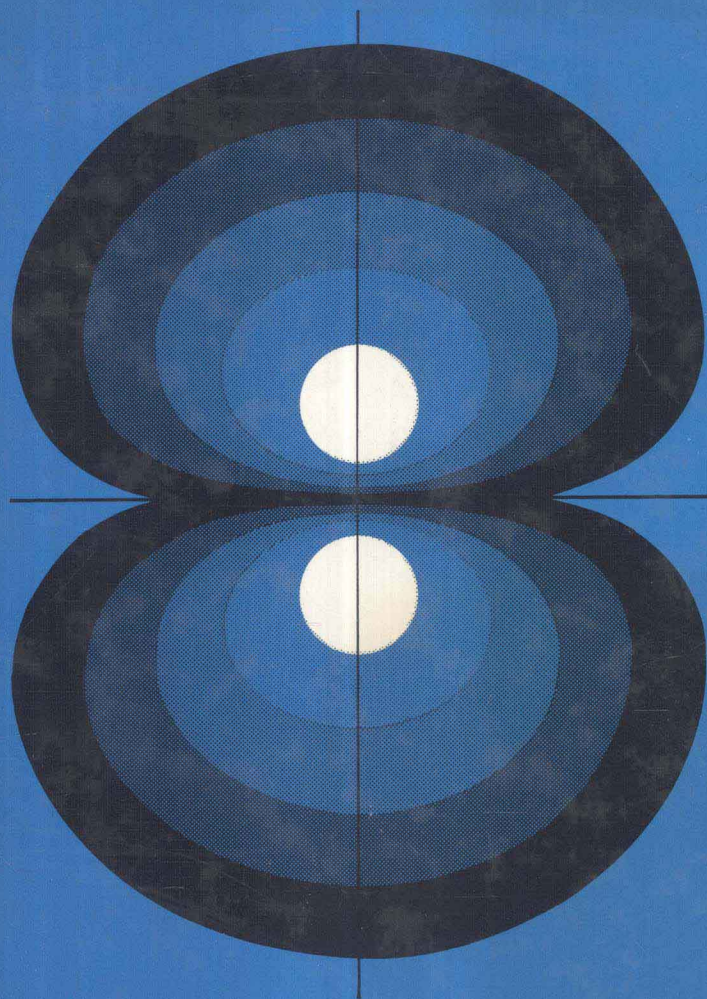


studies in physical and theoretical chemistry



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ATOMIC AND MOLECULAR CLUSTERS

Edited by
E.R. Bernstein

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Edited by

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Preface

Atomic and molecular clusters have been studied for nearly fifty years. Nonetheless, the last 15 years has seen a veritable explosion of clusters research, brought about by two relatively new experimental advances: supersonic jet expansions creating cold high density atomic and molecular beams and laser (mass and optical) spectroscopy. The success and power of these two techniques, taken together, and applied to the study of atomic and molecular clusters, are chronicled in this volume.

The field of cluster study is indeed a very broad one, propelled by both the potential application of cluster results to many bulk systems and the interest in clusters as systems in their own right. The eclectic nature of the collection of chapters in this volume reflects well the diverse nature of this area of chemical physics.

We begin this volume with perhaps one of the most surprising (and controversial) of recent cluster studies - those for the carbon system. As with bulk and molecular carbon chemistry, the chemistry of carbon clusters seems to be unique. Nonmetallic main group clusters also form a very interesting set of systems and their structure and chemistry are as fascinating as they are varied. Diatomic/atomic clusters and small polyatomic clusters demonstrate an incredible amount of spectroscopic detail and thus structure, dynamics and, in some instances, chemistry can be characterized for them. Clusters of larger molecules also yield information on structure, dynamics and chemistry but can in addition give information on changes in molecular structure with degree of solvation. As clusters become larger they begin to assume the properties of bulk systems. Finally, some of these chapters discuss the nucleation and growth of clusters, each from its own unique perspective and point of view. Current efforts involve following these processes from the formation of a two molecule cluster to liquid drop.

