ELSEVIER

International Journal of Mass Spectrometry 200 (2000) 459–478

International Journal of Mass Spectrometry

Mass spectrometric implications of high-pressure ion sources

John B. Fenn*

Department of Chemistry, Virginia Commonwealth University, Richmond, VA 23284-2006, USA

Received 1 August 2000; accepted 30 August 2000

Abstract

The nature of supersonic free jet expansion of a gas from high pressure into vacuum is reviewed and characterized in this article. The increasingly widespread applications and implications of this jet expansion process in mass spectrometry are described. Particular attention is paid to prospective advantages and possible problems when such jets are used to transport ions from a source at high pressure into the vacuum environment of a mass analyzer. (Int J Mass Spectrom 200 (2000) 459–478) © 2000 Elsevier Science B.V.

1. Introduction

Mass spectrometry can be regarded as the art of weighing individual molecules. Its practice consists of endowing those molecules with an electric charge to form ions and then measuring the effects of electric and/or magnetic fields on the trajectories of those ions in a vacuum. The determination and interpretation of trajectory response is frequently referred to as mass analysis. Thus, a mass spectrometer comprises an ion source and a mass analyzer as its principal components.

For many decades, the ions for mass analysis have most often been produced by gas phase encounters between neutral molecules and electrons, photons, or other ions. Under appropriate conditions, such encounters can result in either the removal of an electron from a neutral molecule or, more rarely, the addition of one to it. These ionizing encounters have generally been brought about in the same vacuum system in which the trajectories of the resulting ions are characterized, so the molecules to be ionized are at rather low densities. When ionization is caused by electron impact (EI), long the most widely used method, the probability of ionization for any neutral molecule is typically ≤ 0.0001, so the resulting ion currents are very small.

For a number of years and a number of reasons, it has been found advantageous in many situations to carry out the ionization process in gas at pressures up to 1000 torr or more. Some of the resulting mixture of ions and neutral molecules is then passed into the vacuum system that houses the mass analyzer. So-called electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) are two widely used techniques in which ionization usually takes place in a bath gas at or near atmospheric pressure. The subsequent step of admitting some of the resulting gas–ion mixture from high pressure into a vacuum is simple in concept but in actuality is a complex process whose consequences have too often been unrealized and, therefore, ignored, much to the subsequent dismay of many investigators. The purpose of

---

* E-mail: jfenn@saturn.ucu.edu

1387-3806/00/$20.00 © 2000 Elsevier Science B.V. All rights reserved
PII S1387-3806(00)00328-6

this commentary is to identify and characterize some important features of the process by which gas passes freely through a small-bore orifice or tube from a source at high pressure into a region of low pressure.

1.1. Some historical background

As it happens, a mass spectrometer with a high-pressure ion source is very similar in design, construction, and operation to a modern molecular beam apparatus that uses a supersonic free jet of gas as a beam source. Indeed, the first really successful experiments in both ESIMS and APCIMS were carried out in slightly modified molecular beam systems [1,2]. To provide some historical perspective on what led to these experiments, it will be appropriate to summarize briefly some molecular beam history. The essential components of a classical effusive molecular beam apparatus are illustrated in the upper panel of Fig. 1. Chamber A, often called an oven because it is sometimes at high temperature, is supplied with gas or vapor at density low enough that the mean free path is of the same order as the diameter or width of a source orifice, or slit in the right-hand oven wall through which gas or vapor effuses into the central or collimating chamber B. To minimize scattering losses, the gas density in B is kept low enough to provide a mean free path larger than the distance between the source and the collimating orifices. When those orifices are circular, the effusive flux intensity vectors in chamber B have cosine distribution for which the envelope is a sphere tangent to the source orifice, as shown. For such a distribution, the maximum intensity for I_0 is along the axis normal to the plane of the orifice. The value of I_0 at distance x along that axis is given by

$$I_0 = n_0(c_0/4)A/\pi x^2, \qquad (1)$$

where n_0 is the number density of molecules in the oven, c_0 is their average thermal speed, and A is the source orifice area. The resulting collimated beam or ray of molecules in test chamber C can be scattered from a surface, scattered by a cloud of other molecules, or deflected by a field of some sort. Response of the beam to such interactions can provide a great deal of information about the structure and behavior of both the beam molecules and their targets.

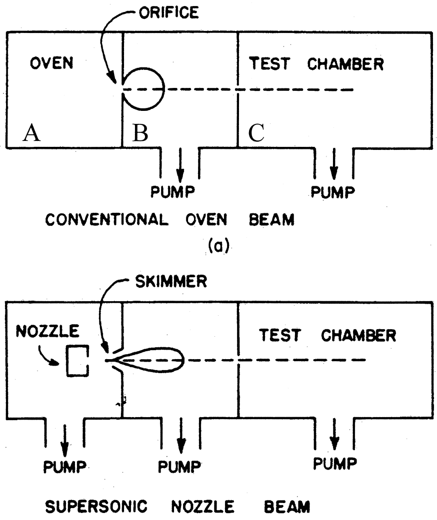


Fig. 1. Schematic representations of the two general types of molecular beam systems. Upper panel (*a*) shows a classical system in which gas or vapor effuses from a source cavity A, often called an oven, through a small orifice into a collimating chamber, and thence to a test chamber where the beam molecules interact with various kinds of targets or fields before being monitored by a detector, which is not shown. The envelope of molecular flux vectors is represented by a sphere tangent to the source orifice. Lower panel (*b*) shows so-called nozzle beam apparatus. Gas from a high-pressure source flows into an evacuated region A through a small orifice emerging as a supersonic free jet. The convective velocity of the flow is superposed on the thermal velocities of the molecules so that the envelope of flux vectors in the gas entering the collimating chamber comprises an elongated ellipse. The ratio of the major axis to the minor axis of the ellipse represents the ratio of axial velocity to radial velocity in the beam molecules. The net result is a beam with much higher intensity and much narrower velocity distribution than is possible with the effusive source of the upper panel (*a*).

It was Otto Stern who first realized and then began demonstrating the power of such molecular beam techniques in experiments carried out in Frankfurt in 1919. After a move to Hamburg in 1922, his laboratory became the Mecca of molecular beam researchers, though at any one time his group comprised only half a dozen or so colleagues. In 1933, Stern left for America and, with Immanuel Estermann, started a small program in molecular beam research at Carnegie Institute of Technology in Pittsburgh. After becoming emeritus in 1945, he retired to Berkeley, California, where he had received an honorary degree from the University of California, Berkeley, in 1930, and remained there until his death in 1969. Meanwhile, the laboratory of one of his protégés, Isadore Rabi at Columbia University, had become a worthy successor to the title of a molecular beam Mecca. In 1943, Stern received the Nobel Prize in Physics for his experiments with Gerlach on the magnetic deflection of a beam of Ag atoms showing that space is quantized and for those with Estermann and Frisch on the diffractive scattering of He atoms and H_2 molecules from an LiF crystal, which demonstrated the reality of the wave properties of particles as massive as atoms. Rabi was similarly honored 1 yr later for discovering the resonance method of measuring magnetic moments by deflection of a molecular beam. Since then, the trail blazed by these pioneers has led nine more scientists to Stockholm to be honored for research with molecular beams. It is interesting that although they are both renowned as physicists, Stern's chair at Hamburg and Rabi's first academic degree were both in chemistry. Moreover, of the 11 Nobel prizes thus far awarded for research with molecular beams, five have been in Chemistry.

The results obtained with beams from these effusive sources were impressive, but the technique suffered from fundamental limitations because of the relatively low intensities of the beams that could be produced. Consequently, a lot of intensive effort was devoted to the production of more intense beams. As has often happened in other fields of research, the idea that finally led to the much-sought increases in beam intensity came from outside the community of molecular beam research, arriving in the form of a landmark paper in 1951 by Kantrowitz and Grey [3]. This paper presented an analysis showing that expansion of a gas from a high-pressure source into a low-pressure region through a small converging-diverging nozzle should produce a supersonic jet of gas with a very narrow velocity distribution and a very high flux per unit area. Moreover, in a well-designed nozzle, all the exit stream lines are parallel, so that the resulting beam could comprise a large fraction of the total flow. Thus, the ratio of beam intensity to required pumping speed could be very high, thereby minimizing the size and cost of the required vacuum pumps. The first successful reduction to practice of the Kantrowitz-Grey idea was reported in 1954 by Becker and Bier, then at the University of Marburg [4]. They had found empirically that better beams were obtained if the diverging section of the nozzle was eliminated. The reason is that the Kantrowitz and Gray analysis had neglected viscosity. The Reynolds number (the dimensionless ratio of inertial forces to viscous forces in a ducted flow) of such tiny nozzles is so low that viscous interaction of gas with the walls of the diverging section produces a boundary layer of thermalized molecules that invades and destroys most or all of the isentropic core flow whose existence was assumed by Kantrowitz and Grey. Removal of the diverging section eliminated much of the viscous gas-surface interaction, so that most of the gas could expand isentropically except for interaction with the background gas. However, its absence also meant that instead of being directed into parallelism with the jet axis, the stream lines were free to diverge. Consequently, the centerline intensity of any beam formed by downstream collimation of the jet core flow decreased with the square of axial distance from the nozzle exit. Even so, the actual centerline intensities were so much higher than those intensities that effusive sources could provide that practitioners have been using simple orifices, converging nozzles, or straight tubes, with no diverging section, ever since the Becker-Bier paper. Not only do these simpler geometries work better than converging-diverging nozzles, they are much easier and cheaper to fabricate. The beams they produce are also much more intense and have much narrower velocity distributions than those produced by effusion of low-pressure gas through an orifice or slit as taught by Stern and his disciples.

