# Analytical Spectroscopy in Supersonic Expansions

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## Contents

## I. Introduction

In 1951, Kantrowitz and Grey[1] proposed that a dramatic increase in the intensity of molecular beams could be realized by replacing the effusive oven source then in widespread use with a high-velocity (supersonic) nozzle. An experimental demonstration of such a device was published as a companion paper.[2] However, attainment of the full increase in intensity predicted by Kantrowitz and Grey was prevented by insufficient pump capacity. Indeed, applications of supersonic nozzles were very limited due to the pumping requirements of even small nozzle systems. Over a decade later a review of supersonic nozzle beams stated that nozzle beams were still at the point of development of a principle into a useful tool.[3]

In the analysis of Kantrowitz and Grey, it was demonstrated that the directed mass flow characteristic of such a supersonic expansion would precollimate the beam upstream of the first slit of a molecular beam chamber. This precollimation would result in an intensity increase of ~2 orders of magnitude. In addition to the expected intensity gain, other characteristics of nozzle sources were also given. For molecular beam studies a particularly advantageous property of a nozzle source is that the distribution of velocities in the beam is narrowed relative to the velocity distribution in an effusive source. This "monochromatizing" of the distribution meant that velocity selection devices, with their consequent diminution of intensity, could be eliminated. Accompanying this effect was an increase in the average velocity of the beam, which was viewed, at that time, as being a disadvantage in most cases. Finally, nozzle sources produce a beam in which the population of low-energy rotational levels is increased at the expense of higher energy levels. It was suggested that this might be of help in certain types of experiments.[1,2] It is ironic that it is this latter property which has led to a virtual explosion in the use of nozzle sources in the past decade.

In 1974, Levy, Wharton, and co-workers[4] took advantage of the rotational cooling effect of a seeded nozzle expansion to drastically simplify the fluorescence excitation spectra of $NO_2$. Subsequently, these workers and others showed that the spectral narrowing and simplification due to depopulation of higher energy rotational, vibrational levels could be applied not only to di- and triatomic molecules but also to polyatomic species with molecular weights of several hundred. It has been primarily in the area of high-resolution gas-

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phase spectroscopy that nozzle sources have proliferated.

Analytical applications of nozzle spectroscopy were proposed and demonstrated not long after the popularization of nozzle spectroscopy.[5,6] However, the analytical applications have not developed as rapidly as the spectroscopic. Indeed, analytical jet spectrometry is at about the stage of nozzle sources at the time of the review by Anderson et al.,[3] i.e., the development of a principle into a useful analytical tool.

This review will assess the present state of analytical jet spectrometry, paying particular attention to the shortcomings of the technique, which have hindered its analytical development, and also to recent work that has been addressed to overcoming those limitations. In the next section the physics of nozzle expansions will be presented along with a discussion of the limitations of various nozzle sources of analytical relevance. Following that, a brief summary of spectroscopy in supersonic jets will be presented. Spectroscopic applications of jets have been too numerous to be reviewed exhaustively within this paper. The intent is therefore to demonstrate the range of spectroscopic applications and the relevance of those applications to analysis. Following the section on spectroscopy will be a section on analytical jet spectrometry. This section will first address qualitative analysis and then consider the few quantitative applications tht have appeared. Limitations of jet analysis will be considered next, followed by possible methods of overcoming those limitations which are currently being pursued.

As will be seen in the next section, the end result of a jet or nozzle expansion is rarefaction of the gas being expanded. Thus, jets are an obvious device to use in interfacing a continuum fluid with a detector requiring vacuum operation, e.g., ion detectors. There are numerous instruments that take advantage of jets to effect this interface. For example, the thermospray liquid chromatograph–mass spectrometer interface of Vestal and co-workers[7] is essentially a jet expansion through a capillary; similarly, the supercritical fluid chromatograph–mass spectrometer of Wahrhaftig[8] and the inductively coupled plasma–mass spectrometer[9] both use a nozzle or jet to introduce the continuum phase into the mass spectrometer vacuum region. Such apparatus are beyond the scope of this review. The apparatus under consideration herein are those in which advantage is taken of the cooling effect of the expansion as opposed to simply utilizing the rarefaction properties.

## *II. Dynamics of Gas Expansions*

### A. Pure Gases

A large majority of the situations encountered in gas dynamics can be accurately described with the use of two simplifying assumptions. These are that the gas can be approximated as a continuum, compressible fluid and that the gas flow is inviscid. By continuum fluid it is meant that a microscopic, molecular understanding of the gas is not required, but rather that gas properties can be approximated as varying continuously from point to point within any region of the gas. By inviscid it is meant that viscosity effects that occur as the gas flows over surfaces can be neglected or considered only for a thin boundary layer at the surface. Unfortunately, neither of these assumptions can be used in an accurate description of a nozzle or jet expansion. However, although a complete mathematical description of jet expansion has not yet been accomplished, there is sufficient understanding that the design of jet systems can be guided by firmly based principles. To illustrate these principles two limiting cases, namely, effusive and supersonic expansions, will be considered.

#### *1. Effusive Expansions*

Consider a pure gas confined to a reservoir with an initial pressure $P_0$. Then the velocity distribution of the gas is determined solely by the reservoir temperature, $T_0$, and the atomic weight of the gas according to the Maxwell–Boltzmann distribution function. Now, if the gas is allowed to escape from the reservoir into a region of lower pressure via a hole in the reservoir wall, there are two possibilities. The hole diameter is either larger or smaller than the mean free path, $\lambda_0$, of the atoms in the reservoir. In the latter case, a molecule in the vicinity of the hole can pass into the low-pressure region without undergoing any collisions. Such a situation corresponds to an effusive expansion. Because, in an effusive flow, the transition from the reservoir to the vacuum takes place without velocity-altering collisions, there will be no change in the temperature in the vacuum which characterizes the velocity distribution of the gas. In addition, and more important for its spectroscopic implications, for a polyatomic gas there is no mechanism by which the distribution of population among the various internal (rotational, vibrational) energy states of the gas can be altered. In sum, in an effusive expansion the state of the gas is not influenced by the presence of the hole. The gas has simply gone from a region of high pressure, which can be characterized by the continuum approximation, to a region of low pressure in which the gas density is markedly decreased but in which thermal properties are characterized by the reservoir temperature, $T_0$. For large molecules that have both a large density of low-energy rotational-vibrational levels and low vapor pressures, $T_0$ will be large enough that any spectroscopic investigation of an effusive expansion will result in extremely broad absorption or emission due to severe spectral congestion and hot band absorption. Additionally, an effusive expansion is nearly isotropic, so that the gas number density at any point within the vacuum chamber is extremely low. Effusive expansions have not been used for analytical spectrometry and so will not be considered further in this review.

#### *2. Nozzle Expansions*

A more interesting situation obtains when the hole diameter is much larger than $\lambda_0$. Now, since the hole dimensions are large compared to $\lambda_0$, there will be many collisions among molecules in the vicinity of the hole. With regard to driving molecules out of the reservoir, the most effective of these collisions will be those that have a large velocity component in the direction perpendicular to the hole area. Moreover, the effect of a large number of collisions in the orifice vicinity is to monochromatize the velocity. Additionally, since most measurements of the beam are done along the axis defined by this perpendicular, there is also a geometric factor contributing to the velocity narrowing.[10] The geometrical contribution to cooling is dependent upon the distance from the source and independent of collisions. It arises from the fact that the probability of finding molecules with velocity components perpendicular to the beam propagation direction will decrease with increasing distance from the nozzle. Thus, its effect is to narrow the distribution of velocities in this direction. Although this contribution to velocity narrowing continues throughout the expansion, it does not contribute to cooling of internal degrees of freedom in the absence of collisions. The net effect of these factors is that the velocity distribution is narrowed, which corresponds to a lowering of the temperature that describes the velocity distribution equation.

In addition to this velocity narrowing, there is also an increase in the most probable velocity. This increase in velocity together with the decrease in number density which accompanies the expansion produces a supersonic flow condition. It should be emphasized that the flow is supersonic primarily due to the temperature decrease, which causes a corresponding decrease in sonic velocity, rather than to the velocity increase. However, the importance of establishing a supersonic flow condition is that as the gas propagates supersonically a shock wave due to collisions with background gas molecules is established around the flow. The effect of this shock wave is to develop a region around the beam protected from intrusion by warm background gas in the vacuum chamber. The components of the shock wave are referred to as the barrel shock which extends outward from the orifice to the Mach disk, which is a circular shaped area perpendicular to the flow direction. The protection of the expanding jet from collisions with warm background gas allows the spectroscopist to take full advantage of the cooling effects of the expansion.

A third important characteristic of a supersonic expansion is that the expansion is isentropic, i.e., that the various degrees of freedom (translation, rotation, vibration) of the gas remain in equilibrium, at least during the initial portion of the process. Actually, three distinct regimes have been identified in a supersonic expansion. The first, termed continuum flow, is characterized by a large number of collisions and can be treated by ordinary methods of fluid dynamics; in this regime the isentropic nature of the expansion is maintained by the high collision frequency. The second regime is referred to as the transition flow region and is characterized by the falling out of equilibrium of the various internal molecular degrees of freedom. In general, this loss of equilibrium varies inversely with the energy of the mode involved, so that the population of higher energy modes, which initially were less highly populated, becomes established, or "frozen", earlier than the population of lower energy modes. The mathematical description of this flow region is not as well understood as that of the other two regions. The final region is termed the free molecular flow region. In this regime, the populations of all of the various degrees of freedom have become fixed, and the frequency of collisions is approaching zero. It is in this region that the spectroscopist wishes to work. Expansion conditions must thus be arranged so that the free-flow regime can be protected by the supersonic shock wave. Fortunately, it is not difficult to achieve this, especially in unskimmed expansions.