We hope this volume proves helpful to the researcher in the field as a survey of current status and to the student who may discover a new and exciting area of investigation.

I wish to thank all of those who helped bring this book to fruition: the authors for their cooperation, patience and understanding; Elsevier for its careful attention to detail and form; and R. Jaramillo for the final assembly of the completed text.

Elliot R. Bernstein

Fort Collins, Colorado
June, 1989

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CHAPTER 1

SUPERSONIC CARBON CLUSTER BEAMS

R. E. SMALLEY

I. INTRODUCTION

Advances in laser and supersonic molecular beam techniques over the past 5-10 years have produced a flood of new results and insights as to the nature of small clusters. Within the sub-field of strongly bound (non van der Waals) clusters, certainly one of the most active and intellectually exciting areas has been the study of carbon. Although many of these new experiments are still in the process of verification, extension, and further interpretation, a remarkable new picture is beginning to emerge as to the processes of carbon condensation and the nature of the species involved. It is an interesting story both from what it tells us about carbon, and more generally as testimony to the power (and limitations) of the new generation of supersonic cluster beam techniques.

Perhaps the most concise way to introduce this subject is simply to list some of the key features of the emerging new view of the small clusters of carbon.

- (1) Carbon nucleates to form small clusters far more readily than any other element in the periodic table (including such refractory elements as tungsten and tantalum).
- (2) The smallest clusters (C_2 through C_{29}) are essentially one-dimensional: they are most stable in the form of linear chains or monocyclic rings (depending on the charge state and temperature).
- (3) Even-numbered clusters in the 32-100+ atom size range often take the form of entirely closed, hollow spheroidal shells (the "fullerenes").
- (4) Odd-numbered clusters in the 33-101+ atom size range often take the form of nearly-closed spheroidal shells (the "semifullerenes").
- (5) The prototypical fullerene, C_{60} ("buckminsterfullerene"), prefers the shape of a truncated icosahedron. Because of its size and perfect symmetry, it is extremely stable (chemically, thermodynamically, photophysically).
- (6) A spiraling shell is a good model for the active nucleus involved in carbon grain growth (and soot formation).
- (7) The fullerenes are side products (dead ends) in the process of soot formation.

(8) The fullerenes are made whenever carbon condenses, including sooting flames.

(9) Metal ions may be trapped inside completely closed fullerene shells.

When compared to the view prevalent in the carbon literature only a few years ago, these 9 points (with the possible exception of the first two or three) are quite divergent -- perhaps even wildly divergent. Nonetheless, my colleagues and I have found the new experimental evidence compelling. To our knowledge this picture is the only one consistent with all experimental results, both new and old.

Aside from the intrinsic interest all small clusters have for chemists and spectroscopists, there is an extra depth and intensity of interest in carbon. Astrophysically, carbon is one of the most abundant elements in the universe -- after hydrogen, helium, and (possibly) oxygen. In the current model of stellar nucleosynthesis of the elements, ^{12}C is the first stable element that can be synthesized in fusion reactions involving the hydrogen and helium produced in the original "big bang". All other elements are then derived from this critical ^{12}C starting point. Of all the abundant elements carbon is by far the most refractory, and in the carbon-rich red giant stage large stars are known to pour vast quantities of carbon dust into the interstellar medium. Carbon grains of one form or another are thought to constitute the prime refractory cores of interstellar dust, vast tracts of which obscure major portions of our galaxy (particularly its center). In the interstellar medium the largest currently known molecules are, in fact, long carbon chains.

