

HIGH SENSITIVITY MASS SPECTROMETRY of TRANSIENT SPECIES

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Introduction

TRANSIENT SPECIES, SUCH AS FREE RADICALS and electronically excited molecules, play very important roles in fundamental chemical processes. These species are ordinarily present in extremely small concentrations primarily because they are the active participants in the reaction and, therefore, have short lifetimes. Since one is obviously much more interested in the low concentration highly-reactive components than in the large concentrations of relatively inert molecules, there is a definite requirement for a versatile analytical instrument having high sensitivity.

In addition to the extremely reactive short-lived components, there is a class of relatively stable components which is encompassed by the same analytical umbrella and is of current interest in environmental problems. In particular, atmospheric pollutants have recently been the subject of

considerable attention in connection with the proposed establishment of national air quality and emission standards.¹

Under the influence of sunlight, hydrocarbons and nitrogen oxides from automobile exhausts combine to form a complex variety of photochemical oxidants which, together with the solid and liquid particles in the air, form the pollutant mix commonly known as smog. The principal photochemical oxidants are ozone, nitrogen dioxide, various peroxyacyl nitrates, aldehydes, and acrolein. Studies have shown that eye irritation becomes noticeable when the oxidant levels reach about 0.10 part per million. Plants are often more susceptible than man to injury by these oxidants. For example, tobacco plants can be damaged by ozone at a level of 0.03 part per million and radish

¹ *Environmental Quality*, "The First Annual Report of the Council on Environmental Quality," 1970, U.S. Government Printing Office, Washington, D.C.

The detection of low concentration transient chemical species presents several formidable problems not encountered in ordinary analysis. This paper discusses the various factors involved in high sensitivity mass spectrometry of transient species and describes a mass spectrometer that incorporates design features based on these considerations. The successful integration of the mass spectrometer with a crossed molecular beam system has permitted the study of important elementary gas phase reaction mechanisms.

yields have been reduced 50% by prolonged ozone exposure at 0.05 part per million.

Sulfur oxides, principally sulfur dioxide and sulfur trioxide, are produced primarily by combustion of coal and oil in electrical power generating plants and can cause injury to the respiratory system. The President's Council on Environmental Quality Report¹ states that health may be imperiled when the annual mean concentration of sulfur dioxide rises above 0.04 part per million.

Carbon monoxide is the single greatest pollutant by weight that is injected into the atmosphere (estimated at over 100 million tons per year in the U.S.) and almost two-thirds of this is emitted by internal combustion engines. It is interesting to note that studies have shown that an exposure to 10 parts per million of carbon monoxide for approximately 8 hours may dull mental performance, and that such levels are commonly found in cities throughout the world. For short periods of time in

heavy traffic it is not uncommon for carbon monoxide to reach levels of 100 parts per million.

The analytical interest in atmospheric pollutants, thus, covers a broad range of concentrations, extending from about 100 parts per million down to perhaps 1 part per billion. Some pollutants, while stable in the atmosphere, being buffered from contact with catalytic surfaces by an essentially inert gas environment, may not be able to survive the rigors of sampling in conventional instruments and, for this reason, would have to be treated with the care usually reserved for free radicals.

Of the many techniques available for gas analysis, mass spectrometry stands closest to providing high sensitivity universal detection of all the chemical constituents present. Each constituent has a characteristic mass spectrum that can be used in much the same way that a fingerprint is used for identification. The universal detection capability of the mass spectrometer is a mixed blessing. On the one hand, it permits analysis of all the components in the sample. On the other hand, when many components are present, the overlapping of the spectral lines can cause confusion, and in ordinary analytical work this is solved by using a tandem arrangement of a gas chromatograph in series with a mass spectrometer, so that the components are separated before they enter the mass spectrometer. In searching for small concentrations of transient species, such as free radicals, one obviously cannot use a gas chromatograph, which would destroy them, and so has the arduous task of detecting the desired components in a large background of stable molecules.

Some aspects of high sensitivity mass spectrometry have been discussed in two articles that have been published in the *APL Technical Digest*.^{2,3}

General Considerations

A mass spectrometer produces a beam of ions from the material under study and sorts the ions out according to their mass-to-charge ratios into a spectrum. What is not generally appreciated is the enormous potential increase in detectability which

² S. N. Foner and R. L. Hudson, "Mass Spectrometry of Free Radicals and Metastable Molecules," *APL Technical Digest* 5, No. 4, March-April 1966, 2-11.

³ S. N. Foner and R. L. Hudson, "Mass Spectrometry of Very Fast Chemical Reactions," *APL Technical Digest* 7, No. 6, July-August 1968, 2-9.

results from the first step in the analytical process, converting the molecules into ions. Prior to ionization, the molecules are an indifferent lot having kinetic energies of about 0.04 eV and, figuratively, it would take a bucketfull of them to produce an observable indication on an instrument, such as a pressure gauge or thermocouple gauge measuring gross physical properties. For example, the world population equivalent, 3×10^9 molecules, in a volume of 1 cm^3 would produce a pressure of 10^{-7} Torr ($1 \text{ Torr} = 1 \text{ mm Hg}$), which would be barely detectable with a non-ionizing pressure gauge. A molecule on being ionized becomes a distinguishable entity. The ion can be accelerated and directed through various electric and magnetic selector fields, and finally detected by a particle counter as a discrete event.

