Spectroscopy of Jet-Cooled Ions and Radicals

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Received September 11, 1990 (Revised Manuscript Received January 28, 1991)

Contents

Paul C. Engelking became an undergraduate at California Institute of Technology in 1966, in the state in which he was born 18 years earlier. There George Hammond and Harry Gray enticed Paul into chemistry in the course of their introductory class, Chem 2. Upon completing his Ph.D. studies on laser-induced fluorescence of molecular ions at Yale, in 1975, he joined Carl Lineberger's group in Boulder, CO, investigating ions with photoelectron spectrometry. He has been at the University of Oregon in the department of chemistry since 1978 and is currently a member of the Chemical Physics Institute there. The work he has performed on jet cooling of ions and radicals results from his fascination with open-shell molecular systems, including those with degeneracies giving rise to symmetry breaking.

I. Introduction

The advent of spectroscopy of jet-cooled radicals and ions came barely a decade ago. With jet cooling, old problems of the structures and internal dynamics of radicals and ions are now successfully being resolved; questions that would have been beyond technique only a few years ago are now amenable to spectroscopic study. One has to look back to the late 1960's and early 1970's, the time of the introduction of the laser to molecular spectroscopy, or to the 1950's, when flash photolysis entered the scene, to find comparable excitement and optimism about experimental studies of open-shell molecular systems.

A. Why Jets?

To apply jet cooling, one forms radicals or ions in a high-pressure carrier gas near an open gas nozzle. As the gas expands into a low-pressure vacuum, it cools the entrained radicals or ions. Much of the internal energy of these selected species is now absent. These cold species may then be probed by nearly any of the methods of modern spectroscopy.

Free jet expansions prove useful both in producing interesting radicals and ions and in simplifying the analysis of their spectra.

1. Versatile Preparation of Radicals or Ions

Most techniques of radical or ion production can be adapted to the miniature dimensions of nozzle geometries, and a good deal of this review will show how experimentalists have prepared radicals and ions in numerous ways.

New species, for which no chemical method of preparation was previously available, have been produced and examined in jets. Highly labile radicals and novel metal clusters are among these novel species. Nozzle cooling may stabilize delicate species; for example, in the study of van der Waals molecules, expansions have become indispensible. The short microsecond time scale of the expansion allows the preparation and investigation of short-lived transients or metastable species. Jet cooling has permitted entrance to new regions of chemistry.

Molecules complete an expansion in a vacuum, an ideal environment for stabilizing highly reactive, possibly very labile, species. This isolation becomes important in the study of easily perturbed systems, such as those with degeneracies that exhibit Jahn–Teller effects. In such cases, almost any perturbation would lift the degeneracies, and even weak interactions can

0009-2665/91/0791-0399$09.50/0

have significant effects on the spectra. Matrix interactions, and even infrequent collisions in the gas phase, may complicate an already complicated situation, and it is for good reason that most of the well-analyzed Jahn–Teller systems have been studied by using jet cooling.

2. *Simplification of Spectra*

As demonstrated in this review, radicals and ions prepared in nozzle expansions are amenable to investigation by a range of spectroscopic techniques, ranging all the way from optical spectroscopy with high dispersion grating instruments and photographic plate detection, with which gas-phase molecular spectroscopy began, to mixed optical–microwave spectroscopy with modern klystrons and lasers.

For spectroscopic analysis, the greatest usefulness of jet cooling lies in the reduction of the internal rotational temperatures of the absorbing or emitting species. Broad, complex rotational bands collapse at low temperatures into simple progressions of a few narrow lines, enormously simplifying molecular spectroscopy. A perenial problem in analyzing spectra is that of locating each band "origin", corresponding to the energy of the transition if the molecule were not rotating. These band origins are more easily identified in spectra of very cold, almost irrotational, molecules.

In addition to simplifying spectra, rotational cooling aids detection by concentrating the transition strength into narrow spectral regions. Rotational bands spread over a spectral region of width that scales approximately as $(kT)^{1/2}$, containing an average number of lines that scales as kT. Detection of either a band envelope (at low resolution), or a single rotational line (at high resolution) is aided by a reduction in rotational temperature.

Upon cooling, vibrational bands that would ordinarily overlap become well separated and easily identified. Rotational analyses of spectra of complex, high-spin radicals simplify enormously: instead of two or three dozen overlapping subbranches with hundreds of individual lines each, cooling reduces this to a half-dozen lines in each recognizable subbranch.

The analysis of intramolecular perturbation is facilitated in jet-cooled spectra, and badly perturbed systems have become clear as a result of this new weapon in the spectrosopist's armory.

This review will provide many examples of spectral structure simplifying upon cooling of rotations.

B. How Did We Get Here?

Jet cooling is a technique borrowed from the field of molecular beams. Nozzle expansions have generated beams of stable molecules, both for investigation of their properties and for studies of their subsequent reactions. In one of its earliest spectroscopic application, jet cooling has produced molecular beams used in Rabi- or Townes-type microwave spectroscopy. Molecules readily form clusters under the very low temperature conditions present in a jet, and the spectroscopy of hydrogen-bonded or van der Waals bonded clusters in molecular beams depends upon this.

The low temperatures attained in expansions simplifies the spectra of even large, stable molecules. Almost every issue of *The Journal of Physical Chemistry* now contains at least one study of molecular spectra assisted by the technique of jet cooling.

Workers enter the field of jet-cooled spectroscopy of radicals and ions from two directions. The development of my personal interest is perhaps typical of that of about half of the workers in this area. While diatomic ions showed that they could be detected in a flowing afterglow by laser-induced fluorescence even when warm,[1] subsequent attempts on larger systems with more complex spectra demonstrated to me the usefulness of rotational cooling in producing analyzable spectra.[2] With similar motivations, other groups working on radicals and ions independently have made the same transition into jet spectroscopy.[3-15]

The other half of workers entering this field, previously experienced with nozzle expansions containing closed-shell molecules, subsequently developed interests in radicals and ions and have brought with them the jet techniques to which they are accustomed.[16-30]

C. Scope of This Review

The material selected for review here consists of electromagnetic spectroscopies of jet-cooled radicals or ions. Photoelectron or exclusive use of mass spectrometry is excluded. Background material useful to understanding the operation of an expansion has been included but this material is not intended to be comprehensive. Reference to spectra of warm radicals or to mass spectrometry of jet species may be made in passing to clarify a point.

Selective summaries covering aspects of early work on molecular radicals or ions cooled in expansions have been available.[31-37] While the subject matter of those summaries is included here, they provide valuable information not present here. An excellent recent review of the spectroscopy and structure of organic free radicals depends upon jet cooling for much of its material and places the results of this technique in context.[38] Several reviews of ion spectroscopy[39-43] touch on nozzle cooling. Finally, anyone interested in the spectroscopy of open-shell radicals and ions should be aware of the recent compilation "Electronic Energy Levels of Small Polyatomic Transient Molecules," by M. E. Jacox,[44] which already incorporates much of what has been learned through jet cooling.

In light of the excellent reviews on jet-cooled molecular clusters published here in *Chemical Reviews*,[45] closed-shell clusters have been excluded entirely. Open-shell clusters and cluster ions have been included only to the extent that they are a logical extension of ion or radical studies detailed here, or only when they illustrate a particular point for which studies of smaller systems are not yet available. For metallic systems, anything containing two or more metal atoms is considered to be a cluster. Diatomic alkali metals, which can be considered to be formally closed-shell and have a specialized literature, were not reviewed. An excellent review of metallic clusters is that of Morse,[46] and a recent review brings the subject of main-group clusters up to date.[47]

I would like to warrant that this review is complete up to mid-1990, but must warn the reader that in such a rapidly growing field some newly developing work may have escaped notice. Some authors now consider jet cooling to be a standard technique, and make no

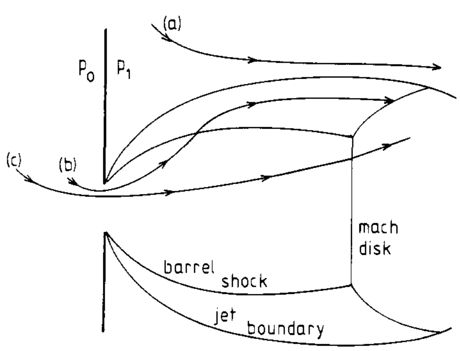

Figure 1. Free jet stream lines in an expansion from high initial pressure p_0 to low final pressure p_1. The surrounding gas follows a stream line (a) outside of the jet boundary. Gas passing near the edges of the nozzle leaves the isentropic core of the expansion through an axisymmetric "barrel shock", entering the mixing region between the shock and the jet boundary, as shown by stream line b. Gas flowing through the nozzle near the axis (c) expands unhindered until it encounters a "Mach disk" standing shock. This Mach disk is located downstream where the impact pressure of the expansion becomes comparable to p_1. The cold molecules desired by the spectroscopist are found in the isentropic core, surrounded by the barrel shock and before the Mach disk.

particular mention of it in either title or abstract. I apologize for any unintended oversight, and would enjoy having any new developments brought to my attention.