On earth carbon is, of course, rather important as well. Aside from all of organic chemistry and most of biology, one ancient and still vital (and still rather mysterious) area is simply the business burning carbon things. Outside the community of combustion chemists and engineers, few are aware of the fascinating processes that occur even in the simple candle flame. At the top of the conical region at the center of the flame where the color changes abruptly from blue to yellow, soot is formed. In fact it is the incandescence of these tiny soot particles in the 1200-1700K temperatures of the flame that produces the beautifully soft yellow light which gives the candle its value. How does it happen that such large "super-molecules" of carbon form so readily in such hot regions where entropy normally favors the destruction of all large molecules? The answer critically depends on the special nature of small carbon particles.

So both from an astrophysical standpoint and the more mundane terrestrial issues surrounding the technology of combustion, research into the processes and species involved in carbon condensation are of vital interest.

The following sections of this chapter present an account of the current state of carbon cluster research in supersonic beams. Throughout the interpretation emphasized is that of the 9 points summarized above. The reader is cautioned that some aspects of this interpretation are still controversial, and a degree of scientific skepticism is useful.

II. LASER VAPORIZATION CLUSTER BEAMS & ABUNDANCE DISTRIBUTIONS

Figure 1 shows a schematic of the sort of laser-vaporization cluster source used for the new carbon cluster experiments. This new technique was developed at Rice particularly for the study of small clusters of transition metals, but turned out to be rather general in scope¹⁻⁴. Here a pulsed laser is directed at the surface of solid rod of the material to be studied. With currently available pulsed lasers one can easily generate temperatures on the target material in excess of 10,000K in this apparatus, readily vaporizing any known substance in such a short period of time that the rest of the source can operate at room temperature. The cool, high density helium flowing over the target then serves as a buffer gas in which clusters of the target material form, thermalize to near room temperature, and then cool to near 0 K in the subsequent supersonic expansion as this helium emerges into a well-pumped vacuum chamber. Collimated beams skimmed from these supersonic cluster expansions then provide useful sources for detailed study of a vast set of fascinating new cluster species.

In order to probe the contents of these refractory cluster beam one of the easiest and most useful approaches has been to photoionize the clusters with an excimer laser, and examine of the mass spectrum of the resultant photoions with a time-of-flight (TOF) mass spectrometer. An early example of the sort of cluster distributions produced by the laser vaporization beam source is shown in Figure 2. Note that clusters of even the most refractory metals such as tungsten and molybdenum are readily produced in fashion.

The first such experiment on carbon was performed by a group at Exxon⁵ using an apparatus originally developed and built at Rice. As shown in Figure 3, a rather dramatic result is obtained in such an apparatus: there are two distinct cluster distributions. In the higher mass distribution only even-numbered clusters are observed. The Exxon group was uncertain as to the reason for the prominence of this second, even-numbered distribution, although they suggested it may be evidence for the formation during vaporization of a hypothetical "carbyne" form of carbon consisting of linear chains of triply-bonded carbon, much as had been reported previously (see ref. 6 and references therein). As it turned out, the real reason for this bizarre bimodal distribution appears to be even more interesting.

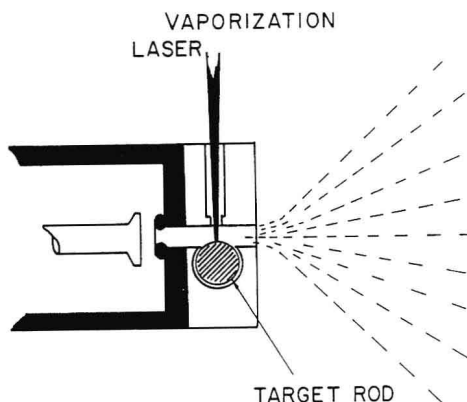


Figure 1. Cross-sectional view of the original pulsed laser-vaporization supersonic metal cluster nozzle source. Helium carrier gas in the reservoir on the left is pulsed down a 0.2 cm diameter channel, passing over a rotating, translating rod of the material to be studied, then freely expanding into a vacuum to form a supersonic jet. A pulsed laser beam (usually the 2nd harmonic of a Q-switched Nd:YAG laser, 5 nsec pulse duration, 5-50 mJ pulse energy) is used to vaporize the target rod. The vapor entrained in the flowing helium condenses rapidly to form the desired small clusters.