The essential features of a molecular beam apparatus based on the Kantrowitz-Grey idea of a supersonic free jet as a beam source are shown in lower panel of Fig. 1. Gas at high density (mean free path much less than the nozzle diameter) expands from sonic velocity at the exit of the nozzle in chamber A, forming a supersonic free jet in chamber A that is exhausted by a vacuum pump of substantial speed.

The role of the source orifice in the effusive beam system of panel a is assumed by the aperture in the tip of a conical collimator known as a skimmer. The component of free-stream convective velocity in the jet superposed on the random thermal motion of its molecules transforms the envelope of flux vectors from the sphere of the effusive source system in panel a to that of the ellipsoid aft of the skimmer in panel b. The ratio of the major axis to the minor axis of the ellipsoid is the ratio of convective velocity to the thermal velocity of the molecules, that is, the speed ratio equivalent to the Mach number, the latter being defined as the ratio of the convective velocity to the speed of sound in the gas which is $(\gamma RT/M)^{1/2}$, where γ is the heat capacity ratio of the gas, C_p/C_v. The net result is that a much greater fraction of the molecular flux stays close to the centerline and contributes to the beam intensity. It turns out that for Mach numbers >4, the beam intensity at a distance x downstream from the skimmer inlet is approximated by

$$I_x = n_s u_s A_s \gamma M_s/(2\pi x^2), \tag{2}$$

where n_S is the number density of molecules in the jet, u_S is the convective velocity, A_S is the area, and M_S is the Mach number, the subscript S referring to conditions at the skimmer inlet. If n_S in Eq. (2) equals n_0 in Eq.(1), $u_S=2c_0$, where c_0 is the most probable molecular velocity, $A_S=A_0$, and $M_S=20$, the intensity of the convective beam of panel b is 5000 times higher than the intensity of the effusive beam of panel a. Unfortunately, to avoid perturbation of the flow by the skimmer (i.e., skimmer interference), the gas density must be lower by a factor approximately equal to $1/M$ so that the realizable gain in this case is only 250. However, already at $M-20$, 90% of the molecules are within 5% of the most probable velocity. Thus, if one wants a narrow velocity distribution in the beam, which is almost always the case, essentially all of the flux intensity in the convective beam is useful intensity. To obtain a similarly narrow velocity distribution in an effusive beam, one must use a velocity selector that, at best, can pass only ~2.5% of the total intensity. Moreover, it is easy to obtain Mach numbers much higher than 20. Consequently, the effective gain in useful intensity for a convective beam over an effusive beam is usually at least several hundred to several thousand.

Clearly, the molecular beam community owes a lot to Kantrowitz and Grey; but in the interests of historical accuracy, it should be noted that in 1927–1928, 25 yr before their landmark paper, T.H. Johnson, a postdoctoral fellow at Yale, found that very high beam intensities could be produced by raising source pressures in his effusive beam apparatus to well over 100 torr [5]. Unfortunately, neither he nor the rest of the molecular beam community understood the expansion of high-pressure gas into a vacuum, so Johnson's results were ignored, and he never received the credit he deserved. History passed him over once again after he left Yale to become a research scientist at the Franklin Institute in Philadelphia. There he built a molecular beam apparatus and, contemporaneously with Estermann, Frisch, and Stern at Hamburg, was attempting to observe diffraction in the scattering of hydrogen and helium molecules from the surface of lithium fluoride crystal. As in Hamburg, the surface of the crystal was oriented so that the planes of the atoms were perpendicular to the plane of the incident molecular beam. Also as in Hamburg, no evidence of diffraction was found. One day in Hamburg when the apparatus was being reassembled, the technician by mistake oriented the crystal so that the atom planes were parallel with the plane of the incident beam instead of perpendicular. It was then that diffraction was observed for the first time. Eight weeks later, Estermann was in the United States and visited Johnson's laboratory. He recounted the story of how the accidental rotation of the crystal in Hamburg had resulted in diffraction patterns. Johnson then rotated his crystal, and he too saw diffraction. Twenty-five years too early with his high-intensity beams and 8 wk too late in rotating his crystal surface, this very able scientist is today an unknown, a victim of bad luck.

1.2. Enter mass spectrometry

The focus of this discussion is on mass spectrometry, but as was pointed out earlier, a modern mass spectrometer with an ion source at high pressure is

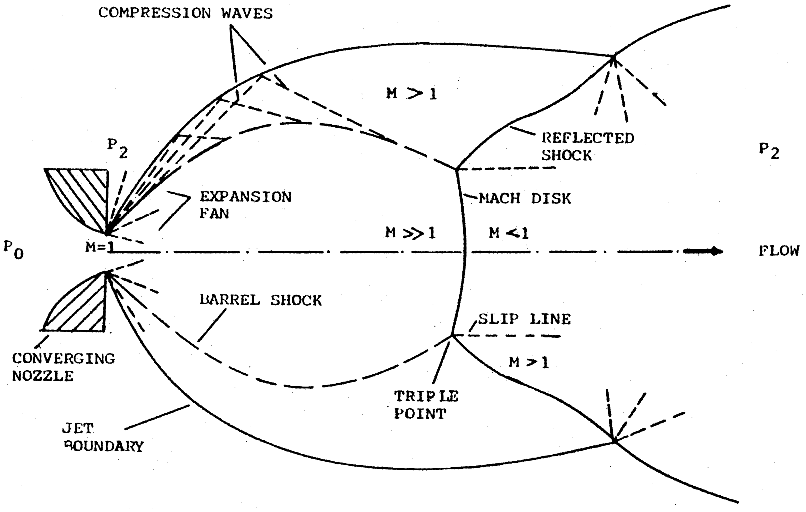


Fig. 2. Schematic representation of a supersonic free jet. When the ambient pressure p_2 is very low, as in a vacuum system, the shock wave structure becomes very diffuse and the isentropic core bounded by the barrel shock and the Mach disk includes most of the flow.

functionally and operationally almost identical to a modern molecular beam apparatus that uses expanding free jets as a beam source. Consequently, many of the lessons learned in experiments with molecular beams from nozzle sources have a substantial relevance to mass spectrometry with ions from high-pressure sources. The similarity is clear from the schematic diagram of such an apparatus in Fig. 1. In form and function it differs from an ESI or APCI mass spectrometry system primarily in the absence of an ionizer in the source gas and, thus, in the absence of ions in the resulting beams. (As shown, it also is without a mass analyzer, but in fact, small mass spectrometers were often used as detectors in molecular beam experiments, the ions being formed from the neutral beam molecules by electron impact or laser photons after those molecules had been scattered, deflected, or otherwise processed for the purpose of the experiment.) Unfortunately, many mass spectrometrists are unfamiliar with the large body of information and understanding that has been accumulated by many investigator-years of experience with free jets as sources for molecular beams. Nor has that ignorance been blissful. For example, it doomed to failure the pioneering efforts of Malcolm Dole in reducing to practice the revolutionary idea of ESIMS, which he proposed in 1968. [6]. It is to be hoped that this article may help repair some of this deficiency in the understanding of free jet characteristics, some of which deficiency still persists in the siblinghood of mass spectrometrists.

1.3. The anatomy and behavior of supersonic free jets

Fig. 2 depicts the structure of a jet formed by gas issuing from the exit of a simple converging nozzle into a region of lower pressure when the exiting velocity is sonic; that is, it equals the local speed of sound in the gas. This happens when the ratio of pressure p_0 upstream of the nozzle to the pressure downstream (i.e., p_2 in chamber B of panel b) in Fig. 1 is equal to or greater than $([\gamma+1]/2)^{\gamma/(\gamma-1)}$; γ is the heat capacity ratio C_p/C_v. For a monatomic gas, $\gamma=5/3$ and decreases to 1.0 for a gas of molecules with an infinite number of atoms. In other words, as long as the ratio of pressures across a nozzle or duct is ≥ 2.05, the velocity of the gas in the plane of the duct or nozzle with the smallest cross-sectional area will equal the speed of sound in the gas; that is, $(\gamma RT/M)^{1/2}$, where T is the temperature of the gas. That critical value of 2.05, as the sufficient requirement to achieve sonic velocity in any gas, is increased to the extent that the viscous dissipation contributes to the pressure drop across the orifice or nozzle. Once sonic velocity is reached at the minimum cross-sectional area of any duct or nozzle, the flow is said to be choked. Any further increases in upstream pressure will increase only the density of the gas in the plane of smallest cross section, not its velocity, which equals the speed of sound in that gas $(\gamma RT/M)^{1/2}$. Our interest is in the cases for which the minimum flow area occurs at the exit of a duct or nozzle exhausting at sonic velocity into a region whose walls, if any, are many nozzle diameters away. In all such cases, the emerging gas makes up an underexpanded free jet in which the pressure of the jet gas is greater than the ambient pressure in the region it enters. Consequently, the jet gas expands radially and axially, accelerating axially to a supersonic velocity, that is, faster relative to a stationary observer than the speed of sound in the gas because the gas was already at the speed of sound when it started its expansion-driven acceleration on leaving the nozzle or duct.