## B. Gas Mixtures

For gas mixtures, ideally the expansion can be approximated as the expansion of a pure gas with molecular weight and specific heat ratio, $\gamma$, determined as the concentration-weighted average for the mixture. Thus a monatomic gas, such as helium, can be seeded with a low concentration of the species of interest and, due to the concentration weighting, show essentially the expansion properties characteristic of helium. Although some use of this effect has been made in accelerating beams of atoms to higher kinetic energy,[11] seeded beams have been used most extensively for spectroscopic applications. Within the isentropic portion of the expansion, the seed species will also be in equilibrium with the expanding gas. Indeed, it has been this property that has been primarily responsible for the explosion of interest in jet applications. The seed molecule is cooled not only translationally but also in its internal energy. By careful choice of expansion conditions, the seed molecule may be prepared in a state in which virtually all of the excited vibrational levels are depopulated and in which only the lowest energy rotations are populated. Furthermore, it can be arranged so that the transition to free molecular flow occurs upstream of the Mach disk, so that the prepared molecule can be probed within the free jet region protected by the barrel shock, a truly isolated molecule.

Several factors enter into the choice of carrier gas into which the analyte will be seeded. Because the freezing in of the temperature characterizing the various degrees of freedom depends upon the number of modes into which energy may be partitioned, a monatomic carrier is indicated. (A monatomic gas does not itself have any internal energy levels requiring cooling.) Further, since a light gas can be more easily accelerated and hence attain a lower ultimate $T_{\mathrm{trans}}$, it might be thought that helium would be the gas of choice. However, although it is true that the lowest $T_{\mathrm{trans}}$ for a pure expansion has been attained with helium,[12] helium does not always produce the most efficient cooling of seed molecules. For seeded beams with large differences in size and weight between the seed and the carrier (e.g., $m_{\mathrm{heavy}}/m_{\mathrm{light}} > \sim 50$), there is a velocity slip effect,[13-16] that results in the terminal velocities for both the seed and the carrier differing significantly from calculated values. The slip effect has been measured for both iodine and aniline expanded in hydrogen and in helium. The translational temperatures for both the seed and the carrier were much higher than calculated from the equivalent pure-gas expansion. Under the same conditions no slip effect could be observed for expansions in argon. For large, heavy, rigid molecules Amirav et al.[15] found that cooling varied in the order Xe > Kr > Ar > Ne > He.

Thus one might expect the heavier noble gases to be used exclusively in spectroscopic jet expansions. For a number of reasons this is not true. First, in principle, any desired degree of cooling can be attained for any expansion gas. If velocity slip is occurring, one can, in principle, increase the reservoir pressure of the carrier gas and thereby increase the number of binary collisions to compensate for the slip effect. Of course this necessitates a larger pumping capacity to handle the increased gas flow. Thus, comparisons of cooling efficiencies should be made at fixed pump speed. However, as the reservoir pressure is increased to increase cooling, the tendency to form van der Waals clusters also increases. In ref 15, Amirav et al. were careful to point out that a sufficient degree of cooling ($T_{\text{vib}} \sim 30$ K) was reached with pressures below those at which clustering was observed to occur. However, Even et al.[17] found that in both argon and neon vibrational cooling was not sufficient to depopulate the low-energy phenyl torsion modes of magnesium tetraphenylporphyrin at the moderate pressures needed to avoid complexation. They were able to freeze out these vibrations by using a high-pressure helium expansion.

As the above example indicates, the defintion of "a sufficiently low vibrational (rotational) temperature" depends upon the experiment at hand. In some cases, light carrier gases have been found to produce sufficient cooling and are still used. A third reason for using a light carrier gas is compatibility with ancillary equipment, e.g., for use with a gas chromatograph utilizing a helium carrier. More recently, several workers[18-20] have utilized supercritical fluid jet expansions to try to take advantage of the solvation properties of these carriers (vide infra).

## C. Apparatus

### 1. Continuous Expansions

a. **Low Background Pressure Expansions**. Not surprisingly, the earliest attempts to realize the Kantrowitz–Grey type of expansion utilized systems originally designed for an effusive source by simply replacing the oven with a skimmed nozzle source. This type of system, illustrated in Figure 1 (top), usually consists of a least two large vacuum chambers, each pumped by a large diffusion pump or a cryopump. The nozzle output is skimmed relatively close to the nozzle, and the deleterious effect of penetration of the beam by warm background gases is minimized by maintaining the lowest possible vacuum in the expansion chamber. This design has been referred to as a Fenn-type expansion[21] in recognition of the development efforts of Fenn and co-workers.[22] Because of the necessity of maintaining very low chamber pressures, the Fenn-type nozzle system is not satisfactory for use with low molecular weight species due to a lack of pumping capacity needed for accelerating such species to low $T_{\text{trans}}$. Such systems are, however, useful in expansions in which the lowest attainable temperatures are limited by cluster formation rather than by pump capacity.

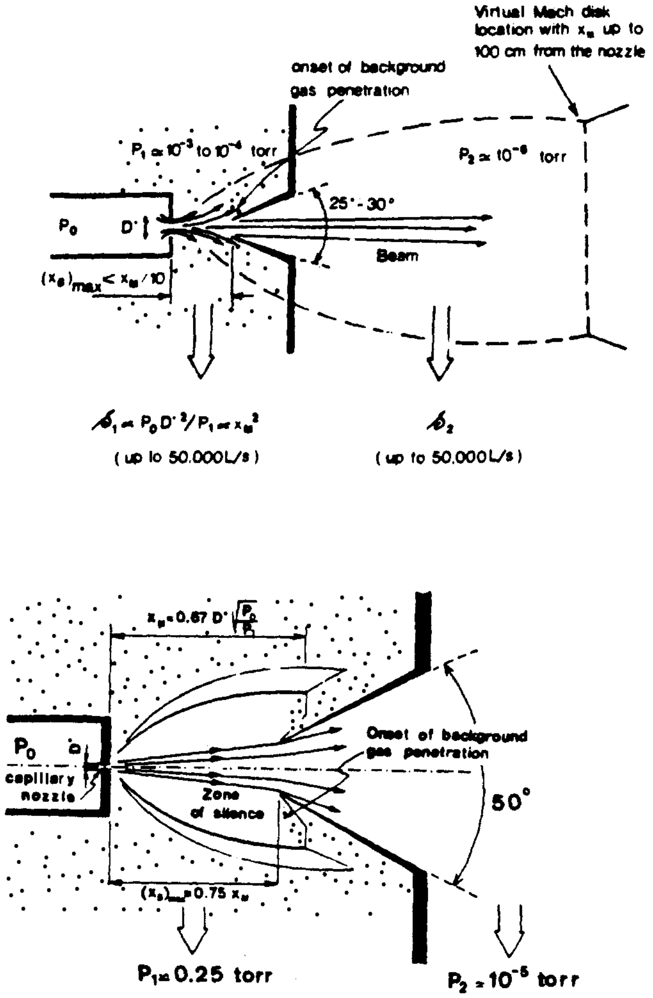

Figure 1. Schematic representations of Fenn-type (top) and Campargue-type (bottom) continuous flow nozzles. Reprinted with permission from ref 21. Copyright 1984 American Chemical Society.

b. **Moderate Background Pressure Expansions**. In contrast to the Fenn-type nozzle system is the Campargue-type system pioneered by Roger Campargue at the University of Saclay and depicted in Figure 1 (bottom). In the Campargue design, the pressure, $P_1$, in the expansion chamber is typically in the range $10^{-2}$–1 Torr, i.e., 2–3 orders of magnitude higher than in the Fenn-type expansion. At these higher pressures, the developing free jet is encased in a shock-wave structure. This shock wave extends from the nozzle tip to the Mach disk. At typical operating pressures, this shock wave is thick enough and dense enough to prevent penetration of the core of the jet by warm background gas. As the chamber pressure is decreased, at constant ratio $P_0/P_1$, the shock wave becomes more diffuse, so that background gas intrusion into the jet begins to occur. However, at the higher pressures the cold, isentropic core of the jet is completely unaffected by the background. The volume of the jet within the shock wave has been referred to as a "free jet zone of silence" by Campargue.[21] Since photon probing of the shock system does not alter the jet properties in any manner, it is within this zone of silence that spectroscopic measurements are ideally made.

The relaxed vacuum requirements of the Campargue nozzle mean that smaller pumping systems can achieve effective cooling. Indeed, Campargue has produced helium expansions in which $T_{\text{trans}} = 6 \times 10^{-3}$ K in a system with a pump speed of 350 L s$^{-1}$. In addition to the reduced pumping requirements, chamber dimensions can also be reduced dramatically from the near room-sized chambers characteristic of effusive beam systems to a chamber with dimensions on the order of 10–20 cm. This size reduction is due to interrogating the beam within the zone of silence, i.e., upstream of the Mach disk. Since the position of the Mach disk is dependent on the square root of the ratio of reservoir pressure to expansion chamber pressure, the Mach disk is much closer to the nozzle in a high-pressure Campargue-type system.

c. **Nozzle Designs**. In continuous flow systems, a variety of nozzle designs have been used. Early work, based on ref 1, utilized a converging-diverging Laval nozzle, designed so that a particular exit Mach number was reached. However, Becker and Bier[23] found that removing the diverging section of the nozzle did not appreciably affect the beam intensity. Thus, in the Fenn-type systems, converging nozzles have now almost entirely replaced Laval nozzles.