II. Jet-Cooled Radical and Ion Production

A. Cooling in Jets

The temperature disequilibrium that may be achieved by very rapid expansion cooling in a jet of the translational modes of a gas was first investigated by Kantrowitz.[48] It was recognized that very cold rotational and translational temperatures could be attained without necessarily aggregating molecules or quenching internal vibrations, and that unusual, nonequilibrium states could be achieved in an expansion. It was also recognized that the translational velocity distribution would become very narrow, with the overall bulk motion away from the nozzle becoming a bit over the initial speed of sound in the preexpanded gas. This was a significant improvement in molecular beam characteristics over that available with an effusive source, since a narrow velocity distribution could be achieved automatically, without having to introduce a mechanical velocity selector in the beam path. Several proposals were made to utilize an expansion for a molecular beam source.[49-52]

Although much of the subsequent work using nozzle expansions studied reaction dynamics, a portion of the nozzles became used for spectroscopy of molecules. The basic motivation was the low rotational temperature that could be attained. Much of this work with stable molecules seeded into rare gas expansions is reviewed by Levy.[53] Spectroscopists naturally would wish to introduce unstable species into these nozzle flows and have done so over the last few years. However, they needed to understand the basic mechanism of cooling in a jet to take full advantage of this technique.

1. Circular Nozzles

Most studies use an unconstrained free jet expanding into a vacuum chamber from a circular hole, without introducing "skimmers" for separating out a free molecular beam. A simple free-jet expansion is diagramed in Figure 1.[54] Since most researchers do not have infinite pumping speed available, the jet expands into a low pressure. Much work has been done on the aerodynamics of a similar situation, a rocket exhaust plume at high altitudes.[55,56] A good deal of theoretical and experimental work on axial symmetric jets has been summarized by Love.[57]

TABLE I. Free Jet Scaling Parameters

specific heat ratio	angular s	radial f	apparent origin x_0/D
1.67	1.15	0.150	0.075
1.40	0.95	0.086	0.40
1.286	0.83	0.059	0.85

Many of the theoretical predictions of flow structure have been experimentally confirmed by methods of shock visualization and Pitot tube pressure measurement. Recently, optical tomography of Cl_2 expansions using arc lamp UV sources have directly confirmed predictions of the density distribution in the flow.[58]

The basic structure of the expansion consists of subsonic hydrodynamic flow on the high-pressure side of the nozzle toward the constricting throat. At the throat, the flow conditions becomes sonic and, subsequently, supersonic in the expansion into the vacuum. As the flow expands away from the nozzle throat, it gains only a little in additional speed, but rapidly reduces its internal temperature, as is consistent with rapid adiabatic expansion.

After a few nozzle diameters, to a good approximation the flow appears to be expanding radially away from a virtual point source a distance x_0 just outside the nozzle throat (see Table I). The gas density is greatest on axis, but the exact density profile depends upon the exact nozzle shape. The density $n(R,\Theta)$ for a given distance R from a thin circular nozzle is well modeled (within 3%) by a modified cosine squared distribution,

$$n(R,\Theta)/n(R,0) = \cos^2(s\Theta) \qquad (1)$$

depending only on the angle Θ deviating from the flow axis, the distance R from the apparent origin, and a nearly unit scaling parameter s given in Table I.[59] Along the axis, the density falls off quadratically with distance:

$$n(R,0) = fn_0(R/D)^{-2} \qquad (2)$$

Here D is the nozzle diameter, n_0 is the preexpansion density, and f is the scaling parameter dependent upon the ratio of specific heats γ found in Table I.

It should be reemphasized that the flow field may be significantly altered by nozzle shape.[60] Since most elongations of the nozzle tend to confine flow closer along the axis, eq 1 may be thought of as an ideal, limiting, maximum for angular spread of the jet density.

In an adiabatic expansion temperature scales as $n^{\gamma-1}$; the above scaling relations for density, n, can be used to calculate the limiting translational temperature, and hence the minimum rotational temperature, expected. Table II shows the minimum distance downstream one must operate for three expected amounts of cooling.

Predicting the actual rotational temperature is more problematical. Rotational cooling becomes less efficient as densities decrease and collisions become less frequent as the expansion proceeds. In addition, internal vibrations and the formation of clusters may release additional energy during the expansion.

TABLE II. Minimum Distances Downstream Producing Adiabatic Cooling on Axis for Circular Nozzles (Distances Expressed in Nozzle Diameters)

specific heat ratio	T/T_0		
	0.1	0.03	0.01
1.67	2.21	5.35	12.1
1.40	5.33	23.7	93.1
1.286	14.0	114	773

Internal molecular motions, especially those with high frequencies, can become "frozen in" on the time scale of the expansion. The achieved state distributions can become dominated by the kinetics of cooling. Typically, translations are coldest, followed by rotations, while high-frequency vibrations are most resistant to cooling. Several studies[61-65] have shown that cooling of rotations is state dependent, leading to non-Boltzmann distributions. Generally, except for the widely spaced energy levels of hydrides, rotational "temperatures" in typical expansions are typically within a factor of two of translational temperatures.

Additional energy may become available during an expansion if significant clustering occurs. The release of binding energy has been found to increase both flow velocities and translational temperatures in strongly clustering ammonia expansions.[64]

Outside of the expansion core, the flow from the nozzle interacts with the background gas, giving rise to two structures. Outermost is the jet boundary, the limit of mixing of the expansion gas with the background gas. Across this boundary, background gas is entrained into the jet flow. Marking the inner boundary of this region of mixed gas is the flow-shock boundary, upon which terminates the radiating flow lines from the nozzle. At this shock boundary, the flow lines change direction abruptly, reflecting the momentum transfer from the inflowing boundary gas. It is within this "barrel shock" that the spectroscopist finds the cold molecules desired.

On axis, flow is unaffected until it encounters the "mach disk" located, for free jets from circular apertures, at the distance

$$x_{\mathrm{m}} = 0.67D(p_0/p_1)^{1/2} \qquad (3)$$

where D is the nozzle diameter, and p_0 and p_1 are the pre- and postexpansion chamber pressures.[59]

The region available for spectroscopic purposes within the isentropic expansion core typically starts five or 10 nozzle diameters downstream from the nozzle and extends to the mach disk. For example, for an expansion of 1000 Torr into a chamber of 0.1 Torr out of a nozzle of 0.1-mm diameter, one expects to find the mach disk at 6.7 mm downstream. Thus, a 5-mm long region, extending between 1 and 6 mm downstream from the nozzle is available, an adequate dimension for a variety of spectroscopic experiments. Only moderate vacua are needed whenever experiments are conducted here, in the core of the expansion in front of the nozzle, and for these cases a mechanical blower pump, as pioneered by Campargue[66] is often the choice of pumping apparatus.

Some experiments involve actual molecular beams, requiring chamber pressures 10^{-6} Torr or lower. These high vacua are most easily achieved with diffusion pumps. Although the *volume* throughput of a diffusion pump is large, the overall *mass* throughput is limited, and many diffusion pumped expansions have pulsed nozzles, first pioneered by Gentry.[67] Infrequent, short, gas pulses allow low ultimate pressures to be attained without overloading the average pumping speed. Pulse duration must be sufficient to allow development of hydrodynamic flow through the nozzle; the time required to establish steady flow has been investigated by Saenger and Fenn.[68]

2. Planar Nozzles

Nozzle neometry need not be cylindrically symmetric about the flow axis. Recently, planar nozzle geometries have been introduced to attempt to match the properties of the expansion to the needs of the spectroscopist. The engineering literature refers to these as "slot" nozzles; molecular spectroscopists lean toward the term "slit" nozzles.

Flows from slit nozzles have been experimentally studied[69] and summarized.[70] The density in an expansion from a thin slit falls off only inversely with distance from the nozzle, leading to milder cooling over longer dimensions than in an jet from a circular nozzle. This has been useful in reducing the rate of cooling.[71]

On first examination, a planar jet would appear to offer the advantage of a longer path length for absorption studies, which have now been conducted over the electromagnetic spectrum from IR[72] to VUV.[73] A careful study of this question by Veeken and Reuss[74] shows that the column density along a path parallel to the long dimension of the slit increases by only 17% over that offered by a circular nozzle operating at the same mass throughput! Column densities of molecules is not the major advantage of a planar nozzle.