A typical mass spectrometer operating at a source pressure of 10^{-4} Torr and an ionizing electron current of $100 \mu\text{A}$ at 75 eV will produce about 5×10^{11} ions/sec. Assuming that 20% of the ions could be focused onto the detector, one would have an ion current of 10^{11} ions/sec. Therefore, an easily measured signal of one ion count per second would represent an impurity or minor component present only in 1 part in 100 billion.

Actually, as we shall see later, the experimental situation is generally complicated by other considerations, so that this sensitivity is not achieved in practice. Nevertheless, the inherent sensitivity of the method is so high that one can afford to yield several orders of magnitude in sensitivity before running into serious trouble on many problems.

Ionization by Electron Impact

A simplified diagram of a mass spectrometer ion source is shown in Fig. 1. Electrons emitted from a heated filament, usually tungsten or rhenium, are accelerated by appropriate potentials on the electrodes and are constrained by an externally supplied axial magnetic field to move in essentially straight line paths (actually tightly wound spirals about the magnetic field lines). Ions produced by electron bombardment of molecules introduced into the ionization chamber are extracted by a small cross-field applied between the upper and lower plates of the ionization chamber. Since the ion beam intensity is proportional to the electron current, the electron collector current is used in a high-gain feedback circuit to control the filament temperature and thereby maintain

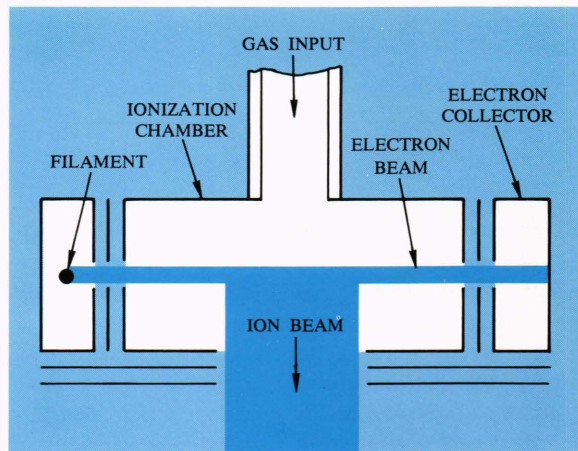


Fig. 1—Schematic diagram of a mass spectrometer ion source.

the electron current constant, typically to about 1 part in 10,000.

In the ionization process, the molecules can be considered stationary targets for the much faster electrons. For example, an electron even at the relatively low energy of 10 eV has a velocity of 1.8×10^8 cm/sec which is 1000 times that of a hydrogen molecule at room temperature and 4000 times that of an oxygen molecule. Accordingly, the number of ions produced by any component will be proportional to its number density in the ionization chamber and to its ionization cross section.

In general, the ion current can be written as

$$i = i_e n \sigma \ell F / (1.60 \times 10^{-19}) \text{ ions/second, (1)}$$

where i_e is the electron current in amperes, n is the number density (molecules/cm³) in the ionization chamber, σ is the ionization cross section (cm²), ℓ is the ionizing path length, F is the collection efficiency (fraction of the ions produced that are finally detected), and the numerical factor 1.60×10^{-19} is the electronic charge in coulombs.

The ionization cross section σ , which appears in deceptively simple guise in Eq. (1), actually is a function that depends strongly on electron energy and is different for different molecules. The typical behavior of the ionization cross section as a function of electron energy is illustrated in Fig. 2. Below the ionization potential, no ions are formed. Above the ionization potential, the cross section curve rises very rapidly, then goes through a more or less linear region, bends over and goes through a broad maximum, and slowly tails off at higher energies. For most of the molecules en-

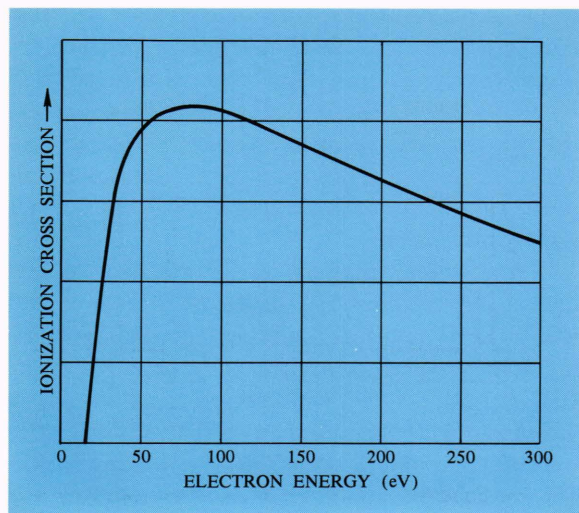


Fig. 2—Ionization cross section as a function of energy for a typical molecule.

countered in chemical analysis, the cross section maximum occurs in the neighborhood of 50 to 100 eV, and analytical instruments are usually standardized to operate in this energy range. Catalogs of mass spectra of thousands of compounds taken at 50 and 70 eV have been compiled and are useful in correlating instrumental performance at various laboratories. The ionization cross section maximum for typical small molecules often encountered in gas analysis ranges from about $2 \times 10^{-16} \text{ cm}^2$ to about $10 \times 10^{-16} \text{ cm}^2$. Incidentally, the estimated ion current of 10^{11} ions/sec for a gas sample at 10^{-4} Torr and an electron current of $100 \mu\text{A}$ at 75 eV mentioned in the previous section can be obtained by inserting the following values into Eq. (1): $i_e = 10^{-4}$, $n = 3.2 \times 10^{12}$ (molecules/cm³ at 10^{-4} Torr and 300°K), $\sigma = 2.5 \times 10^{-16} \text{ cm}^2$ (cross section for N₂ at 75 eV), $l = 1 \text{ cm}$, and $F = 0.2$.