In the Campargue-type systems, in which small orifice diameters (typically 10–100 μm) are utilized, both converging nozzles and flat orifices ($l/D \ll 1$; $l$ is the length and $D$ the diameter of the orifice) have been used, although Campargue claims that the most efficient type of nozzle is a capillary with $l/D > \sim 2$. Miller et al.[24] support this contention, although they reported enhanced clustering of Ar and $CO_2$ at $l/D = 128$. For helium, however, Campargue argues that $l/D \simeq 2$ provides maximum beam performance without clustering.

**d. Skimmers.** Although unskimmed free jets are ideal for spectroscopic applications in which photon emission or absorption is detected, attempts to improve sensitivity and interests in nonfluorescent compounds have led to fairly widespread use of resonantly enhanced multiphoton ionization. Operation of ion detectors is often incompatible with the high-pressure expansion of a Campargue-type free jet. Thus, the expansion is usually skimmed to produce lower pressure in the detection region. However, care must be taken in converting a Campargue type expansion to a skimmed expansion. Extensive work on skimmed Fenn-type expansions has been done, and high transmission through the skimmer without forming a shock wave at the skimmer can be attained. Primarily this is accomplished by using a conical skimmer with a sharp orifice edge to minimize disturbance of the gas flowing through the skimmer and by varying the skimmer-to-nozzle distance so that the skimmer is in a relatively low-density region of the expansion. In the low-density region molecules back-scattering from the skimmer do not collide with subsequent molecules in the flow, and the dependence of skimmer interference on skimmer geometry is reduced.[25]

*The above principles do not apply to Campargue-type expansions skimmed in the free jet zone of silence.* Systematic study of the various skimmer parameters has been done by Campargue,[21] and a skimmer design that minimizes interference has been proposed. Although Campargue states that the skimmer problem has been solved,[21] the point here is that those doing jet spectroscopy and analysis must exercise care in designing skimmed free jet expansions. In particular, care must be exercised in converting, e.g., a fluorescence-based detection system in which the zone of silence is probed to a skimmed system. Unless care is taken, intensities much less than expected can result.

### 2. Pulsed Expansions

One early solution that attempted to realize the promise of increased intensity of a supersonic expansion without straining pumping capacity was the pulsed valve of Hagena.[26,27] This early pulsed valve utilized a solenoid-driven plunger with a minimum opening time of 1.6 ms. Although this valve did indeed demonstrate the feasibility of this method of reducing pumping needs, pulsed valves did not come into widespread use until much more recently.

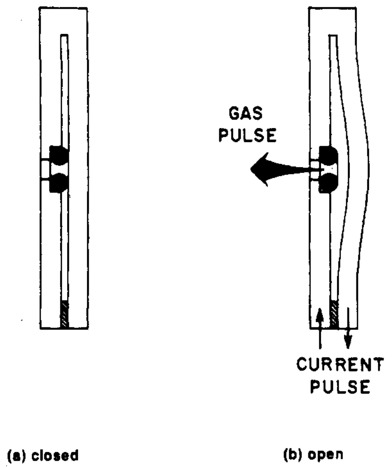

**Figure 2.** Diagram of the Gentry–Giese "hairpin" valve: (a) closed valve; (b) when a current pulse flows through the bar, the repulsive forces cause the bar to flex. Reprinted with permission from ref 28. Copyright 1978 American Institute of Physics.

Two developments spurred an increase in the use of pulsed valves. First was the demonstration by Gentry and Giese[28] of large increases in signal-to-noise ratios attainable with very high speed valves. The second was the proliferation of laser spectroscopic applications. With pulsed tunable dye lasers having relatively low (10–30 Hz) repetition rates and short pulses ($\sim 10^{-8}$ s), a pulsed valve provides an increase in duty cycle rather than the decrease that it would in a continuous signal situation. Numerous designs for pulsed valves are now extant and most are commercially available.

The Gentry–Giese design has been adapted by others,[29,30] and at least two commercial versions are available.[31,32] The basic feature of this design is an electrical "hairpin" with one side and both ends fixed so that when a current pulse flows through the bar the opposing flow in each arm causes the free arm to flex, thus opening the orifice. The operating principle is illustrated in Figure 2. The original Gentry–Giese design produced 10-μs pulses at 1 Hz. Subsequent variations were operated at repetition rates up to 10 Hz and pulse widths of ~100 μs.[29,30]

Automobile fuel injection valves have been adapted for pulsed jet expansion valves by numerous workers.[33-35] These valves are similar to the design used by Hagena,[26] in that current flow through a solenoid is used to provide the opening force. Typically the valve is modified to improve its sealing properties. This modification may consist of simply regrinding the seat or changing the seating material from the steel–steel seat, which is adequate for gasoline but not for vacuum operation. Generally, these valves provide fairly long pulses (~500 μs) but can be operated at 50–100 Hz.

Shorter gas pulses can obtained from solenoid valves that incorporate two solenoids: one for opening the valve, the second for closing it. Several valves of this type have been described.[36-38] When the overlap between the electronic pulses through the two solenoids is varied, open times of 10–100 μs can be obtained at frequencies of up to 35 Hz. A commercial version of this design is available.[39]

Higher repetition rates (up to 750 Hz) have been obtained with a pulsed valve using a piezoelectric actuator.[40,41] Pulse widths of ~100 μs have been obtained. A commercial version is also available.[42]

A design limitation of almost all of the above valves is that the maximum operating temperature is ~150 °C. This limit is due both to the materials used in the valve construction and to the difficulties inherent in maintaining a seal between dissimilar materials over an extended temperature range. Aside from the seat, O-ring seals and electrical insulation are the most heat-sensitive areas in the design. There are literature references to valves that claim to provide higher temperature operation, although for many of these details are sketchy. Even et al.[43,44] used a valve capable of attaining temperatures of 20–520 °C with a width of 200 μs. No additional details were given. Similarly, Chan and Dantus[45] have used a valve described as a "modified Bosch design" for which they claim a maximum operating temperature of 400 °C. The Bosch design refers to the use of a fuel injection solenoid valve, most variations of which produce pulses $\gtrsim$600 μs. Imasaka et al.,[46] for example, have published a complete description of a modified fuel injection valve that can be heated to ~300 °C with a repetition rate of 100 Hz, but with a minimum pulse width of 1.3 ms and a measurably less than perfect seal. Syage et al.[47] and Keelan and Zewail[48] have used a "low inductance solenoid modified to deliver pulse widths of 250 μs", with repetition rates of up to 50 Hz, heatable to <200 °C. Sack and Gross[49] have used a commercially available valve[50] for GC/FTMS that appears to be adaptable to pulsed-jet applications. The valve is a solenoid type with a minimum pulse width in the millisecond range. In a subsequent paper, Sack et al.[51] reported satisfactory operation at 250 °C.

One other high-temperature valve that has been described is the rotating slit nozzle of Amirav et al.[52–54] This consists of two stainless steel cylinders each containing a rectangular slit. The inner cylinder rotates so that a gas pulse is produced when the slits are aligned. Operation at temperatures up to 200 °C is possible with pulse width of 150 μs at 12 Hz.

Regardless of the particular valve type, an important consideration with any valve is the ultimate cooling attained in the expansion. With reduced pumping requirements, larger orifices that, in principle, would give lower temperatures can be used. In order to realize this improved cooling, the flow must reach the "choked flow regime". This refers to the flow velocity becoming limited by the orifice diameter and the pressure differential across the orifice. In this regime the flow properties are the same as would be attained in an equivalent continuous expansion. Empirically, the attainment of choked flow is determined by flat-topped gas pulses. A model that provides a means for determining the minimum time to attain choked flow is also available.[55,56] Care must also be taken to ensure that the gas is probed within the choked-flow part of the pulse.

## *III. Spectroscopy in Jets*

### A. Monomers

By far the largest use of supersonic jets at the present time is in spectroscopic applications. A complete review of spectroscopy in jets is far beyond the scope of this paper; nevertheless, a brief summary of the range of spectroscopic investigations and some findings relevant to spectrometry is apropos. Three attributes of supersonic expansions are responsible for the ubiquity of jet systems in medium to high resolution spectroscopy. First, the molecules in the beam are cold; second, they are isolated; third, their number density is high. To these three attributes must be added the relative simplicity and low expense of a jet system.

For probing within the zone of silence of a rudimentary jet system, laser-induced fluorescence is the simplest method, requiring only a scannable dye laser, a minimum number of lenses, and an appropriately filtered photomultiplier. Indeed, it was the success achieved with such a system by Levy and co-workers[57–60] that spurred the spectroscopic developments. Initial experiments on di- and triatomic molecules soon gave way to high-resolution spectroscopy of polyatomics such as *s*-tetrazine[61] and free base phthalocyanine.[62–64] For the latter molecule, fluorescence emission spectra and fluorescence excitation were obtained for both the $S_0 \rightarrow S_1$ region and for the $S_0 \rightarrow S_2$ region. Interestingly, the fluorescence emissions were virtually identical for the two regions with only an increase in line width and emission intensity when $S_2$ was excited. This was interpreted as being due to rapid internal conversion from the excited level in $S_2$ to isoenergetic states in $S_1$ followed by fluorescence from the high vibrational levels in $S_1$ to the corresponding ground-state vibrational levels. The single strong peak in all the fluorescence spectra was assigned to the $\Delta v = 0$ transition. The very small frequency shifts in the position of this band were due to nearly identical ground- and excited-state frequencies, and the line broadening and intensity increases were ascribed to vibrational relaxation and increased oscillator strengths, respectively.

