10 February 1984, Volume 223, Number 4636 SCIENCE

Chemistry and Chemical Intermediates in Supersonic Free Jet Expansions

Terry A. Miller

The concept of a reactive intermediate, sometimes called a free radical, is an old one in chemistry. To illustrate, a textbook of organic chemistry, first published in 1887, states, "Radicals are groups of atoms that play the part of elements, may combine with these and one another and may be transferred by exchange from one compound to another" (*1*). Our concept of a chemical intermediate has been refined only a little in the intervening 100 years.

Summary. Short-lived intermediates often play key roles in determining the course of chemical reactions. Recently the combination of sophisticated laser techniques and supersonic free jet expansions has offered new insight into the structure and reactivity of such intermediates. Because of their extremely reactive nature the intermediates are produced in situ in the expansion. The free jet expansion provides cooling of the intermediates to very low temperatures, so that even complex organic free radicals and molecular ions can be identified and characterized. Radical-radical reactions and ionic cluster formation likewise proceed in the expansion and can be monitored by laser spectroscopy.

We would now call any molecular or atomic species that is produced during the detailed mechanism of an overall chemical reaction, but is not an isolable end product of that reaction, a chemical intermediate. Generally speaking, such intermediates will be chemically unstable (that is, highly reactive) but physically stable (that is, the unperturbed species will not spontaneously decompose) (*2*).

Most common chemical intermediates can be classified into several categories that include reactive atoms such as H, O, and N; neutral free radicals such as CH, ClO, C_5H_5 (cyclopentadienyl), and C_7H_7 (benzyl); and charged molecular ions such as N_2^+, Cl_2^+, $C_6H_2^+$ (benzene cation), and $C_6H_3F_3^+$ (sym-trifluorobenzene cation). An important facet of modern physical chemistry is to devise methods of detecting, characterizing, and monitoring the dynamics of these chemical intermediates. This is an extremely important task for two general reasons. Often these chemical intermediates are simpler and much more reactive "pieces" of larger molecules. Their physical characterization can play a key role in the fundamental understanding of molecular bonding and reaction. In addition, the capability to detect and monitor the transient populations of these intermediates is important in the understanding of the detailed mechanisms, and hence the control, of many complicated chemical reactions of commercial and environmental importance.

Because of their transient role in chemical reactions, the concentrations of such chemical intermediates are frequently quite low. Often sophisticated spectroscopic techniques are used for their detection and characterization. In this article, I describe some recent work done by our group and by others that combines, for the first time, the power of laser spectroscopic techniques with supersonic free jet expansions for the study of chemical intermediates. The laser techniques give us extremely powerful and sensitive ways in which to produce and detect chemical intermediates. The free jet expansion provides, in many ways, an ideal environment for the study of both the physical characteristics of the intermediates and their reactions.

The Free Jet Expansion

The properties of a free jet expansion, and their potential usefulness, probably were first recognized by Kantrowitz and Grey (*3*). The correctness of their ideas was almost immediately demonstrated experimentally by Kistiakowsky and Slichter (*4*), with at least part of the motivation provided by the desire to determine the structure of one of the simplest chemical intermediates, the methyl free radical, CH_3. After that seminal work over 30 years ago, much of the attention to free jet expansions centered on the details of the gas dynamics occurring therein, rather than on their potential use for the study of chemical intermediates.

Before discussing the advances that have made possible the present studies of chemical intermediates I shall summarize some of the relevant properties of free jet expansions themselves. This discussion will be brief and heuristic; there are several fine reviews (*5, 6*) the reader can consult for additional details. The key feature of the free jet expansion is a small-nozzle orifice that separates a high-pressure gas sample behind the nozzle from a downstream region kept at low pressure by a vacuum pump. The diameter, *D*, of the nozzle orifice is usually 0.01 to 1 millimeter; the pressure upstream from the nozzle, the stagnation pressure, P_0, ranges from 100 atmospheres to less than 1. Figure 1 depicts the conditions for a typical expansion, one with 10 atmospheres of room-temperature He behind the nozzle. The conditions downstream from the nozzle are

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The author is at Bell Laboratories, Murray Hill, New Jersey 07974.

indicated for various multiples (X/D) of the nozzle diameter. As indicated in Fig. 1, the pressure 50 nozzle diameters downstream is less than 10^{-7} that of the stagnation pressure. To maintain such a large differential places great demands on the pumping system, and often available pumping speed is the limiting factor in experiments. [To some extent, pumping speed limitations can be overcome by using a pulsed valve on the nozzle, thus limiting the total gas load on the pump—see, for example, the pioneering work of Gentry and his co-workers (*7*).]

From a molecular point of view, the free jet expansion converts random thermal motion in the gas reservoir to directed motion in front of the nozzle. This is illustrated in Fig. 1 by the conversion of the arrows indicating velocity from random length and direction behind the nozzle to uniform length and direction beyond it. It has been said that the free jet expansion "monochromatizes" the gas velocity. Even though this velocity may be dependent on the details of the expansion, it can be shown to reach a terminal, limiting value. For He, this corresponds to 2×10^5 centimeters per second, which can be compared to 1.3×10^5 centimeters per second, the arithmetical average velocity (*6*) in a random direction for a static gas of He at 300 K.

Such jets are often referred to as supersonic expansions, which may seem a little surprising since the limiting jet flow velocity is only slightly greater than the average bulb velocity, which indeed is close to the speed of sound (*6*). However, the local speed of sound is proportional to the square root of the temperature. Thus as the expansion proceeds, the Mach number, M, which is the ratio of the flow velocity to the local speed of sound, increases dramatically. For the portion of the expansion shown in Fig. 1, M has already reached 50. However, M will not increase indefinitely as a function of X/D; the decreasing frequency of collisions causes M to approach a limiting value. Nonetheless for He, M values over 200, which is truly supersonic, have been reported (*5*).

