Chapter XI

PULSED METHODS FOR CLUSTER ION SPECTROSCOPY

Mark A. Johnson
and
W. Carl Lineberger

1 Introduction
2 A Brief Retrospective: “Traditional” Methods of Ion Spectroscopy
3 Pulsed Ion Sources
   3.1 Positively Charged Clusters
       3.1.1 Molecular or “van der Waals” Ionic Clusters
       3.1.2 Cluster Ions of Metals and Semiconductors
   3.2 Negatively Charged Clusters
       3.2.1 Molecular Ion Clusters
       3.2.2 Cluster Ions of Metals and Semiconductors

2 Mass Selection
   4.1 Primary Ion Beam
   4.2 Interaction of the Ion Beam with a Pulsed Laser

5 Determination of Charged Photofragments Using Tandem Time-of-Flight Mass Spectrometry
   5.1 Tandem TOF Using a Reflectron
   5.2 Tandem TOF Using Two Pulsed Fields

6 Pulsed Photoelectron Spectroscopy Using Time-of-Flight Electron Energy Analysis

7 A Few Results
   7.1 Mechanism of Optical Absorption in “van der Waals” Cluster Ions: Localization of Charge within Large Clusters
   7.2 Statistical Photodissociation Dynamics of Large Molecular Ion Clusters
   7.3 Formation of “Magic Numbers” in Cluster Ion Mass Spectra
   7.4 Size Dependence of the Br$_2^-$ Recombination Quantum Yield upon Photodissociation of Br$_2^-$ Within Br$_2^-$ (CO)$_n$ Clusters: Observation of “Caging” of the Atomic Fragments

8 Outlook
References
1. INTRODUCTION

A central goal of physical chemistry is the explanation, on a molecular level, of chemical and physical processes occurring on a macroscopic scale. Traditionally, researchers have been divided into two groups: one primarily interested in the exact details of very small systems and one interested in understanding very complex systems as they occur in nature. The themes of each endeavor are correspondingly different, with small molecule research being directed toward observation of single eigenstates in order to determine empirically the molecular Hamiltonian and with condensed phase research relying heavily on ensemble averaging in modeling "real" physical processes. Over the past few years, these two approaches have been converging as experimentalists are increasingly able to carry out a variety of laser spectroscopy experiments on very selectively prepared ensembles of molecular aggregates or clusters containing from 2 to about 100 molecules. At the same time, theoretical techniques are becoming available that can handle small aggregates at Hückel [1], ab initio [2–8], and molecular dynamics [9] levels, and the forthcoming decade promises to be rich in interaction between theory and experiment.

Ionic clusters play an important role in this field since mass spectrometry allows ionic clusters of precisely determined composition to be selected for study. Indicative of this importance is the virtual explosion of experiments over the past 5 years, all aimed at elucidating the properties of ionic clusters. [10,11] In a recent review article on ionic clusters, for example, Castleman and Keesee [10] catalog over 450 recent publications in this field. In fact, whereas in 1983 only one report appeared [12] on the photodissociation of a cluster ion containing more than two monomer units, in 1987 at least 12 research groups [12–23] have been directing major efforts toward the photodissociation spectroscopy of mass selected ionic clusters. The topics of these studies range from ion solvation using van der Waals [14] type clusters such as (CO₂)₅⁺ to the elucidation of semiconductor [24] and metal [25] band structures as a function of cluster size and composition. A number of novel experimental approaches have contributed to the rapid development of this field, and the purpose of this chapter is to review several of these techniques using pulsed ion beams in conjunction with pulsed lasers. Indeed, a primary dividend arising from these methods has been a simplification of ion-beam experiments to the extent that they are now generally applicable to a wide range of chemical species.

One of the most important recent developments is the generation of pulsed beams of clusters ions based on the ionized free jet. This advance has been paralleled by recent tandem time-of-flight (TOF) techniques allowing the efficient overlap of ion beams with low duty cycle pulsed lasers. The combination of these methods makes it relatively easy to mass select a specific size ionic cluster of either positive or negative polarity, to interact nearly 100% of the selected ions with a pulsed laser, and, finally, to detect all of the photofragments—daughter ions, photodetached electrons, and fast neutrals.

This flexibility is especially important in the investigation of cluster ions
since these species are likely too complex for application of high-resolution spectroscopic techniques common in molecular physics, yet they are also small enough that statistical averaging and periodicity, so useful in understanding the behavior of bulk systems, are not directly applicable. Therefore, a large effort is being made to characterize the behavior of systems as the size and composition is systematically varied. The goal of this effort is to extract regularities in behavior from the database in order to gain an empirical understanding upon which to build more sophisticated models and more detailed experiments. In this review, we catalog some recent developments in experimental techniques that are currently making a major impact and summarize some representative trends that have been observed using these techniques. We also mention some important remaining challenges for experimentalists.

2 A BRIEF RETROSPECTIVE: "TRADITIONAL" METHODS OF ION SPECTROSCOPY

The pulsed instruments outlined here are fundamentally different in character from the continuous ion-beam experiments discussed in a previous review [26]. Traditionally, ions are formed in a discharge environment and are continuously extracted and mass selected, typically by a Wien filter, quadrupole mass filter, or magnetic sector and steered into a long arm for collinear interaction with a continuous laser. An example of such an experiment is shown in Fig. 1, which depicts a fast ion-beam apparatus developed by Huber et al. [27] and used for very high-resolution photofragmentation spectroscopy of molecular ions. Such instruments have also been productive in studies of negative ion threshold photodetachment, where Doppler broadening can be reduced to \( \sim 20 \text{ MHz} \) using the kinematic compression in a fast beam. In addition, there have been some reports on cluster ion spectroscopy using these techniques. Fayet and Wöste [18] have studied \( \text{Ag}_{\text{n}} \) photodissociation in a continuous ion beam where photodissociation was carried out in an octupole trap; Okimura et al. [20] have obtained infrared (IR) photodissociation spectra of \( \text{H}_{\text{n}}^{+} \) and \( \text{H}_{\text{3}}^{+} \cdot \text{H}_{\text{2}} \) also using an ion trap, and Castileman et al. [12] have studied the photodissociation of \( \text{CO}_{2}^{-} \cdot (\text{H}_{2}\text{O})_{\text{n}} \) clusters with continuous beams and a photofragment energy analyzer. Helm et al. [17] used a photofragment energy analyzer to study the spectroscopy of \( \text{Cs}_{\text{n}}^{-} \) clusters. Much of the existing spectral data on binary and ternary molecular ion complexes was obtained by Peterson and co-workers [28] at SRI using mass-spectrometric sampling of a high-pressure drift tube ion source in which the ions are irradiated at the entrance aperture of the mass spectrometer chamber. Bowers et al. [29] have used a continuous apparatus to obtain the photofragment angular distributions from a number of cation dimers and trimers [e.g., \( \text{(NO)}_{\text{2}}^{+} \)] . Using a triple quadrupole instrument equipped with a sputtering ion source, Magnera et al. [19] have obtained a structured electronic spectrum for the \( \text{N}_{\text{2}}^{+} \cdot \text{Ne}_{\text{n}} \) system. Ion cyclotron resonance (ICR) experiments have also been useful in obtaining data on binary ion-solvent systems [30], metal ion complexes [31], and the photochemistry of
organic cations [32]. The experimental methods enumerated above each offer special advantages that complement the pulsed beam methods discussed in this review. ICR experiments, for instance, afford an unparalleled capability of measuring decay rate constants and can also obtain extremely high mass resolution. This review presents a new, complementary method, which we expect to join these proven techniques in the field of cluster ion research.

3 PULSED ION SOURCES

3.1. Positively Charged Clusters

For 20 years, the ionized free jet has been recognized as the method of choice for forming cluster ions. Until recently, however, most cluster ion experiments have used the jet as a source of neutral clusters that were then converted to cationic clusters either by electron impact or photoionization. The ionic mass spectrum has typically been used as an indication of the neutral cluster distribution formed in the jet. Such experiments have been very successful in determining the bimolecular reaction kinetics of clusters with small molecules
[33–35]. These experiments all depend upon the ability to relate the intensity of a given ion observed in the mass spectrometer to the concentration of a neutral precursor(s). As a consequence, there is always concern over the extent to which fragmentation occurring in the ionization process may complicate or even invalidate the analysis. Very few studies have yielded definitive results regarding fragmentation branching ratios for the nascent ions. Buck and Meyer [36] have used elegant momentum transfer experiments to establish the fragmentation of argon clusters upon ionization. They report that clusters at least as large as \( n = 6 \) form primarily dimers upon electron impact ionization. This extensive fragmentation is actually responsible for the appearance of intensity anomalies (magic numbers [37]) in the ion cluster distribution, as we elaborate below. A second problem with neutral ionization methods (more important from the perspective of the techniques described here) arises from the internal energy content of the ionic cluster formed after ionization and fragmentation of a neutral. The sequence of events that likely occurs is vertical ionization of the neutral cluster to an internuclear configuration of the ionic cluster far from its equilibrium geometry [38]. The ion then relaxes toward the equilibrium geometry with concomitant vibrational excitation of the cluster. If the vibrational excitation exceeds the binding energy of neutrals, monomers may be ejected by the process

\[
M_n + e^- \rightarrow [M_n]^{+*} \rightarrow (n-\rho)M + M^+_\rho + 2e^-
\]

until the internal energy of \( M^+_\rho \) is below the bond dissociation energy \((M^+_{\rho-1}) - M\). We therefore expect that the product ionic cluster will be in general internally excited to an extent roughly comparable to the bond energy of one neutral monomer unit.

In order to overcome difficulties associated with the internal excitation inherent in direct ionization sources, a significant effort has been devoted to develop alternative preparation schemes yielding controlled internal energy ion clusters. The technical demands on the source are quite different for forming clusters of volatile species as compared to the case of refractory precursors, so we review the methodology of each type of source separately.