The spectroscopy of phthalocyanine is somewhat anomalous among the spectra of large molecules. Several groups, building upon the results of the Chicago group, extended jet spectroscopy to larger and heavier molecules. In almost all cases there were sufficient shifts between ground- and excited-state vibrational frequencies to provide more complex spectra than that of phthalocyanine. Although in most cases the spectral analysis is straightforward, there are some differences between isolated gas-phase spectra and the corresponding condensed-phase spectra. The problem of relating mixed crystal spectra to gas-phase spectra where medium-induced distortions are absent has been discussed by Warren et al.[65,66] for β-methylnaphthalene and phenanthrene.

The polycyclic aromatic hydrocarbons (PAH) and their alkyl derivatives are by far the largest class of molecules that have been studied. For all of these molecules, narrow absorption lines are observed for the $S_1$ absorption origin and vibronic bands within ~ 1000–2000 cm$^{-1}$ of the origin. As the vibronic energy approaches this level, the bands begin to broaden due to vibrational relaxation processes from the optically excited level to the vibrational continuum of optically inactive levels.[67]

Somewhere in the vicinity of 50–75 molecules in the above class have been characterized spectroscopically in jets. This accounts for somewhat over half of the total number of polyatomic species characterized. Clearly the relatively small number of well-characterized molecules has important implications for analytical spectrometry. The development of jet spectrometry as a mature analytical technique will require an extensive increase in this quantity, and much of this increase will have to be accomplished by the analytical practitioners.

## B. Complexes

The very high incidence of collisions that occur in the initial stages of a supersonic expansion can produce molecular clusters of species which are not possible to synthesize by any other means. Indeed, the spectroscopy and dynamics of these weakly bound species are very active areas of jet research. This research ranges from synthetic studies whose goal is the synthesis of "exotic" compounds[68] to the microscopic studies of solvation and bonding phenomena.[69-71] For analytical jet applications cluster formation would most often fall into the category of nuisance, as analytes forming clusters would decrease the concentration of unclustered analyte and hence decrease sensitivity. Thus, the intent of the present section is to provide only an overview of cluster formation with emphasis on methods of avoiding clusters.

The study of $I_2He$ and $I_2Ne$ van der Waals clusters was one of the earliest applications of jet spectroscopy.[59,60] In that work it was shown that supersonic expansions of $I_2$ in helium with helium pressures up to 100 atm could be used not only to produce $I_2$ with $T_{rot} \simeq 0.4$ K but also to investigate the spectroscopy and binding of the molecules $I_2He_n$ ($n = 1, 2$). The intensity of spectroscopic features due to these species varied as $\sim P_0^{2n}$, and these features were always blue shifted from the corresponding uncomplexed $I_2$ features, indicating that the dissociation energy of the upper vibronic state is less than that of the lower vibronic state. It was later established that for complexes of the type $I_2He_aNe_b$ that the spectral shifts were additive, i.e.

$$\Delta\nu(I_2He_aNe_b) = a\Delta\nu(I_2He_1) + b\Delta\nu(I_2Ne_1) \quad (1)$$

Jortner and co-workers[69,71-75] have investigated the complexes formed between large aromatic hydrocarbons such as anthracene, tetracene, and pentacene and the rare gases argon, krypton, and xenon in order to model microscopic solvent effects. For these molecules complexes of the type $MR_n$ were observed with $n$ up to 7 for tetracene·argon.[69] For all these species the bands due to the complexes were found to be red shifted relative to the bare-molecule transitions, and band intensities were found to be proportional to $P_0^{2n}$ (see Figure 3). On close examination of the positions of the peaks of the complexes, it was found that the additivity relation (eq 1) was not followed. This fact led the authors to conclude that successive additions of a rare gas atom did not occur to the same geometry.

Complexes with non rare gas species, such as water, benzene, aniline, ammonia, and anisole, have also been investigated by numerous workers.[76-85] In general, two types of behavior have been observed for the complexes. In most cases, the observed absorption bands are sharp, and the bands are red shifted a few wavenumbers from the corresponding bare-molecule feature. These facts are explainable by assuming that the binding to the parent molecule is weak and has only weakly perturbed the ground and excited states of the parent species. More rarely, either the absorption or emission bands of the complex are diffuse and significantly shifted from the bare molecule bands, indicative of a strong interaction between the complex partners. Such strong interactions correspond to charge-transfer[82,85] and exciplex situations.[82,83]

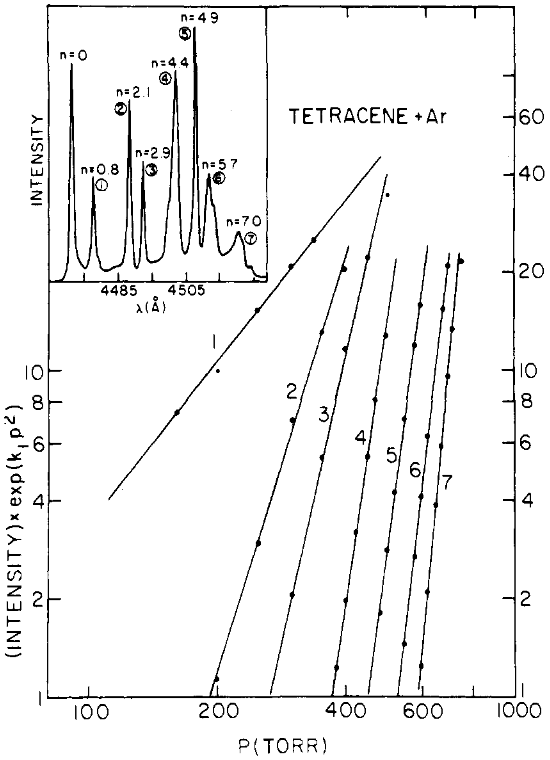

**Figure 3.** Argon pressure dependence of the normalized intensity of peaks due to tetracene·argon van der Waals clusters. The inset shows the fluorescence excitation spectrum with the values of $n$ obtained from fitting the pressure dependence data to the form $P^{2n}$. Reprinted with permission from ref 69. Copyright 1981 American Institute of Physics.

## C. Biomolecules

For molecules that can be vaporized, supersonic expansions are the method of choice for high-resolution spectroscopy. For many biologically important molecules, jet spectroscopy is the only high-resolution technique available. Thus, even biological molecules with very small vapor pressures are being forced into supersonic expansions whenever possible. Jortner and co-workers,[17,43,86-89] for example, followed studies on large and heavy polycyclic aromatic molecules with a series of papers on porphyrins. Among the compounds studied were free base porphyrin and free base tetraphenylporphyrin, magnesium tetraphenylporphyrin, and zinc tetraphenyl- and tetrabenzoporphyrins. As discussed above, for the tetraphenyl species, the low-energy phenyl torsions could not be effectively cooled in either argon or neon expansions at pressures below which significant complexation occurred. Helium expansions did produce cooled spectra. For each of the porphyrins the spectra of at least two excited electronic states with resolvable vibrational structure were recorded. The lowest singlet excited state of porphyrins has been labeled the Q state. The next higher energy state of the metal-containing porphyrins is called the Soret band, labeled B. In free base porphyrins in which the molecular point group symmetry is reduced from $D_{4h}$, the Q and B states are split into $Q_x$, $Q_y$ and $B_x$, $B_y$ states. For the metal porphyrins studied in the jet,

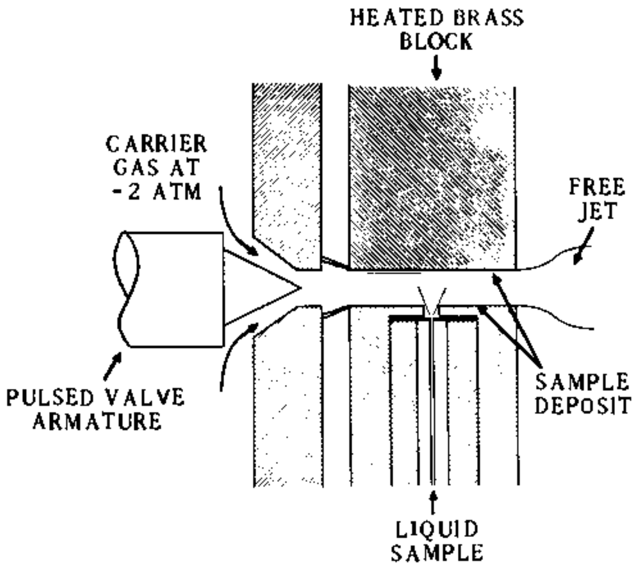

**Figure 4.** Apparatus for thermospray deposition of thermally labile samples. Reprinted with permission from ref 91. Copyright 1986 American Institute of Physics.

resolvable vibrational bands were recorded for both Q and B states. For free base tetraphenylporphyrin, $Q_x$, $Q_y$, and $B_x$ states with resolvable structure were detected; for free base porphyrin only the two Q states were reported. In every case, the vibrational bands of the upper states were significantly broader than the bands of the lowest energy excited state. Assuming that the nuclear potential energy surfaces and, hence, the rotational level structures do not differ greatly between the Q and B states, the increased width was assigned to homogeneous, lifetime broadening of the upper states. The observed broadening corresponded to upper state lifetimes in the range 0.5–5 ps. It was emphasized that this value corresponds to a lower limit of the lifetime and was consistent with solution fluorescence quantum yield data as well as observed solution fluorescence lifetimes for porphyrins for which such data were available.