Veeken and Reuss point out a more subtle advantage for the slit nozzle. Because the velocity components parallel to the long dimension are more uniform and smaller, the resulting doppler line width is correspondingly narrower. This has two effects: first, individual spectral lines can be better resolved; second, the optical density at the line maximum increases. Thus the slit nozzle shows to best advantage in high-resolution measurements.

While slit nozzles have been predominantly used for studies of stable molecules and clusters, investigators studying molecular ions at high resolution[75] have shown the suitability of planar nozzles for ion spectroscopy.[76]

B. Radical Production in Jets

Introduction of radicals into jets started with extensions of atomic beam techniques. The first method used for radical generation was oven evaporation or decomposition of a radical precursor. Metal vapor ovens had become pressurized with rare gases by the late 1970's, and the more exotic species NaNe and NaAr yielded interesting spectroscopy.[3,17] A generalization of oven techniques involved thermal dissociation of fluorine in a nickel oven, which, when pressurized with Xe, formed the excimer lasing molecule XeF.[16] The expansion cooling of this radical permitted examination of the vibrational progression all the way to the dissociation limit, giving the proper dissociation energy. These measurements showed how expansion cooling could produce spectroscopic information complementary to that obtained in other ways, even on otherwise well-studied systems.

Laser photolysis generated a radical of organic chemistry interest, CH_2 in the high-pressure region of an expansion.[77] Ketene, upon irradiation, gave both a diffuse emission and decomposition into CH_2 and CO. When the photolysis took place late in the expansion, well after any significant collisions, the CH_2 was found to be produced rotationally hot. Photolysis early in the expansion, so that the CH_2 experienced many collisions with cold background gas, produced rotationally cold CH_2 radicals.

Photodissociation of BrCN, which had been well characterized as producing hot CN radicals, gave rotationally, but not vibrationally, cold radicals when conducted early in the expansion.[78] These laser photolyses demonstrated the versatility of photolytic radical production and also established the general principles of rapid rotational, but slow vibrational, cooling of radicals in an expansion.

Other means of radical production have been accomplished in a nozzle, followed by expansion cooling. A typical radical production method is that of abstraction. Farthing et al.[79] demonstrated fluorine atom abstraction at moderate (100 Torr) pressures behind a nozzle, and subsequent cooling of the radical products. Obi et al.[11] demonstrated photolysis without use of a laser in the production of cold HNO radicals.

Heaven et al.[80] showed that photolysis could be quite complex, involving bimolecular reaction. They were able to form S_2, in addition to the primary photolysis product SH, in photolysis of H_2S in the high-pressure region of the expansion.

Laser vaporization is an effective technique for introducing low-vapor pressure material into the initial stages of an expansion. Originally a technique to produce clusters (see below), it can produce small diatomics and radicals. That the rotational temperature could be quite low has been repeatedly demonstrated. For example, Rohlfing carefully measured the rotational temperatures which result after ablation from graphite and expansion in a He flow.[81]

A number of discharge techniques have been applied to nozzles. Several groups[82-84] have attempted to form metastable molecular beams with an electrical discharge in the high-pressure region of the expansion. A corona-excited supersonic expansion was demonstrated for the production of OH molecular radicals,[85] but at the time it had not been clear that a fragile, polyatomic radical could be produced in similar manner. The question of the effectiveness of a discharge for producing even polyatomic molecular radicals was answered by the generation of methyl nitrene in a corona-excited supersonic expansion.[86] Not only was the radical produced, but it was produced in an electronically excited state, which was subsequently rotationally cooled in the expansion on a time scale which was short when compared to the fluorescence. The spectroscopy of this radical indicates that this upper state is very fragile, rearranging or dissociating with a barrier of about 1000 cm^{-1}, suggesting the usefulness of the corona-excited expansion in producing other, fragile species. Figure 2 shows the important features of this source. Electrical considerations for stable operation have been established;[87] a corona-excited supersonic expansion has even been used in conjunction with a Fourier transform spectrometer,[88] for which stable, continuous radical production and emission was imperative.

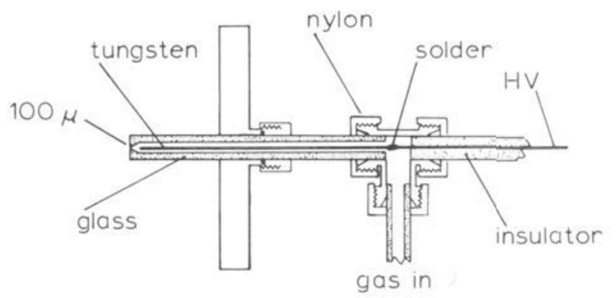

Figure 2. Corona excited supersonic expansion. Reprinted from ref 85. Copyright 1983 Elsevier Science Publishers.

The method of corona excitation was extended by Sharpe and Johnson to a pulsed configuration used in conjunction with a pulsed nozzle.[19,20] Although charged species were present in such an arrangement, neutral radicals and triplet metastables still could be examined by multiphoton ionization and subsequent detection of their ionized products.

The electric fields in the expansion produced by a discharge in the throat of a nozzle are milder than one might first imagine. The plasma outside of the nozzle is far out of equilibrium, with more charge carriers than could be sustained in a static gas at that low-current density. This leads to high conductivity and space-charge shielding of electrical fields. An electron beam can pass within a millimeters of the operating discharge nozzle without noticeable deflection; ions produced in the expansion are rotationally cold, which would not be the case if accelerated by strong electrical fields and colliding against slower neutrals. Thus, a discharge configuration in which most of the excitation occurs in the high-pressure region of the expansion appears to have the favorable characteristics of other cold radical sources.

Discharges operating at low pressures farther down stream in the expansion suffer from warm rotational and translational state distributions. A mass spectrometry ion source, the capillaritron, works by sustaining a glow discharge between a metal nozzle (or nozzle holder) and the extractor of a typical molecular beam apparatus. Both the translational and internal energy distributions of radicals produced in this manner are significantly hotter than if they had experienced the cooling of the full length of the expansion.[21]

Less is known about the production and internal energy distribution of radicals that would be produced in a transverse discharge across a slit. Baldwin et al. have reported the intense UV radiation from helium or argon excimers, under certain conditions, can be comparable to that of the atomic resonance lines.[89]

Recently, flash pyrolysis has been demonstrated as a method of producing radicals from a pulsed nozzle, by passing a gas mixture through a hot preexpansion chamber. The products are then cooled by expansion into a vacuum. Methyl radicals thus generated were probed by multiphoton ionization, and an estimate of 40 K was obtained for the temperature.[18] A design is shown in Figure 3. Currently, the only observed disadvantage of this method of radical generation is pyrolytic "tarring" of the slow, effusive tail of the gas charge delivered to the oven. This may be remedied in the future; one possible approach might be postpyrolysis purging of the nozzle with a "clean" gas. Multiple valve nozzles have already been developed for reaction studies.[90] It may be expected that the technology of nozzle design will evolve to accommodate

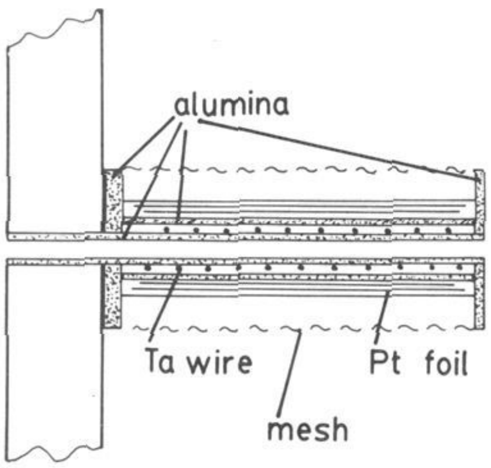

Figure 3. Schematic cross section of a flash pyrolysis nozzle, after the design of Chen and co-workers.

more careful control of the chemistry of radical production. Other recent entries into this area of jet-cooled flash pyrolysis indicate the attractiveness of this technique.[91,92]

C. Ion Production

Ionization by electrons or photons imparts little angular momentum, and the cations of stable parents are easily produced cold by direct ionization at low pressures. This fact has been used by hydrodynamicists to measure the amount of rotational cooling of their expansions. Typically, a molecule such as N_2 is subjected to electron impact, and the resulting ion produced in its A state is examined by wavelength-resolved fluorescence.[93-98] There has been some discussion about the amount of warming produced by electron impact.[22,99,100] The general consensus is that "low energy" electrons (what is meant by "low" is debated) are capable of exciting several quanta of rotation by ionizing through temporary negative ion resonances and by participating in long-range charge-quadrupole interactions with the ion core, while "high-energy" electrons just remove an electron directly, without specific rotational interactions with the core.