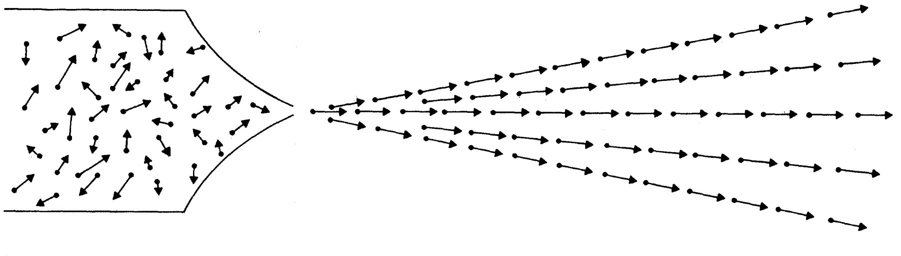
From our point of view, the most important physical property is not the absolute velocity but the width of the velocity distribution, which constitutes a direct measure of the gas's translational temperature. For the expansion in Fig. 1, this width corresponds to a temperature of less than 10 K at $X/D = 10$ and subsequently drops to less than 1 K; under more extreme conditions the translation temperature can approach 0.01 K. Since the distribution of molecular velocities is narrow, the energies of the collisions that occur in the expansion will be characteristic of these low temperatures. As a result of these collisions, the internal degrees of freedom of the molecules—that is, the vibrational and rotational energy levels—will relax toward these same low temperatures.

As the expansion proceeds, the density of the gas and the probability of collisions decrease. Thus the ultimate distribution of internal excitation in the molecule may not reach precise equilibrium with the translational temperature of the molecule. As a rough rule, rotational-translational equilibrium is usually rapid, and rotational temperatures are rarely greatly different from translational ones in a simple expansion. Vibrational-translational equilibrium is usually less efficient and often dependent on the details of the vibrational structure. Nonetheless, substantial vibrational cooling is also typically observed.

The collision processes in the jet deserve more discussion. The number density drops by a factor of more than 500 in the first ten nozzle diameters, and then, as Fig. 1 shows, drops by a comparably small factor of less than 40 in the next 50 nozzle diameters. Although, it is not possible to draw completely distinct boundaries, it is reasonable to assume that most of the n-body ($n \geq 3$) collisions occur at $X/D \lesssim 5$ for these expansion conditions. Because the initial step in molecular condensation requires n-body ($n \geq 3$) collisions, condensation must initiate mostly for $X/D \lesssim 5$. (The degree of condensation can be reduced by using a mixed gas expansion—for example, an inert gas like He or Ar dilutely seeded with the molecules of interest. In this case, most of the collisions occur among inert gas atoms, between which the intermolecular forces are relatively weak. Thus, in comparison with a pure molecular expansion, condensation is greatly lessened.)

The region very close to the nozzle is difficult to model theoretically and may vary considerably from expansion to expansion because of details in nozzle design. However, the region beyond $X/D \gtrsim 5$, where 2-body collisions predominate, can be rather accurately modeled. Lubman *et al.* (*8*) reported very useful results describing the collision frequency in this region. In Fig. 1, the flow velocity was used to convert this collision frequency into the number of 2-body collisions suffered by a typical molecule downstream from the point $X/D = 5$. Most of the collisions have occurred by $X/D = 30$ to 40, but inside this region they are quite frequent.

From our perspective, this region of 2-body collisions may be the most interesting. If "hot" radicals are injected into the jet, these collisions can thermalize them to the low temperature characteristic of the expansion. Similar collisions between reactive species can lead to bimolecular chemical reactions.



Distance (X/D)	10	20	30	40	50	60
Mach number	15	24	32	38	44	50
Temperature (K)	4.0	1.6	0.9	0.6	0.5	0.4
Density (S.T.P. torr)	15	3.7	1.6	0.9	0.6	0.4
Pressure (mtorr)	150	15	3.5	1.5	0.7	0.4
Collisions (5 → X)	80	106	112	115	117	119

Fig. 1. Schematic diagram of a free jet expansion. Shown below the expansion is a scale measuring distance (X/D) downstream in units of the nozzle diameter (D). Given at various positions downstream are the Mach number, the temperature, the density [in torr at standard temperature and pressure (*S.T.P.*); 1 S.T.P. torr = 3.54×10^{16} molecules per cubic centimeter], the pressure (in millitorr), and the number of collisions between $X/D = 5$ and the indicated point. It is assumed that the stagnation pressure behind the nozzle is 10 atmospheres of He at 300 K; for the collision calculation, $D = 0.15$ mm, and a collision cross section of 50 square angstroms is assumed.

Detection of Species in Jets

In many ways the free jet expansion produces an almost ideal source of molecules for study. They are at a very low temperature, so that even complex molecules have only a few populated rotational or vibrational levels. Yet they are isolated in the gas phase, free from any condensed-phase effects. The problem for the chemist is how to sample and interact with these exquisitely prepared molecules. The introduction of most mechanical devices into the jet will cause turbulence, destroying the ordered flow and raising the temperature of the seeded molecules. Great effort has been expended to design carefully shaped "skimmers" to sample physically the cold core of the expansion without introducing undesirable turbulence. Usually these skimmers serve as high-intensity (because of the jet's directed flow), low-temperature sources for molecular beams.

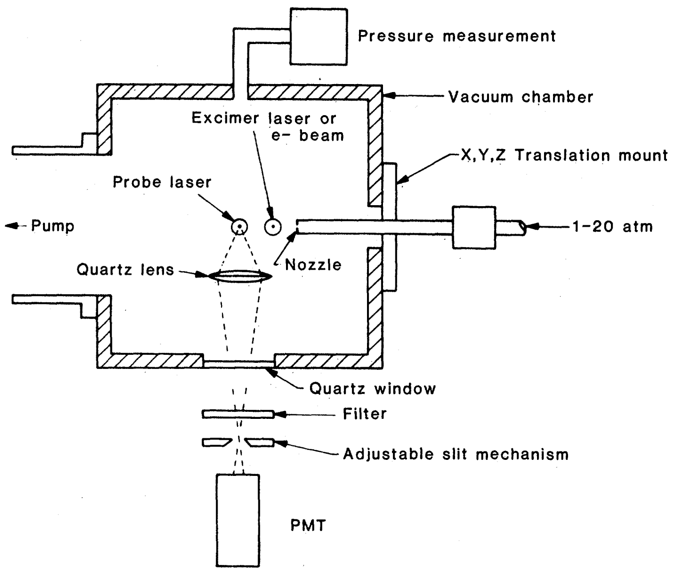


Fig. 2. Experimental apparatus used to study chemistry and chemical intermediates in a free jet expansion. The photolysis laser or electron beam is typically positioned between ~ 5 and 25 (*X*/*D*). The probe laser will usually be positioned at the photolysis laser position to ~ 80 (*X*/*D*). For experiments employing only an electron beam and no probe laser, the simple photomultiplier (*PMT*) detection will be replaced by a monochromator and photomultiplier. Similarly, in some cases laser-induced fluorescence may be dispersed by a monochromator.