An interesting technique for vaporizing thermally labile biological species has been reported by Rizzo et al.[90,91] for studying the spectroscopy of the amino acid tryptophan. The apparatus used is illustrated in Figure 4. A solution of the sample is first thermosprayed[7] through a heated stainless steel capillary terminated by a 50-$\mu$m orifice into a cylindrical channel in a brass block. The block is then dried at 170 °C and inserted into the vacuum chamber. The block is heated to 250 °C, and a free jet is formed by pulsing argon or helium through the channel. The jet is skimmed and probed by a resonant two-photon ionization process with time-of-flight mass detection. The necessity of using a gentle vaporization technique was demonstrated by comparison of the nonresonantly ionized mass spectrum produced in this way with the mass spectrum produced in a direct thermal vaporization process. The mass spectrum of the thermosprayed tryptophan (Figure 5) contains two peaks: a weak peak at *m*/*e* 130 due to photofragmentation (as determined from its dependence on ionizing laser intensity) and a peak at *m*/*e* 204 corresponding to tryptophan. On the other hand, when it was attempted to seed tryptophan directly into the expansion by thermal vaporization, the mass spectrum shown in Figure 6 resulted. The major peak observed was attributable to decarboxylated tryptophan (tryptamine); additional peaks at the masses of indole and 3-methylindole were also prominent. Only a weak mass 204 signal that disappeared more quickly with time than the other peaks was seen. The energy-resolved, resonantly enhanced spectrum of tryptophan was found to be similar to the spectrum of more volatile indole derivatives to which it is structurally similar but more dominated by low-frequency vibrational structure than are the spectra of those species.[92] Some of these low-frequency modes were attributed to nonconvertible rotational conformers of tryptophan. The existence of such conformers is consistent with a model for the solution photophysics of tryptophan. Small amounts of methanol could be added to the expansion, and mass peaks due to one, two, and three molecules of methanol complexed to tryptophan were detected in the mass spectrum. This ability to form complexes can be combined with high-resolution spectroscopy to determine the geometries of the complexes and thereby better understand solvation and reaction dynamics in these species.

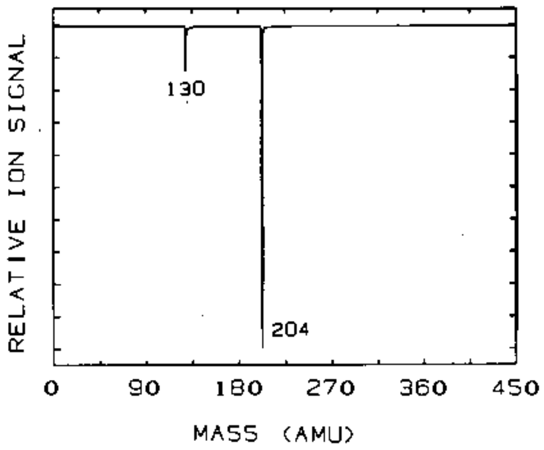

**Figure 5.** Nonresonant two-photon ionization mass spectrum of thermospray deposited tryptophan. Reprinted with permission from ref 91. Copyright 1986 American Institute of Physics.

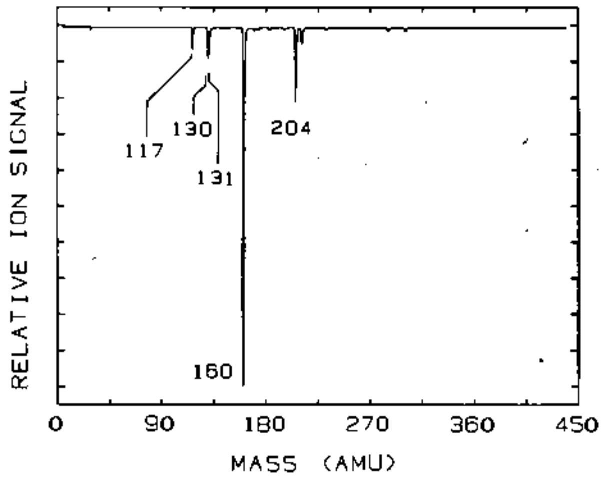

**Figure 6.** Nonresonant two-photon ionization mass spectrum of thermally vaporized tryptophan. Reprinted with permission from ref 91. Copyright 1986 American Institute of Physics.

The pyrimidine uracil has been investigated in a supersonic jet by Ito and co-workers.[93] A pulsed valve with a ceramic solenoid wound with polyimide-coated wire and with heat-proof O-rings was used. This valve was reported to be heatable to 260 °C. Uracil was vaporized at a temperature of 200 °C and expanded with 4 atm of helium through a 0.4-mm orifice. Both fluorescence excitation spectra and dispersed fluorescence spectra were obtained. Absorptions assigned as the $n\pi^*$ states of two tautomeric forms were detected. No thermal decomposition was reported.

Another promising method of vaporizing thermally labile biomolecules is laser desorption, which is discussed in a later section of this review.

## *IV. Analysis*

### A. Qualitative

#### *1. Laser-Induced Fluorescence*

By straightforward extension of the high-resolution jet spectroscopy work of Levy and co-workers,[57-61] Warren et al.[94] showed that laser-induced fluorescence (LIF) in a jet expansion could be used to obtain fingerprint spectra from mixtures of organic species. In that work, a multicomponent mixture consisting of naphthalene and methylnaphthalenes was expanded continuously with helium through a 160-$\mu$m orifice. The expansion was crossed ~30 nozzle diameters downstream by a pulsed tunable laser. Fluorescence was collected at right angles to both laser and molecular beam propagation directions and imaged into a 0.3-m monochromator. When fluorescence at ~29 700 cm$^{-1}$ was monitored as the laser energy was scanned from 31 600 to 32 600 cm$^{-1}$, a spectrum spanning the $S_0 \rightarrow S_1$ absorption origin for the three species was obtained. The three origin bands were well resolved, and characteristic vibronic bands of each species were identified. It was further stated that fluorescence spectra characteristic of one component of the mixture could be obtained without interference from the other analytes by selective single vibronic level excitation. Detection limits were not given, although it was stated that ~250 ppm of naphthalene could be identified in $\beta$-methylnaphthalene.

Results similar to the above were reported by Amirav et al.[6] utilizing a continuous expansion. According to these authors characteristic fluorescence spectra could be obtained in such an expansion for molecules with vapor pressures in excess of 10$^{-3}$ Torr at the nozzle operating temperature. A 100–1000-fold increase in sensitivity was demonstrated by utilizing a pulsed slit nozzle rather than the continuous expansion. By use of the slit nozzle, fluorescence excitation spectra were obtained for fluorene present at ~1 ppm in biphenyl. Basic requirements for LIF analysis of large molecules were deemed to be an emission quantum yield exceeding 10$^{-3}$, a volatility such that a vapor pressure >10$^{-5}$ Torr (10$^{-7}$ Torr for a slit nozzle) is attainable, and chemical stability at the nozzle operating temperature.

An LIF supersonic jet fluorometer has been described by Imasaka et al.[95] A continuous expansion of argon through a 300-$\mu$m nozzle was used. The nozzle was heatable to 500 °C, although temperatures of 400 °C were more commonly used in order to avoid sample decomposition. A detection limit of 100 ng was claimed for perylene, and it was also demonstrated that benzo[*a*]pyrene could be detected in the presence of perylene, although selective excitation was not achieved.

#### *2. Lamp-Induced Fluorescence*

In order to simplify the instrumentation required for analytical jet spectrometry, attempts to replace the commonly used laser excitation source with a lamp excitation source have been reported.[96-99] Lamp excitation had previously been reported in a number of spectroscopic applications, most often to directly obtain absorption spectra either because of low fluorescence quantum yield[100] or in conjunction with fluorescence spectra to determine quantum yields.[101,102] In the analytical applications, however, the lamps were proposed as excitation sources for fluorometry.

Imasaka et al.[95,96] utilized a 150-W xenon lamp to excite fluorescence in a pulsed (100 Hz) argon expansion. The lamp output was dispersed in a 1-m scanning monochromator and then focused onto the jet 5 mm downstream of the orifice. Fluorescence from analytes in the jet was measured with a bare photomultiplier tube and gated photon counting. A base-line correction was made by subtracting the counts due to light scatter as measured during the valve close cycle from those of the valve open signal. With this apparatus the authors were able to identify well-resolved fluorescence excitation features from each component of a mixture of aniline, *N*-methylaniline, and *o*-, *m*-, and *p*-toluidine. However, this system was nearly 7 orders of magnitude less sensitive than a similar laser-excited system. The sensitivity differences were almost entirely due to the differences in source intensity. The laser-based system also had the advantage of better signal-to-noise ratio and narrower fluorescence line widths.