The technique of ion production by electron impact has been combined with fluorescence emission spectroscopy to examine parent molecular ions of stable species.[4,101] This has been one of the more fruitful methods of examining molecular ion spectra, especially when electron impact ionization is combined with laser-induced fluorescence.

Lasers may also be used for ionization. This was demonstrated in a jet with a multiphoton ionization of fluorinated benzene, followed by laser-induced fluorescence of the rotationally cold molecular ion produced.[102,103] Vibrational "hot bands" present in these spectra reflect the vibrational Franck–Condon factors for the ionization process, allowing one to probe vibrations of the ground state without dispersing the laser-excited fluorescence.

For production of cold ions that do not have a stable parent compound that can be cooled prior to ionization, formation and ionization must precede rotational cooling in the expansion. That ionization can be asymptotically locked into an expanding plasma appears to have been pointed out first by Raizer.[104]

On the basis of density alone, since the rate of recombination is proportional to the product of the electron and ion densities, each of which falls off with the inverse square power of distance from a circular aperture, recombination can be expected to rapidly turn off as the expansion proceeds. The temperature dependence of the recombination rate coefficient complicates this simple view, but as long as this coefficient does not diverge at low temperatures faster than $T^{-3.75}$ for a gas with $\gamma = 1.67$, or $T^{-6.25}$ for $\gamma = 1.4$, ionization is locked in, just as density arguments alone predict. For a planar nozzle, where density falloff is slower, the low-temperature divergence of the recombination coefficient must be less than T^{-3} for $\gamma = 1.67$ or T^{-5} for $\gamma = 1.4$.

The explicit kinetics of reactions in expansions have been explored more closely by Mazely and Smith.[105]

A few variations of discharge sources have been tried for the production of rotationally cold molecular ions. Beuhler et al.[106] have produced ions in a 10–100 Torr corona behind a metal nozzle. Y. T. Lee's group has used sources of similar design for preparing clusters of H_n^+ and solvated protons.[107,108] These designs appear to reproduce many of the features of the design of Searcy and Fenn.[109] The corona discharge terminates on the inside of the high-pressure metal nozzle. The dimensions must be rather large (1-cm diameter) in order to avoid striking an arc, and the excited volume ionized is rather large. A great number of ion clusters may result. The ion density outside of the nozzle is lower than can be obtained by other techniques, since all ions must be entrained in the flow through the nozzle.

Ions have also been produced outside of the nozzle by discharge in the capillaritron.[21] The ions appear with large thermal spreads, and do not appear to be very cold. The high fields present probably account for this.

In a modification of the source of metastables of Brutschy and Haberland,[84] ions have been generated by electron impact in a clustering source for a photodetachment apparatus. At this time it is not known how cold the ions are, but the sharp photodetachment spectra suggest a low temperature.[110] More experience with this source may eventually tell how cold ions generated in this manner may become. The configuration of the hot cathode loop just outside of the nozzle, near the barrel shock, complicates the use of this as an ion source for spectroscopy experiments which would probe this expansion region. Its use may be limited to molecular beam studies.

Midway between discharge excitation inside the nozzle and excitation outside the nozzle, the flow in the throat of the expansion can be excited with a corona discharge, if the nozzle is itself an electrical insulator. Not only radicals, but ions may be produced in this manner in the high-pressure throat of the expansion with only 10's or 100's of microamperes of current, since all of the excitation is concentrated where it is needed.[87] Several groups have shown molecular-ion spectra may be obtained from jets utilizing such coaxial electrical discharges, including the charge-transfer system of rare gas dimer cations[111] and the A–X system[75] of SO^+. Most recently, Milkman et al. demonstrated the adaption of corona discharge excitation to a slot geometry, thereby reducing the translational doppler width of the individual rotational lines observed in high resolution.[76]

D. Clustering

Nozzles that produce molecular radicals and ions also are capable of producing clusters. Although not the subject of this review, clustering may have a significant

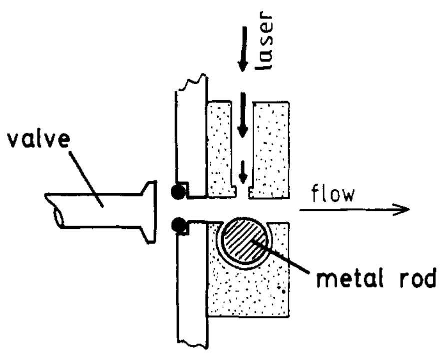

Figure 4. Schematic cross section of a laser-ablation, pulsed nozzle source, after Smalley and co-workers.

effect on chemistry and spectroscopy. Not only are additional spectroscopic features potentially present due to these clusters, but some or all of the radical or ion of interest may be tied up in higher molecular weight clusters. This may have puzzling consequences for the unexpecting researcher. Furthermore, the researcher may find so many clusters that the research may be redirected to the study of clusters themselves. Much of the spectroscopy of molecular radicals and ions is buried in papers primarily focused upon clusters!

The first metal cluster sources were improved versions of alkali metal oven molecular beam sources. Over the years, these have evolved from effusive sources to high temperature supersonic nozzle sources, by using the high-temperature metal vapor as the pushing gas. The adaption of this type of source to an open-shell system was made by Gole and co-workers, who expanded copper dimers and trimers with Cu atomic vapour as the carrier.[15]

Dietz et al.[112] revolutionized the study of metal clusters and that of metal-containing molecular radicals or radicals of refractory materials, by introducing the technique of laser ablation in the high-pressure region of the expansion. (Figure 4.) The first metal clusters produced this way were those of aluminum; impurities in the spectra were fragments of acetone that had been used to "clean" the apparatus. Subsequent work with aluminum vaporization targets has found, and investigated, Al_2 diatomics,[113] Al bound to rare gases,[114] and heteronuclear AlCu diatomics.[115] This technique has evolved to a high degree of specificity, and surface reactions of these clusters have been studied in such a source.[90] Ions may be produced in the metal-vapor plasma produced by the ablating laser pulse, and clustering may ensue about the charged species, so that cluster ions also may be produced by this technique.[116]

Photolysis has been found less useful in producing clusters. Duncan et al.[117] found the dissociation of an organometallic with high-laser powers gave virtually total destruction of the compound and ionization of the metal atoms. Later work at lower laser powers demonstrated that metal atoms were indeed present.[118,119] It might be hoped that a chemically tailored, metal center could be decorated with ablatable ligands, so that a high degree of chemical control would be possible over the composition and structure of a metal cluster. Additionally, it was hoped that the dissociation might impart little momentum to the metal fragment. Doppler measurements of iron atoms produced by multiphoton dissociation demonstrated that large amounts of recoil energy appear in the metal fragments,[120] suggesting that photolysis is not a gentle means of metal production. So far no use of this technique has been made for cold cluster production.

Ions can be formed by electron impact outside a nozzle, early in the expansion, and act as nucleation centers. This appears to be the mechanism of the negative ion cluster source operated by Bowen and co-workers.[110] Alternatively, electron impact upon clusters already formed can form ions in the clusters; excess energy is removed by evaporation, but this can hardly be considered as preparing cold species.

Electrical discharge in the nozzle throat seems to have less usefulness in producing molecular or ionic clusters; at least it has been utilized less for that purpose. Possibly the higher temperatures of the expansion carrier gas in the nozzle throat inhibits clustering, as pointed out by Campargue,[66] who specifically used hot gases in expansions to prevent clusters from forming.

Clustering with the background carrier gas is always a possibility that must be considered. High-backing pressures are primarily the factor responsible in expansions from circular nozzles, since cooling scales as p_0D, while three-body collisions scale as p_0^2D, where p_0 is the backing pressure and D is the nozzle diameter. Clustering is also more severe in slot nozzles, where densities fall off more gradually with distance. Also, the more polarizable, "soft" rare gases cluster more readily than does helium. Since density is highest on axis, clustering occurs there first, and it is possible to "cluster out" the radicals or ions of interest from the core of the expansion. This will be discussed later concerning spectral line shapes.

Clustering of radicals or ions with backing gas has been observed often. Studies of ion spectroscopy of halobenzenes had diffuse shadow bands present with both Ar and He carriers; these were established to be clustering of one, two, or three molecules of the background gas with the molecular ion.[102,103] Argon was found to cluster to methoxy radicals.[121,122] Interesting spectroscopy can be conducted by using the clustering of metal atoms to inert gases[9,123] in an extension of classical pressure broadening of spectral lines: the intermediates responsible are now available for direct study.