The obvious advantages of operating near the cross section maximum are that the ion currents are high and the electron energy need not be known or controlled with great precision. Some auxiliary benefits are that the electron beam is more easily focused at these relatively high energies and space charge effects are less of a problem than at low electron energy.

Having expounded on the advantages of high electron energy operation for routine analysis, one might question why all mass spectrometry is not carried out in this energy range, and, in particular, why when we study transient species we almost

never use high energy electrons, but insist on the disadvantages of working at low electron energies where the cross section is low and is a critical function of energy.

The reason is simply that the mass spectrometer with its universal detection capability does not possess an intrinsic ability to distinguish between ordinary stable molecules and transient species, such as free radicals. The observation of an ion peak at the mass number corresponding to that of an expected transient molecule is only the first step in the analysis. Since, at the electron energies (50 to 75 eV) normally used for routine analysis, the transient ion could be produced by dissociative ionization of various stable molecules in the system, it is generally necessary to exclude this possibility by measurements with low energy electrons.

Ionization and Appearance Potentials

The threshold region of an ionization cross section curve, such as that of Fig. 2, is shown in detail in Fig. 3. The function $P(E)$ is proportional to the ionization cross section and has an onset energy E_0 , the ionization potential. Convolution of the Maxwell-Boltzmann electron energy distribution from the filament and the function $P(E)$ gives the observed ion current $I(V)$ as a function of the electron accelerating voltage V . The ion current curve $I(V)$, in contrast to the ionization probability curve $P(E)$, does not have a sharply defined

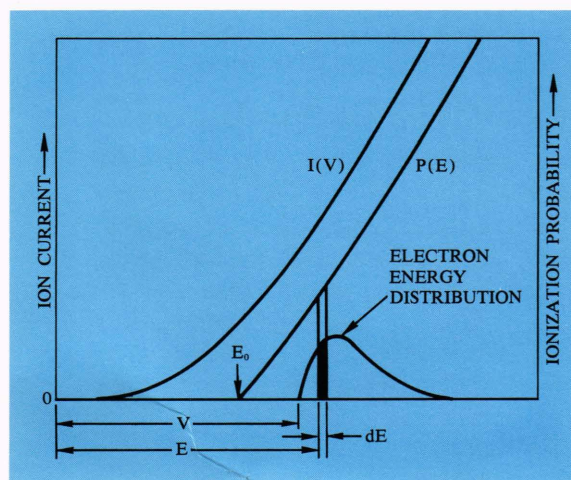


Fig. 3—Ion current as a function of electron accelerating voltage for an arbitrary ionization probability function $P(E)$ with onset energy E_0 . The ion current $I(V)$ at any voltage V is obtained by integrating the product of $P(E)$ and the electron energy distribution function from V to ∞ .

onset, but has instead a long exponential tail which complicates the measurement of ionization potentials.

Consider, now, that we have a gas with a transient species, such as a free radical, R, present in a mixture of stable molecules of chemical composition RR_1 , RR_2 , RR_3 , etc. or, in general RX where X is the molecular fragment left over after we have extracted the radical R. The minimum energy required to ionize the radical R is $I(R)$, the ionization potential of the radical. The minimum energy to produce the radical ion R^+ from the molecule RX is the appearance potential $A(R^+)$ given by

$$A(R^+) \geq I(R) + D(R-X), \quad (2)$$

where $D(R-X)$ is the R-X bond dissociation energy and the inequality includes the possibility that the fragment may possess excess kinetic and excitation energies.

The situation is shown schematically in Fig. 4. Here the curve labeled R^+ from R, the ion current curve for radical ionization, is displaced toward lower energy by an amount $D(R-X)$ from the ion current curve corresponding to dissociative ionization of the molecule RX. The curves have been drawn for roughly equal concentrations of radicals and molecules. Consider a series of measurements made at the voltages V_1 , V_2 , and V_3 . At V_1 , the discrimination of the radical to interference from dissociative ionization, which is given by the ratio

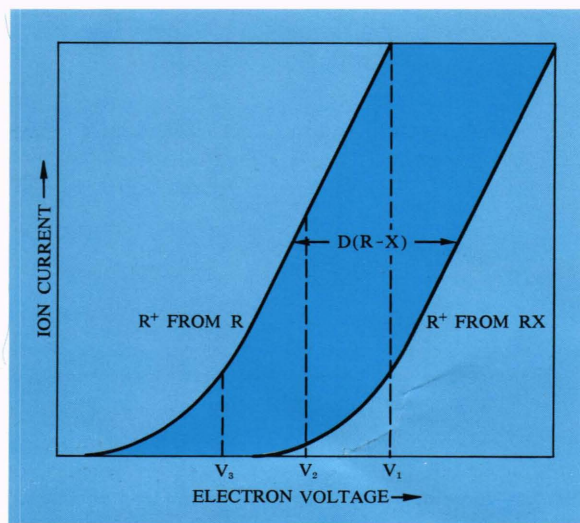


Fig. 4—Appearance potential curves for the R^+ ion from the free radical R and the R^+ ion from dissociative ionization of the molecule RX.

of the curve ordinates, is relatively small. The discrimination against dissociative ionization becomes progressively better as the voltage is reduced from V_1 to V_2 to V_3 . It can be shown that once the voltage has been reduced to the ionization potential of the radical, very little additional improvement in discrimination is obtained by further voltage reduction.