3.1.1 Molecular or “van der Waals” Ionic Clusters

The solution to the internal energy problem was demonstrated as early as 1973, when Searcy and Fenn [39] showed that large, cationic water clusters were formed in an ionized free-jet by sequential association of neutral monomers onto an ionic core. The dependence of the cluster size distribution on jet conditions clearly showed that the three-body association reactions,

\[
H_2O^+(H_2O)_n + H_2O + Ar \rightarrow H_3O^+(H_2O)_{n+1} + Ar
\]

were occurring in the high-density region of the expansion where small ions were forming nucleation centers for the synthesis of the larger clusters. Although
there is at present only indirect evidence regarding the internal temperature of the cluster ions, it is likely that the more probable two-body collisions will relax the nascent cluster before another monomer is added to the cluster and releases another bond energy of internal excitation.

In Fenn’s work, as well as in more recent studies by Beuhrer and Friedman [40] on large water cation clusters and by Harris et al. [41] on rare gas clusters, ionization was effected by a high-voltage pin located on the high-pressure side of the nozzle. Since the ions were formed by a corona discharge and entrained in the jet, it may seem surprising that the clusters are not broken apart due to high energy collisions as the ions are driven by the high electric field. Not only are the clusters intact, but Carrick and Engelking [42] have recently dispersed the fluorescence from molecular ions and neutral radicals created in a discharged nozzle and found that the electronically excited states are rotationally cooled to about 20 K. It is apparent that the expansion is relatively unafflicted by the voltage creating the discharge because a high free electron density forms an overall electrically neutral plasma that shields the core of the jet.

Although the methodology of producing internally cold cluster ions has been in hand for some time, as of 1984 these ion sources were intrinsically continuous and as such were best used in conjunction with cw lasers. The broad tunability of pulsed lasers and the vast reduction in the scale of molecular beam machines using pulsed expansions provided a powerful incentive to develop ways of coupling pulsed expansions to the cold ion-beam techniques based on nucleation.

This coupling was initially carried out by spectroscopists primarily interested in isolating cold monomer ions for high-resolution experiments. The approach envisioned by several spectroscopy groups involved first cooling neutral species and then ionizing them with high energy electron impact to create ions to be studied. High energy electrons (> 100 eV) were used so that high ionization potential species could be studied and so that little angular momentum would be imparted to the cation provided the electron molecule interaction is fast compared to nuclear motion (i.e., within the Born approximation) [43]. Using this method, Miller et al. [44, 45] at Bell Laboratories, Carrington and Tuckett [46] at Cambridge, Klapstein, et al. [47] at Basel, Alexander et al. [48] at JILA and Johnson et al. [49] at Stanford all reported cold spectra of cations in the years 1979–1983. In carrying out these experiments, care was taken to minimize external electric and magnetic fields in order to avoid changes in the ion trajectories resulting in collisional heating of the ions by collision with the neutral expansion. In virtually all of the experiments, a molecular beam was ionized by an electron beam that crossed about 1 cm downstream from a continuous nozzle, in an arrangement in which the filament of the electron gun was floated negative and the electrons accelerated to ground when they crossed the molecular beam, so that cations are created in a field-free environment. Typical electron beam currents are on the order 0.1–1 mA. Moreover, since the ionization is carried outside and independent of the nozzle, the technique is completely compatible with pulsed valves and hence forms a high-intensity pulsed cluster ion source.
Early experiments concentrated on determining the rotational temperature of excited states formed directly by electron impact ionization [45, 46], and the rotational temperature determined for the N$_2^+$ B$^2\Sigma^+$ state is typically 20 K. In 1982, Johnson et al. [49] and Miller [50] obtained laser-induced fluorescence (LIF) spectra of CO$_2^+$ and C$_6$F$_5$H$^+$, respectively, and showed that the ground electronic states of the ions, which drifted for tens of microseconds in the field-free expansion, were also rotationally cooled to about 20 K. In the CO$_2^+$ study, optical–optical double resonance experiments were also carried out that labeled a specific lower state rotational level by selective removal of its population and detection of the "hole" in the rotational distribution with a second laser about 500 ns later. No collisional satellite double resonance transitions were observed. In 1983, Johnson et al. [51] incorporated the pulsed valve into a cold ion apparatus to enhance signal to noise (S/N) and reported the observation of microwave transitions of the CO$^+$ ion. In their microwave-optical double resonance experiment, the ions drift over 10 cm between rotational excitation and detection of the population shift caused by the microwave absorption. No collisional features were observed in the double resonance spectra. These results demonstrate that not only are ions cooled in the low temperature of the jet but that downstream from the nozzle they exist in a nearly collisionless environment. A crude estimate of the ion density based on the LIF signal intensity reveals that the cation density in the pulsed expansion is quite large, $\sim 10^{9}$/cm$^3$ at a distance of 15 cm downstream from the orifice, far in excess of the space-charge limited density.

In addition to establishing that the jet is indeed a collisionless environment for ions, the microwave experiments also showed that small electric and magnetic fields had no effect on the rotational distribution. The ability of the jet to support such large ion densities, the insensitivity of the system to external fields, and the efficiency with which ions are rotationally cooled are explained by the high electron density existing in the ionized jet. The free electron density was directly measured using the Fabry-Perot cavity that introduced the microwave field into the vacuum chamber [51]. Because the microwave frequency resonant with the cavity depends on the index of refraction of the medium in the cavity, the resonant frequency was observed to shift when the electron beam was turned on. The refractive index of free electrons is known to depend on the free electron density [52], and the cavity shift of several Megahertz at 120 GHz reveals a free electron density of about $10^7$/cm$^3$, roughly the same concentration as the cations indicated by LIF. It is also clear that these electrons must have energies much less than 1 eV or the electron–neutral collisions would cause rotational excitation [45]. The free jet is thus a cold, overall electrically neutral plasma with a sufficiently high free electron density to have a short penetration depth (Debye wavelength) for external electric fields.

The pulsed jet cold cation source can be regarded as a partially controlled ionization analog of the high-voltage corona discharge type of apparatus. It is now clear that significant cluster formation must have been occurring in the monomer ion spectroscopy studies but went unnoticed since the cluster ions
usually have completely different electronic structure than the monomer ions and therefore do not absorb near the monomer bands. The external electron beam ionization scheme is ideal for use with a pulsed valve and has the additional advantage of creating the ions in a well-defined environment. The scale of the pulsed ion source apparatus is very much reduced from that of the continuous ion sources and is easily configured for laser spectroscopy experiments.

As an indication of the ease with which clusters are formed with the ionized pulsed jet, Fig. 2 presents mass spectra [14] from the Boulder cooled ion source as a function of the distance Z between the 1-keV electron beam and the orifice (see Fig. 10 for definition of Z). The top trace shows ionization at 2.8 cm, and the cation spectrum contains only the CO$_2^+$ monomer ion. This corresponds to the condition used for the monomer ion spectroscopy experiments. As the electron beam is moved closer to the orifice, the lower traces in Fig. 2 show a gradual shifting of the charged species to larger and larger clusters. The mechanism of the cluster growth is seen to be sequential addition of neutrals, as expected from the nucleation experiments [39–41]. Indeed, we can “fine tune” the cluster distribution with the electron beam position, giving this apparatus great flexibility. In contrast with the corona discharge sources, in which the cluster distribution is altered by varying beam conditions (e.g., backing pressure, stagnation temperature, nozzle diameter, and seed ratio), each requiring a significant change in the experimental configuration, the electron beam effects changes immediately observable when detected with TOF mass spectrometry.

The fact that cations seeded into the expansion form nucleation sites for cluster growth results from the enhanced bimolecular collision rates of the ion–neutral encounters compared with those between neutrals in the low ambient temperature of the jet. For neutrals, the rate of bimolecular collisions suffered by a molecule is given by

$$R = N \cdot V_{\text{rel}} \sigma(V_{\text{rel}})$$  

(1)

where $V_{\text{rel}}$ is the center-of-mass collision velocity, $\sigma(V_{\text{rel}})$ is the velocity-dependent cross section, and $N$ is the collision gas density. For hard sphere collisions, $\sigma(V_{\text{rel}}) \approx \pi D^2$ so that $R \propto \sqrt{T}$ and rate of neutral–neutral collisions falls off rapidly with decreasing temperature. On the other hand, at least in the Langevin approximation [53], the rate of ion–molecule collisions is governed by the long-range ion-induced dipole interaction that yields a cross section proportional to $1/\sqrt{T}$ and a nearly temperature-independent collision rate given by $k_L \cdot N$ where $k_L$ is the Langevin rate constant, usually on the order $10^{-9}$ cm$^3$/molecule-s. An ion can therefore be introduced into the jet in a regime in which the neutrals are essentially collisionless, while an ion still suffers a high rate of collisions.