An interesting outgrowth of clustering two, potentially reactive, species is the photochemical reaction of absolutely oriented species. Zinc and cadmium atoms have been clustered with diatomics H_2, D_2, and HD; when photoexcited, the metal atoms can react with these oriented reagents.[124,125] One can imagine other such reactions, and the clustering of radicals or ions with other background molecules may turn out to be of similar usefulness in understanding their reactivities.

III. Spectroscopic Techniques

A. Line Shapes

Most of the electromagnetic probing techniques involve passing radiation perpendicular to the direction of the expansion. The low translational temperature achieved in an expansion would be expected to give very narrow Doppler line widths; in each locality of the expansion, this is true; however, probing any significant region of the expansion involves a large number of such localities, each moving with its own local velocity. The

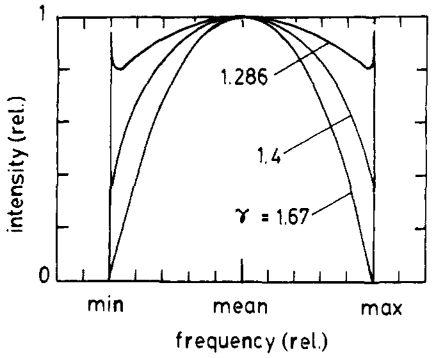

Figure 5. Dopper line profiles for an expansion from a circular nozzle. Optical path is perpendicular to the axis. A parabolic line shape is found for a ratio of specific heats characteristic of a monatomic gas (1.67). Lower specific heat ratios (1.4 and 1.286) increase the intensity in the wings, leading to a "flat topped" line shape.

nonuniform velocity field gives a finite "Doppler spread" that is comparable to the Doppler line width of molecules in the gas before expansion.

Figure 5 shows the expected line shape for a line of sight across a fully developed flow from a circular aperture, by using the density given by eq 1. The maximum frequency shift corresponds to the maximum velocity of the expansion. Notice the parabolic line shape characteristic of a monatomic backing gas, while for gases of lower specific heat ratios, the center becomes depressed relative to the more dominant wings.

The Doppler profile is not the only process leading to peculiar line shapes. Careful studies of ammonia expansions using IR lasers have established that a "double horned" line shape is possible, corresponding to clustering of molecules on the jet axis.[126] When clustering removes molecules from the beam, it shifts the frequencies of their absorption features to those of the clusters. Clustering is always more severe on axis, where densities are greatest. Molecules on the axis have the least Doppler shift; thus clustering preferentially removes this center of the spectral lines, giving a "flat-topped" or "double horned" line profiles. This has been noted in radical spectra by Huber and Sears,[8] especially in the emission of quartet NO.

At high densities additional complications may occur. Radical density can become high enough to cause self-reversal of lines in absorption measurements, or radiation trapping in emission work. It is also possible that the rapid cooling will give rise to a population inversion. Rapid gas dynamic cooling was one mechanism proposed by Hurle and Hertzberg for the population inversion necessary for spontaneous amplification.[127] Gain has been observed in some nozzle expansions.[128]

The major advantage of a planar nozzle is the reduction of the velocity spread, and hence the Doppler width of a transition, viewed parallel to the long dimension of the slot. Otherwise, the sensitivity of any experiment is nearly independent of choice of circular or planar nozzle, as long as the overall throughput is similar.[74]

B. Methods of Spectroscopy

So far, limited use has been made of three standard spectroscopic techniques on jet-cooled molecular radicals or ions: microwave, IR, or visible absorption. The low densities routinely attainable have made direct absorption difficult to observe. Nevertheless, it is possible that, with care, direct absorption can be accomplished. Recent work of Curl and co-workers shows that IR absorption spectroscopy of jet-cooled radicals is now possible, as a result of improved IR technology.[129] Absorption has even been extended into the far IR by using the new techniques of difference frequency generation in a metal whisker diode.[130] Even ions have been seen in direct absorption in a coaxial beam technique; a nozzle source was used for production of the intense beam densities required.[131]

A new technique called "cavity ring down" spectroscopy has located O_2 bands with oscillator strengths of 2×10^{-11} in atmospheric air in a 1-m cavity.[132] Basically, an absorption affects the time decay of light undergoing multiple reflections in a cavity: an intracavity absorber increases the cavity loss rate. Recently, this method has been applied[133] to Cu_2 and Cu_3.

Most of the observational techniques have used the more sensitive methods of fluorescence or ion detection. The original observations of jet-cooled ions depended upon fluorescence stimulated by electron impact.[4,5,6,101]

Later work used active laser probing of ground-state species by laser-induced fluorescence (LIF) for both radicals[77] and ions.[102] This could go to great lengths of sophistication with the use of two or more laser sources, as in optical–optical double-resonance experiments used to sort out perturbations in triatomic spectra.[134]

The high sensitivity of optical or particle detection could be combined with microwave techniques to give both high resolution and high sensitivity. This has been demonstrated on both radicals and ions.[7]

Multiphoton ionization (MPI) is also a technique of both sensitivity and selectivity and has been applied to the spectroscopy of cold open shell species.[135] Photofragmentation often gives unstructured spectra if it proceeds by a direct mechanism, but it is often all that is available in the spectroscopy of larger clusters.[136] Thermodynamic thresholds may be inferred from these types of experiments, but must be viewed with caution. For smaller species, dissociation has been shown to provide valuable, structured, spectra when a predissociation is involved. Morse et al.[137] were able to probe the dissociation of Cu_3 by observing the depletion of the trimer signal, generated by direct one-photon ionization, produced by the wavelength dependence of another predissociating laser.

IV. *Radicals of Nonmetals*

A. Diatomics

Some of the earliest spectroscopy on radicals in a jet was a laser-induced fluorescence (LIF) study on the excimer diatomic XeF.[16] In that work, the vibrational bands $\nu' = 11-22$ of the upper B state were located to an accuracy of half a wavenumber.

The radical SH has been produced and examined in a cold jet.[78] The dimer S_2 has been examined by two groups, one group forming the radical by laser-initiated radical reaction[80] and the other evaporating sulfur in an oven.[10] In the latter study, the weak $B''^3\Pi_u - X^3\Sigma_g^-$ transition was examined by using a lifetime separation method to discriminate the LIF from the stronger bands of the B–X system. The intensity borrowing from the allowed system was examined, and the irregular behavior of the spin–orbit splitting in the B state was shown to result from this interaction with the B″ state.

Laser vaporization of graphite in a pulsed He flow produces copious amounts of carbon species. C_2 evidences the $d^3\Pi_g-a^3\Pi_u$ Swan, the $C^1\Pi_g-A^1\Pi_u$ Deslandres-d'Azambuja, and the $D^1\Sigma_u^+-X^1\Sigma_g^+$ Mulliken systems.[81] An examination of the Swan bands provided rough rotational temperatures and vibrational distributions.

The radicals CN, NH, and OH have been observed in jets, but their well-known spectroscopy has been used more often to characterize the conditions of cooling within jets, rather than jet cooling being used to improve the spectroscopic measurements on these species.[62,78,85,86] An application to the spectroscopy of CN radicals came through the use of microwave–optical double resonance.[7] From this work was extracted the hyperfine constants for the $^{12}C^{14}N$ $X^2\Sigma^+$ ($\nu = 2$) vibrationally excited state. Huber et al. used rotational cooling to help sort out UV emission from the $L^2\Sigma^-$ Rydberg state to the low-lying $A^2\Pi$ state.[138]

Jet cooling of the rotational levels of low J in an excited electronic state of CN have had the interesting effect of revealing otherwise blended transitions originating on high J levels that do not cool efficiently in the jet. This has permitted an extension of spectral analysis to high J.[139]

The radical CCl has been examined by MPI, along with triplet CO metastables, in a pulsed discharge nozzle.[19] High-resolution emission spectroscopy performed with a CW nozzle in front of the UV FT spectrometer at the Kitt Peak solar telescope provided excellent characterization[140] of the $A^2\Delta$ state of CCl.

Emission spectroscopy at high resolution using IR photographic plates has given an unambiguous analysis of the $b^4\Sigma^--a^4\Pi_i$ bands of NO.[8,141a] Inter-Rydberg transitions of an electron surrounding a $^1\Sigma^+$ NO^+ core (4f–3d, 4d–3d) have been examined by using supersonic expansion and a Fourier transform spectrometer.[14b] The N_2 $C''^5\Pi_u-A'^5\Sigma_g^+$ system was reinvestigated by using jet cooling to confirm a previous assignment, which hinged upon the presence or absence of a low J line.[142] It may be expected that this is a forerunner of emission work to be done at high resolution on complex band systems, with jet cooling used to simplify the analysis.