A theoretical analysis on detection of methyl radicals in the presence of methane shows⁴ that with a 2200°K filament and an electron accelerating voltage equal to the ionization potential of the CH_3 radical, 9.843 eV, the discrimination against CH_3^+ from CH_4 is about 10^9 , so that if dissociative ionization from CH_4 were the only limiting factor, one should be able to detect one methyl radical in a background of a billion CH_4 molecules. Although this level of detectability has not been achieved in practice, radicals have been detected in rather low concentrations in selected chemical systems by using low energy electrons. To the author's knowledge, the lowest reported concentration at which a radical could be observed was 1 part in 10^7 , attained in some of our studies of the N_2H_3 radical.

The detection of an electronically excited atom or molecule follows a parallel pattern to that used in detecting a free radical. In this case, the excited atom or molecule requires less energy for ionization than the unexcited atom or molecule. The difference in the ionization potentials, which in the case of an atom is equal to the excitation energy, but is not so simply expressed for molecules, plays the same role that bond dissociation energy plays in free radical detection.

An important benefit derived, almost automatically, from the low energy electron studies needed to identify radicals is the acquisition of information on the ionization potentials of the radicals and bond-dissociation energies of related molecules. A typical example is illustrated in Fig. 5, where the radical being studied is OH obtained by an electrical discharge in H_2O . The ion current curve for the unknown, the OH radical in this case, is compared with the ionization curve of a reference gas, argon, whose ionization potential is known spectroscopically. From the voltage scale shift required to match the curves, 2.59 eV, and

⁴ S. N. Foner, "Mass Spectrometry of Free Radicals," *Advances in Atomic and Molecular Physics*, Vol. 2, Edited by D. R. Bates and I. Estermann, Academic Press, Inc., New York, 1966, 385-461.

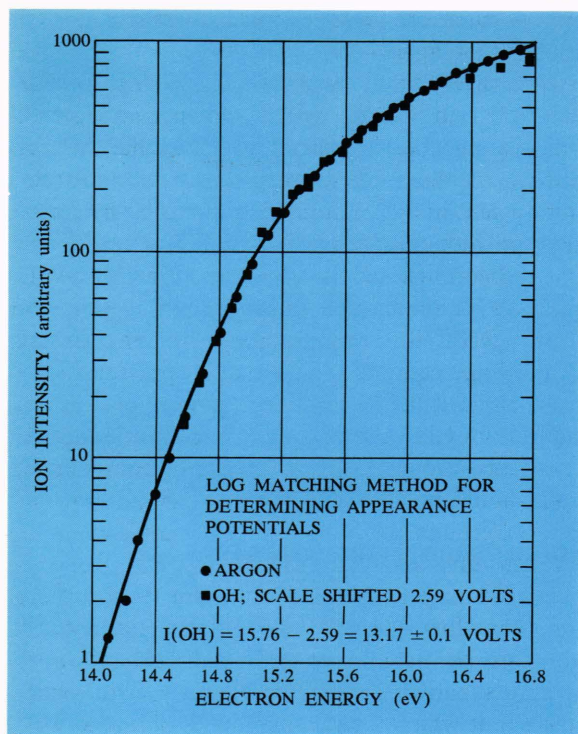


Fig. 5—Determination of the ionization potential of the OH free radical by comparison with argon ionization (reference standard).

the ionization potential of argon, $I(\text{Ar}) = 15.76$ eV, the ionization potential of OH was determined to be 13.17 ± 0.1 eV. The appearance potential $A(\text{OH}^+)$ of the OH^+ ion from H_2O was also measured and found to be 18.19 ± 0.1 eV. This leads directly to a value for the dissociation energy $D(\text{H-OH}) = 5.02 \pm 0.15$ eV = 116 ± 5 kcal/mole, and when combined with thermochemical data to a value of $D(\text{O-H}) = 102.9 \pm 5$ kcal/mole which is in good agreement with the spectroscopically determined value of $D(\text{O-H}) = 101.3 \pm 0.3$ kcal/mole.