As an illustration of the above statements, we estimate the behavior expected for an expansion such as that used in generating the (CO$_2$)$_n^+$ clusters in Fig. 2. The expansion conditions are 2 atm stagnation pressure and a nozzle diameter of 1 mm. We can calculate the density $n(x)$ and local translational temperature $T(x)$
Fig. 2. Time-of-flight mass spectra using a 1-keV electron beam to ionize a CO₂ pulsed free jet expansion, where the distance from the electron beam to the nozzle is varied. Clusters result from successive attachment of CO₂ monomers not from ionization of neutral clusters. Reproduced with permission from Johnson et al. [14].
at a distance \( x \) downstream on the axis of the expansion according to the well-known formulas [54]:

\[
n(x) = n_0 \left[ 1 + \frac{\gamma - 1}{2} A^2 \left( \frac{x}{D} \right)^{2(\gamma - 1)} \right]^{-1/(\gamma - 1)}
\]  

(2)

\[
T(x) = T_0 \left[ 1 + \frac{\gamma - 1}{2} A^2 \left( \frac{x}{D} \right)^{2(\gamma - 1)} \right]^{-1}
\]

(3)

where \( \gamma = C_\mu/C_\nu \), \( D \) = nozzle diameter, \( A \) is related to the Mach number \( M \) by

\[
M = A \left( \frac{x}{D} \right)^{\gamma - 1}
\]

(4)

which is tabulated for various species. Using these expressions, we estimate the density and temperature 5 mm downstream to be \( 2.3 \times 10^{16} \) molecules/cm\(^3\) and 15 K. If we take the hard sphere collision cross section for CO\(_2\) to be about 50 Å\(^2\), Eq. 1 implies that the rate of neutral collisions is \( 3 \times 10^3 \) s\(^{-1}\), whereas ionic collisions occur at the Langevin rate of \( 2 \times 10^7 \) s\(^{-1}\). Thus ion–molecule collisions are about 100 times more probable than collisions between neutrals. For efficient nucleation to take place, these bimolecular collisions must occur during the lifetime \( T_c \) of the ion–molecule collision complex \([\text{CO}_2^- - \text{CO}_2^+]\)*

\[
\text{CO}_2^+ + \text{CO}_2 \rightarrow [\text{CO}_2^- - \text{CO}_2^+]^*
\]

\[
[\text{CO}_2^- - \text{CO}_2^+]^* + \text{CO}_2 \rightarrow (\text{CO}_2)_2^* + \text{CO}_2.
\]

If the stabilizing collision is assumed to proceed with the bimolecular ion–molecule rate, efficient clustering occurs when

\[
\frac{1}{T_c} = n(x) \cdot k_c
\]

For the CO\(_2\) cluster spectrum shown in Fig. 2, clustering is seen to be almost complete at \( x = 3 \) mm from the nozzle, which implies that the complex lifetime must be on the order of tens of nanoseconds. Thus there are two effects that can allow ionic species to dominate clustering: the enhanced bimolecular collision rate and the enhanced complex lifetimes.

Van Koppen et al. [55] have recently investigated the temperature dependence of the three-body association rates for the system

\[
\text{N}_2^+ + \text{N}_2 + \text{M} \rightarrow \text{N}_4^+ + \text{M}
\]

and found that the third-order rate coefficient increases continuously from 450
down to 80 K. Their experimentally determined expression for the rate constant $k$ is

$$k = \frac{k_s \beta k_s}{k_b + \beta k_s [M]}$$

where $k_s$ is the bimolecular collision rate, $k_s$ is the rate of stabilizing collisions, each with efficiency $\beta$, and $k_s$ is the unimolecular dissociation rate of the $[N_4^+]^*$ complex. Using Langevin rates for $k_s$ and $k_a$, these authors find that the temperature dependence is due to the increase in RRKM lifetime of the complex.

![Diagram](image)

**Fig. 3.** Temperature dependence of the $(N_4^+)^*$ unimolecular decomposition rate constant. Calculated for the nitrogen association complex at several values of the total pressure $P_M$. Reproduced, with permission from van Koppen et al. [55].
as the temperature is decreased. The derived values of the rate constant $k_b$ for
dissociation of the $[\text{N}_4^+]^*$ complex,

$$[\text{N}_4^+]^* \xrightarrow{k_b} \text{N}_2^+ + \text{N}_2$$

are plotted in Fig. 3, where the complex lifetimes $1/k_b$ are indeed found to be in the
range of nanoseconds. Interestingly, extrapolation of their data to 15 K (the
temperature of the CO$_2$ jet) yields an estimate of about 20 ns for the $[\text{N}_4^+]^*$
collision complex. This estimate is actually quite consistent with our estimate of
10–50 ns for the (CO$_2$)$_2^+$ complex lifetime based on calculated jet conditions and
the observed loss of the monomer ion.

By moving the electron beam very close to the nozzle, the ion collision
frequency continues to rise, and quite large clusters can be formed with the
nucleation technique. Figure 4 displays the cluster distribution generated from a
pure carbon dioxide expansion, showing cations containing up to 60 CO$_2$
monomers. At least a portion of the falloff at large clusters is due to decreasing
sensitivity of the ion detector. The simple addition of a “conversion dynode” [40]
would likely extend considerably the maximum useful cluster size. In comparision,
the continuous corona discharge used by Harris et al. [41] was able to
generate larger clusters of rare gases containing up to 200 atoms, and Beuhler and
Friedman [40] have made water cation clusters with $m/e \sim 59,000$! Presently, the
pulsed jet techniques appear most useful for cluster sizes below 100, but the use of
more energetic ionizing electrons and higher stagnation pressures would likely
increase this limit substantially.

![Image](image-url)

**Fig. 4.** Large cation clusters of CO$_2$ obtained from 1-keV electron beam ionization of a CO$_2$ pulsed
expansion. Levinger et al., unpublished results.
3.1.2 Cluster Ions of Metals and Semiconductors

The development of metal and semiconductor cluster ion beams parallels that of the molecular ion clusters. In 1972, Takagi et al. [56] reported an apparatus for generating metal cluster ions based on a heated oven to vaporize the metal, followed by expansion of the metal through a nozzle and ionization of the expansion by electron bombardment. The approach is similar to that reported by Searcy and Fenn [39] in their 1973 study of water cation clusters, except that ionization is achieved by passing the beam through a high current ($\sim 1/2$ A) electron shower instead of a discharge. The metal ion cluster beam technique has grown into a large area of activity in materials research, since the beam can be used to prepare many kinds of semiconductor and metallic surfaces otherwise difficult to generate [57]. Although these “hot oven” methods are very productive, they are not readily transferred to the pulsed jet technique, since the valve would be required to operate under extremely corrosive high temperature conditions. They also require large amounts of material and probably do not achieve the cooling available from the hard pulsed expansion. Fortunately, recent results show that the ions of refractory materials may also be introduced into the pulsed-free jet [58, 59].

Laser methods for preparing cations of refractory materials actually date back to 1963 when Honig and Woolston [60] at RCA observed ions emanating from various surfaces (Cu, Mo, Ta, W, C, Ge, SiC, Al$_2$O$_3$) when exposed to a focused 0.4-J pulse from a ruby laser. These authors found that up to $3 \times 10^{16}$ electrons could be ejected per pulse, yielding peak positive ion currents of up to 500 mA. Later in that year, Howe [61] determined the temperature of the plasma to be in the range of 3000–10,000 K by dispersing the CN optical emission. He graphically describes [61] the effect: “It is known that the output beam from a pulsed ruby laser can be focused upon the surface of a suitable target to produce high temperatures and spectacular pyrotechnic displays. When the laser beam was focused on this material [graphite], a mushroom-shaped jet, blue white in color and over 1 cm long, resulted.” In the following year, Berkowitz and Chopka [62] used mass spectrometry to isolate the neutral component of the laser plume in the vaporization of graphite and found a C$_n$ distribution which for $n < 11$ shows significant even–odd intensity alternations. Somewhat prophetically, they warned that this distribution probably did not reflect the primary cluster distribution created by the laser because the local density in the focal region was sufficiently high to create a miniature supersonic expansion, altering the distribution via three-body association reactions! Over the past 30 years, the use of laser vaporization to characterize surfaces has become a standard technique, laser desorption mass spectrometry (LDMS) [63].

Although the ability of pulsed lasers to create ions and cluster ions was known from the earliest days of the ruby laser, the development of effective laser vaporization sources required another dozen years. One obstacle was that the surface is destroyed by the laser after a few pulses, requiring that a fresh surface be presented to the focal point on every few shots. Velghe and Leach [64] overcame this difficulty in 1976 with the apparatus shown in Fig. 5, where a rod of metal is
Fig. 5. Schematic diagram used by Velghe and Leach [64] of the laser vaporization apparatus that incorporated a rotating target. Reproduced with permission from Ref. [62].

Fig. 6. Cluster ion source used by Brucat et al. [58] to generate cold metal clusters by carrying out the vaporization before expansion. Reproduced with permission.
continuously rotated and advanced. The primary interest of these authors was the spectroscopic characterization of small radicals formed in the neat vapor or by subsequent reactions. Cody et al. [65a] have also used the laser vaporization technique as a pulsed ion source for kinetic and spectroscopic studies in the pulsed ICR trap, and Weisshaar and co-workers [65b] have created metal ions using laser vaporization for study in a fast flow reactor.

From the extensive literature on the generation of ions by laser vaporization, it is clear that it is a viable pulsed alternative to the ionized metal oven for cluster ion formation. To use it effectively, however, we must reckon with the difficulty that ions generated in the plume are very hot and as such are not ideal targets for spectroscopic studies. In 1981, Smalley et al. [66] and Bondybey and English [67] demonstrated a method for cooling the metal atoms formed in laser vaporization. The Smalley ion source is depicted in Fig. 6. In this approach, the metal is vaporized inside a channel about 2 mm in diameter, and the vapor is entrained in a high-pressure burst of helium from a pulsed valve. The rotating rod is incorporated into the channel of the jet. The laser is timed to overlap with the peak density of the helium flow, and the atoms are entrained in the channel and cooled to room temperature and then expanded in a free jet. Large, cold neutral clusters are formed after expansion; they are then photoionized with an excimer

![Diagram](image_url)

**Fig. 7.** $C_n^+$ and $C_n^-$ cluster distribution obtained by O’Brien et al. [68] using the laser vaporization ion source. Reproduced with permission.
laser to detect the cluster distribution. High-resolution studies using resonant two photon ionization (R2PI) [66] and laser-induced fluorescence [67] have been carried out on many dimers (e.g., Pb₂, Mo₂, Sn₂) and establish that the clusters are cold. Unfortunately, ionization of cold neutral clusters does not guarantee that the ions will be vibrationally cold, since the ionization step is a Franck-Condon process and the internal vibrational energy of the ion is determined by changes in structure between ion and neutral. Devices based upon the initial Smalley design and its further refinements are now used in many laboratories.