The structure of the resulting jet is depicted in Fig. 2. Its boundary is the locus of points at which the pressure of the expanding gas becomes equal to the ambient pressure p_2. Solid lines starting at the nozzle exit in Fig. 2 represent this locus. They diverge rapidly at first and then converge slightly as the slight overexpansion caused by momentum effects is corrected. We direct our attention to a differential slice of gas just as it issues from the nozzle. Suddenly it is no longer confined by the nozzle wall and starts expanding in both radial and axial directions as it moves downstream. The outermost layer of gas in that first slice of gas expands by a differential amount radially and axially as that slice moves a differential distance downstream with the flow. That differential radial expansion results in an expansion wavelet that propagates back through the slice all the way to the opposite boundary of the jet, where it reflects as a differential compression wavelet. That reflected compression wavelet propagates back through the slice to the opposite boundary of the jet where it pushes back the ambient gas, generating another rarefaction wave that propagates back through the slice to the opposite jet boundary. Meanwhile, the slice has moved a short distance downstream, increasing in thickness as it expands axially in the direction of flow. This process of round-trip expansion and compression wavelets repeats until all the gas in the slice is at the ambient pressure p. At that point, the diameter and thickness of the slice have increased so that its volume equals that corresponding to an isentropic expansion from its pressure when it left the nozzle to the ambient pressure p. The work done by the gas during that differential expansion results in the acceleration of the gas to a readily calculable higher velocity. Each succeeding slice of gas repeats that overall process.

The actual process is somewhat more complicated than the one just described. Each differential compression wavelet causes a slight increase in the temperature, and thus the speed of sound, in the gas it passes through. Therefore, each succeeding compression wavelet travels faster than, and thus overtakes, its predecessor. The net result is that all those wavelets merge into a nearly discontinuous pressure jump, or shock wave that forms what is often called a shock barrel, somewhat inside of the jet boundary, represented by the dashed lines in Fig. 1. At a singularity referred to as the triple point, this barrel shock bifurcates. The inside branch is a plane shock wave normal to the jet axis and known as a Mach disk.

The totality of flow behavior that leads to the free jet structure of Fig. 1 is quite complex and has defied a complete description by the analytical solutions of the governing Navier Stokes equations. However, complete solutions can be obtained by the numerical methods employed in the now highly developed art of computational fluid mechanics. Fortunately for our purposes, the absence of a complete solution to the problem of a real jet has not been a handicap because a simplifying assumption originally proposed by Owen and Thornhill turns out to be both correct and useful [7]. They had addressed the idealized problem of free jet flow into a region of zero pressure. Under such conditions, there are no reflections of expansion waves from the jet boundary, so the complex structure of Fig. 1 does not develop. The gas expansion is thus isentropic, and the governing Euler's equation can be readily solved throughout the jet by the method of characteristics (MOC). This somewhat tedious procedure has also been tremendously eased by modern computers and requires much less effort than does the nonisentropic expansion of the bounded jet that leads to the complex structure shown in Fig. 1. Owen and Thornhill [7] reasoned that in real situations the gas on the centerline of the jet does not become aware of a finite ambient pressure until it encounters the Mach disk. Thus, within the region bounded by the shock barrel and the Mach disk of Fig. 2, which Sherman, following von Karman, dubbed the zone of silence, the gas behaves as if the ambient pressure were indeed zero, and the MOC solutions should apply. In many situations where free jet expansions are used, it is important to know the position of the Mach disk relative to the source orifice of the jet. Theory has not been of much use in predicting this position, but an abundance of experimental evidence over a wide variety of conditions has confirmed the generality of the empirical relation

$$x = 2/3(p_0/p_2)^{1/2}, \tag{3}$$

where X is the axial distance in orifice diameters from the plane of the orifice exit to Mach disk. This relation is apparently independent of γ. At least it applies to experimental results for monatomic, diatomic, and triatomic molecules reported by Ashkenas and Sherman [8], Bier and Schmidt [9], and Crist et al. [10].

Implicit in this discussion but not explicitly indicated until Eq. 3 is that all these jets have the convenient property of being self similar, in that their scaling factor is the diameter of source orifice. In other words, at any point in the jet at a distance of, for example, *N* orifice diameters away from the orifice exit plane, the state of the jet gas will be the same from jet to jet no matter whether that diameter is a micrometer, a millimeter, a centimeter, or a meter.

Supersonic free jets of the kind described are not at all uncommon. They are formed by exploding volcanoes, the venting of boilers and other containers of gases at high pressure, the flow from gas wells and rocket motors, the discharge of firearms, and even vigorous sneezes. Indeed, structures analogous to the one shown in Fig. 1 have been seen on television by millions who have watched the launching of the space shuttle and other rocket-powered vehicles. In those situations, one often sees a sequence of Mach disks, sometimes referred to as Mach diamonds because of their shape, which is often nonplanar. These subsequent disks or diamonds are caused by the jump in density and pressure that the gas undergoes as it passes through the Mach disk shock wave. If the source pressure is high enough, the recovered pressure aft of the shock is enough above the ambient pressure for the gas to repeat the expansion scenario of Fig. 1. As the rocket climbs, the ambient pressure decreases and the overall ratio of source (engine) pressure to ambient pressure becomes high enough for this process to repeat several times. The result is a sequence or series of disks or diamonds that can often be seen on television screens.

In the situations of interest in mass spectrometry, the free jets of ion-bearing gas often expand into a region where the pressure is so low that the mean free paths of the molecules in the background gas are of the same order as, or larger than, the dimensions of the jet. Because shock waves are several mean free paths in thickness, the barrel shock and Mach disk are not abrupt discontinuities but, rather, broad diffuse regions in which molecules from the jet gas mingle and collide with those from the background gas. The experiments of Anderson and Fenn showed that in these circumstances, background gas diffuses into the jet, arriving at the centerline at about the same distance downstream from the nozzle as is predicted for the Mach disk by Eq. 2 when the jet and background gas are both at high density [11]. This finding is entirely reasonable because the rates of both diffusion and wave propagation in a gas relate to the thermal velocities of the constituent molecules. The important take-home message from these early findings is that the state of a pure gas in a free jet expansion is well defined and readily calculable within the zone of silence bounded by the barrel shock and the Mach disk. Therefore, if one extracts a sample of the jet gas through an orifice probe (skimmer) whose entrance is within that region, that is, upstream of the Mach disk and near the jet axis, the state of that gas as it enters the probe can be predicted with reasonable accuracy and confidence. Note that when the background pressure is so low that the mean free path of the molecules is very large relative to the jet dimensions, the wave patterns and jet boundaries disappear completely, and the density distribution of the gas can conveniently and with useful accuracy be modeled as an assembly of rectilinear molecular trajectories radiating from a point source. The trajectories diverge so that their envelope comprises a cone whose tip is located on the jet axis very close to the exit plane of the nozzle. This point source model provides a remarkably accurate description of the flow field beyond a few nozzle diameters from that source, the actual number depending on the density of the jet gas in the source [8].

1.4. The spatial distribution of jet gas properties

We now examine in somewhat more detail the state of the gas and its dependence on location in the jet flow field. Some bare and important essentials will be summarized here. For further information, see the review articles mentioned. Anderson, Andres, and Fenn reviewed the early development of molecular beam systems based on free jet sources [12,13]. Ashkenas and Sherman provided a fairly complete description of the structure of continuum free jets [8]. Anderson, in what is probably the most revealing and complete description of free jets for the production of molecular beams, enlarged on the continuum picture with some considerations of the transition from continuum to free molecule regime [14]. Miller discussed in substantial detail the methods for calculating the structure and properties of free jets with more details on relaxation times for molecules with vibrational and rotational degrees of freedom [15]. His article is the first chapter in a comprehensive treatise, *Atomic and Molecular Beam Methods*, edited by G. Scoles, which contains 26 other chapters on all phases of molecular beam methods, many of which will be of interest to mass spectrometrists [15].

To be remembered is that specification of values for any two properties of an ideal gas fixes the values of all the other properties. Therefore, to the extent that any flow field is isentropic, one has only to know the value of any one property at any point to characterize the state of the gas completely at that point. In the algebra of compressible flow, it turns out that the Mach number M, defined as u/a, where u is the flow velocity and a the local speed of sound, is a convenient choice of independent variable, and most solutions to the governing Euler's equation obtained by the MOC are expressed in terms of this variable. The results of MOC calculations by Owen and Thornhill [7] for equilibrium jets are shown in Fig. 3 as a plot of Mach number against distance along the axis measured in nozzle diameters, $X=L/D$, where L is the axial distance and D is the nozzle exit diameter. Each curve relates to a particular value of γ, the heat capacity ratio. Note that the indicated value of a gas property at a given value of X refers to that value on the axis of the jet. Because the jet flow field can be reasonably represented as radial flow from a point source located on the jet axis near the exit plane of the nozzle, an acceptably accurate value of a gas property at any location off the centerline of the jet is the same as the value on the jet axis that is the same distance X

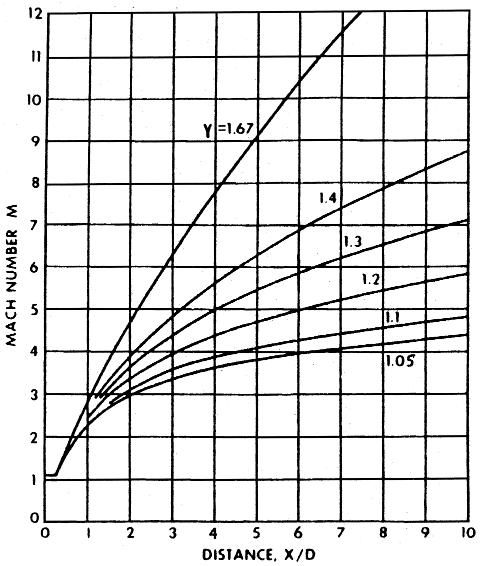


Fig. 3. Mach number distribution along the center line of a supersonic free jet for gases of varying values of γ, the heat capacity ratio, C_p/C_v. Note that the dimensionless axial distance is expressed in nozzle diameters. Thus, at X nozzle diameters downstream, the Mach number is the same for any nozzle, no matter what its diameter is.