Although considerable work has been done with such molecular beams, probably the most important advance has been the realization that the simplest, least perturbing way to study molecules is in the free jet itself, by using photons that can pass through the expansion without causing any perturbation to the medium.

The first clear demonstration of this fact was a precedent-setting experiment on NO_2. The visible, electronic absorption spectrum of NO_2 under ambient temperature conditions had long been regarded as so complicated and overlapped that a successful analysis was impossible. In the experiment of Smalley *et al.* (*9*) a supersonic expansion of NO_2 seeded in Ar was produced. The translational temperature of the beam (where interrogated) was 2 K and the rotational temperature of the NO_2 was 3 K, leaving only two rotational levels with significant populations. The expansion was crossed by a tunable dye laser. The fluorescence generated by the interaction of the laser beam and the cold NO_2 was collected in the third orthogonal direction. Tuning the laser frequency over the NO_2 absorption spectrum resulted in a fluorescence excitation spectrum of NO_2 that for the first time permitted a clear separation, and rotational analysis, of the otherwise badly overlapped vibronic bands.

Since this initial experiment, the use of laser-induced fluorescence for the detection of molecules in free jet expansions has become widespread (*5, 6, 10*). The low temperatures in the jet have permitted the obtainment of greatly simplified spectra of many complex molecules (*11*), among them tetracene ($C_{18}H_{12}$), pentacene ($C_{22}H_{14}$), ovalene ($C_{32}H_{14}$), and phthalocyanine ($C_{32}N_8H_{18}$), with molecular weights even exceeding 500. Radiationless transitions have also been studied in simpler molecules. Because of incipient condensation, very weakly bonded molecules—van der Waals molecules—are found to some degree in typical expansions. Because of the low temperatures and collision energies present, these species can survive in the jet. This has opened up a wide area of research (*5, 6, 12*) on their spectroscopy and photochemistry.

Although not yet as widespread, spectroscopic techniques other than laser-induced fluorescence have been used to study molecules in jets. These include Raman scattering, direct absorption, and multiphoton ionization.

Chemical Intermediates

The combination of optical, particularly laser techniques, with supersonic free jet expansions was initially widely used for the study of chemically stable molecules and their van der Waals adducts. Recently, however, such work has been extended to include highly reactive chemical intermediates. Figure 2 shows a schematic diagram of the apparatus constructed in our laboratory for this purpose. Apparatuses based on similar principles have been developed in other laboratories.

The key complication in studying chemical intermediates is that they cannot simply be entrained in the carrier gas behind the nozzle because of their extreme reactivity. Rather, they must be produced, at some stage, in situ in the expansion either immediately before or after the nozzle. Electron beam irradiation and laser irradiation downstream from the nozzle (Fig. 2) have been the most popular techniques for the production of chemical intermediates in the expansion.

Electron impact production and excitation of ions. In the first experiments producing chemical intermediates, an electron beam was used to produce ions, particularly N_2^+ from N_2. Two features of these experiments (*13*) set them apart from the rest of the work discussed in this article. First, the objective of these experiments was not the elucidation of either the structure or reactions of N_2^+. Rather this work was motivated by a desire on the part of fluid dynamicists to develop a convenient temperature probe for the free jet expansions. The way in which it was hoped that N_2^+ might provide such a probe rested on the second feature that differentiates this work from the rest. The electron impact process both creates the N_2^+ and provides for its detection in that it creates a fraction of the N_2^+ in an excited electronic state, which decays by the emission of photons to the ground state of the ion. Dispersing this optical emission through a monochromator shows clearly the rotational structure of this spectrum. From an analysis of the relative intensities of the transitions the rotational temperature of the excited B state can be determined.

It was originally hoped that the rotational temperature of the B state would be the same as the translational temperature of the jet at the point sampled. Although this appears to be roughly true, there has been great difficulty establishing the exact relation between these quantities. Recent work (*14*) shows there is apparently a slight "warming" of the temperature upon electron impact excitation, especially if the energy of the electrons is low.

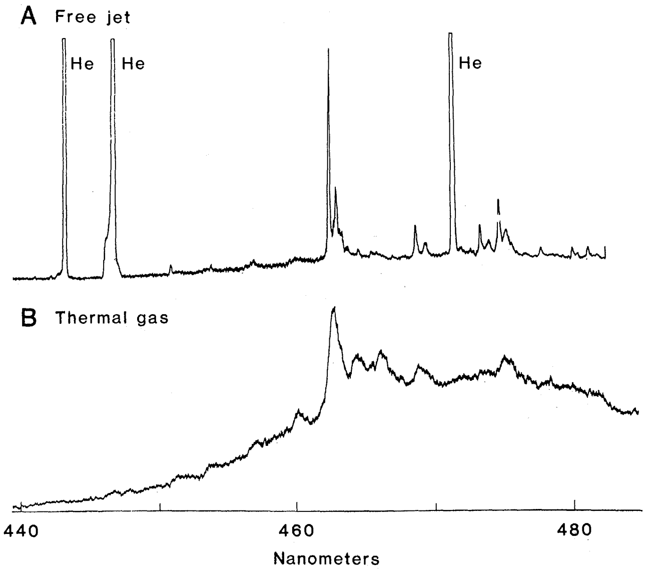
In the present context, probably the most important aspect of the N_2^+ work is the demonstration that chemically reactive species could be produced within the expansion without grossly distorting its unique properties such as directionality and low temperature. Being a simple diatomic species, N_2^+ had been well characterized in previous, traditional spectroscopic work. However, the electron impact techniques have recently been used by several groups to characterize reactive positive radical ions of triatomic neutrals and larger organic molecules. Species studied (*14–19*) in this way now number well over a dozen and include such diverse cations as those of CO_2, H_2O, N_2O, hexadiyne (C_6H_6), dichloroacetylene (C_2Cl_2), bromodiacetylene (C_4HBr), trichlorobenzene ($C_6H_3Cl_3$), and hexafluorobenzene (C_6F_6).

Figure 3 shows the simplification in the emission spectrum that can be achieved in a free jet expansion for a typical, relatively large, organic cation, $C_6F_6^+$. Clearly the resolution provided by the "cold" spectrum of $C_6F_6^+$ can be invaluable in analyzing vibrational structure that can probe the changes in chemical bonding from the neutral to the ion in an aromatic molecule. For systems like the dichloroacetylene cation (*17*), similarly improved resolution yields the fine structure splitting caused by the spin-orbit interaction. Even for a relatively small ion like CO_2^+, the cold jet spectrum can be useful (*18*) for probing, for example, perturbed rotational structure.