Brucat et al. [58] and Bloomfield et al. [59] have recently shown that the plasma initiated by the vaporization laser is itself an efficient ion source. Thus, with the laser vaporization cluster sources, cluster ions are directly produced so that photoionization of neutral clusters is not required. High-resolution studies of the Nb₂⁺ system confirm that cationic clusters are indeed rotationally cold. In addition, the shower of free electrons generated by the vaporization laser via the photoelectric effect allows efficient production of a neutral plasma described in the earlier discussion of van der Waals clusters. Because the electrons move much more rapidly than the clusters, vaporization in the high molecular density region as shown in Fig. 6 seems essential to confine the electrons before they fly away from the plume. O'Brien et al. [68] have used this source to obtain the mass spectra of ionic clusters of carbon shown in Fig. 7, indicating that both positive and negative ions are efficiently produced. As we will see in the next section, the presence of a high density of low energy electrons in the jet plasma generally creates a very fertile medium for synthesizing negative ions and cluster ions. The formation mechanism for negative cluster ions is significantly different than that operative for cations, however, as we discuss in the next section.

3.2 Negatively Charged Clusters

3.2.1 Molecular Ion Clusters

Negatively charged clusters have generally been considered more difficult to prepare, since they cannot be created by simple ionization of a parent neutral as can positive ions. Two processes commonly exploited [69] for negative ion production are three-body stabilization

\[ RA + e^- + M \rightarrow RA^- + M \]  \hspace{1cm} (5)

and dissociative attachment

\[ RA + e^- \rightarrow A^- + R \]  \hspace{1cm} (6)

An example of the dissociative attachment mechanism for molecular species is the formation of O⁻ from N₂O [70]:

\[ e^- + N_2O \rightarrow O^- + N_2 \]
which is often used as a starting reagent in negative ion flowing afterglow reactors.

In general, we might not expect 6 to be very efficient since the time scale for electron motion is much faster than that for the nuclei, and this mechanism requires “catching” the electron while it is transiently attached to the molecule. Therefore, it may be surprising that Klots and Compton [71] have demonstrated a cluster variation of dissociative electron attachment, “evaporative attachment,” where the “third-body M” in 5 is actually a part of a cluster. Thus the process is

\[ \text{e}^- + M_n \rightarrow M_m^- + (n - m)M \]  \hspace{1cm} (7)

where the negative ion is stabilized by ejection of neutral monomers. This evaporative attachment mechanism 7 can be considered to be a combination of 5 and 6, where the incipient M\(^-\) species is stabilized by collision with monomers already attached to the cluster.

The formation of oxygen negative ion clusters affords a good example of how the electron attachment occurs. First, consider the inelastic collision of a low energy electron with an isolated O\(_2\) molecule

\[ \text{e}^- + \text{O}_2(v = 0) \rightarrow \text{O}_2(v = 1) + \text{e}^- \]

Spence and Schulz [72] have determined the electron energy dependence of this process and found that the cross section for vibrational excitation shows several peaks occurring at collision energies corresponding to resonant formation of autodetaching vibrational states of O\(_2^-\) with \(v > 3\),

\[ \text{e}^- + \text{O}_2 \rightarrow \text{O}_2^-*(v > 3) \rightarrow \text{O}_2(v = 1) + \text{e}^- \]

Now these transient O\(_2^-\) \((v > 3)\) negative ion states are estimated [73] to be rather long lived (about 100 ps) so that at resonant energies we might expect an enhancement of the three-body association reaction,

\[ \text{e}^- + \text{O}_2 + \text{O}_2 \rightarrow \text{O}_2^- + \text{O}_2 \]

Such an enhancement is indeed found, as shown by the experimental results of Spence and Schulz [74] where the electron energy dependence of the inelastic scattering process is seen to be nearly identical with that of electron attachment. In 1978, Klots and Compton [71] realized the implication of these data on the possibility of forming negative ion clusters. They reasoned that attachment to neutral clusters such as O\(_2^-\)·O\(_2\) should be very efficient since the capture cross section for the electrons is likely to be similar to that of the monomer, whereas the stabilization step is very efficient, owing to the long lifetime of the resonance and the expected short vibrational predissociation lifetimes that stabilize the cluster ion before the electron detaches. Klots and Compton [71] demonstrated that
negative cluster ions of light molecular gases such as CO₂ and N₂O are efficiently formed when low energy electrons are injected into a supersonic expansion of pure CO₂ or N₂O. Shimamori and Fessenden [75] find that the oxygen dimer has a significant effect on the thermal electron attachment rate to oxygen as evidenced by the anomalous temperature dependence of the three-body rate constant.

In light of the above discussion, it is clear that the efficiency of negative cluster ion formation will depend on the electron energy. Märk and co-workers [76–78] have recently reported the electron energy dependence of cluster formation for the CO₂, N₂O, and O₂ systems. For all three systems, it is clear that large negative ion formation is optimized with low energy (effectively zero energy) electrons. Thus the problem of negative ion formation lies in finding efficient ways to inject low energy electrons into the jet.

Many ingenious approaches have met with varying degrees of success with the problem of injecting the low energy electrons. The inherent problem with producing the ions with an electron gun is, of course, that the coulombic repulsion limits the electron density and hence low energy electron beams typically have very low flux. Bowen and co-workers [79] have used electron transfer from alkali atoms to species such as (Cl₂)ₖ to create a variety of negative molecular ion clusters. Haberland et al. [80] have been particularly successful in forming clusters of (NH₃)ₖ⁻ and (H₂O)ₖ⁻ using both the photoelectric effect to inject electrons in the high density region of the expansion and discharging the expansion with a heated filament. More recently, Bowen and his students [81] have used a variation on Haberland's filament approach to generate a variety of clusters of both metals and nonmetals.

Perhaps surprisingly, the high energy (∼1 keV) electron impact ionized jets described in the previous section are excellent sources of negative ion clusters. This could have been anticipated based on the description of the characteristics of the ionized jets as a dense free electron plasma. Moreover, since these jets have been observed to preserve the rotational cooling achieved by the expansion, the average electron energies must be low (<1 eV) or the electron neutral collisions would result in rotational excitation. The mechanism for production of these low energy electrons starting with keV electrons must involve the secondary electron formed in the initial ionization step:

\[ e^- + O_2 \rightarrow O_2^+ + e^- (<10 \text{ eV}) + e^- (~990 \text{ eV}) \]

That is, one electron comes off slowly, and the high energy electron loses only a small fraction of its original energy and continues on through the jet. For ionization in the dense part of the jet, the high energy electron beam penetrates through the gas, leaving a trail of low energy electrons. Since the jet is observed to be electrically neutral, the high energy electron must eventually scatter out of the jet, whereas the low energy electron cools in the jet through inelastic scattering events.

For example, the electron impact ionization cross section [82] of N₂ for a 1-keV electron is about \(10^{-16}\) cm\(^2\), so that at a density just outside the throat of a 1-
mm nozzle of about $10^{17}/\text{cm}^3$, each primary fast electron suffers an average of about one ionizing collision, producing one cation and one low energy electron. At higher molecular densities, the low energy electron yield can, in principle, exceed that obtained from the 1-keV gun. For oxygen, the electron thermalization rate has been determined [83] to be 1.7 torr-µs so that just outside the nozzle where the density is equivalent to about 10 torr pressure we expect rapid thermalization of the electrons resulting from ionization. Note that rare gases are about two orders of magnitude less efficient [83] at electron thermalization, so that helium expansions may well be less favorable negative ion sources.

To illustrate the performance of this source, the top trace in Fig. 8 presents the negative ion mass spectrum obtained from a CO$_2$ expansion [84] ionized under similar conditions as the cation cluster spectrum shown in Fig. 2. The peak intensities of the anion spectra are about a factor of 10 lower than the cations. Ionization at 2.5 cm from the nozzle creates very different size cluster ions in the positive and negative channels. Large negative ion clusters (up to 17 monomers) are produced in a regime in which only the monomer cation is evident in the mass spectrum. The implication is that the production mechanisms

![Fig. 8. Dependence of negative cluster ion distributions on the distance Z from the electron beam to the nozzle taken from Alexander et al. [84] Unlike the positive ion clusters (Fig. 2), the negative cluster ions are relatively insensitive to the ionization distance. Reproduced with permission.](image-url)
are different since the negative ion clusters can be formed by evaporative
attachment to neutral clusters, whereas cations are formed by nucleation of
neutral clusters onto monomer ions. This is particularly evident in the CO$_2$
case since the monomer ion CO$_2^-$ is not observed in the mass spectrum and in fact is
not a stable species [85]! It has been observed as a long-lived species, however,
in both ion-molecule reactions and charge exchange with Cs [85] and by low
energy electron attachment to neutral carbon dioxide clusters [77]. The anion
cluster spectrum in Fig. 8 can also be used to establish a bound on the electron
energy. Knapp et al. [77] have shown that the energy threshold for production
of CO$_3^-$ is about 3 eV. This ion is absent from the 1-keV electron impact
ionized jet mass spectrum, indicating that most of the electron in the expansion
are less than 1 eV. The anion spectrum can be affected by the position of
ionization, however, and the bottom trace in Fig. 8 shows the (CO$_2$)$_n$-
distribution for ionization at 0.5 cm, indicating that larger clusters can be formed
by nucleation reactions. Negative ions appear to be different from cations in that
the nucleation ions are themselves clusters.