An example of the observation of metastable molecules is shown in Fig. 6. In this experiment, nitrogen in a high-speed flow system was subjected to a microwave electrical discharge and studied within 2 milliseconds. The ionization curve, labeled N_2^* , is significantly different from the ionization curve for ordinary N_2 molecules, obtained when the discharge was turned off, and indicates the presence of a large proportion of metastable molecules in the discharged nitrogen. In order to explain the complex structure in the metastable N_2^* curve, it was necessary to assume that, in addition to many vibrationally excited ground state

molecules, a substantial fraction of the N_2 molecules were in various vibrational levels of the $A^3\Sigma_u^+$ electronic state (6.169 eV above the ground state). A comprehensive discussion of the complexities in the mass spectra of metastable nitrogen atoms and molecules has been published.⁵

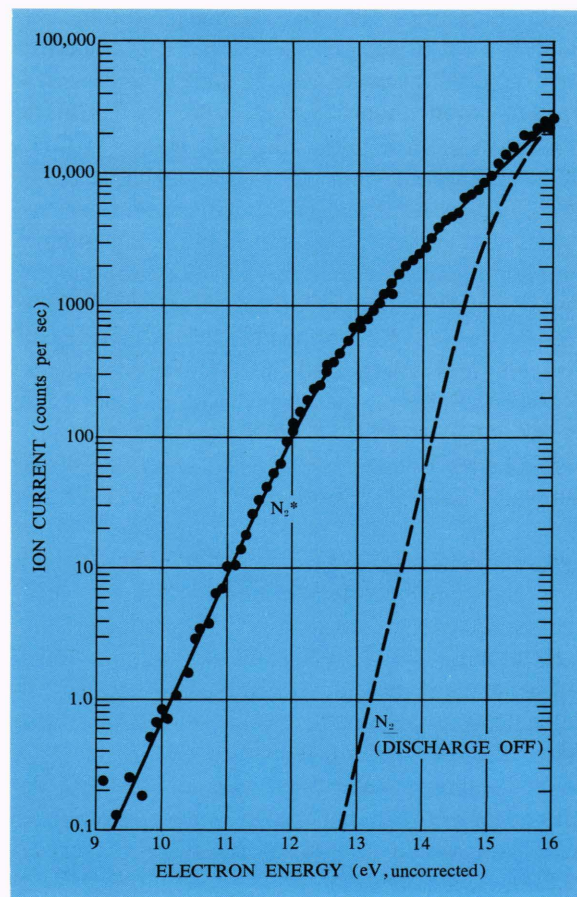


Fig. 6—Metastable nitrogen molecules from an electrical discharge in nitrogen at 0.45 Torr. The dashed curve is the ionization curve for unexcited N_2 molecules.

Mass Resolution Requirements

In searching for a small component, it happens all too frequently that there is an interfering peak nearby which has the same nominal mass number. Since the chemical elements do not have exactly integral masses except for ^{16}O , which is exactly 16 by definition, all compounds made up of different atomic combinations giving the same nominal

⁵ S. N. Foner and R. L. Hudson, "Mass Spectrometric Studies of Metastable Nitrogen Atoms and Molecules in Active Nitrogen," *J. Chem. Phys.* **37**, 1962, 1662-1667.

mass will, in fact, have different exact masses. With an instrument having sufficient resolving power, they would be completely separated. For example, in looking for the O atom at mass 16, one has to consider the possibility of interferences from NH_2 which has a mass of 16.02382 atomic mass units and CH_4 which has a mass of 16.03640 atomic mass units. To separate the largest spaced and most likely occurring doublet, CH_4 -O with $\Delta M = 0.03640$, would require a resolving power $M/\Delta M$ of 440. Other examples of possible interferences in the low mass range are mass 17: OH, NH_3 , $^{13}\text{CH}_4$; and mass 29: N_2H , CHO, CH_3N , C_2H_5 , ^{13}CO , $^{13}\text{C}^{12}\text{CH}_4$. As the mass number increases the variety of possible interfering atomic combinations proliferates rapidly. For example, at a nominal mass number of 210 there are 45 different possible combinations of carbon, hydrogen, nitrogen, and oxygen; and this tabulation excludes contributions from the heavy isotopes of these elements.

The heavy isotopes of H, C, N, and O have the following natural abundances: D = $1.49 \times 10^{-2}\%$, ^{13}C = 1.107%, ^{15}N = 0.366%, ^{17}O = $3.74 \times 10^{-2}\%$, and ^{18}O = 0.204%. The doublet mass differences corresponding to some of the isotopic species are quite small. In particular, the H_2 -D spacing is only 0.001549 atomic mass units which makes it difficult to distinguish between H_2 and D in a compound by mass measurement alone. For example, to separate OD from H_2O would require a resolving power of 13,000. To distinguish between H_2 and D in a compound of mass 100 would require a resolving power of 65,000.

The mass spectrometers that have been used for studies of free radicals and reactive molecules have been, almost without exception, low resolution instruments with resolving powers ranging from 100 to about 300. This is often inadequate for mass discrimination of possible interfering compounds. If the interfering molecule has a higher appearance potential than the searched-for component, the background interference can be wiped out by using low energy electrons. In many instances in free radical studies this is actually what happens and lack of resolution is not a problem. A contrary example that can be cited is the NH radical which has a relatively high ionization potential (13.1 eV) and may have to be detected in the presence of CH_3^+ ions which can be produced at lower energies from various compounds in the sys-

tem. To separate these two peaks would require a resolving power of 1200.

The reason that high resolution instruments have not found favor with workers studying free radicals and other transient species is that there is an enforced trade-off between sensitivity and resolution. A high resolution instrument has narrow slits and transmits a much smaller fraction of the ions than a low resolution instrument with its wide slits. With the marked improvement in detector sensitivity recently brought about by ion counting techniques, it would appear that a high sensitivity instrument with a resolving power of several thousand, which is adequate for discrimination against the vast majority of interfering compounds, could be built.