Laser production and detection of ions. Although the technique of electron impact ionization with simultaneous electronic excitation is a simple means for obtaining spectra of both small and large jet-cooled ions, it is relatively limited with respect to versatility. Because of the very short lifetimes (nanoseconds to microseconds) typically associated with radiating, excited electronic states, production and detection are nearly superimposed in space and time. For many applications, it is desirable to separate these two events.

Figure 2 illustrates the means by which this may be accomplished. Rather than monitoring the emission associated with the ionization process, the detection of the ions is accomplished downstream in the jet by laser-induced fluorescence. This part of the experiment is essentially identical to that described earlier for the observation of cold NO_2. The only substantial difference is that the ionic species being monitored is now being produced in situ in the free jet expansion. Other detection schemes could be envisioned, but laser-induced fluorescence has the key advantage of being able to monitor selectively different quantum states of the ion.

Thus far, two methods of ion production have been shown to generate high enough ion densities for successful downstream monitoring of laser-induced fluorescence. One of these is the electron impact ionization (*18, 19*) used in the emission studies. The other is the production of the ions by multiphoton photoionization. A large number of organic ions have been produced in our laboratory by the absorption of two excimer laser (ArF) photons. At present the two techniques appear to be somewhat complementary. The electron impact method appears to be better suited for light species with high ionization po-



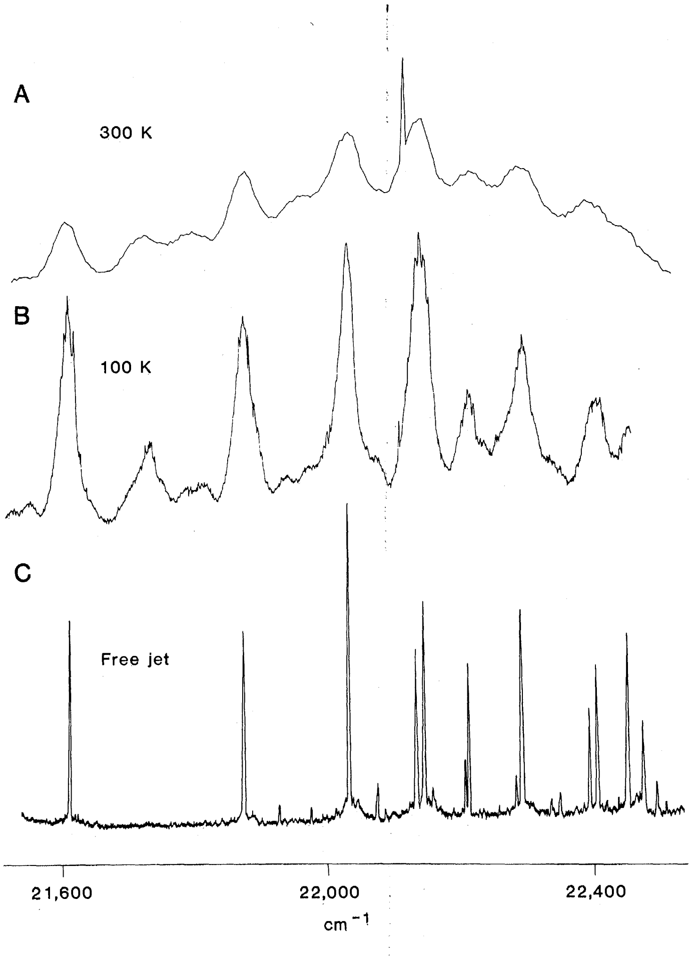


Fig. 3 (left). Experimental traces of the emission spectrum of $C_6F_6^+$ excited by electron impact. In (A), the sample is a free jet expansion of He seeded with C_6F_6, whereas that in trace (B) is a room-temperature sample of pure C_6F_6. The instrumental resolution is similar in the two traces. Lines marked He are due to electronic transitions in the carrier gas. Fig. 4 (right). Laser excitation spectra of $C_6F_6^+$. In (A) and (B), the $C_6F_6^+$ was produced by Penning ionization in a flow system; (A), the flow was at room temperature, whereas in (B) it was cooled by liquid N_2. For (C), the $C_6F_6^+$ was produced by two-photon photoionization through the use of an ArF laser interacting with C_6F_6 dilutely seeded in a free jet expansion in Ar. The probe laser line width is the same for all three traces; the sharp line in (A) is due to an atomic impurity.

tentials requiring the absorption of many photons. Laser photoionization, however, is a cleaner and less intrusive technique, and it has been successfully applied to a number of larger organic ions.

Figure 4 shows a laser excitation spectrum of $C_6F_6^+$ that was obtained in a jet after production of the ion by two-photon photoionization (*20–22*). For comparison, the laser excitation spectrum of $C_6F_6^+$ is also shown under conditions in which the ion's temperature was approximately 100 K and 300 K.

Spectra such as those shown in Figs. 3 and 4 have greatly increased our understanding of $C_6F_6^+$ and related organic ions. For instance, it has been established (*22*) that several substituted benzene ions retaining a degenerate ground electronic state by virtue of either a threefold or sixfold axis of symmetry [for example, $C_6F_6^+$ (sixfold) and sym-trifluoro- or sym-trichlorobenzene cation (threefold)] suffer an interaction between the nuclear and vibrational motion, called the Jahn-Teller effect. The existence of this Jahn-Teller interaction causes the electronic state to be stabilized by 500 to 1000 cm^{-1} in energy and to be geometrically distorted. Experiments have shown that the minimum energy configuration of these benzenoid ions does not correspond to a regular hexagon but rather to one with the internal ring angles distorted from 120 degrees by 1 or 2 degrees, and the C–C bond length alternating in length by approximately 0.02 angstrom. The implications of such geometric distortion for the chemical reactivity of these ions is being explored.

Ionic clusters. The role of ions as preferred sites for nucleation has long been recognized. Indeed, the venerable Wilson cloud chamber is perhaps the example that first comes to mind. In this case a supersaturated vapor is exposed to ionizing radiation such as cosmic rays. The cosmic rays produce ions along their path that serve as nucleation sites for droplet formation, giving rise to the well-known particle track in the chamber.

Ions, of course, constitute preferred nucleation sites because the strongest of the long-range, intermolecular forces are those involving the lowest order multipole, namely, the point charge. The microscopic origin of charged droplets are molecular clusters with one or a few neutral molecules bound to an ion by intermolecular forces. Such ionic clusters have long been thought to have a role in the chemistry of the upper atmosphere, some aspects of combustion, and certain electrical discharges. Indeed the widespread existence of ionic clusters has been demonstrated in numerous mass spectrometric experiments.