This asymmetry between positive and negative ion formation is caused by the
kinetics of the ion formation step. For positive ions, the association rates are
likely to be similar for the monomer ion and small cluster ions, and the rate of
formation of monomer ion relative to cluster ions by direct electron impact is
governed primarily by relative abundances in the jet. Since under typical
conditions (1-atm backing pressure, 300 K, nonhydrogen bonded species) neutral
clusters are only about 0.1% of the monomer density [86], most cation clusters
are formed from the monomer ion. Note also that ionization usually takes place
close to one nozzle diameter away from the orifice, implying that only mild
cooling has occurred and clustering of the neutral is not complete. For the
negative ions, there is no direct monomer channel leading to ion production, so
the competing processes are binary and ternary electron–molecule collisions:

\[ e^- + O_2 + O_2 \xrightarrow{k_1} O_2^- + O_2 \]

\[ e^- + (O_2)_n \xrightarrow{k_2} (O_2)_n^- + (n-m)O_2 \]

These processes lead to an expression for the relative rates $R_1$ and $R_2$ for $O_2^-$
formation:

\[ \frac{R_1}{R_2} = \frac{[O_2]^2 k_1}{[(O_2)_2]} k_2 \]

If the density of O$_2$ monomers is about $10^{17}$ cm$^{-3}$ just outside the nozzle and the
percentage of dimers in the beam is 0.1%, $k_1 \sim 10^{-31}$ cm$^3$/s [75] and $k_2 \sim
10^{-9}$ cm$^3$/s, the rate for anion formation by three-body addition to a monomer
is one-tenth that for evaporative attachment to a neutral cluster: Most negative
ions are thus created from neutral precursor clusters in the jet. The suggestion
that the negative cluster ions are created by evaporative attachment in the pulsed expansion is confirmed by the cluster size distributions shown in Fig. 8. This figure shows that the size distribution is relatively insensitive to changes of over an order of magnitude in the neutral concentration at the point of ionization.

The role of neutral clusters in negative ion formation is also supported by comparing the electron beam generated cluster size distribution with that obtained using controlled low energy electron impact [76] and electron transfer from Rydberg states in collision with rare gas atoms [87]. The \((\text{CO}_2)_n^\text{−}\) distribution obtained from the low energy attachment,

\[
e^- + (\text{CO}_2)_n^\text{−} \rightarrow (\text{CO}_2)_m^\text{−} + (n-m)\text{CO}_2
\]

was recently determined by Stamatovic et al. [76], and their spectrum is quite similar to the \(\text{CO}_2\) negative cluster ion formed by the high energy electron impact source shown in Fig. 8, including the intensity anomalies described as “magic numbers.” This similarity is also observed for water clusters, where the low energy electron injection distribution is observed [88] to create clusters beginning at about \(n = 13\), a pattern that is also observed for the 1 keV electron beam source [89].

3.2.2 Cluster Ions of Metals and Semiconductors

The essential features of the electron beam ionized jet that lead to large negative cluster ion formation and extensive cooling are duplicated in the pulsed jet-expansion chamber version of the laser vaporization experiments. Zheng et al. [90] at Rice and Bloomfield et al. [59] at AT&T Bell Laboratories have recently shown that indeed the laser vaporization technique is capable of generating intense, pulsed negative cluster beams of refractory materials. The group at AT&T Bell [59] has reported negative ions of carbon and silicon and the Rice group [15, 58, 90] has applied the technique to Ag, Cu, Nb, Ni, and C. Based upon the results of these experiments, the evaporative attachment mechanism involved for negative ion formation from neutral van der Waals clusters may not account for cluster negative ion formation in metals. This fact is due to the much larger binding energy of metal atoms in the cluster ion compared to that of the van der Waals case. In the \(\text{Cu}_n^\text{−}\) system, for example, the binding energy [15, 58] is on the same order as the electron affinity of the cluster. Therefore, the incipient ion cannot eject multiple neutral atoms but rather must be stabilized by collisions with helium.

Finally, an advantage of either version of the negative ion jet ion sources is that the cluster ions are likely to be cooled internally to an extent that high-resolution spectroscopy experiments may be attempted. Certainly, significant cooling occurs since clusters of weakly bound species such as argon and neon atoms can be formed with both metals and nonmetals. In the case of cations, spectroscopic experiments [58] indicate that the clusters are vibrationally and rotationally cold. However, we know of only one direct determination [22] (on \(\text{O}_2^\text{+}\)) of the internal energy distribution of anion clusters and therefore caution against
presuming that these species are cooled to the translational temperature of the jet. Indeed, such experiments would be extremely valuable and represent a significant challenge for experimentalists. It is likely that internal energy measurements will use spectroscopic methods. With this in mind, the next section summarizes the pulsed spectroscopic techniques currently in use to characterize the cluster ions.

4 MASS SELECTION

4.1 Primary Ion Beam

Although the use of pulsed jet cluster ion sources is well established, there is an intrinsic disadvantage when using such sources in conjunction with mass spectrometry to select a specific cluster size for study. This disadvantage results from the necessity of allowing the ions to continue to expand in the jet until the neutral density is sufficiently low that the ionic clusters are not collisionally activated upon extraction from the expansion. In addition, the plasma that acts to shield the ions in the expansion from external fields must be broken down by the extraction voltage as well. A free drift region of about 15–20 cm is sufficient to allow extraction, but because of the 1/r^2 fall off of the density, the initially compact ion cloud is now spread out over about 5 cm on either side of the flow axis. Thus, although TOF mass spectrometry is the natural choice for mass selection, we are faced with two problems before it can be effectively implemented for laser experiments: first, the inherent mass resolution limit caused by the large spatial spread, and, second, the necessity to obtain spatial compression of the mass selected ions in order to achieve efficient overlap with a pulsed laser beam.

These problems are simultaneously overcome using a space-focusing TOF mass spectrometer first demonstrated by Wiley and McLaren [91] in 1955. These authors show that the resolution loss due to the spatial extent of the ions in the source can be compensated, to the order of the first moment of the spatial distribution, simply by accelerating the ions through two regions with appropriately chosen, different electric fields, followed by the usual drift region. Wiley and McLaren [91] were interested in improving the resolution of an electron bombardment ion source, where the spatial extent of the ions was on the order of a few millimeters, the diameter of the electron beam. Since the ions in the jet source are spread over several centimeters, the focusing conditions must be altered somewhat from the Wiley-McLaren condition. We consider the spectrometer to be optimized when the arrival time T of an ion is nearly independent of its initial transverse position in the source. Figure 9 presents the arrival times as a function of transverse position in the source for an optimized configuration, such as exists (Fig. 10) on the Boulder apparatus. It is clear that the optimum condition only exists for ions distant from the extraction hole. In this mass focusing technique, mass peaks are quite narrow at the half-width, but the line shape is generally asymmetric. There is a sharp edge on the long time side, but the peak has a significant tail toward shorter times extending over several microseconds, and we must guard against the possibility that a low-level
Fig. 9. Calculated arrival times as a function of the initial transverse position of ions in the source for an optimized Wiley-McLaren [91] TOF mass spectrometer, From M. J. DeLuca and M. A. Johnson, unpublished results.

A background of ions from nearby masses might contribute to the observed signal in photofragmentation experiments.

To couple this two-field TOF spectrometer to the cluster ion source, the ions prepared in the high density region close to the nozzle are allowed to drift 15–20 cm in a field-free region in the flow of the free jet. The expanding plasma passes between two plates separated by about 15 cm to avoid substantial interruption of the flow, since this could cause collisional dissociation or fragmentation. When the ion cloud passing between the plates reaches maximum intensity, the potential of one of the plates is rapidly switched with respect to the other, causing ions to accelerate toward the plates. Most ions simply collide with the plates; however, a cylindrical volume of ions passes through a 4-mm-diameter aperture, is accelerated in a second region about 5 cm long, and is then allowed to drift 1.5 m where the beam is focused in a plane perpendicular to the drift axis.

The apparatus used by Johnson et al. [14] is shown schematically in Fig. 10, and typical mass spectra are shown in Figs. 2, 4, and 8. The time evolution of ions of a given mass is indicated by the small dots in Fig. 10, and the compression of the ion beam as it nears the focus is illustrated by the density of the dots. A mass resolution \( m/\Delta m \) of 200–300 can be obtained for the parent ion whose energy spread is about 500 eV (resulting from the differing formation positions in the first transverse field) with a mean energy of order 3 keV. For mass spectral characterization of the beam, an electron multiplier is placed at the focus, whereas the laser experiments are carried out by timing the laser to intersect the ion beam at this space focus at the precise time that the ion of interest is transiently focused.
Fig. 10. Schematic diagram of the tandem TOF photofragmentation mass spectrometer used by Alexander et al. [107]. Reproduced with permission.
This does not require physically removing the multiplier, however, since the position of the focus can be varied in a calculable fashion with the voltages used in the two-stage acceleration region.

Note that there is no necessity to pulse the ion formation (e.g., with a pulsed electron beam) since the leading edge of the draw out pulse initiates the TOF process, and the extraction voltage remains on until well after the pulsed valve closes. As long as this voltage is on, subsequent ions entering the region between the plates are accelerated into the plates well before the aperture and are not injected into the mass spectrometer.

4.2 Interaction of the Ion Beam with a Pulsed Laser

The space focusing described above that improves the resolution of mass spectrometry also creates an ideal ion target cloud for interaction with pulsed lasers. A 50-ns wide mass peak for a 2-keV ion beam implies that the ion cloud is less than 0.5 cm long. If a simple Einzel lens is used to focus the beam, about $10^5$ ions can be compressed into the focal volume of the laser beam with an area of 0.5 cm$^2$. Essentially 100% overlap can be achieved between the mass selected ion cloud and a pulsed laser. Since the pulse width of most common pulsed lasers (Nd:YAG and excimer, pulse width < 20 ns) is less than the time an ion is focused, mass selection of the parent ion can be achieved by timing the laser to pick off the desired mass at the focus during the 20-ns pulse width of the laser. Thus, with this relatively simple technology, the most difficult problem of using pulsed lasers in an ion-beam apparatus—poor beam overlap owing to the duty cycle of the pulsed laser—is substantially overcome. The TOF method in essence compresses about 20 μs of ion output from the jet down to 50 ns for optimal compatibility with the pulsed laser.

This new compatibility has significantly opened up the possibilities for laser studies on cluster ion beams. We now review two areas that have already benefited from application of these pulsed techniques: photofragmentation and photoelectron spectroscopies.

