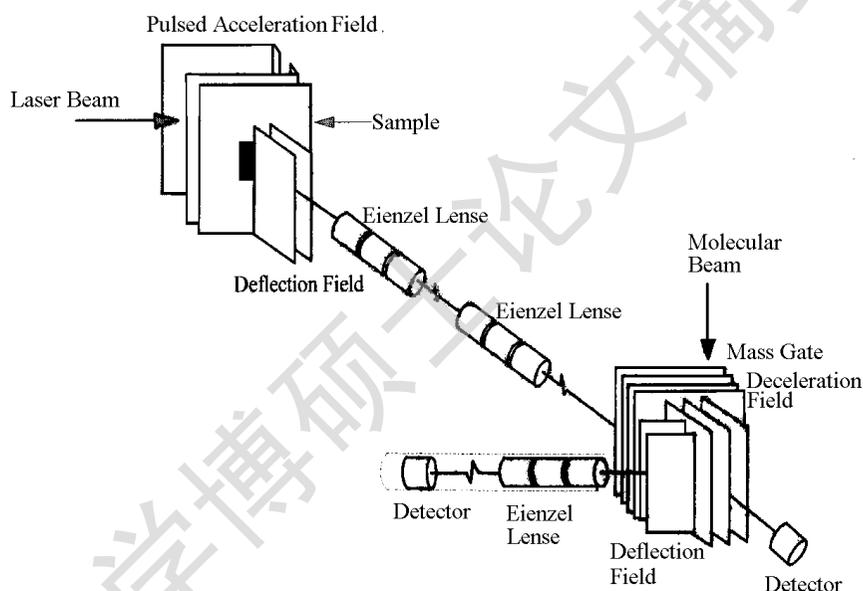
Figure 2.1 Schematic diagram of the crossed ionic/molecular beam tandem time-of-flight mass spectrometer. Vacuum chambers and flight tubes of the spectrometer are not shown on the diagram. The function of each stack of electrodes is labeled.

chamber formed a dual-stage acceleration stack. The pulsed voltage applied on the stack is 1 kV with a 300 ns rise time. On the end of the first drift tube is another stack of four electrodes, of which the first and third are grounded. The second electrode is connected to a high voltage pulse (100 ns for both rise and drop times, pulse width adjustable) which is maintained at 1050 V at most times and pulsed down to 900 V at selected times. The three electrodes function as a "mass gate" to select the cluster ions with a specified mass. The electrostatic potential applied on the fourth electrode forms the deceleration field between the third and fourth electrodes. The second acceleration stack is next to, and perpendicular to, the mass gate/deceleration stack. The first and second electrodes are kept at the deceleration potential at most times to form a field-free region where collision reactions take place. As the ions enter the exit of the

second acceleration stack, the potential on the first electrode is pulsed up 500 V to accelerate the ions. The third electrode of the stack is at 2500 V potential so a total 4 kV acceleration potential can be applied.

Each of the four vacuum chambers of the apparatus is evacuated by a 7001 s^{-1} diffusion pump. A pulsed piezoelectric valve produces a supersonic beam for colliding with the selected cluster ion beam. The pulse molecular beam with a pulse width adjustable from 150 μs upward crosses the ion beam between the deceleration and the second acceleration zones. Back pressure of the valve is typically $1 - 3$ atm. When the pulse valve is inactive, the whole vacuum system operates under a vacuum of 2×10^{-6} Torr. Under normal operating conditions, the background pressure of the collision chamber is about 4×10^{-5} Torr and the pressure in the two transition chambers can be kept at 8×10^{-6} Torr.

The sample probe is 7 cm away from the first acceleration region and the laser-generated plasma diffuses into the region by its initial kinetic energy. The deflection field and the Einzel lenses direct the ion beam to the collision chamber where the cluster ions are mass selected, decelerated and crossed with the molecular beam. The parent ions and their products after the collision are then accelerated again and mass analyzed by the secondary TOF mass analyzer. Ions are detected by a dual micro-channel plate (MCP) detector and its output signal is digitized by a 100 megasample s^{-1} transient digitizer after preamplification. Mass resolution of the apparatus routinely exceeds 400 in the first mass analysis and is near 150 in the second stage.

The pulsed laser beam used in the experiments was the second harmonic of a Quantary Nd:YAG laser. The wavelength of the laser beam is 532 nm with pulse width 7 ns. The power density acting on the sample was of the order of 10^{8} Wcm^{-2} after being gently focused by a long focal length lens. The samples should be purified before the experiments. Nitrogen or Argon gas of high purity was selected as buffer gas to collide with cluster ions.