Some Interfering Effects

In mass spectrometry of transient species there are two effects which, though not particularly troublesome in ordinary analytical work, conspire to limit sensitivity. The two effects are ion-molecule reactions and space charge.

Ion-molecule reactions can take place in the ion source of the mass spectrometer to produce ions corresponding to the ion of the transient species, and may even produce ions whose neutral counterpart does not exist in nature. The reason these reactions can be troublesome is that they often have cross sections that are many times larger than gas kinetic cross sections. Since they are secondary reactions, they are pressure dependent and one can eliminate the effect by operating at sufficiently low pressures, which, of course, reduces sensitivity. In the molecular beam system to be described later, the pressure is about 10^{-7} Torr and the effect of ion-molecule reactions is negligible. However, at the pressures normally used for ordinary analytical work these reactions cannot be ignored in searching for free radicals at low concentrations. A recently developed analytical form of mass spectrometry called chemical ionization mass spectrometry actually utilizes ion-molecule reactions at high pressure to simplify the spectra obtained for stable molecules.

Space charge in the electron beam is an effect that influences the accuracy of ionization measurements that are usually carried out to identify transient species, such as free radicals. The effect is proportional to the electron current and to the inverse square root of the electron energy. This places a limit on the electron current that can be

used in appearance potential measurements. Calculations on a typical system show⁴ that for a 10 μA electron current, the space charge induced error in a measurement of the ionization potential of the methyl radical when using an argon standard would be about 0.03 eV, which is acceptable. However, at an electron current of 100 μA , the error would be 0.3 eV, which would be excessive. In our work, we have generally restricted the electron current to 5 μA or less.

Gas Sampling Systems

The only reliable method for introducing transient species into a mass spectrometer is by a collision-free molecular beam. This approach eliminates the loss of reactive components in sampling lines and allows the measurement of species that have short lifetimes, essentially being limited only by the molecular beam flight times. The system being sampled is generally at a pressure that is several orders of magnitude higher than the maximum allowable pressure in the mass spectrometer ion source. Thus in sampling from one atmosphere pressure a reduction of about 10^8 is required, while sampling from a system at 0.1 Torr only requires a pressure reduction of about 10^4 .

Very similar to the staging arrangement used for launching rockets into space, molecular beam sampling systems generally employ two or more stages of differential pumping to accomplish the desired pressure reduction in an efficient manner. In some of the early work on free radicals, only a single stage of differential pumping was used between the reaction region and the ion source. An analysis⁴ shows that it is extremely difficult to achieve a favorable ratio of molecular beam pressure to background pressure with such an arrangement.

The three-stage molecular beam sampling system that has been used successfully for many years at the Applied Physics Laboratory is shown schematically in Fig. 7. Gas enters through Slit 1 (which is usually a small circular aperture in a thin metal plate or quartz cone rather than the long narrow slit normally employed in molecular beam work, in order to minimize wall collisions) and is collimated into a molecular beam by Slits 2 and 3. A vibrating reed beam chopper is placed in front of the second slit to discriminate against background. By changing the size of the first aperture one can accommodate a wide range of

sample pressures. A practical difficulty encountered in high pressure sampling is the plugging of the necessarily small-sized orifice by dust particles, etc. The three sections of the system are separately evacuated by high-speed diffusion pumps and the operating pressures under full gas sampling load conditions are typically 10^{-3} Torr in the first region, 10^{-5} Torr in the second region, and 10^{-7} Torr in the ion source. In the absence of a molecular beam input the mass spectrometer pressure is about 3×10^{-9} Torr.

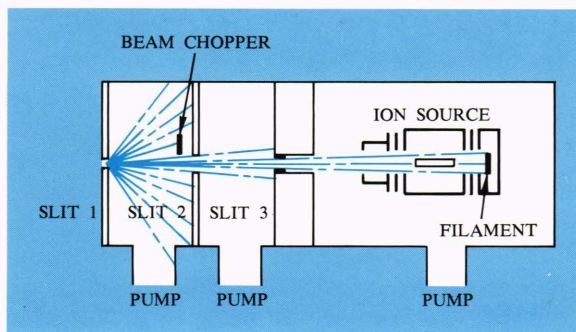


Fig. 7—Schematic diagram of three-stage molecular beam sampling system.

A feature of molecular beam sampling which is quickly recognized is that the available ion source pressures (or more precisely, molecular number densities) developed by a beam are rather small compared to the pressures usually used in analytical mass spectrometry (10^{-4} to 10^{-5} Torr). Another point worth noting is that most of the background pressure observed when the beam is on is developed by the molecular beam input. The background, thus, consists mainly of scattered and reacted beam molecules which under electron impact could often produce ion fragments at precisely the mass peaks corresponding to the transient species being sought.

Modulated Molecular Beams

The discrimination of a mass spectrometer against background interference is greatly enhanced by using modulated molecular beams. The technique of modulated molecular beam mass spectrometry was originally developed for studying atoms and free radicals in flames,⁶ and has

⁶ S. N. Foner and R. L. Hudson, "The Detection of Atoms and Free Radicals in Flames by Mass Spectrometric Techniques," *J. Chem. Phys.* **21**, 1953, 1374-1382.

since been applied to many systems, including ordinary stable molecules, where it is necessary to observe a small beam in the presence of a large background.