5 DETERMINATION OF CHARGED PHOTOFragments USING TANDem TIME-OF-FLIGHT MASS SPECTROMETRY

Whereas the resolution of the parent mass selection can be quite good, as described in the previous section, obtaining the mass spectrum of the photofragments is again complicated by the large energy spread of the parent ions. Two approaches have been used to overcome this difficulty:

1. Laser interaction with the high energy beam followed by fragment analysis using a reflecting field or “reflectron”

2. Deceleration before laser interaction followed by a second pulsed Wiley-McLaren mass spectrometer to mass analyze photofragments

Each approach has advantages, and we discuss them in turn.
5.1 Tandem TOF Using a Reflectron

In 1984, Johnson et al. [14] demonstrated the reflectron method on photofragmentation of \((\text{CO}_2)_n^+\) clusters with the apparatus shown in Fig. 10. Photofragments are separated from parent ions by reflecting the ions back at a 170° angle using a weak electric field so that the ions penetrate far into the reflecting field region before turning around. The first use of the reflectron technique was reported by Mamyrin et al. [92] in 1973, who demonstrated a resolution improvement of about a factor of 10 in TOF mass spectrometry by incorporating the reflecting region. The reason for this improvement is that, like the Wiley-McLaren scheme, the arrival times of ions are essentially independent of the energy of the ion. Boesl et al. [93] used this device for high-resolution multiphoton ionization experiments, and in 1981 they pointed out that the reflectron is also useful for determining the decomposition products from metastable decay of ions in the drift region before the reflecting field. Echt et al. [94] used a reflectron to observe collisional and metastable decay of ammonia cation clusters formed by multiphoton ionization of neutral ammonia clusters. Thus, based on the success of these workers in determining fragmentation patterns, the reflectron was a logical choice for the photofragmentation experiments. In addition, the reflectron does not require decelerating the ion beam, so that the focusing characteristics of the high energy cluster beam could be maintained.

The principle of the single field reflectron is that higher energy ions of a given mass spend longer in the reflectron field than lower energy ions of the same mass, but the higher energy ion traverses a drift region more quickly. Therefore, at some distance down the drift tube the faster ions delayed in the reflectron will catch up to the slower ions, at which point the ions at this \(m/e\) will be focused. If \(E_r\) is the reflectron electric field tilted at angle \(\phi\) with respect to the axis of the ion beam, \(L\) the length of the drift region, \(E_b\) the ion beam energy, the arrival time of an ion with mass \(m_p\) is

\[
T(m_p, E_b) = \frac{2m_p \sec \phi}{eE_r} \sqrt{\frac{2E_b}{m_p}} + L \sec 2\phi \sqrt{\frac{2E_b}{m_p}} \tag{8}
\]

If we impose the condition that \(dT/dE_b = 0\), i.e., the arrival time of a fragment ion with mass \(m_f\) is independent of initial energy, we find

\[
T(m_f, E_b) = L \left( \frac{m_f \sec \phi}{2 \langle E_f \rangle} \sqrt{\frac{2E_b}{m_p}} + \sec 2\phi \sqrt{\frac{2E_b}{m_p}} \right) \tag{9}
\]

where \(\langle E_f \rangle\) is the average energy of the fragment ions which penetrate a distance \(L/4\) into the reflectron. Equation 9 shows different mass ions with identical initial velocities are dispersed so that the photofragmented ions are indeed mass resolved. A resolution of about 150 has been demonstrated for the daughter ions in the reflectron experiments.
5.2 Tandem TOF Using Two Pulsed Fields

Bloomfield et al. [13] first carried out pulsed photofragmentation experiments with a tandem TOF instrument, investigating the Si$_2^+$–Si$_2^+$ systems. Brucat et al. [58] use a similar technique, and their apparatus is shown in Fig. 11. In their approach, the parent beam is decelerated before injection into the second mass spectrometer, which allows similar drift lengths and extraction voltages to be used on each spectrometer. Both spectrometers use the Wiley-McLaren focusing, and the second stage has been oriented either parallel and perpendicular to the first. Since the ions are decelerated before laser interaction, the laser timing cannot be used to achieve high mass resolution, since the focus of the first spectrometer occurs when the beam is at high energy. Therefore, a “pulsed mass isolator” or “mass gate” was used for parent mass selection, a device that consists of a short region that is electrically isolated and houses a set of pulsed deflector plates. This region is placed at the focus with the plates normally set to deflect the ion beam but when the desired mass passes through the plates are pulsed off so that this mass continues undeflected into the deceleration region. The resolution m/Δm reported using this technique, is greater than 100 for parent and photofragment ions.

The Smalley group [15, 58] has conducted several careful power dependences of the photofragmentation and photodetachment process for the metal cluster ions and has found multiphoton phenomena are prevalent at moderate laser powers. Studies of the fluence dependence of Fe$_6^+$ photodissociation [58] show that only Fe$_5^+$ is a one-photon product, with all of the smaller cation fragments resulting from two- and three-photon absorption. Strong nonlinear behavior is apparent at fluences below 10 mJ/cm$^2$, demonstrating that extreme caution must be exercised in carrying out the pulsed experiments to avoid multiphoton effects.

Smalley et al. [15] have used careful determination of the onset of one-photon

![Fig. 11. Schematic of the tandem TOF photofragmentation mass spectrometer used by Brucat et al. [58] that uses two pulsed acceleration regions. Reproduced with permission.](image-url)
induced photodissociation to measure the sequential bond dissociation energies and electron affinities of copper clusters and are presently pursuing this method on several transition metal systems. This group has also carried out photodetachment studies of negative metal cluster ions of copper and silver. Interestingly, $(\text{Ag})_{10}^+$ only photodetaches, whereas the $\text{Ag}_7^-$ photodissociates exclusively to $\text{Ag}_5^-$ and $\text{Ag}_5^-$. Both photodetachment and photodissociation channels are competing in the trimer anion.

6 PULSED PHOTOELECTRON SPECTROSCOPY USING TIME-OF-FLIGHT ELECTRON ENERGY ANALYSIS

The marriage of the pulsed laser and ion source has created new possibilities for photoelectron spectroscopy. Photoelectron spectroscopy (PES) of negative molecular ions was demonstrated first on $\text{O}_2^-$ and $\text{NO}^-$ in 1972 by Celotta et al. [95] using a continuous ion beam and the intracavity 488-nm radiation of an argon ion laser. Until 1986, all negative ion PES machines used concepts derived from this first device. Much of the work on photodetachment of molecular ions has recently been reviewed [97]. The groups have demonstrated that the continuous methods can also be applied to cluster ions. Bowen [21, 81] has reported spectra of $\text{NO}^-(\text{N}_2\text{O})_n^-$, $(\text{N}_2\text{O})_n^-$, $(\text{H}_2\text{O})_n^-$, $\text{H}^-\text{(NH}_3)_n$, and $\text{NO}^-(\text{RG})_n^-$ (RG = rare gas and $n \leq 3$), and Leopold and Lineberger [25] have recently obtained photoelectron spectra of $\text{Cu}_n^-$ with $n \leq 11$. The desirability of ultraviolet (UV) photons for PES studies of clusters derives from the typical solvation energies of ions. An ion with an electron affinity of 1 or 2 eV is readily studied with the 488-nm line from an argon laser, but each solvent molecule clustered to the ion will increase the electron affinity roughly by the solvation energy, usually in the range of 0.25–0.7 eV/solvent molecule [98]. Thus, after the first few solvent molecules the electron affinity approaches the photon energy and the clusters do not photodetach. The photon energy available from continuous wave (cw) sources is also not an intrinsic limitation since ion lasers can be operated with (marginally) adequate flux on several cw ion laser lines between 350 and 370 nm. Moreover, new materials, such as $\beta$-BaBO$_3$, hold the promise of frequency doubling with adequate intensity, provided that the doubled light is injected into a buildup cavity located totally inside the vacuum container. These approaches aimed at improving cw PES spectroscopy for use on cluster ions are, however, rather substantial undertakings, whereas the pulsed methods described below allow PES to be easily carried out with conventional pulsed UV lasers and intense pulsed nozzle sources.

Posey et al. have constructed the apparatus shown in Fig. 12, a machine that first demonstrated [22] negative ion pulsed photoelectron spectroscopy. The principle of this instrument is quite simple—the ions are photodetached at the space focus from the extraction TOF mass spectrometer. The electron spectrometer on this apparatus is very similar to TOF photoelectron spectrometers used in multiphoton ionization experiments on neutrals [99] except that the photodetachment spectrum of the ions is usually a one-photon event. The
Fig. 12: Schematic diagram of the pulsed negative ion photoelectron spectrometer developed by Paces et al. [22]. Reproduced with permission.
Fig. 13. Pulsed 532-nm photoelectron spectra of (a) $O^-$, (b) $O_2^-$ and (c) $O_4^-$ obtained with the spectrometer shown in Fig. 12. The peaks labeled a, b, c, d in the inset of the bottom trace were recorded at 10 times the laser power (40 mJ/pulse) as the full trace and result from photodetachment of an $O_2$ photofragment.
electron drift region is a 60 cm long, magnetically isolated drift tube. The arrival times are recorded in a transient digitizer to generate the photoelectron spectrum. Typical spectra of $O^-$, $O_2^-$, and $O_4^-$ are shown in Fig. 13. The resolution of this spectrometer is about 35 meV at 1 V, compared to state-of-the-art cw PES spectrometers with resolution of 3–8 meV [100]. The collection efficiency of the TOF spectrometer is about $10^{-7}$, comparable to that of the cw instruments. The PES spectrum also yields an independent estimate of the ion density at the laser crossing region, since the charge density in the focused ion beam is sufficiently large to cause a shift in the position of electron peaks owing to the coulombic repulsion between the departing electron and the ion cloud [22].