GaAs has been the subject of recent work of Morse and co-workers.[143]

B. Triatomic Radicals

The methylene radical CH_2 has been examined in the jet-cooled photodissociation products of ketene.[77] The $\tilde{a}^1A_1$ state, examined by LIF, showed considerable vibrational excitations. Recently, the vibronic assignments on the $\tilde{b}^1B_1$ state of CH_2 have been extended by using LIF in a jet.[144] Similar work was done independently by two groups on the substituted halocarbene CCl_2, using again LIF to obtain frequencies and $\tilde{A}^1B_1$ and $\tilde{X}^1A_1$ state geometries.[145,146] The naturally occurring isotopes provided a sufficient set of independent rotational constants for the geometry determinations.

Several different techniques have been applied to emissions from two different states of C_3. Using resonant 2-photon MPI, Morse and co-workers[147] found analogous, but higher energy $^1\Pi$ or $^1\Delta$ states, with intensity borrowed by vibronic coupling from the allowed transitions in the VUV. Rohlfing[148] used LIF to help sort out the vibrational assignments of this new $\tilde{A}$-$(^1\Pi,^1\Delta)-\tilde{X}^1\Sigma_g^+$ band system, extending our knowledge of the ground-state vibrations, including high anharmonicity and barriers to linearity when even quanta of the asymmetric stretch are excited. In contrast, the symmetric stretch appears to increase rigidity against bending. Rohlfing and Goldsmith have introduced stimulated emission pumping, using the $^1\Sigma_u^+-\tilde{X}^1\Sigma_g^+$ system[149] and $\tilde{A}^1\Pi_u-\tilde{X}^1\Sigma_g^+$ system[150] to access additional bands and to resolve rotational features. These show the vibronic dynamics to be complicated; the possibility of the asymmetric vibrations inducing rearrangements makes this problem fascinating.

Another carbon-centered radical of astrophysical interest is CCN, which has been investigated recently by using UV FT spectroscopy coupled with jet cooling.[151] Unlike the diatomic CCl previously examined in the same manner, and which has a similar pattern of excited electronic states, this radical has a bending vibration that shows extensive progressions and combinations. A large Renner effect further complicates the situation. Expansions primarily cool rotational excitations, leaving considerable vibrational excitation; by reducing the extent of each band, jet cooling simplifies the identification of each vibrational band in the spectrum. Here, in addition to permitting rotational analyses of three vibronic bands, vibrational bands were sorted out and vibrational frequencies obtained.

The HNO radical was prepared by a Hg-photosensitized photolysis upstream of the nozzle.[11] By using LIF on the $\tilde{A}^1A''-\tilde{X}^1A'$ system, the lifetime of the $\tilde{A}$ state fluorescence was determined for single rovibronic levels. One advantage of this technique was the ability to measure the lifetimes unperturbed by collision.

In the following year, another nitrogen-centered radical, NH_2, was investigated by LIF in a jet.[153] This was followed recently by two IR absorption studies—one with an IR color-center laser[142] and another using tunable far IR.[130] The first of these extended the rotational analysis of the vibrational states of NH_2; the second study extended the precision of the rotational analysis of the ground state.

The 340-nm band system of S_2O was investigated[154,155] by LIF in a supersonic jet. From this, unambiguous vibrational assignments give the three vibrational frequencies 407, 253, and 380 cm^{-1}. The proximity of these three frequencies to one another gives a rather congested spectrum of band progressions and combinations, and jet cooling was helpful in isolating and identifying individual bands, whose relationship to others could be determined by LIF.

C. Polyatomic Radicals

The methyl radical CH_3 has been examined cold, in an expansion, after production by flash pyrolysis in a nozzle.[18,157] The method of MPI was used to examine the $3p^2A_2''-\tilde{X}^2A_2''$ spectroscopy. Estimated temperature of 40 K gave spectra with resolvable rotational features. Of significance was the generation of CH_3 from *tert*-butyl nitrite, and the lack of overlapping NO bands: the byproducts of the pyrolysis were also rota-

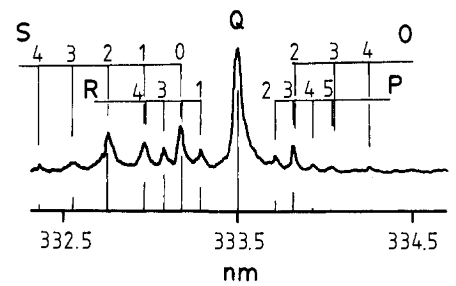

Figure 6. MPI spectrum of the methyl radical produced in a pyrolysis nozzle. Reprinted from ref 18. Copyright 1986 American Chemical Society.

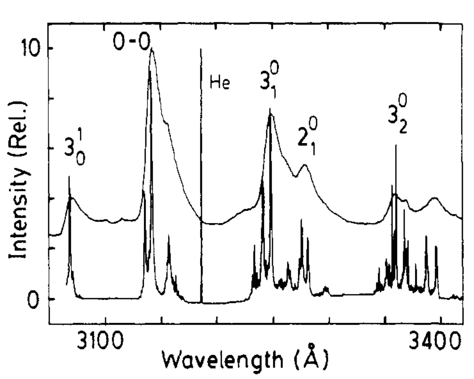

Figure 7. Methylnitrene spectra, comparing nozzle-cooled emission (lower trace) with room-temperature emission (upper trace). Reprinted from ref 163. Copyright 1985 American Physical Society.

tionally cold, significantly reducing the congestion of the spectrum. A MPI spectrum of methyl radical is shown in Figure 6. Examination of the photolytic product channels by laser ionization mass spectrometry identified the production of CH_2 from excited methyl Rydberg states.[158]

The study of linear hydrocarbon radicals has progressed with the demonstrated production of ethyl, allyl,[159] vinyl, and ethynyl[180] radicals in supersonic expansions. Since these do not appear to fluoresce, studies have been restricted to "dark" techniques, such as MPI. Vibrational assignments for some bands have been made, while rotational assignments of high-resolution spectra still awaits experimentalists.

Recently, C_5 has been observed by IR diode laser absorption in supersonic expansions seeded with carbon by laser ablation.[161] Detection utilized the ν_3 stretch centered at 2169.44 cm^{-1}; the simple spectrum of just P and R branches indicated the carrier was a linear $^1\Sigma_g^+$ species, as expected for C_5. Further information on this radical is the subject of another study.[162]

If one oxygen atom is added to methyl, the methoxy radical is obtained, CH_3O. The jet-cooled spectrum of this radical has been studied by three groups. Powers et al.[121] has examined the LIF spectrum of these radicals expanded with both Ar and He, finding considerable clustering with Ar. Significant perturbation of each band made the analysis difficult, and the spin-orbit splitting in the $\tilde{X}^2E$ ground state was not observed, presumably having been cooled away. Carrick, Brossard, and Engelking,[2a] and later Brossard et al.,[2b] examined the emission from this radical at low dispersion, clearly establishing the spin-orbit splitting in this radical as 62 cm^{-1}. Upon deuteration, this splitting decreases to 55 cm^{-1}. An analysis of this effect shows that much of the orbital angular momentum in the radical is quenched by the 3-fold static geometry to about 98 cm^{-1} from about 140 cm^{-1} found in OH; the angular momentum is further reduced by a dynamic, Jahn–Teller quenching effect to the value that is observed. It is this dynamic quenching that is sensitive to deuteration. Several vibrational progressions were identified; one progression was found in the Jahn–Teller active mode ν_5, which corresponds roughly to an asymmetric hydrogen scissors motion. Assuming most of the effect was concentrated in mode 5, the Jahn–Teller coupling constant could be estimated, showing that the Jahn–Teller stabilization in this radical is only about 200 cm^{-1}.

The LIF spectrum of jet-cooled methoxy radical was also examined by Fuke et al.[122] Two additional vibrational modes in the upper $\tilde{A}^2A_1$ state were assigned to the ν_1 and ν_5 modes. The vibrations in the CO stretch were followed all the way to dissociation.

In a series of papers from Miller's group,[164-166] jet cooling was combined with LIF to provide rotationally resolved methoxy vibronic bands. The vibrational origin band of the $\tilde{A}^2A_1$–$\tilde{X}^2E$ system is now clearly established,[165] and the rotational analysis of this band has improved upon the microwave rotational constants of the $\tilde{X}$ state.[167,168]

Currently, full sets of six vibrational fundamental frequencies are known for both the upper and the lower electronic states; the Jahn–Teller effect allows transitions between all vibrational levels of the upper and lower states, leading to numerous vibronic band progressions and combinations. Just between upper and lower state vibrational fundamentals, there are nearly 50 bands; without cooling, the over 300 observed bands in the $\tilde{A}$–$\tilde{X}$ system are badly overlapped: jet cooling has been essential to sorting out this spectrum.