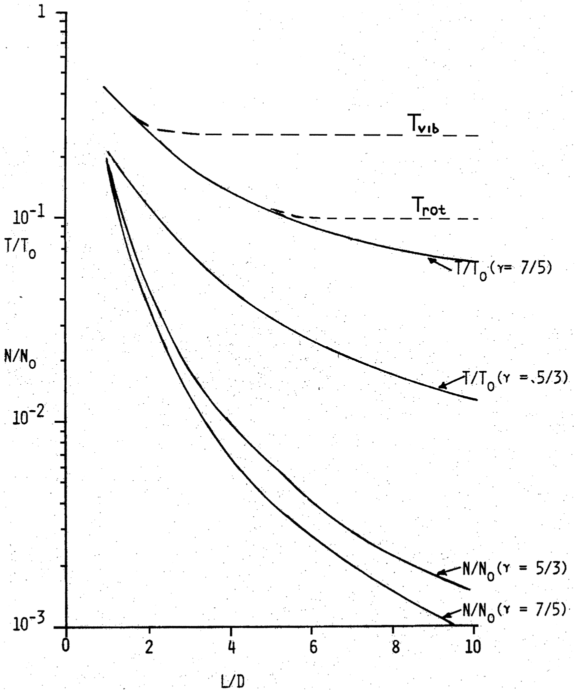


Fig. 4. A transform of the curves in Fig. 3 showing the axial distribution of temperature and density along the center line for a monatomic gas ($C_p/C_v=5/3$) and a diatomic gas in which two rotational degrees of freedom are active, so that $C_p/C_v=7/5$.

along the jet centerline as the arbitrary location is from the point source along the radial streamline from that source. Some of the cited references [8,14] provide convenient algebraic fitting formulas that reproduce the numerical results with acceptable accuracy. (Some investigators prefer the average molecular speed to the speed of sound as the reference velocity. In their algebra, Mach number is replaced by speed ratio, Sr, as the independent variable, where $\mathrm{Sr}=3\gamma M/2$.)

The curves in Fig. 4 are transforms of Mach number into the more familiar properties of density and temperature along the jet centerline for gases with γ values of 5/3 and 7/5, corresponding, respectively, to monatomic molecules with only translational degrees of freedom and to diatomic molecules having two rotational degrees of freedom also contributing to the heat capacity. (For diatomic molecules such as H_2, N_2, and O_2, the vibrational mode does not contribute to C_p or C_v except at very high temperatures.) Fig. 4 reveals features that make small free jets so interesting and useful, that is, the rapid decrease in both temperature and density with distance from the nozzle exit. At a distance of only 10 nozzle diameters downstream from nozzle exit (only 1 mm if the nozzle diameter is 0.1 mm in diameter), the temperature of a monatomic gas is only 1% or 2% of its source value. Because the flow velocities are a few times 10^4 cm/s, the cooling rate of the gas is well over 10^8 K/s. Nozzles with the even smaller diameters that are often used lead to correspondingly higher cooling rates. Meanwhile, the gas density falls even more rapidly, decreasing to only 0.001 of its source value at 10 nozzle diameters downstream from the nozzle exit. Thus, there is a catastrophic decrease in collision frequency, so that all the kinetic collision processes required to maintain equilibrium are stopped cold, as it were.

For a gas at thermodynamic equilibrium, the energy in each of the degrees of freedom has a Boltzmann distribution among the molecules so that the energy in each of the degrees of freedom can be characterized by a temperature. Thus, we can refer to a translational temperature T_{tr}, a rotational temperature T_{rot}, and a vibrational temperature T_{vib}. One of the consequences of decreased collision frequencies is a difference in the extent to which T_{tr}, T_{rot}, and T_{vib} relax, that is, a difference in the stage of the expansion at which they no longer track the equilibrium temperature expected for an isentropic expansion. As the collision frequency in the jet is reduced by the decrease in density, the exchange of energy among the various degrees of freedom slows down and ultimately stops, with the result that the distributions within each degree of freedom remain fixed for the remainder of the expansion. Such freezing occurs at different collision frequencies and, thus, different stages of the expansion for each degree of freedom. The order of freezing and, thus, the frozen value for each temperature is generally in the order $T_{\mathrm{vib}}>T_{\mathrm{rot}}>T_{\mathrm{tr}}$. This sequence of events is indicted in Fig. 4 by the departure of horizontal lines from the equilibrium curve for a diatomic molecule $\gamma=7/5$ at the ordinate value of T, at which the collisional frequencies have become so low that these internal degrees of freedom no longer give up energy to translation. T_{vib} freezes earlier in the expansion than does T_{rot} because, on average, a greater number of collisions is required to remove a quantum of vibrational energy from a molecule than is required to remove a quantum of rotational energy. As shown in Fig. 4 and as will be discussed in the next section, the collision frequency ultimately becomes so low that T_{tr} also freezes. The particular values in Fig. 4 for these freezing points are only illustrative and do not relate to any particular species.

1.5. Terminal conditions in free jet expansions

When a population of molecules comprises two subpopulations, each with a different rotational temperature, for example, collisions between and among the molecules in the differing populations will ultimately decrease the difference in rotational temperatures of the two subpopulations to zero. The time it takes for those collisions to reduce the difference in the two rotational temperatures to 1/e of its initial value is known as the characteristic relaxation time for rotational energy exchange in that species. The number of collisions that an average molecule of a population undergoes during that characteristic relaxation time is called the rotational collision number, Z_{rot}, which is a convenient measure of that rotational relaxation rate. Translational and vibrational relaxation rates can be similarly characterized by Z_{tr} and Z_{vib}. We have already considered somewhat superficially the freezing of T_{vib} and T_{rot}.

1.5.1. Terminal translational energies

Translational energy is the most easily exchanged of the three kinds. Except when there is a very large difference in mass between two colliding molecules, there is a substantial transfer of translation energy with almost every collision between them so that, generally, Z_{tr} is near one. Z_{rot}, however, ranges from 3 or 4 to 300 or so, while Z_{vib} can be as high as a million or more. These wide variations in collision numbers simply reflect the wide variations in the size of the quanta involved when a molecule changes its energy level. Thus, a quantum of vibrational energy is generally much larger than a quantum of rotational energy, for example. These quantal differences can be crudely rationalized in classical terms as relating to differences in characteristic velocity or frequency of the involved mode of motion. A bowling ball can impart appreciable translational energy to a ping-pong ball only if its velocity in laboratory coordinates is near that of the ping-pong ball. A steamboat whistle at a very low pitch, no matter how loud, does not excite vibrations in a harmonica reed that emits sound at a very high pitch when it is vibrating.

Whatever the value of Z_{tr}, if the collision frequency in a gas becomes negligibly small, *RT* is no longer coupled to PV, and the gas is said to be in the free molecule flow regime. It continues to expand in the sense that the number of molecules per unit volume continues to decrease, but temperature as reflected in the distribution of molecular velocities does not change as long as all the molecules in the jet are included in the averaging process. However, if one measures the velocity distribution of the molecules in a particular sample of jet gas, the result depends on where in the jet the gas was sampled. Thus, in a beam formed by a collimating orifice on the jet centerline, the distribution of velocities in the axial direction can be quite different from the distribution in the radial direction. The extent of the difference depends on the axial distance from the nozzle exit at which the collimating orifice is placed. In the collisionless free molecular flow regime, the molecules with large radial velocities remove themselves from the axial region more rapidly than do the slower ones. Consequently, as the distance of the collimating orifice from the nozzle exit increases, the average component of radial velocity in the molecules near the beam axis decreases while the distribution of velocities in the axial direction remains unchanged. This sampling bias results in what has been dubbed geometric cooling, an apparent decrease in the so-called perpendicular temperature that characterizes the distribution of the radial components of molecular velocities in the beam. Similarly, the distribution of axial velocities corresponds to the parallel temperature of the beam molecules. In the limit of very large axial distances from the nozzle, only those molecules whose radial velocity components are zero will reach a detector at which their perpendicular temperature will be zero. The parallel temperature, however, will correspond to the axial velocity distribution on the jet centerline when the jet density became so low that the molecular collision frequency became zero. This terminal velocity distribution or temperature can be determined from time-of-flight measurements of the axial velocity distribution for molecules in a beam defined by a collimating orifice at substantial axial distances from the nozzle exit. An extensive experimental study by Anderson and Fenn led to the following expression for what they called the terminal Mach number, M_T

$$M_T = 1.17 \times \mathrm{Kn}^{(1-\gamma)/\gamma}, \tag{4}$$

where *Kn*, the nozzle Knudsen number, is the ratio of mean free path in the source gas (i.e., at T_0 and p_0) to the nozzle throat diameter [17]. M_T is the maximum Mach number reached before the gas density becomes so low that the collision frequency is insufficient to continue the transformation of thermal energy (more properly enthalpy) to streaming kinetic energy of the expanding jet gas. A measured value for M_T is perhaps the best indicator of the transition to the collisionless flow regime, but the value calculated from Eq. 5 is usually a very good approximation and fits the data of most investigators. However, it must be admitted that most testing has been done only with monatomic gases in which there is no ambiguity about the value of γ because of incomplete relaxation of internal degrees of freedom, which is to be discussed next.