However, until recent jet experiments, no other physical identification or characterization of these clusters had been accomplished. Consequently, almost nothing is known about their structure, and much remains to be learned about their growth and role in chemical reactions.

The picture is starting (*20, 21, 23*) to come into focus with the obtainment of optical spectra for model cluster systems, one or more inert gas atoms bound to an organic cation. For example, distinct spectra have recently been obtained for the addition of one, two, and three He atoms to $C_6F_6^+$. The addition of each of the first two He atoms produces almost equal spectral shifts, implying nearly equivalent bonding sites. However, the spectral shift upon the addition of the third He is only about 15 percent of the value of the first two. It is appealing to suggest that the first two He's are binding equivalently above and below the benzene ring. The third He must then go into a second "solvation sphere," probably binding around the edge of the ring or to another He atom. Similar but somewhat more complicated data are now available for heavier inert gas atoms, and it seems likely that many different kinds of cluster ions can be studied by this technique. Although the picture still is not completely clear, it appears that our knowledge of ionic clusters should increase dramatically in the near future.

Simple neutral free radicals. The discussion to this point has focused almost

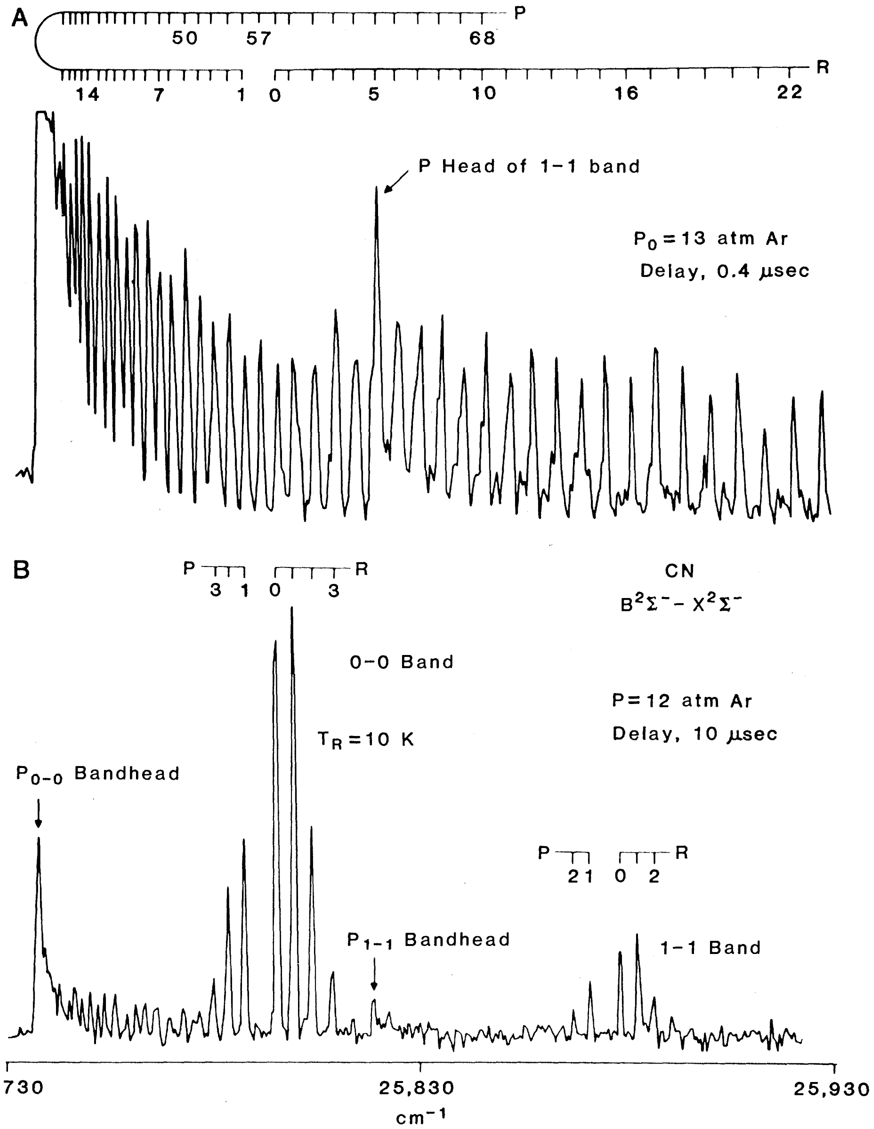


Fig. 5. Laser-induced fluorescence spectra of the CN free radical produced by the ArF laser photolysis of BrCN in an Ar free jet expansion. In (A), the probe and photolysis laser are nearly overlapped in space and time, and the CN distribution detected is nascent or near nascent. In (B), the probe laser has been displaced downstream by 10 μsec in time and 6 mm in distance. Large redistributions in rotational populations are clear. The rotational assignments for the R and P branches are as indicated.

exclusively on the study of charged chemical intermediates in free jets, but many chemical reactions have, as intermediates, neutral species—usually free radicals. It is not obvious that the techniques applied so successfully to the study of molecular ions in jets can be applied to the study of free radicals. To produce a reactive parent ion from a neutral precursor, one need only remove an electron. As mentioned earlier, removal of an electron will always approximately conserve the rotational and often the vibrational state of the precursor. Thus, given a cold precursor, it is relatively easy to produce a cold parent ion.

In contrast, to produce a neutral free radical (or charged) fragment from a precursor requires the rupture of a chemical bond. Excess energy must be converted into the translational and internal degrees of freedom of the fragments. Thus, in general, a cold precursor will produce vibrationally and rotationally hot, not cold, free radicals (*24*), as well as imparting a velocity to these species very uncharacteristic of the expansion.

Such a result would at first glance appear to destroy most of the jet's desirable characteristics. There is, however, the possibility that the free radicals, although initially produced hot, can be "thermalized" to the jet's temperature before they are detected or used. Figure 1 indicates that many collisions are possible if the fragments are produced near the nozzle exit. Indeed if radicals are initially formed translationally hot, they will suffer even more collisions than is shown in Fig. 1, since they will be "out of step" with the rest of the molecules in the jet. However, the extent to which thermalization can be accomplished under normal expansion conditions, is not a priori clear.