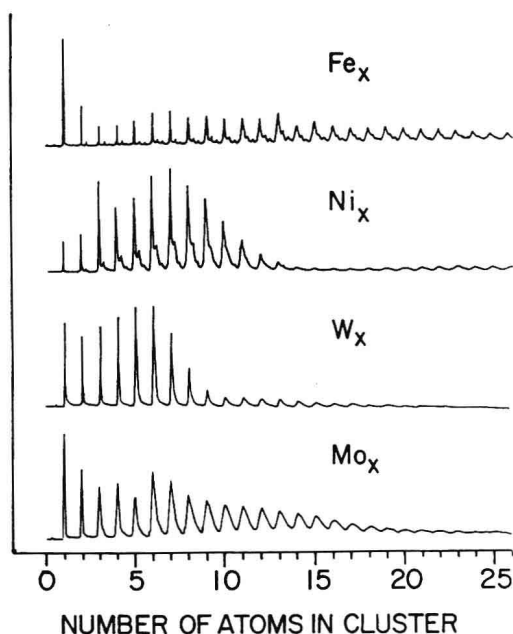


Figure 2. Typical time of flight (TOF) mass spectra of various transition metal clusters prepared in a supersonic beam by the laser vaporization method.

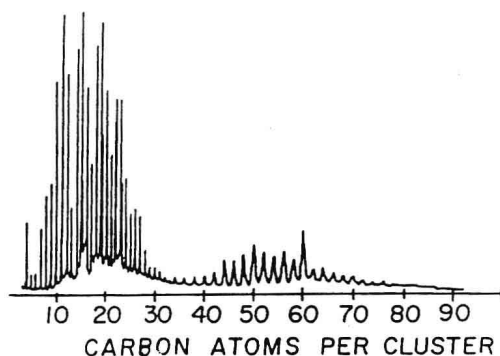


Figure 3. TOF mass spectrum of carbon clusters prepared in a supersonic beam by laser vaporization of a graphite target. Ionization of the neutral clusters was done by photoionization with an ArF excimer laser beam (1930 \AA , 6.4 eV).

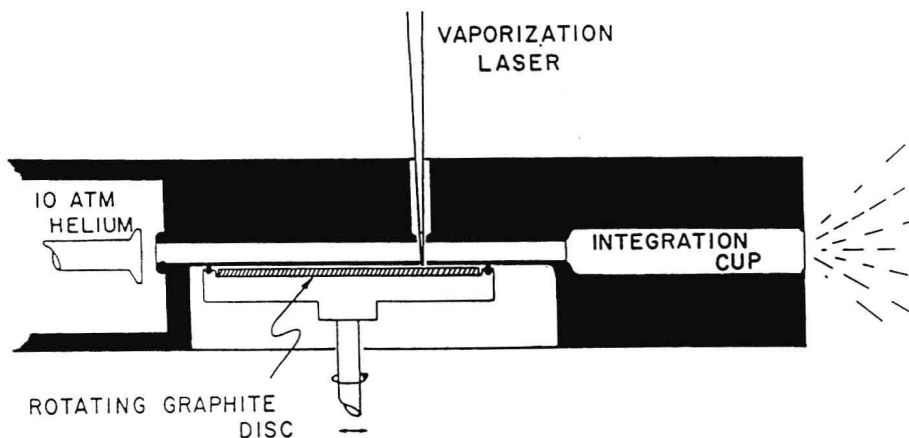


Figure 4. Schematic of more recent rotating disc variant of the pulsed laser vaporization nozzle source. This was the principal nozzle design used for production of the supersonic carbon clusters beams discussed in this chapter. Reprinted by permission from *Nature*, Vol. 318, No. 6042, pp. 162-163 Copyright (c) 1989 Macmillan Journals Limited.