1.6. Terminal rotational energies

Rotational energies are somewhat more resistant to change than translational energies, as indicated by values for Z_{rot}, which range from 4 or 5 to a few tens for most species except when the colliding partners have very different masses, as is the case in translation relaxant. Molecules containing hydrogen atoms also have somewhat higher values for Z_{rot}. Indeed, for diatomic hydrogen molecules, Z_{rot} is several hundred. It follows that the rotational energy content of free jet molecules freezes earlier in the expansion than does translational energy. It is noteworthy that velocity analysis of the terminal translational energy in a free jet expansion provides a measure of the translational energy of the jet gas. The total energy of the jet gas can be determined from the temperature of the gas in the source. The difference between the two indicates the total amount of rotational and vibrational energy that is retained by the gas in its terminal state. In the cases in which vibrational energy does not relax and/or is not contributing to energy content, it plays no role in the expansion process. Therefore, it is possible to integrate the collision frequency during the expansion and obtain the total number of collisions that occurred. One can thus determine the effective value of Z_{rot} for the expanding gas. Gallagher and Fenn carried out such studies on number of molecules and were able to obtain values of Z_{rot} that are difficult or impossible to determine by other methods [18].

1.7. Terminal vibrational energies

By far the most resistant to collisional exchange, vibrational energy relaxation in small stiff molecules is characterized by very large collision numbers. In nitrogen and hydrogen, for example, Z_{vib} has values on the order of 10^6. The reasons for these remarkably large differences in collision numbers for the various kinds of energy are readily explained by quantum mechanics but need not concern us here. The important point is that the time scale of free jet expansion from small nozzles together with the substantial differences in relaxation rate for various kinds of energy means that the terminal states can be far removed from equilibrium and have very interesting and sometimes useful properties that have not yet been completely explored. One application of the ability of free jets to distinguish between rotational and vibrational energy has had a tremendous impact on molecular spectroscopy. In 1975, Smalley et al. showed that the rotational cooling in free jet expansion could essentially eliminate the rotational broadening of vibrational lines [19]. They cooled NO_2 in a free jet of helium and obtained a spectrum of the laser-induced fluorescence. What had always previously been an almost featureless continuum in traditional spectrometric measurements became a collection of well-resolved lines for which the vibrational frequencies could be readily inferred. That landmark discovery of the ability of free jet expansion to eliminate rotational broadening of spectroscopic lines has made free jets the darlings of molecular spectroscopists. There are many more such jets at work in spectroscopy experiments than in the molecular beam scattering experiments for which they are such excellent beam sources.

For mass spectrometrists, the take-home message from these studies of energy relaxation in free jet expansions is that the terminal vibrational energy of polyatomic molecules is usually a substantial fraction of its source value. Therefore, when one wants to produce fragmentation of parent ions for MS-MS experiments, simple heating of the source gas can often greatly enhance the vibrational energy content of a mass-selected ion. Collisions of those ions with inert target molecules or surfaces will, therefore, produce many more fragments for subsequent mass analysis than would be the case if the vibrational energy relaxed during the free jet expansion by which they are introduced into the vacuum system. It is noteworthy that in early experiments with MS-MS of proteins and peptides, investigators found little or no appreciable fragmentation of the ES ions of these complex species unless they were heated before they entered the vacuum system. In this connection, it is worth noting that a very effective method for producing vibrationally excited ions is to apply a potential difference between the nozzle and the skimmer. The resulting axial field in the free jet accelerates the ions relative to the neutral carrier gas molecules, bringing about suprathermal collisions that can excite the vibrational modes of the ions. Indeed, the excitation obtained in this way can be sufficient to fragment the ions, thus making possible some MS-MS measurements with single quadrupole or magnetic mass analyzers. However, the advent of ion traps and ICR instruments has provided convenient and effective production, storage, dissociation, and analysis of parent ions and their fragments in the same cell or cavity so that several stages of MS-MS can be readily carried out. In these systems, the extent to which vibrational energy is retained by large molecules during free jet expansion becomes a much less important question.

1.8. Solvation and clustering

Explicitly revealed in the preceding discussion and in Fig. 4 are the remarkably low temperatures that can be and are attained in gases undergoing free jet expansion. It thus becomes natural to wonder to what extent condensation can and does occur in the jet gas. That condensation was a phenomenon to be reckoned with in free jets was first noticed by Becker and Henkes in their TOF studies of hydrogen beams. They found a discontinuity in the dependence of the velocity distribution on source pressure that was also accompanied by a dramatic increase in apparent beam intensity, which they attributed to the onset of condensation in the jet [20]. In 1961, Henkes and Bentley independently reported the mass spectrometric detection of dimers in free jets of carbon dioxide [21,22]. Within the next few years, several other groups had become active in using small free jets in vacuo to produce and study clusters ranging in size from dimers to thousands and millions of molecules. A useful reference for an overview of that early work and some later developments can be found in the February 1984 issue of *Berichte der Bunsen-Gesellschaftfuer Physikalische Chemie*, which contains the papers presented at a Symposium on “Experiments on Clusters” in Koenigstein, Germany, October 12–14, 1984 [23]. In all the early work on cluster formation in free jets, the jet gas contained no ions, so the clusters were neutral and had to be ionized before they could be sized by mass analysis. Because of an unknown amount of fragmentation in the ionization process, there was always some uncertainty in mass of the parent cluster.

The pioneering experiments of C.T.R. Wilson in the 1890s revealed that ions were extremely effective condensation nuclei. That discovery led to the widely used Cloud Chamber method for detection of particles produced by high-energy accelerators for which Wilson received a Nobel Prize in 1927. Almost 50 yr later, Searcy and Fenn carried out the first experiments under controlled conditions on the cooling of ion-bearing gas by free jet expansion [24]. They passed a corona discharge through a source chamber containing a mixture of argon and small amounts of water vapor. After the resulting source gas was cooled by free jet expansion into a vacuum chamber, mass analysis (with no further ionization) showed an abundance of ions comprising protons solvated with varying numbers of water molecules. A striking feature of the spectra was the outsized abundance of ions comprising a proton with 21 water molecules of solvation, indicating that clusters of that size were unusually stable. This result was the clearest evidence up to that time for the reality of magic numbers—a phenomenon of much interest in the now major discipline of cluster science and technology, in which free jet expansions have played a major role in the production of clusters. The most famous example of this magic number stability is fullerene, the 60-atom cluster of carbon that was discovered by Smalley et al. during mass spectrometric analysis of free jets of helium containing traces of carbon because of laser ablation from an adjacent graphite surface [25].

For our present purpose, the significance of the Searcy-Fenn result is its showing that in the mass spectrometry of ions from high-pressure sources, one has to be very concerned about possible distortion of the masses of ions by solvation during transfer by free jet expansion from the scene of their production at high pressure to the low-pressure environment of their interrogation. One of the main reasons for the failure of Dole's original experiments with ESIMS was that he did not realize or appreciate the extent to which resolvation could occur during the free jet expansions by which his ions went from atmospheric pressure into the vacuum where he attempted to perform mass analysis. Another reason for his lack of success had to do with his method of mass analysis, which will be discussed in the next section.

In Dole's experiments, all the vapor caused by evaporation of solvent from the electrospray droplets was included in the ion-containing gas that underwent free jet expansion into vacuum. Consequently, the ions whose masses he tried to measure had been resolvated to a substantial but undetermined extent during transfer into the vacuum system. Moreover, that resolvation problem haunted him again in later experiments by which he tried to characterize his ES ions by mobility measurements [26]. The ion gas mixture containing the solvent in the electrospray droplets went from atmospheric pressure into a drift cell that was maintained at pressures of 730, 570, 440, or 360 torr. With the advantage of hindsight, inspection of the results that puzzled Dole leave little doubt that even expansions through those relatively small pressure differences produced enough cooling to bring about substantial solvation of the ions, with marked effects on their measured mobilities. (After a talk by J. B. Fenn at a meeting session on ESIMS in which he explained the solvation phenomenon, Dole came up and thanked him profusely for explaining why his mobility measurements were not consistent with the size of his analyte molecules. He realized that he had been looking at highly solvated cluster ions.)

During unreported exploratory studies in the mid 1970s, M. J. Labowsky in our lab at Yale repeated both the MS and mobility measurements of Dole. He found that the resolvation problem could be solved by using the electric field in the ES chamber to drive the droplets and ions to the orifice into the vacuum system against a counter-current flow of bone-dry bath gas. As a result, both the ions and the bath gas that entered the orifice leading into the vacuum system were devoid of solvent molecules so that resolvation could not occur. Other solutions to the resolvation problem have since emerged. One is to heat the bath gas so that its temperature remains above the saturation value during free jet expansion. Another is to apply an axial potential gradient in the free jet expansion to bring about suprathermal desolvating collisions between ions and neutral bath gas molecules. Some systems employ both of these tactics. These alternatives can prevent desolvation but do not have the ability of counter-current flow to prevent any nonionized material from entering the vacuum system. As a result, counter-current flow systems are much more tolerant of dirty samples and require less frequent cleaning.