Smalley's group at Rice performed the first experiments on free radicals in jets. In the initial experiment (*25*), they photolyzed ketene, CH_2CO, to produce the methylene free radical, CH_2. They observed that the nascent rotational temperature of CH_2 was moderate but could be seen to cool even further by subsequent collisions in the expansion. Under certain photolysis conditions, considerable vibrational excitation appeared in the CH_2, which was only inefficiently cooled by the expansion.

To try to ensure more efficient cooling, the Smalley group developed (*26*) a two-stage expansion, which permitted precursor photolysis in a region of moderately high pressure, just before final free expansion. Using this technique, the group observed the methoxy radical, CH_3O, so cold rotationally that only the lowest two or three levels were populated. When the carrier gas was Ar, a van der Waals complex, $Ar \cdot OCH_3$, was also observed.

The pressure in the photolysis region of the two-stage expansion is sufficiently high that newborn radicals can reach roughly a room-temperature equilibrium. Depending on the experiment, this high-pressure section may or may not have desirable effects. It ensures more complete vibrational relaxation than might be expected in the expansion itself. Likewise, the room-temperature equilibrium apparently facilitates van der Waals complex formation in the expansion. On the other hand, the high-pressure region may lead to radical reactions that alter or destroy the species of interest. Moreover, this technique does not permit following the relaxation of the radical from a nascent to cold distribution. (Other techniques involving preexpansion production are discussed below.)

Heaven *et al.* (*27*) performed several experiments in which it was possible to produce hot nascent radicals and follow their relaxation in the jet. Using the apparatus shown in Fig. 2, they studied the photolysis of BrCN with an ArF excimer laser. This technique produces the CN free radical with a very hot rotational and vibrational distribution. Figure 5A shows the laser-induced fluorescence spectrum of CN, with the probe laser nearly superimposed in space and time with the photolysis laser. The observed distribution approaches, if it is not equal to, the nascent distribution. Although the rotational distribution is not exactly a Boltzmann, it can be approximated by a Boltzmann distribution with a temperature of about 4000 K. The fraction of population in the $v = 1$ vibrational level is about 20 percent of that in $v = 0$, which is equivalent to that expected for a vibrational temperature of about 1800 K.

If the probe laser is translated downstream from the photolysis laser, the trace of Fig. 5B is obtained. The CN has now suffered many collisions with the cold Ar carrier gas, causing a massive

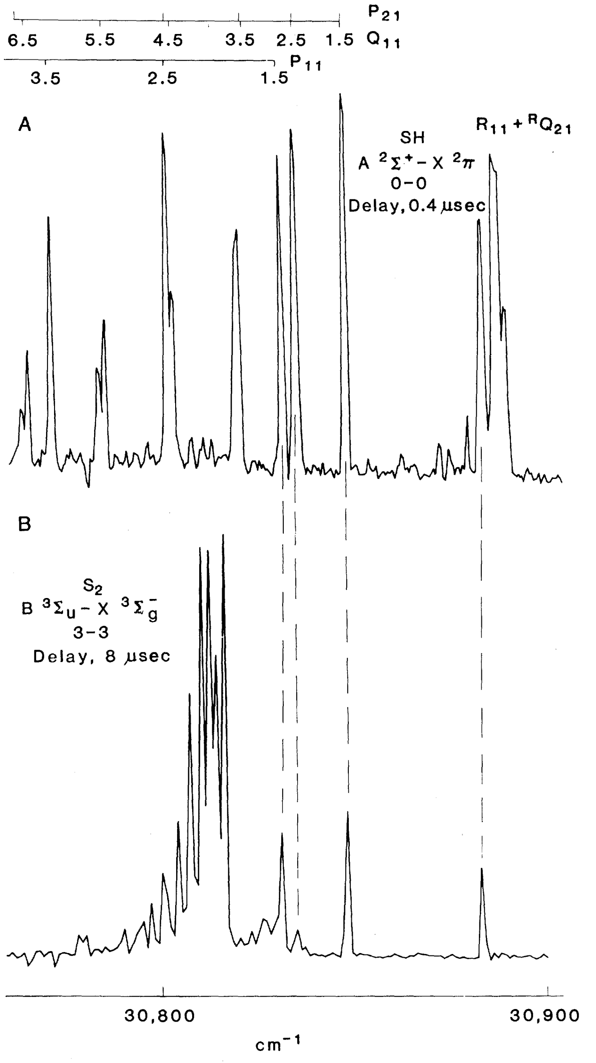


Fig. 6. Laser-induced fluorescence spectrum of the products of an ArF laser photolysis of H_2S seeded in an Ar free jet expansion. In (A), the probe and photolysis lasers are nearly overlapped. The spectrum observed is for the SH free radical with a nearly nascent population distribution. The rotational assignments of the lines are as indicated. In (B), the probe laser is delayed about 8 µsec in time and moved 5 mm downstream. The SH is considerably colder than in (A). The new, denser spectrum can be attributed to the S_2 molecule.

redistribution of rotational population. The overall distribution is now strongly non-Boltzmann. However, the lowest half-dozen or so levels are in equilibrium with a temperature of about 10 K. The ratio of populations in the $v = 1$ and $v = 0$ levels is essentially unchanged.

If the number of downstream collisions is increased by raising the Ar stagnation pressure toward 20 atmospheres, the only detectable CN radicals are in the lowest J levels characterized by a temperature of about 7 K. If He replaces Ar as the carrier gas, then rotational relaxation is not as complete, but all of the $v = 1$ population is efficiently relaxed.

Radical-radical reactions. For CN, the collisions relaxed the radical's internal energy but were chemically nonreactive. However, it is also possible to study reactive collisions with similar techniques. An example of such a chemical reaction is the one (*28*) forming the S_2 molecule. In this experiment, H_2S is photolyzed by an excimer laser to form predominantly SH+H. Laser-induced detection of SH, immediately after the photolysis pulse, is shown in Fig. 6A. The rotational distribution is nearly nascent and characterized by a rotational temperature of 300 to 400 K.

Figure 6B shows the same spectral region but the probe laser is now displaced downstream by about 5 millimeters in distance and delayed by about 8 microseconds in time. The SH spectrum is now much colder, only the lowest two or three rotational levels having observable populations. However, by far the most interesting feature in Fig. 6B is the newer, much denser spectrum now present, but absent in Fig. 6A. If the probe laser is narrowed by insertion of an etalon, this denser spectrum can be completely resolved and its carrier can be unambiguously identified as the S_2 molecule. Analysis of the spectrum shows that the S_2 present has comparable populations in the lowest five or so vibrational levels, but its rotational and fine structure populations can be described by a Boltzmann distribution with a temperature of about 20 K.