Thiomethoxy has $\tilde{A}^2A_1$ and $\tilde{X}^2E$ electronic states analogous to those of methoxy itself, and the corresponding $\tilde{A}$–$\tilde{X}$ transition has been seen in jet-cooled emission.[169] The main vibrational progression corresponds to mode 3, the C–S stretch, indicating a significant lengthening of the C–S bond in the upper state, as in also the case in methoxy. The analysis of jet-cooled LIF spectra, combined with microwave results, allow estimating the spin–orbit splitting of the ground state as 255 cm^{-1}. Interestingly, this is two-thirds of the splitting found in SH, showing that the thiomethoxy radical's electronic angular momentum is not greatly reduced, suggesting that the radical site remains well localized on the heteroatom. This contrasts to the situation in CH_3O, where a combination of static angular momentum quenching and a further angular momentum reduction caused by the Jahn–Teller distortion leaves a spin–orbit splitting less than half of what it is in the analogous OH radical.

If the oxygen atom in methoxy is traded for a nitrogen, the elusive methylnitrene radical CH_3N is obtained. This has been examined in emission in a jet.[163] Figure 7 shows the spectral simplification that can be obtained by jet cooling in comparison to the emission obtained in a flowing afterglow. In spite of the potential to rearrange to methyleneimine $CH_2{=}NH$, the triplet ground state is stable to rearrangement. The upper state is more labile, and appears to rearrange or dissociate: only one vibration is present in the upper state. A full set of vibrational frequencies and a geometry[88] derived from the jet-cooled spectra allows the determination of a harmonic, vibronic force field.[170]

Some summarizing comments about the bonding in CH_3X radicals are appropriate here before moving on to other systems. In all cases studied, the C–X bond was stronger than that found in closed-shell analogues. This is evidenced in shorter bond lengths or greater vibrational forces. In addition, considerable reorganization occurs in the bonding at the methyl. Overall, these radicals are not well represented by standard bond lengths and bond angles that usually apply to closed-shell organic molecules.

Another pentatomic nitrogen-containing molecule has been examined[8] in jet-cooled emission: ND_4. This was examined in the red and in the near IR on the Schüler band, $3p^2F_2$–$3s^2A_1$, a Rydberg–Rydberg transition.

LIF spectra have been taken of jet-cooled vinoxy, cyclopentadienyl, and benzyl radicals.[171] In subsequent work,[172] the vinoxy radical $\tilde{B}^2A''$–$\tilde{X}^2A''$ spectrum was analyzed, giving three vibrational frequencies in both upper and lower states, a full set of rotational inertial constants, and one spin-rotation constant.

The lifetimes of the excited electronic states of cyclopentadienyl and methyl cyclopentadienyl have been measured, showing a clear decrease in lifetime with vibrational excitation.[173] There appears to be a significant nonradiative mechanism for decay in the excited state. This has complicated the use of intensities in understanding the Jahn–Teller effect in the ground-state radical.

Partly motivated by a desire of researchers to better understand the Jahn–Teller effect in C_5H_5, work on this radical has pressed ahead. It has been easier to approach the rotational analyses of individual bands, rather than to first obtain a comprehensive vibrational analysis.[174,175]

Benzyl radical emissions have been reexamined by jet cooling.[176] Vibrational band assignments are still not complete; jet cooling reveals a more complicated situation than had been suspected. Benzyl has also been introduced into jets by the reaction of Ba atoms, produced by laser vaporization, with benzyl chloride seeded in He expansions.[177]

The trimer SiC_2 has been observed in conjunction with laser ablation studies in nozzles.[156] It may be expected that the ablation work on metals and metal compounds (described below) can be extended to produce oxides, nitrides, silicides, etc. of nonmetals.

V. Molecular Ions of Nonmetals

A. Diatomics

Most of the electron-impact ionization of N_2 has used the fluorescence of N_2^+ to characterize the cooling conditions of the jet. A significant exception to this is the use of optical–optical double resonance to obtain new information about the molecular nitrogen cation.[24]

The similar diatomic CO^+ has been looked at in a microwave–optical experiment in a jet,[7] confirming other measurements of uncooled CO^+.

Huber and co-workers have examined the charge-transfer band systems that occur in emission from mixed rare gas diatomic cations.[178] An example of the usefulness is the establishment of the ground-state dissociation energy of $ArXe^+$ as 0.179 ± 0.004 eV.

The emission $A^2\Pi_i$–$X^2\Pi_r$ band system of rotationally cold SO^+ was observed and analyzed. Combining the data from 60 bands involving $\nu'' = 0$–10 and $\nu' = 0$–11 with those from previous measurements extended the accuracy of the rotational constants of these levels.[75]

Recently, the HF^+ cation was formed in a Haberland-type[81] jet expansion, electron-impact ion source. The ions were extracted and acclerated into a fast ion beam, which was then seen in direct IR absorption.[131]

A corona-excited supersonic expansion of SH^+ was placed inside an LMR cavity as a means of producing magnetically tuned far IR spectra of a rotationally cold (10 K) ion.[179]

B. Triatomics

A strongly perturbed emission observed from CO_2^+, until jet cooling,[180] was difficult to understand. An optical–optical double resonance experiment helped sort out the problem, which was an interaction between the $\tilde{A}$ and the $\tilde{B}$ states.[134] This work was further pursued to resolve both the issue of perturbations, and the seeming paradox of the $\tilde{A}$ state emission that occurs upon excitation of the $\tilde{B}$ state. The explanation for these problems lay in the perturbation of specific rotational levels of the $\tilde{B}$ state by the $\tilde{A}$ state, giving rise to red-shifted emission that was attributed at lower resolution to emission from the lower energy $\tilde{A}$ state.[181]

Nozzle cooling of H_2O^+ has provided emission spectra of the water cation under conditions comparable to those present in comets.[182] The spectra observed in the lab and in space show similar intensity patterns.

A problem of the spectroscopy of the halocyanide cations had been around since first observation by electron impact in effusive jets.[183] LIF on ions trapped in radio frequency quadrupole traps showed that cooling would be essential.[184] Two complementary approaches, ion trapping in matrices[185] and nozzle expansions,[186,187] finally yielded an understanding of these spectra, including a set of vibrational stretching frequencies. There still are unanswered questions about these species, with indications of perturbations similar to those occurring in carbon dioxide cation.

C. Polyatomics

A very similar set of halogenated cations are the haloacetylenes. There is an indication of radiationless transitions occurring in the haloacetylenes, giving rise to long and short decay lifetimes.[188] In electron-impact fluorescence[189] and LIF[190] on chloroacetylene, the spin–orbit splittings and vibrational frequencies in the $\tilde{A}$ and $\tilde{X}$ states were measured. However, a full set of vibrations was not obtained; especially missing were the hydrogenic motions, for which the transition is nearly vertical, as found in calculations.[191] The vibrational frequencies and their progression intensities agree well with calculations. Emission work on the more strongly spin–orbit coupled iodoacetylene has recently been performed.[192]

More recently, the hydrogen in the chloroacetylene has been replaced by a methyl group, and emission from the cation has been observed.[193] The bromine-substituted species was also examined. Here, the complication is the ability of the end methyl group to hyperconjugate with the π electron degeneracy, giving vibronic interactions and spin–orbit quenching.

Similar studies have involved the dichloro-[194-197] and dibromoacetylenes.[183] Here the spectroscopy is even more complex, due to the longer conjugation length of the π system and more available states.

It is interesting to note that the acetylene cation itself is nonemissive. This is understandable from the aspect of calculations showing the excited $\tilde{A}$ state correlating to a strongly bent geometry, with possible crossing with the ground state.[198]

Fluorescence is possible from longer conjugated carbon chains. In the gas phase, 2,4-hexadiyne cation and its substituted analogues[199,200] show considerable detail, which becomes clearer upon jet cooling.[187] One interesting development is the appearance of a bending mode, not observed in a matrix.[202]

The classical diacetylene cation emission spectrum had some ambiguity remaining in the rotational numberings, and hence an uncertainty in the derived rotational constants. Jet cooling allows unique rotational assignments, and locates the weak Q branches, from which an unambiguous set of rotational constants may be determined.[203]

Unlike the phosphaethynes[204-206] HCP^+, DCP^+, and FCP^+, the phosphapropyne cation CH_3CP^+ has a gas-phase emission spectrum which is heavily congested, and benefits greatly from jet cooling.[207] The spin-orbit coupling is significantly smaller in the methyl-substituted compound than in the linear species, presumably reflecting conjugation of the off-axis hydrogen with the π electrons.