Despite the problems that it can cause, ion solvation can provide useful information if it is carried out in a controlled way. Fig. 5 shows a spectrum for the

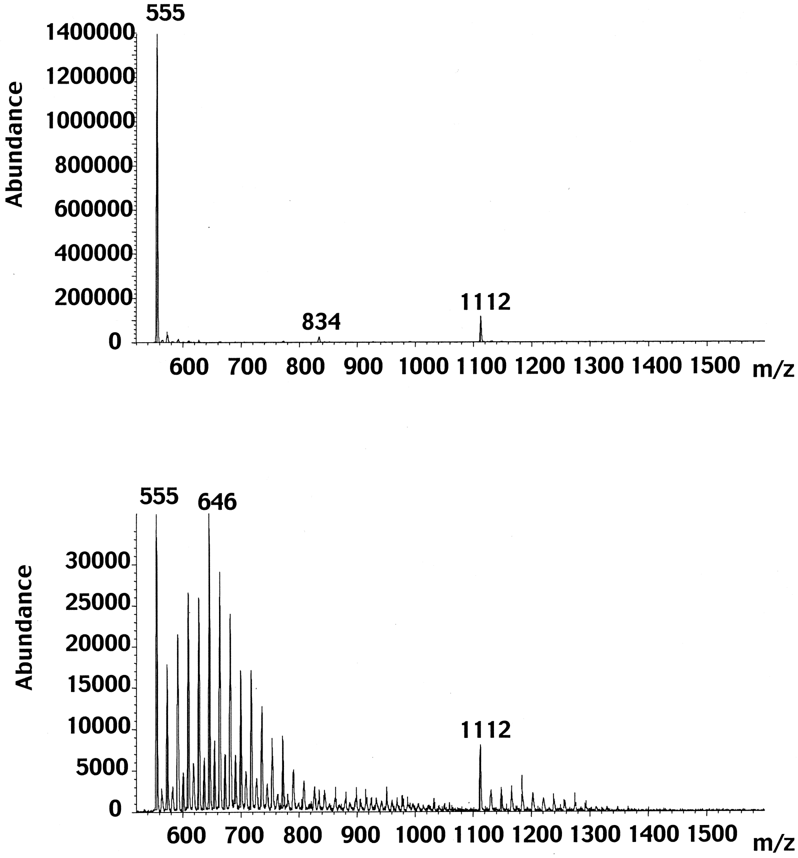


Fig. 5. Electrospray mass spectra for the peptide leucine enkephalin. The upper panel shows the result when the ions are completely desolvated and in a dry carrier gas before they undergo free jet expansion. For the lower panel, everything was the same as in the upper panel except that the carrier gas contained 0.166% water vapor.

peptide leucin-enkephalin obtained in our laboratory with an apparatus in which ES ions are completely desolvated before being mixed with bath gas containing precisely controlled amounts of solvent vapor, or any other species whose interaction with ions might be of interest [27]. The upper panel shows the spectrum obtained when the expanding carrier gas was solvent-free nitrogen. The major peak at 555 corresponds to singly charged monomers, the tiny peak at 834 to doubly charged trimers, and the small peak at 1112 to singly charged dimers. The lower panel shows the spectrum obtained under identical conditions except that the bath gas contained only 0.116 mole% of water vapor. That small amount of water clearly resulted in extensive solvation, even though the bath gas was significantly above room temperature. A noteworthy bit of information resulting from this solvation experiment is that a substantial fraction of what seemed in the upper panel to be singly charged monomer was revealed in the lower panel to be doubly charged dimer. In sum, controlled solvation can reveal information about the nature of ions that is otherwise obtainable only with mass analyzers capable of resolving peaks with differing isotopic content. Clearly, there are many other ion-neutral interactions that can be studied by this general procedure.

1.9. Molecular beams with suprathermal translational energies

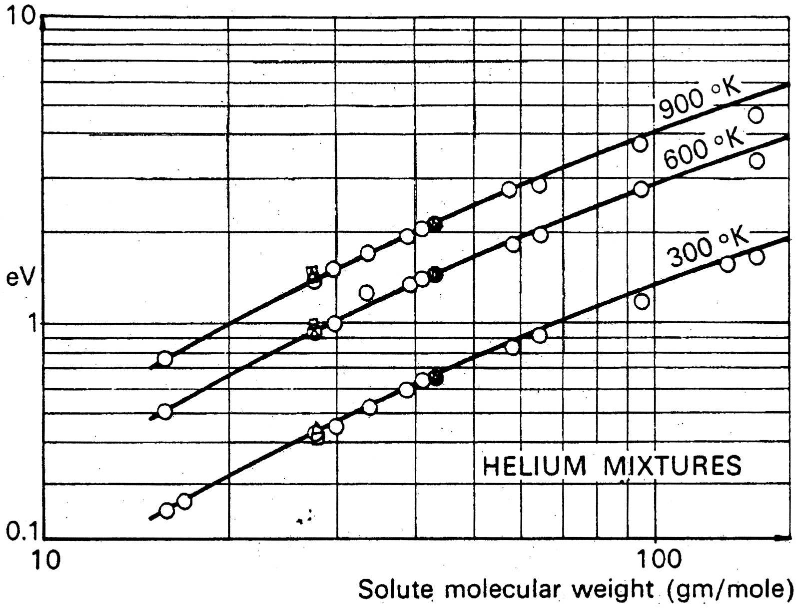
Another attraction of free jet sources for molecular beams has been their ability to produce beam molecules with much higher translational energies than could their effusive oven forbears. Each molecule in the low-density gas of an effusive oven source (e.g., chamber A in the upper panel of Fig. 1) has many collisions with the oven walls before it passes through the source orifice into collimating chamber B. The net result is that the gas temperature cannot be higher than the wall temperature, which has an upper limit of about 3000 K for feasible materials of construction. At this temperature, the most probable translational energy of a beam molecule is ~0.5 eV. Moreover, most polyatomic molecules undergo fairly rapid decomposition of some sort at such high temperatures. Even so, what has been suggested as comprising the chemical regime of the energy spectrum includes energies up to the ionization potential of helium, 24.5 eV. Free jet sources provide two tunnels through this energy barrier of 0.5 eV for effusive sources. The first one takes advantage of the high density of the source gas in the nozzle plenum chamber, which means that the gas temperature can be very much higher than the temperature of the walls because the latter can be cooled to well below the gas temperature. Thus, heating the gas with electric arcs or shock waves makes feasible the use of gas temperatures thousands of degrees above the melting point of the containing walls [28,29]. The use of very high temperature sources along with other possibilities for achieving high translational energies are described in two review articles [30,31]. However, all these approaches have given way to a much simpler and more effective way to produce beams of molecules with high translational energies, namely, the aerodynamic acceleration of heavy molecules by a light carrier gas in the so-called seeded beam technique.

In its simplest terms, the free jet expansion of any gas is a process that converts the thermal enthalpy of that gas to streaming kinetic energy. It follows, and is easy to show, that the maximum velocity that a gas can reach during an adiabatic expansion is:

$$u_{\max} = (C_p T_o \boldsymbol{M}_r)^{1/2}, \tag{5}$$

where M_r is the molecular weight. That maximum velocity is reached when all the thermal enthalpy of the gas in the source (C_pT_0) has been converted to kinetic energy so that $T_T = 0$. Absolute 0 K is never, in fact, reached in an expansion, but temperatures as low as 10^{-4} K have been achieved. Moreover, below a few tens of K, the amount of enthalpy remaining in the gas is so small that its equivalent in terms of a velocity increase is negligible. Thus C_pT_0 is a good approximation for the total amount of enthalpy that can be converted to streaming kinetic energy, the square root of which is the velocity.

If the source gas comprises a dilute solution of a gas with high molecular weight in a carrier gas of low molecular weight, the molecules of heavy species during free jet expansion should be swept along by the carrier gas, like wind-blown dust particles, to a much higher velocity than if they were expanding by themselves. The translational kinetic energy of the heavy species in the final beam is, thus, higher than that for a pure gas by a factor that in the limit of infinite dilution approaches the ratio of the molecular weights of the heavy and light species. In the case of argon in helium, for example, this energy multiplication factor is 10, so that the argon molecules would reach a translational energy approaching 6.25 eV, slightly more than 10 times the value from an effusive oven at 3000 K because in the free jet expansion it is the enthalpy of the gas rather than just its translational energy that becomes transformed into streaming kinetic energy. Abuaf et al. made the first definitive demonstration of this aerodynamic acceleration with careful measurements of the terminal velocities obtained with helium-argon mixtures over a range of concentrations from pure helium to pure argon [31]. Fig. 6 shows the results they later obtained with a variety of seed species in hydrogen and helium [29]. (The solid line in the graph for the case of hydrogen as the carrier gas indicates the energy that a seed species would reach if the rotational energy in the hydrogen molecules were converted into streaming kinetic energy. Because of the high value of Z_{rot} for hydrogen, the rotational energy remains frozen so that the actual energy that could in principle be achieved by a seed species is shown by the dashed lines.) Subsequently, by combining source heating and aerodynamic acceleration, Campargue et al. achieved