A xenon arc lamp based jet fluorimeter has also been described by Yamada et al.[97,98] In contrast to the apparatus of Imasaka, described above, which dispersed and scanned the lamp output to generate a photoexcitation spectrum of one species at a time, this instrument utilized the full spectral output of a 300-W lamp focused to a spot of ~1.5-mm diameter, 1–3 mm downstream of a continuous flow nozzle of 80-$\mu$m diameter and an argon expansion. The lamp was chopped and fluorescence detected through a 1-m spectrometer with a lock-in amplifier in order to reduce spurious background light. The spectral line widths attainable with this system were not reported; however, the spectra obtained were characterized by narrow lines built upon a broad background that was attributed to being due to the bandwidth of the excitation source. In spite of the broad background signal the authors were able to distinguish three of four anthracene derivatives in a mixture. No estimate of sensitivity was given, although the same instrument was also used for evolved gas analysis[99] with a claimed limit of detection of 10 $\mu$g.

#### *3. Multiphoton Ionization*

Regardless of the source used, fluorescence-based methods are by their nature at the mercy of fluorescence quantum yields and photon collection efficiencies. One approach to avoiding these limitations is multiphoton ionization (MPI), which is being developed by several groups as a jet analytical technique. In the simplest case MPI is an *n*-photon absorption process leading to ionization and obeys the condition

$$nE_{\mathrm{ph}} > \mathrm{IP} \qquad (2)$$

where $E_{\mathrm{ph}}$ is the photon energy and IP is the molecular ionization potential. In such a case the number of ions produced will be proportional to $I^n$, where $I$ is the laser intensity. Such a process is entirely nonselective: any species in the sample for which eq 1 is satisfied will be ionized. In such a nonselective ionization scheme, supersonic cooling would be of little use.

Resonantly enhanced MPI processes have become widely used in conjunction with supersonic expansions. In this case at least one of the virtual absorption processes is replaced by absorption by a real excited electronic state of the molecule. A great enhancement of the ion signal can be obtained in such a case. In the most favorable case

$$\mathrm{IP} < 2E_{\mathrm{S}_1} \quad (3)$$

Then in a one-color experiment a single photon will excite $S_1$ followed by ionization by a second photon of the same energy. The ion-yield enhancement will be equivalent to the ratio of the absorption cross section for a real state relative to the corresponding cross section for a virtual state. This type of process is generally referred to as one-color, resonance-enhanced, two-photon ionization or R2PI.

When eq 3 is not satisfied, resonantly enhanced ionization can be effected with a two-color R2PI process, provided the energy of the second photon exceeds IP $- E_{\mathrm{S}_1}$. Alternatively, a three photon or higher order process can be used. The latter processes are commonly designated $n_1 + n_2$ MPI processes, where $n_1$ is the number of photons required to achieve excitation into a real excited state and $n_2$ is the number of additional photons required to achieve ionization. Processes with $n_2 > 1$ are generally of low efficiency. The two-color process, on the other hand, is theoretically as efficient as the R2PI process but experimentally demands exacting spatial and temporal coincidence of the two laser beams.

An early report on the analytical potential of MPI processes in beams is contained in the paper by Boesl et al.[103] Although done in an effusive beam (i.e., without supersonic cooling), it was demonstrated for six different organic molecules that soft ionization could be obtained. By soft ionization it is meant that the molecule is ionized without fragmentation. The ions were detected with a quadrupole mass filter after resonance-enhanced ionization in a one-color experiment. For five of the six compounds examined, the condition $E_{\mathrm{S}_1} > \mathrm{IP}/2$ held, and the cross sections for both the excitation and ionization steps were determined. For the sixth compound, furan ($C_4H_4O$), there are no excited states in a convenient spectral region for R2PI. For this compound two alternate ionization schemes were compared: a totally nonresonant two-photon ionization through a virtual intermediate and 2 + 1 MPI. The direct two-photon ionization was more efficient than the three-photon process, even though no resonance enhancement was involved.

Lubman and co-workers have published a number of papers in the area of jet-MPI spectrometry. All of these experiments have utilized a pulsed expansion at 10 Hz, the unskimmed expansion then being ionized within the ion extraction grids of a time-of-flight mass spectrometer (TOFMS). In an early experiment, Tembreull and Lubman[104] utilized R2PI to demonstrate the ability of jet-REMPI-TOFMS to discriminate among the isomers of cresol. They succeeded in showing that the three isomers could readily be distinguished with discrimination limits of 1:300–500. The detection limit was extrapolated to be ~20 ppb. Additionally, the extent of cooling in various gases was investigated. Although the coldest spectra were obtained in argon, narrow spectral features were also observed for other gases. In particular, nitrogen and air were nearly identical in the extent of cooling, and that cooling was sufficient that the technique could be applied to the direct analysis of air samples.

In a paper by Sin et al.,[105] a variety of disubstituted benzenes was examined. The species studied were selected because of their spectral and mass similarities and low fluorescence quantum yield. By taking advantage of the multidimensional selectivity of jet-TOFMS, the various species could be distinguished with high discrimination factors, e.g., a discrimination limit of 1:5000 for a mixture of *p*-cresol and fluoroaniline was demonstrated.

Tembruell et al.[106] examined the R2PI spectroscopy of halogenated aromatics. The compounds examined consisted of mono- and dihalobenzenes, -toluenes, and -anilines. These compounds are of interest because of their decreased fluorescence quantum yields relative to the nonhalogenated species. This decrease primarily is due to the internal heavy atom effect. Efficient R2PI was observed for all the species examined except for the iodo compounds, compounds with a halogen ortho to an electron-donating group (e.g., $NH_2$ or OH), and ortho-dihalogens. These results were generalized into a set of rules for predicting ionization efficiencies.

A number of azabenzenes have been investigated by the same group.[107] The azabenzenes are of interest because of their $n\pi^*$ excited states in addition to the $\pi\pi^*$ states of nonheteroatomic aromatic molecules. In the absence of solvent effects, the $n\pi^*$ states are usually the lowest energy singlet excited states. Narrow bands in jet expansions are often observed for only the lowest energy vibronic transitions of the first excited state. As vibronic excitation energy is increased and for higher excited states, radiationless processes into an increasingly dense manifold of nearly isoenergetic levels cause band broadening. The $n\pi^*$ states are also characterized by reduced fluorescence quantum yields due to enhanced intersystem crossing and ionization potentials greater than $2E_{\mathrm{S}_1}$. Nevertheless, Tembreull et al.[107] reported that they were able to obtain soft ionization of these species in a one-color, one-photon resonant process. From the power densities necessary to produce ion signals, it was concluded that the two-photon ionization process was more efficient than could be explained by ionization through a virtual state. This efficient ionization was interpreted as being due to another state at $2E_{\mathrm{S}_1}$. It was postulated that this was either a Rydberg state or a valence state of the molecules and that it must have a dense level structure at $2E_{\mathrm{S}_1}$ since the bands observed in the spectrum correlated with the known $S_1$ vibrations of the compounds.

Rohlfing[108] has evaluated both LIF and REMPI for the discrimination of chlorinated naphthalenes. For 2-chloronaphthalene, LIF spectra were obtained in spite of a reduction in $\phi_{\mathrm{fl}}$ by ~30 relative to naphthalene. A detection limit of 30 ppb was estimated. For dichloronaphthalenes, however, a further reduction in $\phi_{\mathrm{fl}}$ precludes the observation of any LIF signal. $E_{\mathrm{S}_1}$ for the chlorinated naphthalenes is less than IP/2, hence ionization must proceed via a one-photon resonant, two-photon ionization mechanism. In order to achieve sensitive detection with such a scheme, high laser intensities were used. These high intensities induced considerable fragmentation along with ionization. In contrast to the dihalobenzene results,[106] ionization was observed for *o*-dichloronaphthalenes, although an increase in the ratio of fragments to parent ion was observed in this case. Figure 7 illustrates application of

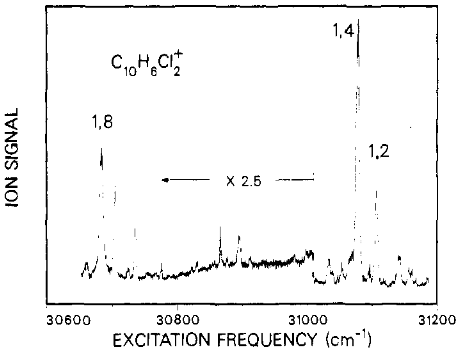

**Figure 7.** Parent ion MPI spectrum of a mixture of dichloronaphthalenes. Reprinted with permission from ref 109.

the 1 + 2 REMPI process to distinguish among the components of a mixture of three dichloronaphthalenes. The sensitivity has been estimated to be ~30 ppb.[109]

## B. Quantitative

Although detection limits are cited in several of the reports summarized in the previous section, truly quantitative investigations have been few. The difficulties involved in obtaining quantitative data as well as one solution to the quantitation problem were first proposed by Hayes and Small.[5] They noted that in a continuous expansion of a complex mixture the intensity of a peak in the LIF spectrum is proportional to the vapor pressure in the reservoir of the component responsible for that absorption. However, the partial pressure of each component can depend upon the partial pressures of other species in the mixture and the partial pressures are subject to change during the course of an experiment as components become depleted in the reservoir. The quantitation method proposed was to concentrate the total signal from each specific analyte into a small period of time and then to monitor fluorescence as a function of time. As a convenient method of achieving this time concentration, gas chromatography was used. Mixtures of naphthalenes in cyclohexane were injected onto a short (20 cm) packed column with helium carrier gas. The column terminated in a 150-$\mu$m pinhole, expanding into a vacuum of ~5 mTorr. LIF of a single component of the mixture was selectively excited by a tunable dye laser. Discrimination ratios in excess of 1000 were reported for coeluting species. Injections at higher ratios resulted in column overloading. Detection limits of 14–60 ng were reported with a linear calibration curve for over 3 orders of magnitude of amount injected.