Since S_2 contains two S atoms, its formation requires the participation of at least two H_2S molecules. There seem to be only two ways for this to occur. Either the initial species to absorb a photolysis photon is a van der Waals cluster, $(H_2S)_n$ with $n \geq 2$, or subsequent radical-radical reactions occur between the radicals created in the initial photolysis of H_2S.

Experiments (*28*) showed that the product ratio S_2/SH was independent, over a moderately wide range, of the fraction of H_2S in the expansion. This would argue against the cluster explanation for S_2 formation, because species like $(H_2S)_n$ would be expected to increase at least quadratically with H_2S concentration while SH should have only a linear dependence. Similarly, the S_2/SH ratios were measured as a function of downstream position of the photolysis beam. With increasing distance between the photolysis laser and the nozzle, the S_2 concentration fell dramatically. This result is consistent with a radical-radical reaction because, as the photolysis is moved downstream to a lower pressure region of the jet, the probability of reactive collisions rapidly decreases.

The observations are all consistent with the following reaction scheme yielding S_2.

$$H_2S \xrightarrow{h\nu} SH + H$$

$$H + SH \rightarrow H_2 + S$$

$$S + SH \rightarrow S_2(X^3\Sigma_g^-, v'') + H$$

The rate constants for the various steps in the reaction are known from previous work. Use of these constants and a crude model of the expansion embodying the ideas in Fig. 1 shows (*28*) that the observed variation of S_2/SH with photolysis position, stagnation pressure, and so on can be semiquantitatively predicted.

In general, the marked change from energetic, ambient temperature collisions to low-energy, ultracold collisions might be expected to alter profoundly many reaction mechanisms. On a macroscopic scale, the different temperature dependencies of rate constants could be expected to change dramatically the balance between competing chemical reactions. In this case, the final product, S_2, found in the free jet expansion is the species that would be expected from a similar photolysis in an ordinary "bulb" experiment. However, in terms of internal energy content, the S_2 formed in the free jet reaction is very different from the S_2 from any other known source. It is vibrationally quite hot, but its rotational and fine structure distributions are quite cold. This unusual combination allows spectroscopic analysis of S_2 and consequently an understanding of its electronic structure, which had not been previously possible.

Large free radicals. While such unusual distributions may be of specialized interest for simple radicals like diatomic S_2, they have considerably wider utility for larger free radicals. Figure 7 shows (*29*) the spectrum of the vinoxy free radical, CH_2CHO, obtained in a free jet expansion. This radical is widely thought

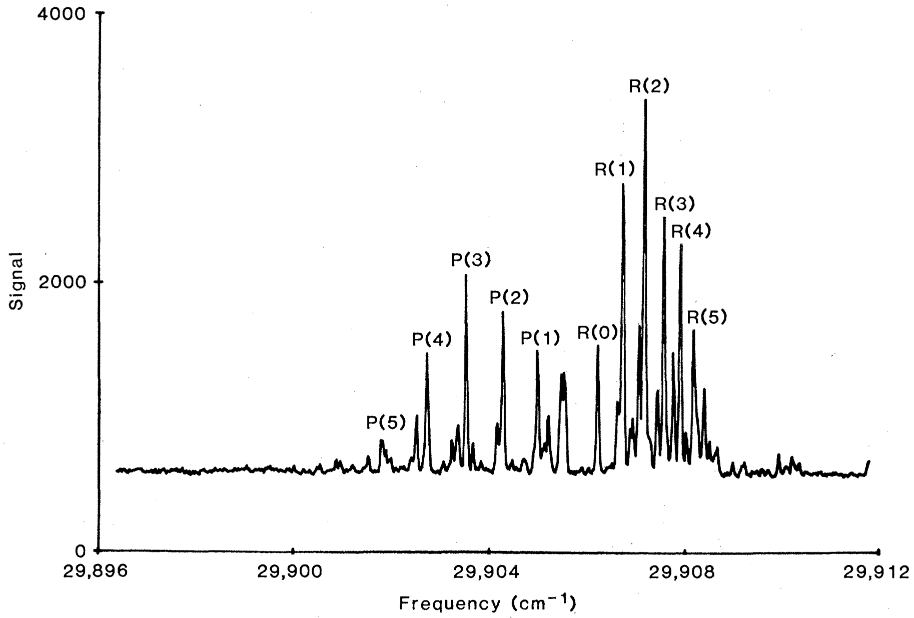


Fig. 7. Laser-induced fluorescence excitation spectrum of the vinoxy free radical (CH_2CHO). The vinoxy was produced by excimer laser photolysis of methyl vinyl ether (CH_2CHOCH_3). The rotationally resolved spectrum of the 010 vibrational band of the $\tilde{B}^2A''-\tilde{X}^2A''$ electronic transition is shown with the probe laser approximately 40 nozzle diameters downstream and the photolysis laser 10 nozzle diameters downstream. A rotational analysis of the spectrum shows the CH_2CHO to have a rotational temperature of ~ 10 K at the probed point. Vinoxy is a near prolate symmetric top and the indicated rotational assignments are in conformance with this approximation.

to be an important intermediate in flame chemistry and was earlier observed by laser-induced fluorescence spectroscopy in a room-temperature flow system. In those experiments, no rotational or fine structure resolution was obtained, largely because of the congested nature of the spectrum at room temperature. As Fig. 7 shows, the free jet photolysis of methyl vinyl ether produces the vinoxy radical with an internal temperature of about 10 K where interrogated. A thorough analysis of this spectrum is possible and has yielded detailed information (*30*) about the geometric and electronic structure of this radical. Recently, similar cold free jet spectra have been reported (*29*) for other large radicals, including the cyclopentadienyl (C_5H_5) and benzyl ($C_6H_5CH_2$) radicals.

Radical generation by other techniques. In the work described thus far, the chemical intermediates have been produced either by electron bombardment or laser photolysis. Until a few months ago, all production of radicals and ions in free jet expansions had been by one of these two methods. However, several experiments have now been performed that indicate that other techniques may be used to form reactive intermediates in jets.