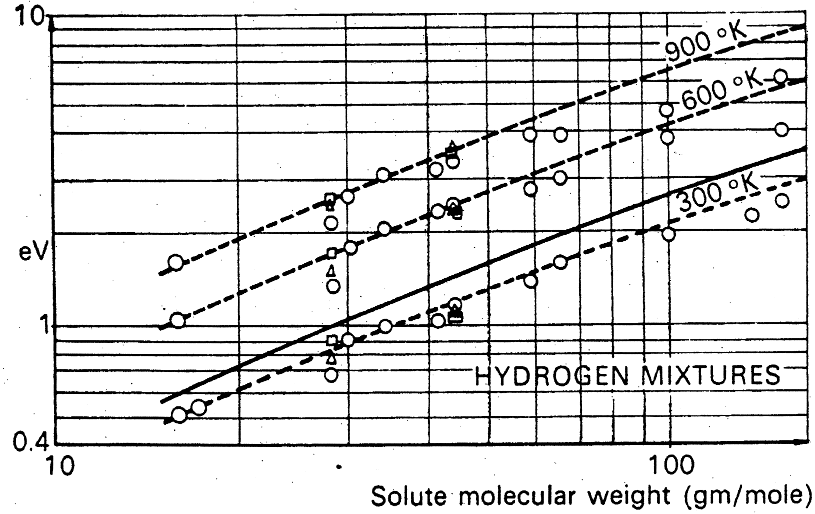


Fig. 6. The translational energies achieved by heavy molecules seeded into a carrier gas of hydrogen or helium at a molar concentration of 1%. The abscissa scale is in terms of molecular weight of the seed species. The ordinate scale shows measured translational energies in units of eV. The solid lines show the energies that would have been achieved if the seed species had reached the velocity that pure carrier gas would attain in a truly isentropic expansion. In the graph for hydrogen the dashed lines show the velocity actually reached by the pure carrier gas. It is somewhat lower than for the isentropic expansion because the rotational energy of the hydrogen molecules does not relax and contribute to the terminal translational energy. Note that as the difference between the molecular weight of the carrier and seed species increases, the difference between measured and calculated velocities increases. This slip effect is particularly apparent in the case of the hydrogen carrier.

translational energies of seed species approaching 40 eV per molecule [32].

This ability to accelerate neutral species in helium or hydrogen would not seem to be of much interest to mass spectrometrists dealing with ions that can be accelerated by electric fields to thousands, even millions, of eV. However, such aerodynamic acceleration was the basis of Dole's attempts to determine the mass of the ES ions he was trying to make from polystyrene oligomers with M_r's from 50,000 to 500,000 K [6]. He had no a mass analyzer that could cover that range of m/z and he apparently did not anticipate the possibility of extensive multiple charging. He was, however, aware of the results from our lab on aerodynamic acceleration, which he referenced in his first paper. He therefore assembled an apparatus in which the ions would be accelerated by free jet expansion to the terminal velocity that would be achieved by the bath gas of nitrogen, which provided the enthalpy to vaporize the solvent from the ES droplets. He placed a retarding potential grid between the nozzle and a Faraday cup electrode and measured the current of arriving ions by means of a sensitive electrometer. The voltage on the retarding potential electrode was gradually increased. When it became equal to the kinetic energy of some of the ions in his primary beam, the ions having that energy or less would be prevented from reaching the Faraday cup and the current would decrease. As the voltage was increased further, the current would show another decrease every time the beam contained some ions having an energy corresponding to that voltage. Because he knew the velocity of the ions, the measurement of their energy was a measurement of their mass. Thus, he could translate the current voltage curve into a mass spectrum of the ions in his beam.

Unfortunately, this very ingenious solution to the problem of measuring mass/charge ratios for very large ions overlooked two serious problems. One, to which we earlier made reference, was the fact that the ions were no doubt highly solvated during the free jet expansion, both in this attempt to measure masses and in his later attempts to determine the mobilities of ES ions. The other was that with increasing difference in Mr between the seed species and the carrier gas species, the difference in terminal velocity between the two could become quite large [33]. Evidence for such slip is already apparent in Fig. 2. The energies of the heaviest seed species (with M_r's between 100 and 200) are appreciably below the lines showing what the energies would be if the velocity of the seed species equaled that of the carrier gas, especially in the case of hydrogen. Dole very probably did not see the results of further studies in our laboratory, shown in Fig. 7, which reveals a marked decrease in the ratio $U_{\mathrm{exp}}/U_{\mathrm{cont}}$ at low values of $(Kn_{\mathrm{slip}})^{-1}$. In that figure, U_{exp} is the experimentally measured velocity for the seed species and U_{cont} the expected velocity in the absence of slip. *Kn* on the ordinate scale, the so-called slip Knudsen number, is in effect a ratio of mean free path in the carrier gas to the size of the seed molecules. It also takes into account the difference in their masses. It is analogous to the conventional Knudsen number (the ratio of mean free path to characteristic dimension of the flow system, e.g., the nozzle diameter), which is a measure of the extent of the departure from continuum flow behavior as a gas becomes more and more rarefied. In simplest terms, as Kn_{slip} increases, the extent of slip increases. The solid curve is calculated from simplified kinetic theory for hard spheres. The points correspond to various concentrations of the indicated species in different carrier gases. We estimate that the actual velocity of Dole's large polystyrene oligomers was probably only about half or less of what he had assumed. It is small wonder, therefore, that his apparent experimental values for m/z and the way they changed with different conditions did not make a lot of sense. This neglect of slip probably contributed much more to the inconsistencies in his mass analysis data than did his neglect of solvation that was mentioned earlier.

We close this review of aerodynamic acceleration with reference to a positive contribution that it has made to the mass spectrometric art. Amirav and his collaborators have found that a variety of molecules can be ionized with high efficiency by what he calls hyperthermal surface ionization (HTS) [34,35]. The idea is that analyte molecules are aerodynamically accelerated to high velocity and then scattered from an appropriate hot surface, for example, rhenium

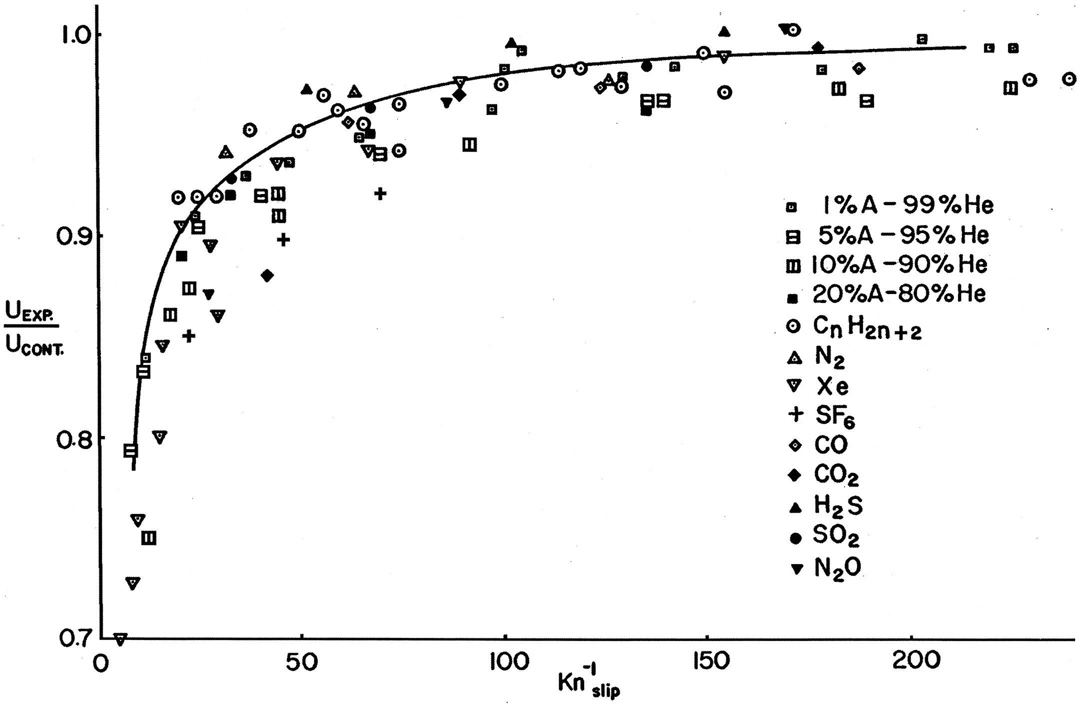


Fig. 7. A correlation for a variety of gas mixtures of the lag in velocity of the seed species relative to the carrier gas in terms of a slip Knudsen number, in effect, reflects the ratio of the mean free path in the mixture to the characteristic dimension of the seed species.

oxide. This technique couples particularly well with gas chromatography, in which the mobile phase is generally helium. Thus, the effluent from the GC flows directly into the vacuum system of the mass analyzer, where it strikes the hot surface. The resulting ions are directed into the analyzer by an appropriately applied field. The combination of HTS with time-of-flight mass analysis can provide extremely rapid GC-MS. Amirav and his colleagues also found that the cooling that takes place in free jet expansion greatly reduces the fragmentation that normally occurs in ionization by electron impact.