Extensive work has been performed on the halobenzene cations, some of it in matrices[208-211] and some in the gas phase, not in jets.[212-216] It is with jet cooling that all workers in the field have come to agree upon the vibrational assignments.[5,12,14,102,103,217] Measurements of the frequencies of vibrational bands in Ne matrices correllate with those in jets. While most band positions correspond to within 1%, some of the bands, particularly those assigned to mode 3, showed significant variability in their matrix shifts.[218] Halobenzene cations have a significant Jahn-Teller effect in the ground state, and it is in these species that the most extensive Jahn-Teller analyses have been conducted, and which have been extensively reviewed.[33]

VI. Radicals and Ions of Metals

This review limits itself to species having no more than a few metal atoms.

Clusters containing many metal atoms have attracted much study of late, and often smaller dimers and trimers are considered in this same category. Yet, dimer and trimer metal-containing species have resolvable spectra resembling that of small molecules, and for this reason dimers and trimers will be discussed here. It should be recognized that this demarcation is only one of convenience: larger open-shell metal-containing species are interesting, too; they are just better discussed in the specific context of large clusters.

Alkali metal dimers have been found in supersonic expansions of neat alkali metal vapor. We wish not to review the voluminous literature on these for three reasons: first, they can be considered formally closed-shell species; second, they are not usually prepared cold in expansions with rare gases; and third, we could not do justice in this space to the voluminous and specific literature on these metal dimers.

A. Open-Shell Diatomics

Alkali metal atoms clustered to rare gases have been studied in jets.[219] This gives direct information about the potential energy surfaces, information which is otherwise indirectly obtained through depolarization, line broadening, or quenching studies.

Other than those of alkali metals, the first metal dimers formed in a rare gas nozzle expansion were Al_2 dimers.[112] These were produced in laser ablation of aluminum metal in the flow of an expansion. Only mass spectra were reported for the ions resulting from MPI of the resultant mixture of products. Acetone impurities in the He backing gas resulted in additional metal-containing species $Al_n(CH_3CO)$ and $Al_n(CH_3)_2CO$. This work demonstrated how one could inject large amounts of metal or refractory material into an expansion without requiring a high-temperature oven.

More recent work[113] on two different electronic transitions of Al_2 produced by laser evaporation provides evidence that the ground state is a $^3\Pi_u$ rather than the previously designated $^3\Sigma_g^-$. Weakly bonded AlAr, AlKr, and AlXe diatomics have been examined by fluorescence excitation and emission spectroscopy.[114] Morse potentials approximate the ground states; dissociation energies were obtained from Birge-Spooner extrapolations. Interestingly, the bonding shows a dependence upon the specific spin-orbit state of the Al atom, with the lower $^2\Pi_{1/2}$ component providing the deeper potential.

AlCu has been recently observed by using time-resolved LIF on products of laser vaporization of Cu-Al alloy.[115]

Cu_2 dimers were found in expansions of Cu vapor. However, the limited backing pressure and the high starting temperature did not achieve a high rate of cooling.[15] Dimer spectra were obtained in LIF. Laser ablation in a nozzle expansion was found to be easier, and provided more substantial cooling.[220] The spectrum could be obtained through MPI, and a new C state was found. Further analysis of the new spectra were conducted in subsequent work.[221] Up to 72 vibrational levels were located in the ground state, and spectroscopic estimates of the dissociation energy were improved.[222]

The next metal dimer observed with this technique[223] was Cr_2, which had been previously characterized. This dimer also was the object of investigation by another group.[224] This work confirmed the short bond length of the chromium dimer, which proved to be formally sextuply bonded with an electronic configuration of $(3d\sigma_g)^2(3d\pi_u)^4(4s\sigma_g)^2(3d\delta_g)^4$, indicating that d electrons would be important in the bonding of these metals.

The molybdenum dimer had similar spectroscopy.[225]

The nickel dimer had not been studied before jet expansion.[226,227] Dissociation of many of the predicted electronic states precludes MPI or fluorescence spectroscopy of these, but there is at least one strong band system. At long wavelengths, the spectrum becomes simple enough to have one analyzable band system.

The heteronuclear diatomics NiCu, NiPt, and NiPd have been the object of a series of studies[228-230] by the Morse group, along with a study[231] of the homonuclear Pt_2.

Vanadium dimer has also been studied.[232] This has a $^3\Sigma_g^-$ ground state, reminiscent of S_2, including an unusually large spin splitting for a Σ state. This dimer is tightly bonded, indicating significant d electron participation, as in the case of neighboring chromium in the periodic table.

Vanadium nitride was formed by reacting V with ammonia. Rotational analysis of the (0,0) band was completed, and vibrational constants were estimated for the intercombination system.[233] A number of recent studies from Hackett's group have focused on diatomics of metals near V in the periodic table. NbS was produced by reacting Nb with CS_2 and two band systems in the visible were observed.[234] TiN was investigated in Stark field experiments involving the X and A states.[235] ZrO has been investigated of the e–a and C–X band systems following nozzle cooling.[236,237] ZrS was produced[238] by reacting Zr with OCS; one of the two observed band systems was assigned as $E^1\Sigma^+$–$X^1\Sigma^+$.

Some of this transition-metal work has been reviewed by workers in the field.[46,239]

To the right of copper in the periodic table is zinc; below Zn are cadmium and mercury. Atomic mercury has long been a spectroscopist's favorite. In a nozzle expansion, species of mercury bound to rare gas atoms can be examined in detail.[9,240] Similarly, cadmium combines with rare gas atoms[241–249] or with itself.[29]

In work similar to that already discussed for aluminum, InAr, InKr, and InXe were probed by LIF.[244]

Sn_2 has been investigated by LIF subsequent to laser vaporization.[245] A spectroscopic value of its dissociation energy agrees well with both calculations and thermochemical values.

Au_2 in a supersonic expansion was the subject of recent studies with sub-Doppler resolution. All J states near the origin were resolved, firmly establishing their numbering.[246]

Recently, the positively charged dimeric species of Fe, Ni, and Nb have been investigated by photodissociation.[247] Fe_2^+ showed no sharp predissociation structure in its spectrum, unlike nickel and niobium dimers.

Calcium dimers have been studied in a jet,[13] which was found to be necessary to its study by LIF, in comparison to the work[248,249] which was possible without expansion on the lighter Be_2. Calcium, strontium, and barium have been studied in expansions clustered to rare gases.[250]

In a show of interest in the top of the periodic table, LiBe has been assigned as the carrier of a spectrum observed in the vapor produced by laser evaporation of a pressed pellet of Li and Be powders.[251] There is a very good agreement with the results of ab initio calculations.

B. Triatomics

Much less work has been done on metal or semiconducting trimers. The most extensively studied are copper trimers[137,239,252–254] and sodium trimers.[255–259] In the observed band system, a Jahn–Teller distortion is expected for the electronically degenerate E-type symmetry states. The analysis of the effect is still not completed. Furthermore, the spin–orbit coupling constant is undetermined. This coupling must be considered in conjunction with the Jahn–Teller effect if the vibrational frequency of the active mode is comparable to the unquenched spin–orbit splitting. This area continues to be one of active research, since these E-type states are prototypical of Jahn–Teller distorted systems.

The analogous electronic transition in Ag_3 has also been noted, exhibiting a similar Jahn–Teller distortion.[260]

Al_3 has been examined by MPI mass spectrometry after the trimer was formed by laser evaporation in a jet.[261]

LIF electronic transitions of Ni_3 have been observed, yet their assignment is less clear, since the open d shell introduces high electronic state densities.[262]

$NiCl_2$ has been examined by dispersing the fluorescence excited by a fixed frequency CW laser in a jet.[263,264] The state density appears to be high enough that bands containing all three ground-state vibrational intervals appear, from which these vibrational frequencies may be determined.

C. Polyatomics

No attempt is made to review the spectroscopy of large metal clusters here.

So far, jet cooling does not appear to have been applied to studies of species such as $CaOCH_3$ or CaC_5H_5, which have extensive emission systems.

Studies of metal atoms clustered to rare gas atoms have been taken into the realm of polyatomics with the replacement of the rare gas atoms by closed-shell polyatomic gases. Thus jet cooling has been used to investigate $HgCH_4$ and $HgNH_3$.[265,266]

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