Shifts on the order 100 meV at 1 eV are routine for the $O_2^-$ system, indicating that the charge density is on the order $10^5$/cm$^3$. Using the pulsed apparatus, Johnson and co-workers have studied three isomers of the $N_2O_2^-$ system, $O_2^-$ with $1 \leq n \leq 10$ and $(CO_2)_n^-$ with $2 < n < 16$. A powerful feature of the pulsed apparatus is illustrated by the $O_4^-$ data, shown on the bottom trace of Fig. 13. It shows that $O_4^-$ is formed by photodissociation of $O_2^-$ and then photodetached by a second photon. It is clear that with a second stage of mass selection, photoelectron spectra of photofragment ions may be recorded and used to evaluate the product vibrational energy disposal in cluster ion fragmentation studies.

**Fig. 14.** Magnetic parallelizer used in the pulsed photoelectron spectrometer described by Cheshnovsky et al. [101]. Reproduced with permission.
Recently, Cheshnovsky et al. [101] at Rice University have also demonstrated pulsed PES of a (Cu₄)⁻ negative cluster ion beam. The copper clusters were formed by laser vaporization, and TOF was again used to energy analyze the electrons. In order to increase the collection efficiency of this spectrometer, however, a magnetic parallelizer was used to achieve an efficiency of about 30%. This device, shown schematically in Fig. 14, is an adaptation of a PES spectrometer used by Kruit and Read [102] and operates by adiabatically turning the electron flight direction without changing its energy. By photodetaching the electron in a region of high magnetic field that expands rapidly into a weak solenoidal field, the electrons are turned and directed along the flight tube axis without changing their energies. Provided the turning radius is small compared to the flight length, good resolution can be maintained with high (up to 98%) collection efficiency. The resolution reported by Cheshnovsky et al. [101] is about 100 meV, but much higher resolution has been obtained by Kruit and Read, and it should be realizable in this context with several obvious improvements.

7 A FEW RESULTS

7.1 Mechanism of Optical Absorption in “van der Waals” Cluster Ions: Localization of Charge within Large Clusters

Lineberger and co-workers [14, 103] have studied the visible and near UV photodestruction cross sections for (CO₂)ₙ⁺ and Ar⁺, finding strong, continuous absorption for each species extending over several hundred nanometers. This finding at first appears curious in light of the fact that none of the species CO₂, Ar, CO₂⁺ or Ar⁺ possesses an optically allowed transition above 350 nm. The (CO₂)⁺ cation is known [28] to have a broad visible absorption band. To understand the origin of this absorption for the larger clusters, relative cross sections were measured for (CO₂)ₙ⁺, 2 < n < 11, with the results displayed in Fig. 15. Interestingly, the cross section for all the clusters is quantitatively similar at 532 nm but is strongly dependent on cluster size for excitation at 1064 nm. The overall picture is that the higher clusters generally absorb in the same spectral region as the dimer cation (CO₂)₂⁺. Smith and Lee [28] have studied the photodestruction spectra of (CO₂)₂⁺ and find broad, continuous photodissociation extending from 400 to 1000 nm. They suggest that it arises from excitation to a potential curve strongly repulsive between the CO₂ centers and involves binding electrons of the dimer (D₀ = 11.8 kcal/mol) [104]. In this model, the nearly Gaussian shape of the absorption spectrum is due to the ground-state vibrational wavefunction corresponding to the relative motion of the two CO₂ molecules. Since the shape of the absorption for the dimer is controlled by the shape of the repulsive surface via the “reflection principle” for dissociative transitions [105], the blue edge of the absorption cross section “probes” the inner turning point of the dimer. Kim et al. [29] have obtained much more complete photodissociation spectra of the trimer (CO₂)₃⁺ and find a spectrum remarkably similar to the dimer cation in the range
Fig. 15. Photodestruction cross sections of $(\text{CO}_2)_n^+$ at (a) 532 nm, (b) 650 nm and (c) 1064 nm, for $2 \leq n \leq 11$. Larger ionic clusters up to at least $n = 26$ appear to absorb in the spectral region as the dimer. Reproduced with permission from Johnson et al. [14].
400–700 nm. The similarity of the photodestruction cross section for the higher clusters with that for the dimer over most of the spectrum leads to the suggestion that the dimer carries the charge within the larger clusters.

Similar studies [103] on photoabsorption of Ar$_2^+$–Ar$_{40}^+$ show a broad absorption band but indicate the complexity to be expected. The species Ar$_2^+$ through Ar$_{70}^+$ all have a similar photoabsorption cross section, but it is larger than Ar$_2^+$ by several orders of magnitude throughout the visible spectrum. Similarly, a new, stronger, red absorption first appears at Ar$_{20}^+$ and persists at least to Ar$_{40}^+$. These results indicate the danger inherent in drawing structural conclusions from a limited set of observations. These data are likely not completely consistent with a model that views Ar$_n^+$ as having a dimer core for all $n$. This difference in core structure would alter existing theories [37] of the ionization dynamics of neutral argon clusters.

Thus, using the characteristic dimer photodestruction spectrum as a diagnostic of the charge distribution, a model for the larger clusters is emerging where the charge is generally contained on a smaller cluster, with the additional monomers adding on to this charged cluster remaining essentially neutral. Substantial changes may occur at “shell closings” in the larger cluster ions, as indicated by the Ar$_n^+$ studies. This result was actually anticipated by workers concerned with the mechanism of “magic number” formation in cluster ion mass spectra, as described in the next section.

7.2 Statistical Photodissociation Dynamics of Large Molecular Ion Clusters

Photofragmentation studies have been carried out on the homogeneous systems (CO$_2$)$_n^+$, (CO$_2$)$_{n-1}^+$, and Ar$_n^+$ by Lineberger and co-workers [14, 84, 103, 106], and a general trend is observed for these systems whereby large clusters (with about 15 or more monomer units) absorb a photon and eject a constant number of neutral monomers independent of parent cluster size. The fragmentation spectra for the (CO$_2$)$_n^+$ system with $2 < n < 26$ have been reported [106], and an expanded region including $2 < n < 46$ recently obtained by Levinger et al. is displayed in Fig. 16. The fragment ions are recorded on the horizontal axis, and the parent ion size is displayed on the depth axis. Above about $n = 15$, it is seen that the CO$_2$ systems all eject about six neutrals for excitation with 1064-nm light, which appears as a “ridge” in the fragment ion patterns. Note that there are no energy constraints limiting the fragment size, so that the entire lined region represents possible fragment channels. Figure 17 shows the dependence of the number of neutrals ejected in the constant loss regime on photon energy. A linear dependence is found, and the slope yields an upper bound for the binding energy for the monomer to the cluster ion of 5.3 kcal/mol, nearly the heat of sublimation of dry ice (5.7 kcal/mol)! The fact that the number of neutrals ejected appears to be governed only by the binding energy points to a model for the photodissociation in which the absorbed photon energy is degraded into thermal energy and finally to evaporation of the CO$_2$ molecules on the surface of the cluster. Presumably the absorber is photodissociated within the cluster, and the recoiling fragments are
Fig. 16. Photofragmentation spectra of (CO$_2$)$_n^+$ taken at 1064 nm, obtained by Levinger, Ray, and Lineberger (unpublished results).

captured by the cluster to effect the energy degradation. This suggestion leads to a series of experiments investigating the "cage effect", experiments that are discussed in Section 7.4.

Interestingly, the negative cluster ions of CO$_2$ are also observed to photodissociate (see Section 7.3), and the number of neutrals ejected is included in Fig. 17. The asymptotic number ejected falls nicely on the line established for the cation data, indicating that the evaporation step is insensitive to charge on the cluster. Further evidence for the evaporation mechanism can be found in the Br$_2^+$-(CO$_2$)$_n$ system, where the Br$_2^+$ component can be photodissociated within the cluster. (The Br$_2^+$ ion, isoelectronic with Xe$_2^+$, will have a continuous absorption similar to that of Ar$_2^+$.) The asymptotic number of CO$_2$ monomers ejected from the Br$_2^+$-(CO$_2$)$_n$ system at 700 nm appears to fall on the same line as (CO$_2$)$_n^+$ and (CO$_2$)$_n$, suggesting that the effect is even independent of interior composition in addition to charge. Actually, the bromine system has an additional feature of interest in that the photodissociation dynamics of small clusters contains information on the "cage effect" on the atomic recombination, as discussed more fully below.

The widths of the fragment ion distributions depicted in Fig. 16 are quite narrow, about 2.5 monomers, and the shape of these distributions contains information on the dynamics of the photodissociation process. Engelking [108] has used a statistical (RRK) model to reproduce these fragmentation patterns and finds qualitative agreement with the experimental results. The photodissociation behavior for all (CO$_2$)$_n^+$ clusters can be reproduced with an average bond energy of 3.6 ± 0.6 kcal/mol for clusters larger than the dimer. The difference between
this value and the slope of the line in Fig. 17 is suggested [108] to result from the translational energy disposal. Another general conclusion of these studies is that the width of the fragment distribution is controlled by the difference between the monomer binding energy and the thermal energy carried off per monomer at a temperature characteristic of the photoexcited cluster. A good illustration of this point is the photofragmentation spectrum [103] of the Arₙ⁻ system. The binding energy in the argon system is only about 1 kcal/mol so that, assuming an equivalent heat capacity for the argon and carbon dioxide systems, the fragment ion distribution would be expected to be much larger for the argon clusters, as is observed [about 2 monomers wide for CO₂ vs. 6 for Ar (see Fig. 20)].