Imasaka et al.[110,111] have also utilized a gas chromatograph as the input into a supersonic jet in order to obtain quantitation. In their earliest work, the GC effluent was continuously expanded through a 500-$\mu$m pinhole, skimmed, and probed by MPI. With this arrangement a detection limit of ~1 $\mu$g was obtained for benzene. The rather poor detection limit was primarily due to the use of an inefficient two-photon absorption, two-photon ionization process. Subsequently, the instrumentation was improved by the addition of a capillary column GC, a high-temperature valve, and a TOFMS detector. With this instrument, resolution of a mixture of aniline, *p*-toluidine, and *N*-methylaniline was demonstrated. The resolution was complicated by the coelution of the latter two compounds, which have identical molecular masses. Selective laser excitation was necessary to the mixture determination. Discrimination factors were not discussed, but a limit of detection of ~5 $\mu$g was claimed.

Pepich et al.[112,113] have also combined a pulsed supersonic expansion with capillary gas chromatography and LIF spectroscopy. In their design, the GC effluent was introduced through an inlet into an antechamber downstream of the pulsed valve. The valve was water cooled so that the antechamber could be heated to 220 °C, while the valve temperature remains near ambient. It was found that adequate mixing of the GC effluent with the expanding gas pulse was obtained when a plug of quartz wool was inserted into the antechamber near the exit aperture. By use of this apparatus, a sample extracted from airborne particulates collected over a 24-h period from the vicinity of a tire conflagration was analyzed.[113] With selective laser excitation, it was possible to quantitatively identify the three isomers of monomethylanthracene in this sample. Detection limits of 2–6 ng were obtained. These results were compared to results of GC-MS analysis of the same sample. The latter technique was more complicated due to the presence of coeluting aliphatics and isomeric monomethylphenanthrenes, which were totally transparent to the LIF technique.

## C. Limitations of Jet Spectrometry

If the studies discussed above have served to demonstrate the potential of jet spectrometry, they have also defined certain shortcomings that have limited the extent of jet applications.

### 1. Sensitivity

Detection limits in the 10–100-ng range were demonstrated in 1982 by Hayes and Small[5] for molecules with $\phi_{\mathrm{fl}} \sim 0.2$ using a continuous jet, selective excitation, and a detection bandpass of ~7.5 nm. For perylene, with a near unity $\phi_{\mathrm{fl}}$, detection limits close to the high end of the above range were observed in supersonic fluorometry, which is less sensitive due to a narrower detection bandpass (0.1–1.0 nm). Near unity detection efficiencies are possible for ion collection compared to photon collection efficiencies of $10^{-3}$ or less. Nevertheless, improved detection limits for quantitative jet spectrometry have not yet been reported for MPI detection. Indeed, the few quantitative MPI reports to date have had detection limits in the microgram range.

Hayes and Small predicted that their detection limits could be extended into the picogram range by increasing the duty factor of the experiment with a pulsed expansion. Such an increase has not been reported. Pepich et al.[112,113] did couple a pulsed expansion to a GC with LIF detection and molecules with fluorescence quantum yields similar to the molecules studied by Hayes and Small. They reported an increase in limits of detection by about an order of magnitude. At least part of the reason for not achieving a more significant improvement can be traced to the lower laser power available in their experiment. A similar capillary column GC, pulsed-valve instrument with MPI detection reported by Imasaka et al.[111] only managed to achieve detection limits in the microgram range.

For jet spectrometry to have more than specialized analytical applications, detection limits in the low picogram range will have to be routinely and reproducibly possible.

### 2. Vaporization

The power and beauty of jet techniques is the ability to produce a beam of molecules that are vibrationally and rotationally cold yet still a vapor. Before this can occur, then, the molecule must be vaporized. Increasingly, the analyst is required to determine high molecular weight species—species with low volatility. In addition to the design constraints imposed by high-temperature operation, such species are often thermally labile and cannot be vaporized by the simple expedient of increased heating. This problem is exacerbated by catalysis of decomposition due to materials needed to construct high-temperature apparatus. Although this problem is not unique to jet spectrometry, the development of techniques for nonthermal vaporization compatible with supersonic expansions would greatly advance the use of jet spectrometry.

### 3. Selectivity

Discrimination factors of several thousand are impressive, but they may conceal a shortcoming of jet techniques. The high discrimination comes about because interfering analytes are transparent to the spectral probe being used. The other side of the coin is that when it is the "interfering" species that is the analyte of interest a change of the spectral probe is necessary. The limited spectral range of tunable lasers, coupled with the necessity of exciting low-energy vibronic features to achieve high discrimination, means that only a relatively small number of compounds (usually of similar or related structure) can be determined in a single experiment. Indeed, to date, quantitative applications have determined only a single compound at a time, requiring multiple analyses to determine multiple components of a mixture. Broader spectral tuning ranges or nonlaser excitation methods will need to be developed to make jet techniques more widely applicable.

### 4. Quantitation

The sequential analysis requirement discussed above is a constraint imposed by the coupling of chromatography to jet analysis. As each compound is eluted from the chromatographic stage into the expansion, it is detected if the spectral probe is sensitive to that compound. Alternative quantitation schemes that could relate spectral peak areas directly to concentrations would relax this constraint. With such a scheme, all compounds with absorption within a spectral range could be quantitatively determined simultaneously. Unfortunately, no simple method of general applicability has been proposed.

A further concern regarding quantitation that has not been addressed in the studies cited above is laser saturation effects. Care must be taken in all laser-based analytical spectroscopies to ensure that electronic transitions are not saturated. This is of particular importance in multiphoton techniques in which high intensities are used to compensate for low-probability processes.

## D. Future Promise

Jet spectrometry is a vital area of research, and the limitations discussed in the previous section are well-known. In this section work in progress addressed directly to alleviating the shortcomings of jet analyses is discussed.

### 1. Direct Absorption

Several groups have demonstrated that electronic absorption spectra in the UV and visible regions can be measured directly in a jet expansion.[6,100–102] In general the sensitivity is low: absorbances of ~0.01 can be measured. For species such as naphthalene or anthracene this corresponds to a detection limit of ~1 ppm in a pulsed expansion through a circular orifice. Most often direct absorption measurements have been used in spectroscopic applications, either due to low fluorescence quantum yields[100] or in conjunction with fluorescence to determine quantum yields.[101,102] Analytical applications with a pulsed planar expansion have been described.[6] Planar expansions can provide an increased absorption path length, thereby increasing sensitivity by up to 2 orders of magnitude.[6] In principle this would allow absorbances as weak as $10^{-4}$ to be measured.

Requirements for an apparatus for analytical jet spectrometry utilizing direct absorption can be readily enumerated. First, in the absence of a more direct quantitation scheme, the apparatus would need to be coupled to a chromatographic instrument. This would not only provide quantitation but also limit the number of analytes to be determined per unit time. Such limitation will minimize interferences from broad absorptions overlapping the narrow features in any particular spectral region. Second, in order to obtain sufficient spectral information to identify each analyte during its elution time, detection of parallel wavelengths would be necessary. This would require either a diode array detector or a Fourier transform detector. Third, to minimize pumping requirements, a pulsed expansion is preferable. This would ideally be used with a pulsed source to maximize the experimental duty factor. (Pulsed signals would of course be more difficult to detect with a Fourier transform instrument.) Finally, in order to acquire, store, and identify spectra, a fast data-handling system would be necessary.

### 2. Sheath Flow Expansions

One approach to increased sensitivity in supersonic expansions is the sheath flow nozzle.[20,114] Based on the principle of sheath flow hydrodynamic focusing pioneered by Keller and Nogar,[115] the sheath flow nozzle is illustrated in Figure 8. The analyte flows through the inner tube, which terminates a few millimeters from the expansion orifice. The bulk of the expansion gas flows around the inner tube; this is referred to as the sheath gas. With the proper ratio of pressures for the sheath gas and the sample-containing gas, the sample flow becomes focused along the center line of the expansion. The focused region is better matched to the dimensions of the excitation laser spot, so that more efficient excitation produces a more intense fluorescence. An intensity increase of ~30 along the center line of a sheath flow expansion can be achieved relative

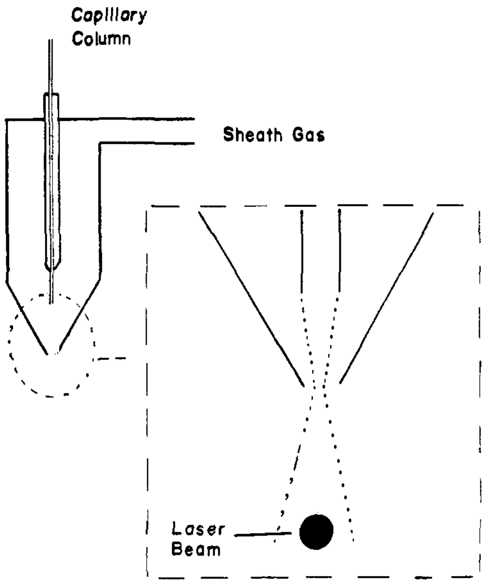

**Figure** 8. Sheath flow nozzle. Reprinted with permission from ref 114. Copyright 1987 American Chemical Society.

to that of an unfocused expansion.