1.10. Species separation in free jet expansions

The last topic to be discussed in this review of what mass spectrometrists can and should learn from the experience of their molecular beam cousins was in fact the first fruit of a collaboration between them. In their first paper on molecular beams of hydrogen from high-pressure sources á la Kantrowitz and Grey, Becker and Bier reported a sixfold gain in beam intensity signal when the hydrogen source gas was contaminated with 4% argon [4]. They knew that their snorkel gauge detector was molecular weight sensitive in that its output signal for a unit beam flux of pure argon should be higher than for a beam of pure hydrogen of the same intensity by a factor equal to the square root of the molecular weight ratios, or about 4.5. But the observed sixfold gain in signal for a beam of hydrogen containing only 4% argon was much too high to be accounted for in this way. They concluded that the beam had somehow been substantially enriched in argon. The next paper from their laboratory reported that experiments had shown that the apparent enrichment was taking place upstream of the skimmer in the free jet [36]. Those observations triggered a series of stimulating and valuable investigations of the separating nozzle or trennduse by Becker and his associates summarized in *Nuclear Energy Maturity*

[37]. Separation effects of remarkable magnitude were found in various gas mixtures, including isotopes of uranium hexafluoride where the mass differences are very small. In most of this work, the skimmer-molecular beam analyzer was replaced by a simple sampling probe immersed in the supersonic jet. The sampled gas could readily be analyzed by any of several methods, depending on the species involved. Similar studies were carried out in this country by Waterman, Stern, and Sinclair [38,39]. The result of all this effort in Germany was a big program in isotope separation, which culminated in the actual construction and testing of a demonstration plant in Brazil for uranium enrichment. Although the jet separation process claimed several advantages over gaseous diffusion, the advent of the gas centrifuge and laser separation methods, along with a decreased demand for enriched uranium, put a stop to further development. However, there was one lasting consequence of interest to the mass spectrometry community. The Swedish chemist Ryhage, who was familiar with Becker's work, found that one of these jet separation elements, or a pair of them in series, provided very effective enrichment of analyte in the effluent from a gas chromatograph before it entered the mass spectrometer [40]. Thus was born the so-called jet separator that was, and still is, widely used in GC-MS.

This story has an ironic twist. For many years, the accepted explanation of these separation effects was preferential diffusive migration of the light carrier gas species, usually helium, radially away from the jet axis, thus leaving a higher concentration of the heavier species on that axis. Then Reis and Fenn undertook an extensive study of jet separation obtained with nitrogen-hydrogen mixtures. They showed that such separation was entirely caused by inertial effects at the entrance to the sampling probe [41]. Such a probe in a supersonic stream results in the formation of a bow shock wave at the probe entrance. If there is an appreciable resistance to flow through the probe, for example, because of viscous effects or deliberate throttling, then the shock wave is detached from the probe entrance, In the region between the detached shock and the probe entrance, the rapid deceleration of the flow results in very large inertial forces by which the heavy species are concentrated in the gas entering the probe while a large fraction of the light species is diverted and flows around outside of the probe back into the free stream. This inertial separation is analogous to what happens when a car drives through a rainstorm at moderate or high speed. The air is readily deflected by the windshield and flows over the roof of the car. Water has a much higher density than air, so the raindrops do not follow the air stream lines but crash into the windshield. Reis and Fenn found that whenever they lowered the pressure in the probe by a small pump so that the shock wave was swallowed, the sampled gas was always identical in composition with the source gas from which the supersonic jet was produced no matter where along the jet axis the probe was placed. When the exit from the probe was throttled, the sampled gas was enriched in the heavy species. A year or two later, Sherman did a theoretical analysis that showed that at the probe Reynolds numbers associated with actual operation, the maximum possible separation by diffusion could only be a few percent of the separations actually observed [42]. It was only after Sherman's theoretical analysis that the Reis-Fenn experimental results gained some respectability and credence. Even to this day, the mechanism of enrichment in the still widely used jet separator is widely attributed to diffusive processes in the jet. The moral: Well-established ideas die hard, even in science, even when they are wrong.

2. Summary and conclusions

The nature of mass spectrometry is such that from its very beginnings its practitioners have quite understandably been preoccupied with the response of ions to electrostatic and electromagnetic forces. With advent of high-pressure ion sources, aerodynamic forces became an important factor in determining ion trajectories. This brief review has touched on a number of phenomena that gas dynamic forces can bring about when a mixture of ions and neutral gas molecules passes from a source chamber at high pressure into a vacuum system containing a mass analyzer. These phenomena are not only interesting per se but can have a substantial effect on the determination of ion mass. Practitioners of mass spectrometry may avoid trouble if they take the trouble to become aware of these effects even if they are not comfortably familiar with them.

References

[1] J.A. Buckley, J.B. French, N. Reid, Can. Aeronaut. Space J. 20 (1974) 231.

[2] M. Yamashita, J.B. Fenn, J. Phys. Chem. 88 (1984) 4451.

[3] A. Kantrowitz, J. Grey, Rev. Sci. Instrum. 22 (1951) 328.

[4] E.W. Becker, K. Bier, Z. Naturforsh. Teil A 9 (1954) 975.

[5] T. Johnson, Nature 113 (1927) 745; Phys. Rev. 31 (1928b) 103.

[6] M. Dole, L.L. Mack, K.R.L. Hines, R.C. Mobley, L.D. Ferguson, M.B. Alice, J. Chem. Phys. 49 (1968) 2240.

[7] P.O. Owen, C.K. Thornhill, Aeronaut. Res. Council UK 1948 2616.

[8] H. Ashkenas, F.S. Sherman, in: De Leeuw, J.H. (Ed.), Fourth Rarefied Gas Dynamics Symposium, 1964 (Academic Press, New York, 1966).

[9] K. Bier, B. Schmidt, Z. Angew. Phys. 13 (1961) 34.

[10] S. Crist, P.M. Sherman, D.R. Glass, AIAA J. 4 (1966) 68.

[11] J.B. Anderson, J.B. Fenn, Phys. Fluids 8 (1965) 780.

[12] J.B. Anderson, R.P. Andres, J.B. Fenn, in I. Estermann (Ed.), Advances in Atomic and Molecular Physics (Academic, New York, 1965, Vol. 1), p. 345.

[13] J.B. Anderson, R.P. Andres, J.B. Fenn, in J.Ross (Ed.), Advances in Chemical Physics (Wiley Interscience, New York, 1966, Vol. 10).

[14] J.B. Anderson, in P.P. Wegener (Ed.), Molecular Beams and Low Density Gas Dynamics (Marcel Dekker, New York, 1974), p. 1–89.

[15] D.R. Miller, in G. Scoles (Ed.), Molecular Beams (Oxford University Press, London, 1985).

[16] G. Scoles (Ed.), Molecular Beams (Oxford University Press, London, 1985).

[17] J.B. Anderson, J.B. Fenn, Phys. Fluids 8 (1965) 780.

[18] R.J. Gallagher, J.B. Fenn, J. Chem. Phys. 60 (1974) 3487.

[19] R.E. Smalley, L. Wharton, D.H. Levy, J. Chem. Phys. 63 (1975) 4977.

[20] E.W. Becker, W. Henkes, Z. Phys. 146 (1956) 333.

[21] W. Henkes, Z. Naturforsch. Teil A 16 (1961) 842.

[22] P.G. Bentley, Nature 190 (1961) 432.

[23] Ber. Bunsen-Ges. Phys. Chem. (1984) 88.

[24] J.Q. Searcy, J.B. Fenn, J. Chem. Phys. 61 (1974) 5282.

[25] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, Nature 318 (1985) 162.

[26] J. Gieniec, L.L. Mack, K. Nakamae, C. Gupta, V. Kumar, M. Dole, Biomed. Mass Spectrom. 11 (1984) 259.

[27] D. Zhan, J.B. Fenn, J. Am. Soc. Mass. Spectrom. 9 (1998) 1241.

[28] G.T. Skinner, Phys. Fluids 4 (1961) 1172.

[29] R.W. Kessler, B. Koglin, Rev. Sci. Instrum. 37 (1966) 682.

[30] J.B. Anderson, Entropy 18 (1967) 33.

[31] J.B. Fenn, Entropy 18 (1967) 11.

[32] R. Campargue, A. Lebehot, J.C. Lemonnier, D. Marette, in S.S.Fisher (Ed.), Twelfth International Symposium on Rarefied Gas Dynamics (AIAA, New York, 1981), p. 823.

[33] N. Abuaf, J.B. Anderson, R.P Andres, J.B. Fenn, D.R. Miller, in C.L. Brundin (Ed.), Fifth International Symposium on Rarefied Gas Dynamics (Academic, New York, 1967, Vol. 2), p. 1317.

[34] A. Amirav, Org. Mass. Spectrom. 26 (1991) 1.

[35] A. Danon, A. Amirav, J. Phys. Chem. 93 (1989) 5549.

[36] E.W. Becker, K. Bier, H. Burghoff, Z. Naturforsch. Teil. A 10 (1955) 565.

[37] E.W. Becker, K. Bier, W. Ehrfield, K. Schubert, R. Schutte, D. Seidel, in P. Zelesky (Ed.), Nuclear Energy Maturity (Pergamon, Oxford, 1976), p. 172.

[38] P.C. Waterman, S.A. Stern, J. Chem. Phys. 31 (1969) 80.

[39] S.A.Stern, P.C.Waterman, T.F.Sinclair, J. Chem. Phys. 33 (1960) 805.

[40] R. Ryhage, Anal. Chem. 36 (1964) 359.

[41] V.H. Reis, J.B. Fenn, J. Chem. Phys. 39 (1963) 3240.

[42] F.S. Sherman, Phys. Fluids 8 (1965) 777.