7.3 Formation of “Magic Numbers” in Cluster Ion Mass Spectra

The anion (CO₂)ₙ⁻ mass spectrum shown in Fig. 8 contains an example of what is called a “magic number” [41], essentially an anomalously abundant cluster in the mass spectrum with respect to the intensity of neighboring clusters. In the CO₂ anion case, the n = 14 cluster is more abundant than 13 or 15 by about a factor of 4. Such anomalies are common, especially in rare gas cation systems [41], and have been the subject of much recent study to determine if they reveal a property of the parent neutral cluster or if they result from kinetic or thermodynamic characteristics of the ionic clusters. Recent work by Haberland [38] and Saenz et al. [37] suggests that the magic numbers in the rare gas cluster ions result from ionization of neutral clusters creating a nascent ion cluster far from its equilibrium internuclear geometry. This displacement is due to the
propensity of the ionic cluster to compress the charge into a small, relatively tightly bound core, as we discussed in the previous section. The energized cluster then relaxes by ejecting neutral molecules until the internal energy of the ion cluster approaches the binding energy of one monomer. If, as the ionic cluster is sequentially ejecting neutrals, an especially stable cluster ion is formed with a substantially higher binding energy, then the activation energy for this cluster to dissociate will be proportionally higher, and a larger portion of the ensemble of ions will be trapped at this cluster size than at adjacent masses. In this view, the magic numbers in the mass spectrum are associated with properties of the ions, not the parent neutrals. Such a model is certainly proven in the case of the formation of the $\text{H}_2\text{O}^+\cdot(\text{H}_2\text{O})_{20}$ cluster, which has been shown [110] to develop in real time after ionization. It is also possible to test this theory further by photodissociating a large cluster ion with a wavelength that creates fragment masses in the size range near a magic number. Since the model does not depend on how the cluster is energized, photolysis should also result in magic numbers in the photofragment distribution and have the advantage that the starting cluster size and initial internal energy are well defined. In addition, there is no possibility of the result being convoluted with the initial distribution of neutral clusters. Alexander et al. [84] have recently carried out such experiments on the $(\text{CO}_2)_n^-$ clusters, with the result shown in Fig. 18. The $n = 14$ cluster is seen to indeed occur with increased intensity compared to neighboring peaks, indicating that an enhanced stability is associated with this cluster.

Saenz et al. [37] have proposed a similar model to account for the magic numbers observed in rare gas cation clusters. Levinger et al. [103] have obtained the fragmentation spectrum of $\text{Ar}_{16}^+$ presented in Fig. 19. The $n = 20$ cluster, which appears weak in the parent ion mass spectrum, is also a minor fraction of

![Figure 18.](image)

**Fig. 18.** Photofragmentation spectra of $(\text{CO}_2)_n^-$ cluster ions following 308-nm excitation. These data show that the intensity anomalies present in the negative ion mass spectra (Fig. 8) are also present in the photofragmentation distributions. Reproduced with permission from Alexander et al. [84].
the photofragment distribution, showing that the effect exists in a single photofragment spectrum. As in the (CO$_2$)$_n^-$ case, the effect is even more striking when all processes leading to a given fragment are summed. Bloomfield et al. [13] have also observed a magic number phenomenon in the photodissociation of Si$_n^+$ clusters, where in this case a propensity is observed to eject the Si$_6^+$ fragment, indicating that this ion is particularly stable.

7.4 Size Dependence of the Br$_2^-$ Recombination Quantum Yield upon Photodissociation of Br$_2^-$ within Br$_2^-$ (CO$_2$)$_n$ Clusters: Observation of “Caging” of the Atomic Fragments

Several experiments have recently been carried out to examine the dynamics of atom recombination upon photodissociation of diatomic molecules in a cluster [111] or condensed phase [112] medium. The solution experiments [112] have been primarily concerned with direct measurement of the time scale of the recombination, whereas cluster experiments [111] have concentrated on the state distribution of the nascent diatomic via dispersed fluorescence. Cluster ion experiments afford the possibility of measuring the complementary process, where the atoms are ejected before recombination can occur. Alexander et al. [107] have carried out such experiments on the Br$_2^-$ (CO$_2$)$_n$ system. The ion is grown by successive CO$_2$ nucleation onto the initially formed Br$_2^-$ ion; the Br$_2^-$ moiety is then photodissociated via a charge resonance band similar to that
found for $\text{Ar}_2^\ast$. The branching ratio for the processes

$$\text{Br}_2^-\cdot(\text{CO}_2)_n + h\nu \rightarrow \text{Br}^-\cdot(\text{CO}_2)_m + (n-m)\text{CO}_2 + \text{Br}^-\cdot(\text{CO}_2)_{p} + (n-p)\text{CO}_2$$

Uncaged products

Caged products

was measured to determine the cluster size $n$ at which the bromine atoms are effectively caged at various excitation energies. The fraction of caged photoproducts as a function of cluster size is shown in Fig. 20 for several photolysis wavelengths. Excitation at 800 and 720 nm corresponds to roughly 0.5 and 0.7-eV bromine atom recoil energies, respectively, whereas excitation at 355 nm provides 2.3-eV recoil energy. The long wavelength data show a sudden onset for caging between $n = 11$ and 12, and uncaged products are not observed from any larger cluster ions. This sharp transition is relatively insensitive to the recoil energy of the bromine atoms between 0.3 and 0.6 eV, demonstrating that it is not due to a peculiarity in the absorption spectrum around 700 nm. The onset of strong caging at $n = 12$ seems likely to be caused by a structural effect, where carbon dioxide monomers surround the bromine molecular ion. This conclusion is reinforced by the observation that the $n = 12$ cluster appears as a magic number in the $\text{Br}_2^-\cdot(\text{CO}_2)_n$ parent cluster ion mass spectrum. Interestingly, a magic number also occurs in the negative ion spectrum of carbon dioxide at $n = 14$. Van de Waal [113] has noted that 13 cluster CO$_2$ neutrals ought to form a stable geometrical structure with 12 CO$_2$ molecules arranged in an icosahedron.
around a central monomer. Recent experiments [107] by Alexander et al. at 355 nm increase the recoil energy to \( \sim 2.3 \text{ eV} \); a sharp increase in caging, to 50\%, is observed near \( n = 12-14 \), but caging is not complete up to at least \( n = 20 \). The reason for the behavior of the ions is by no means clear, and it would be very useful to determine the infrared spectra of these systems to test these structural conclusions. Amar [114] has carried out calculations on the analogous \( \text{Br}_2^+ \cdot \text{Ar}_n \) system and finds evidence for two different types of caging processes, one dominated by attractive forces and another essentially structural in origin.

8 OUTLOOK

Pulsed methods in ion spectroscopy are making a profound impact on the field of cluster ion laser spectroscopy. The intensity and flexibility of the pulsed beam ion sources have been ideally matched by the versatility of pulsed laser sources to produce a scenario in which experimenters have greatly reduced constraints on the types of cluster ionic systems amenable to study. Consequently, the barrier between theory and experiment in this field should erode as experimentalists become able to test subtle theoretical predictions. For instance, it is now plausible to consider experiments in which a chemical reaction is triggered within a cluster in a fashion such that a laser energizes the reactants at a known geometry in a specific chemical environment. The reaction dynamics can then be studied as a unimolecular decomposition problem, and the role of a specific number and kind of solvent molecules can be investigated at a level thought to be out of the question only a decade ago. However, the challenges are commensurate with the goal. A few important unresolved issues that are currently impeding the progress of this field involve finding ways to determine the following characteristics of intermediate size cluster ions:

- Intermolecular geometry and rigidity of molecular clusters
- Internal energy content
- Interatomic geometry of metal clusters
- Electronic structure of both molecular and metallic clusters

Significant progress has been made in some of these areas, such as electronic structure where photoelectron spectroscopy appears to be a useful tool in identifying the molecular orbital or band structure of the aggregate. Other areas, such as the general determination of cluster geometry, have barely been approached and offer substantial opportunities for innovation. A host of interesting questions present themselves as targets of opportunity as we progress in defining the physical attributes of the clusters. Among these are the question of the existence of phase transitions [114] in the microscopic cluster environment and the nature of the free electron in condensed media [115]. High-resolution spectroscopy is on the verge of providing the first glimpse of structural information. Infrared spectroscopy via vibrational photofragmentation appears to be an obvious candidate, as well as the electronic transition excited through.
known chromophores in both the ion and ligands. Non-gas-phase techniques such as electron spin resonance (ESR) and nuclear magnetic resonance (NMR) carried out on matrix-deposited, mass-selected ion beams seem very exciting and may represent powerful avenues to establish symmetry and structure.

In the meantime, mapping out the photochemistry of these new species is certain to provide an immediate return from existing experiments. Other directions that presently appear as opportune targets include subpicosecond pump–probe experiments that record the time evolution of reactions occurring inside clusters of specific composition and high-resolution spectroscopy experiments that probe how the product mix of vibrationally induced reactions is changed by the character of the motion excited. Another area that appears on the verge of delivering a large body of information to be correlated and digested is the photoelectron spectroscopy studies of semiconductors and metals, where the evolution of the band gaps can be directly traced as a function of size and composition. In conclusion, we can look forward to the exploitation of these advances in pulsed technology to move the realm of gas-phase oriented chemical physics research further into the arena of condensed phases, with hope of it converging toward a fundamental understanding of how reactions occur in bulk media.

ACKNOWLEDGMENTS

The authors extend thanks to Professors R. E. Smalley, M. T. Bowers, and P. J. Brucat and to Drs. S. Leach and J. Peterson for providing us with original figures and enlightening discussions regarding the content of this article. Special thanks are due to Meryl Mantione whose tireless attention to detail in the preparation of this manuscript salvaged the effort. W. C. L. acknowledges support from the NSF under grants CHE 83-16628 and PHY 86-04504, and M. A. J. wishes to thank the NSF under CHE 86-02195 and the Office of Naval Research and to acknowledge the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of his research. Professor Johnson’s research is also supported by a grant from Research Corporation and has benefited from his designation as a Shell Faculty Fellow.

REFERENCES

65a. R. B. Cody, R. C. Burnier, W. D. Reents, Jr., T. J. Carlin, D. A. McCrery, R. K. Lengel, and


89. M. DeLuca, L. A. Posey, and M. A. Johnson, unpublished results; (H2O)n clusters were observed in the electron gun ionized pulsed jet with n > 15, similar to the distribution found in Ref. [88] where low-energy electrons were selectively injected into the jet.