The sheath flow has also been demonstrated to be well adapted to interfacing capillary column GC to a jet expansion.[114] Allowance for differences in the optimum flow rates for the GC and the supersonic expansion can be made with the sheath design. A quantitative analysis of naphthalene-containing samples in a continuous sheath flow analysis attained a detection limit of 50 pg following injection into a 30-m, 250-$\mu$m poly(dimethylsiloxane) column.

### 3. Laser Desorption

A promising technique for the vaporization of large molecules is laser desorption. The technique is being used increasingly for mass spectroscopy of solids. Several reviews of this application have appeared,[116-118] and some of the results of LD-MS studies are relevant to jet spectroscopy. In LD-MS, the laser excitation is generally used both to produce desorption and to produce ions for the mass analyzer. Various types of mass analyzers have been used: magnetic instruments,[119] time of flight instruments,[120] and Fourier transform of the current in an ion trap (ion cyclotron resonance).[121] A wide variety of desorption geometries, energy densities, and laser wavelengths have been used, mostly in laboratory-built instruments, although a commercial instrument is available.[122] This wide range of parameters makes data comparison difficult. Nevertheless, several generalizations regarding the desorption-ionization process may be drawn. The most critical parameter in desorption efficiency appears to be laser power density;[118] the desorption process is not strongly wavelength dependent. "True" laser desorption (as opposed to laser-induced thermal desorption) is a nonequilibrium process. Ionization efficiencies are generally low ($\sim 10^{-5}$), although higher efficiencies (0.01–0.1) can sometimes be obtained at high-power densities.

The low ion production ratios in laser desorption make desorption–jet spectrometry an attractive technique. The desorption conditions can be arranged so that primarily neutrals are desorbed and then entrained in a supersonic flow. The full range of jet spectrometric methods is then available to interrogate the desorbed species. Laser desorption followed by entrainment in a supersonic expansion with R2PI detection has been reported by Tembreull and Lubman.[123] They examined desorption of thick (100's of monolayer) layers of pure compounds deposited onto an aluminum rod by repeated solvent evaporation steps. Desorption was induced by several different wavelengths: 249 nm from a KrF excimer laser, 532 nm from a doubled Nd:YAG laser, and 10.6 $\mu$m from a $CO_2$ laser. Power densities for the latter two lasers were in the range $10^7$–$10^8$ W cm$^{-2}$. Ionization was accomplished by a second laser, delayed $\sim$220 $\mu$s relative to the desorption pulse. The ionization wavelength was either 249 or 266 nm, into a dense, nonselective absorption region. The sample-clad rod was mounted 3–5 mm off the central axis of a pulsed argon expansion and a minimal distance downstream from the jet orifice. In the experiments reported, polycyclic aromatic hydrocarbons with molecular masses $\sim$300–400 were desorbed. Two biologically important species, adenine and cytosine, were also studied. The supersonic narrowing of the initial velocity distribution of the desorbed species resulted in narrowing of the time of flight mass ion peaks by a factor of 10 relative to uncooled, desorbed ions generated within the acceleration grids of the apparatus. The most efficient desorption, as determined by both the intensity of the ion signal and the absence of fragmentation, was produced by the $CO_2$ laser desorption. More recently, the same authors reported laser desorption of a variety of clinically important molecules[124] as well as a number of small peptides[125] containing tryptophan, tyrosine, or phenylalanine. Desorption was effected with a $CO_2$ laser with a power density of $<7 \times 10^6$ W cm$^{-2}$ from the face of a rod near the expansion orifice. The desorbed neutrals were ionized by a UV laser at 280 or 266 nm in an R2PI process.

A similar account of laser desorption–jet expansion–MPI has been given by Grotemeyer et al.[126] In their experiment, the desorbed species was a native chlorophyll with a relative molecular mass of 892. Desorption was produced with a $CO_2$ laser upstream of the pulsed valve. The desorbed species were then expanded with argon into the vacuum. The resulting beam was ionized by a frequency-doubled dye laser at 275 nm and the ions directed into a reflectron-equipped TOFMS. Ion peaks due to the chlorophyll and a hydroxylated derivative, which was produced during sample purification, were detected. In addition, a peak due to fragmentation by loss of the pendant phytyl chain was observed as well as a peak due to replacement of the central magnesium by a pair of protons. The fragmentation was assumed to occur during the ionization; the magnesium replacement could have occurred either during desorption or during sample preparation. A mass resolution of 2900 was attained, sufficient to resolve isotopic mass peaks. Good agreement between the intensity of the isotopic peaks and natural isotopic abundances was demonstrated.

### 4. Supercritical Fluid Spectroscopy

Another method of introducing low volatility, thermally labile species into jets involves supercritical fluids (SCF). The solubility of moderate to large molecular weight organic species is considerably higher in such a fluid than it is in a rare gas. Additionally in the expansion process, the supercritical fluid carrier will itself rapidly vaporize as the pressure drops from several hundred atmospheres to subatmospheric. On the other hand, the extent of cooling in commonly used SCF (e.g., $CO_2$, $N_2O$, $NH_3$, $CH_3OH$) will be considerably less than in rare gases. This decrease in cooling is due to two factors. First, being polyatomic species, the SCF themselves have internal energy modes that must be cooled. Second, because of the high-pressure differential involved in the expansion, the terminal Mach number (lowest translational temperature) is not reached within an experimentally convenient distance; thus the beam must be interrogated before the fullest possible cooling can be achieved.

The first report on the use of SCF for introducing samples into a supersonic expansion was by Fukuoka et al.[127] They utilized a continuous jet formed by flowing the SCF through a 0.55-mm-o.d. tube restricted at the end inserted coaxially into a 0.8-mm-i.d. tube that terminated in a 3.0-mm pinhole. Argon was flowed through the outer tube, mixing with the SCF exiting the inner tube just upstream of the pinhole. Although the authors describe the volume where the two flows combine as a mixing region, the design is quite similar to the sheath flow nozzles described by Johnston[114] (vide supra). Expansions with various SCF were evaluated with this system. As expected, the extent of cooling was less for the SCF expansion than for argon expansions. The extent of cooling also decreased as the size (number of internal modes) of the SCF increased. For $CO_2$, for which the most extensive cooling was observed, the line widths for both pure SCF expansions and argon-diluted SCF expansions were nearly the same as those for pure argon expansions. Relative to the pure SCF expansion, however, the intensity was greatly enhanced in the SCF/argon expansion, possibly due to sheath flow focusing.

In a related work, Imasaka et al.[128] used the same design (i.e., coaxial flow of the sample-containing fluid through the expansion gas flow tube) to achieve an HPLC-supersonic jet interface. The HPLC solvent was methanol at near supercritical conditions. A mixture of monochloroanthracenes, for which chromatographic resolution was not attainable for the 1- and 2-chloro species, was analyzed. Sufficient cooling was obtained so that spectral resolution of the three was obtained by wavelength-selective excitation, even though the excitation shifts for the coeluting species are small. The chloroanthracenes were chosen for evaluating this system because at least one of them (2-chloroanthracene) was found to decompose at temperatures below those that would be necessary to achieve thermal vaporization. A detection limit of 40 ng for anthracene was reported. Presumably, the detection limits for the chlorinated species would be poorer due to lower $\phi_{fl}$.

Interfacing of SCF with a supersonic expansion has also been reported by Sin et al.[129] In their apparatus, a pulsed expansion of supercritical $CO_2$ was expanded into the vacuum system. The resulting beam was skimmed and then interrogated by MPI. In order to maintain pressures consistent with ion detection, the bulk of the $CO_2$ was pumped away in the first chamber by four liquid-nitrogen cold traps. The R2PI spectra of acenaphthene, phenanthrene, and carbazole were shown to be cooled in the pure $CO_2$. Although the cooling was less extensive than in argon expansions, the reservoir temperatures needed to introduce the analyte into the expansion gas were much lower for $CO_2$. In addition to obtaining wavelength-resolved MPI spectra of the origin regions of each species, it was also shown that time-of-flight mass spectra obtained with nonselective R2PI (at 266 nm) could mass resolve mixtures of up to five PAH. In a subsequent publication the same authors[130] described modifications of a fuel-injector valve for use with pulsed-SCF jet expansions. The valve was claimed to be useful with expansions of $CO_2$ or $N_2O$ at pressures to 380 atm and temperatures to 100 °C.

## V. Conclusions

Supersonic jet spectrometry is still a developing technique. The high spectroscopic resolution afforded by supersonic expansions is indeed analytically useful. Very high discrimination factors can be obtained even for compounds of similar mass, structure, and electronic states. For mixtures of dissimilar materials, nearly absolute single species selectivity with high sensitivity can be obtained, since interfering species are transparent to the spectral probing. For many biological species, jet spectroscopy is the only source of high-resolution spectral information that is important for uncovering structural and dynamic information.

On the other hand, there remain difficulties with the technique which limit its utility and widespread use. Foremost among these are methods of quantitation which preclude parallel determination of multicomponent mixtures and volatility and stability limits on the materials to which the technique is applicable. Although these same limitations also apply to alternative methods of analyzing large molecular weight species, as a newer method jet spectrometry must demonstrate a clear advantage over those methods to supplant or even to supplement them in routine applications.

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