The general idea behind the method is to modulate the beam with a chopper at a rate which is much faster than the response time of the pumping system and to coherently detect the resulting ion signal modulation. If the modulation is sufficiently rapid, the background pressure cannot follow the beam modulation and, for all practical purposes, remains constant with time. The beam intensity in the ion source, on the other hand, follows the modulation produced by the chopper but with a small amount of rounding due to the dispersion in arrival times caused by the thermal velocity distribution of the molecules. The ion current, which is strictly proportional to the number density of the molecules in the ion source, will faithfully follow the beam intensity modulation. Beam molecules that collide with the walls or react with the filament lose phase coherence with the modulation and become part of the background.

In many systems involving modulated molecular beams the detection system consists of an electron multiplier detector and a phase detector synchronized with the chopper. For low level signals, ion counting techniques are preferable because of the higher sensitivity and accuracy that can be obtained. Furthermore, it is much easier to explain the operation of a modulated beam system using ion counters rather than a phase detector. A modulated ion intensity profile is shown in Fig. 8, accompanied by signal and reference gates used with an ion counting system. The problem is to detect the small signal due to the molecular beam riding on top of the background. The signal and reference gates, in this particular arrangement, control the direction in which a reversible counter totals the number of ions detected by the electron multiplier. When the signal gate is on, counts are added, and when the reference gate is on, counts are subtracted. The signal and reference gates are alternately switched on and off in synchronism with the beam modulation. It is clear that when the system is operating, after a complete cycle the reversible counter will have added the net count due to the signal, and after a large number of cycles it will have totaled up a respectable number of counts, even for a very weak signal. As indi-

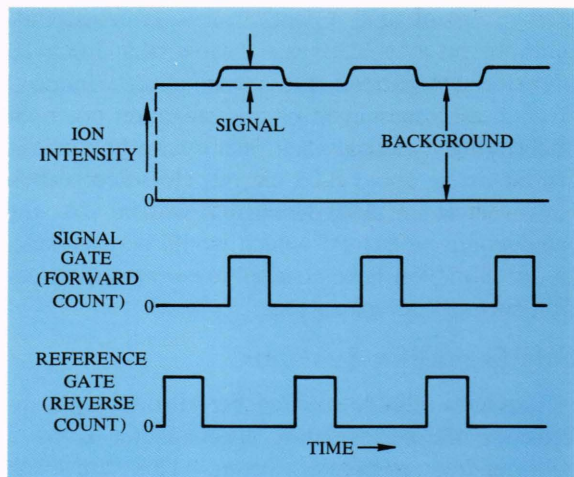


Fig. 8—Ion intensity profile for a modulated molecular beam and the gating arrangement used for detection.

cated in the figure, the signal and reference gate on times, which are identical in duration, are purposely made shorter than the half period of the beam modulation cycle to avoid effects due to jitter in the gating electronics.

There is a fundamental limitation on signal detection which results from inescapable fluctuations in the background ion intensity. Assuming that all system parameters are perfectly controlled and stable, the discrete and statistically independent production of the ions requires that when a total number of N ions is observed, the measurement will have a standard deviation equal to \sqrt{N} . When the background level is large, the statistical fluctuation of the background will also be large and the question is whether the signal exceeds this fluctuation or noise. The signal-to-noise ratio S/N for an optimized system can be written in the form

$$\frac{S}{N} = \left[\frac{i_e \ell T}{\sigma n (1.60 \times 10^{-19})} \right]^{1/2} \left(\frac{\sigma_B n_B}{2} \right), \quad (3)$$

where i_e is the electron ionizing current, ℓ is the ionizing path length, n_B and n are the respective number densities of beam molecules and background molecules, σ_B and σ are the respective ionization cross sections of beam molecules and background molecules, and T is the integrated observation time in seconds. Using the typical values: $i_e = 10 \mu\text{A}$, $\ell = 1 \text{ cm}$, $\sigma_B = \sigma = 3 \times 10^{-16} \text{ cm}^2$, $n = 3 \times 10^9 \text{ molecules/cm}^3$, corresponding to an interfering background pressure of 10^{-7} Torr , and $T = 100 \text{ sec}$, one finds a signal-to-

noise ratio of unity for $n_B = 8 \times 10^4$ molecules/cm³, corresponding to a pressure of 2.5×10^{-12} Torr. Thus, under these conditions one could detect the presence of 1 beam molecule in 40,000 interfering background molecules. To improve the detectability by a factor of 10 would require integration for 10,000 sec, which would be inconvenient.

In searching for a transient species, such as a free radical or excited molecule, the use of low energy electrons in terms of the parameters in Eq. (3) amounts to a signal-to-noise enhancement by a differential reduction in the ionization cross sections. While σ_B might be reduced by a factor of 10^2 , under favorable conditions σ could be reduced by say a factor of 10^{10} , leading to a signal-to-noise ratio of 4×10^7 in the numerical example just discussed. To match the detectability attained by low energy electrons, in this case, would require integration over the practically impossible time interval of 100 days.