§2.2 Computational details

We have mainly performed the calculations using the hybrid density functional

Kohn-Sham method.[2] The effect of exchange and correlation are approximated by the BLYP or B3LYP hybrid density functional, which is a combination of the one or three parameter Becke exchange correlation functional[3-4] with the Lee-Yang-Parr nonlocal correlation functional[5]. The Pople's 6-311G* basis set[6] was used for some heteroatom-doped carbon clusters, while for other species, the CPU time was largely prohibitive with this basis and the structure was optimized with the standard 6-31G* basis set. From prior experience, the use of these basis sets in conjunction with density functional methods leads to quantitatively good results, for pure and heteroatom-containing carbon clusters, especially concerning the structural parameters, the rotational constants and the vibrational frequencies. Geometries have been optimized with analytical gradient techniques. Dipole moments have been calculated with the origin at the center of mass and normal modes of vibration with the fully analytic second derivatives. Moreover, other parameters, such as, the energy difference of the two adjacent clusters, fragmentation energies, were also analyzed at the same level. Simultaneously, the structural parameters of some clusters were optimized with other quantum calculation methods, for example, MP2, QCISD, CCSD these computational results confirmed the efficiency of density functional methods.

Hereinbefore, we generally outlined the computational methods, and the ab initio calculations for each system would be described detailedly in the following discussion.

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Chapter 3 Studies of Linear C_nSe$^-$ (n=1~11) Clusters Produced from Laser Ablation: CID and Ab Initio Calculation

§3.1 Introduction

Because of the discovery[1] and successful preparation[2] of C_{60}, carbon clusters, especially those with large sizes such as fullerenes, have been extensively studied both experimentally and theoretically in the last decade.[3-11] Meanwhile, the small carbon clusters have also attracted much attention in recent years.[12-17] Such an interest is partly due to the involvement of these species in the interstellar medium, which is in the quasi-collisionless conditions. Under these conditions, the small carbon clusters is formed by adding heteroatoms such as nitrogen, oxygen, sulfur, boron or silicon[18], which presents a variety of stability to the carbon chain. The carbon cluster anions containing a heteroatom, C_nX$^-$ (X=H, B, F, Si, Cl, Ti, V, Cr, Fe, Ni, W, Zr, Cs, Rb, Al, N, P, As, Bi, S and *et al.*) were produced by laser ablating the proper samples.[19] Their abundance exhibits odd/even alternation, which varied with the number of clustering carbon atoms and the nature of the heteroatom.[19] It has been found in the observed time-of-fight (TOF) mass spectra that the signal intensities of some C_nX$^-$ clusters, *e.g.*, X=H, B, S, F, Al, with even n are stronger than those with odd n.[20]

Geometry of the small size carbon clusters, including those containing a heteroatom, is generally believed to be linear.[9] Although Zhan *et al.* reported that some C_nX$^-$ anions, such as, C_nB^{-21}, C_nP^{-10} and C_nN^{-22}, of larger n calculated with higher levels are slightly bent in their ground state, most of the structural features calculated in the bent geometry do not exhibit significant difference with those computed with linear structure. However, computations made at much higher levels of theory (CCSD(T)) have revealed that C_nP$^-$ (n=2-7) clusters are linear[23]. G. Pascoli and H. Lavendy[24] also found that C_nN$^-$ (n=2-7) clusters are linear in their ground state. From these calculation results, it seems that the carbon clusters doped with single heteroatom are linear or nearly linear in their ground state.

The polycarbon sulfides C_nS and their protonated forms have recently been investigated both experimentally and theoretically.[25,26] Sulfur polycarbon hydride ions were generated by laser ablating the mixture of sulfur and carbon powder.[27,28] An odd/even alternation in signal intensities was observed, and the cluster cations with even size and the anions with odd size were absent in the recorded mass spectra. The computation results agree very well with the mass spectrometric observations.[28] Recently, the special properties and structural flexibility of $C_2S_m^-$ have been demonstrated with experimental and theoretical methods.[29] Because of the special properties of oxygen and sulfur, it is difficult to generate the C_nO^- or C_nS^- clusters which tend to react further with hydrogen or others to form more stable ions.

Following the study on the carbon clusters doped with sulfide atom, we have generated selenium polycarbon ions by laser ablating the mixture of selenium and carbon powder at the first time. Compositions of the cluster anions are determined by collision-induced dissociation of mass-selected ions. Different than the C_nO^- or C_nS^- clusters, the C_nSe^- cluster anions created in the experiment are relatively stable and can be observed by the mass spectrometer. Thus, although a variety of C_nX^- clusters have been previously studied, the C_nSe^- cluster anions have their special scientific significance. Herein we report the mass spectrometry and ab initio calculations of the C_nSe^- anions. The experimental and theoretical results are compared and correlated, and special attention is focused to the odd/even alternation effect of the clusters.

§3.2 Experimental Section

The experimental technique has been previously described in detail,[30] so only a brief description will be given here. The selenium polycarbon ions, generated by laser ablating the mixture of selenium and carbon powders, diffused into the first accelerated region with their initial kinetic energy and then were accelerated by a pulsed field with a potential of 950 V. After flying through a 2.5 m field-free drift tube, ions with different masses were separated. The ions with a specific mass were then selected by a pulsed field (the "mass gate") and were