Obi *et al.* (*31*) showed that a laser is not necessary for the photochemical production of free radicals in a jet. In their experiment, a simple Hg lamp irradiated a mixture of H_2, NO, Ar, and Hg upstream from the nozzle. The free radical HNO was then formed by the complicated reaction series

$$\mathrm{Hg} + h\nu\ (\mathrm{Hg\ lamp}) \rightarrow \mathrm{Hg}^*$$

$$\mathrm{Hg}^* + \mathrm{H}_2 \rightarrow \mathrm{HgH} + \mathrm{H}$$

$$\mathrm{H} + \mathrm{NO} + \mathrm{Ar} \rightarrow \mathrm{HNO} + \mathrm{Ar}$$

or

$$\mathrm{HgH} + \mathrm{NO} \rightarrow \mathrm{HNO} + \mathrm{Hg}$$

Laser-induced fluorescence spectra well downstream from the nozzle detected HNO cooled to a rotational temperature of approximately 16 K.

In a recent experiment by Droege and Engelking (*32*), a corona discharge was established upstream from the nozzle in a mixture of H_2O and He. In this work, optical emission from the discharge afterglow was observed downstream from the nozzle. The emission showed the presence of OH radicals in their excited $A\ ^2\Sigma^+$ electronic state cooled to about 11 K rotationally, but with a vibrational temperature of approximately 3400 K. Although the mechanism for the production of the OH is not firmly established, it has been suggested that $^2\Sigma^+$ OH is produced in the discharge upstream from the nozzle and rotationally cools before it radiatively decays downstream from the nozzle.

Farthing *et al.* (*33*) have produced the reactive species, NH_2, BrF, and IF, in a free jet. Their technique involved the reaction of F atoms, produced in a microwave discharge with NH_3, Br_2, and CH_3I, respectively, to produce the above-mentioned species. The chemical reaction takes place immediately behind the nozzle and the reactive intermediates expand through the orifice. Moderate cooling to approximately 100 K is reported by this technique.

It is rather difficult to assess the impact of each of these very recent experiments on the overall field. A major advantage of each of these techniques is continuous, rather than pulsed, production of intermediates. A clear limitation of the techniques is that they all rely on chemistry behind the nozzle. Overall, these techniques clearly add considerable versatility to our methods for the production of chemical intermediates in free jets.

Conclusions

Observation of chemistry and chemical intermediates under the singular conditions of a supersonic free jet expansion has wide-ranging implications. The spectroscopy of large reactive species can be studied at low temperature at which the number of populated quantum states is few. Such simplified spectra usually allow a detailed physical characterization of important chemical intermediates. Several relatively large organic intermediates, both ions and neutral free radicals, have already been studied in this manner. Prospects for future work in this direction are good.

Although the existence of small ionic clusters has been established by mass spectrometric work, their structural characteristics are largely unknown. Their detection by laser-induced fluorescence techniques in free jet expansions opens the door to a much better understanding of the bonding and structure of these important species.

In some cases, chemical intermediates produced upstream from the nozzle survive passage through the nozzle with subsequent cooling in the expansion. Evidence has been presented, in addition, for the occurrence of ion-molecule and radical-radical reactions in the jet itself. The implications of these observations are considerable. For example, the jet may serve as a laboratory prototype capable of simulating the isolation and low temperatures of interstellar chemistry. It also may be possible to develop entirely new chemistry based on the uncommon properties of the jet expansion. At the least, it gives us an opportunity to study old chemical reactions in a new environment, with the likelihood that a more thorough understanding of them will develop.

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Communications Satellites: Countdown for INTELSAT VI

L. Pollack and H. Weiss

Summary. Since the formation of COMSAT 20 years ago, the number of international telephone circuits made through satellites has grown 400 times and the cost of a telephone call has decreased by 12,000 percent. Worldwide communications linking 109 nations are achieved with 14 satellites in earth-synchronous orbit. Advances in microwave technology have expanded the transmission bandwidth per satellite from 50 to more than 3000 megahertz. Improvements in solar cell, battery, stationkeeping, and microwave amplification technology have increased satellite lifetime from 1.5 years to 10. The sixth generation of INTELSAT satellites, now being manufactured, will be introduced into the system in 1986, and each satellite will carry more than 40,000 telephone channels plus two television programs. The next generation of satellites, now under design for expanded capacity, will be needed by the middle 1990's to meet the traffic demand. These satellites are likely to add new frequencies (20 and 30 gigahertz), onboard signal processing and switching, and more bandwidth-efficient modulation, to achieve larger communication capacity at each orbital location.

In the two decades since the formation of the Communications Satellite Corporation (COMSAT), the number of active international satellite telephone circuits, worldwide, has grown 400 times and the cost of a telephone call has decreased by 12,000 percent, while the quality of service has improved. The timely exchange of televised news and cultural events via satellite is now commonplace among most countries worldwide. This dramatic progress has been made possible because of the introduction of geosynchronous communications satellites.

In 1964 COMSAT joined together with communications entities of 15 nations to form an international body known as INTELSAT, the International Telecommunications Satellite Organization. The organization which now includes 109 members is preparing for the introduction of its sixth generation of satellites. INTELSAT's global system provides communications along 1132 paths with earth stations in 169 countries and territories through more than 670 antennas, to which about 100 are added each year. In addition to seven full-time television channels and 5550 hours of occasional television, more than 31,000 simultaneous telephone circuits carrying voice, Telex, facsimile, and data are now in service.

Basic Technology

A geostationary satellite being an active radio relay repeater at a point 35,786 km above the equator, the early technology requirements were of a kind still of importance today. The four fundamental elements provide the means to (i) place the satellite in orbit; (ii) keep it stationary and stable in attitude; (iii) provide the repeater with a housing, thermally controlled environment, and operating power; and (iv) perform microwave amplification of signals received and transmitted between points on the earth by the satellite relay. While these technologies were available to inaugurate a modest satellite service in 1965, subsequent progress has been made possible by major research and development advances.

Supporting Technologies

Launching satellites. Although the first basic technology area (that associated with the launch vehicle, the launch process, and the transfer and injection of a satellite into geostationary orbit) is essential for the establishment of a network—a satellite and its associated earth stations—in INTELSAT planning it is considered mainly in the dimensioning of the payload. Dimensioning refers to both the physical dimensions of the satellite and its "wet" mass, which is the total mass to be carried by the launch vehicle at lift-off and includes the fuel needed to manipulate the satellite after it has separated from the launch vehicle for the remainder of its mission. Satellite dimensions must be commensurate with the mass-lifting and size limitations of the launch vehicle. In the case of the NASA Space Transportation System (the space shuttle), its lift capability of 29,480 kg and cargo bay measuring 4.5 m in diame-

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L. Pollack is vice president, INTELSAT Technical Services, World Systems Division, and H. Weiss is senior director, R & D Policy and ITU Matters, Communications Satellite Corporation, Washington, D.C. 20024.