A simplified schematic diagram of the APL modulated molecular beam mass spectrometer is shown in Fig. 9. The molecular beam is modulated at 170 Hz by a vibrating reed mechanical chopper whose position is monitored by a capacitive probe. To compensate for the transit time of the molecules into the ion source (about 200 μ sec) a corresponding time delay is introduced into the gating circuits by the phase shifter. The ions produced in the ion source are extracted by a small cross field, accelerated, passed through a 90° magnetic sector analyzer, post accelerated by a few keV, and detected by a 13 stage beryllium-copper electron multiplier. Pulses from the electron multiplier are amplified and shaped into uniform rectangular pulses suitable for counting purposes. The gating circuits which control the reversible counter are used as indicated in Fig. 8 to detect the modulated molecular beam. The background signal level, which is needed for statistical error analysis, is readily obtained by inhibiting the reversing feature

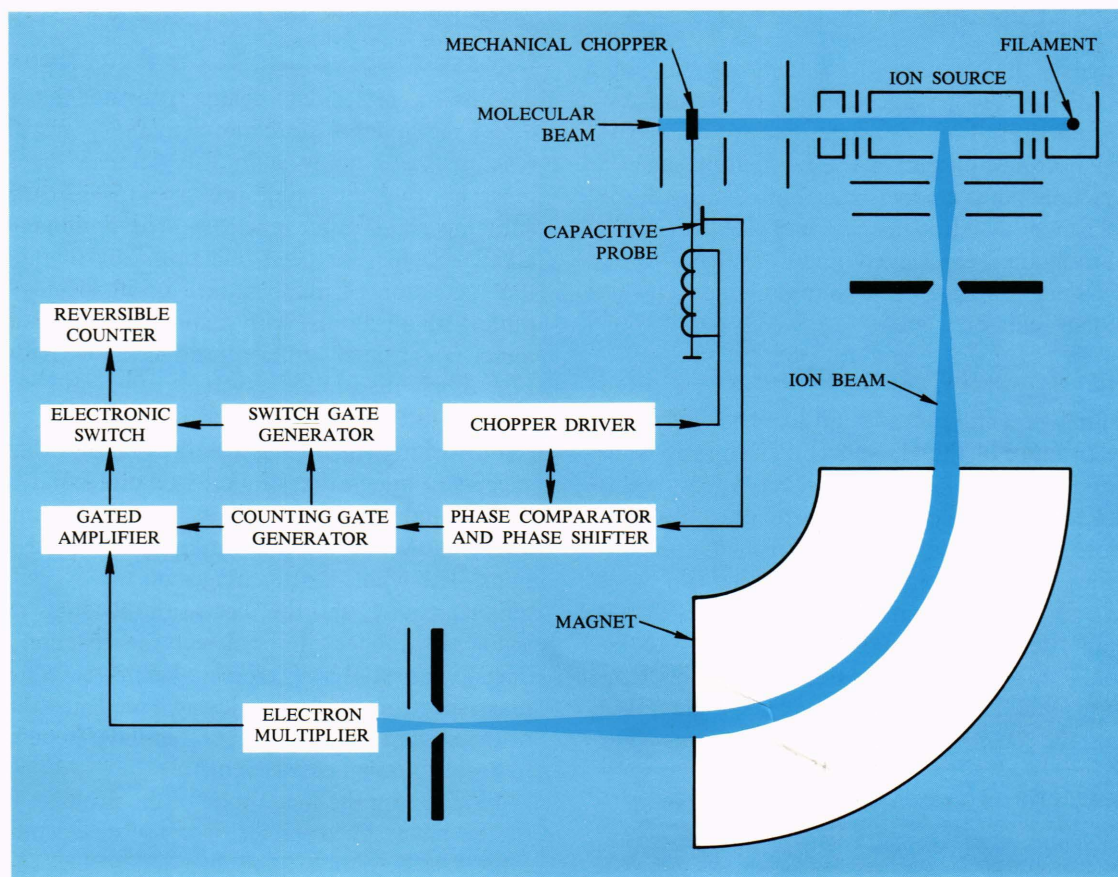


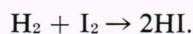
Fig. 9—Simplified schematic diagram of the APL modulated molecular beam mass spectrometer.

of the counter and counting both signal and background for a known short time interval.

Elementary Gas Reactions

One of the current areas of investigation by high sensitivity mass spectrometry that shows great promise is the study of elementary gas phase reactions. Most of the available information on chemical reaction mechanisms has been indirectly derived from kinetic data on overall reaction rates. It has been established that chemical reactions usually proceed by a series of elementary reaction steps involving atoms and free radicals as intermediates. Direct observational evidence for the actual presence of the atoms and free radicals assumed to be present in the reacting systems, unfortunately, is rarely available. In complex reactions, this often leads to some difficulty in choosing between different reaction schemes that fit the data. Even in some simple reactions, without direct observation of the reaction intermediates, there is always the nagging feeling that something important may have been overlooked in the analysis.

Probably the best recent example of the difficulties that may be encountered in relying too heavily on overall reaction rate data for establishing reaction mechanisms is the fascinating saga of the reaction between hydrogen and iodine. Since the early work of Bodenstein⁷ in 1899, this reaction was studied extensively and considered to be the classical example of a simple elementary bimolecular reaction



The rate of reaction was found to be proportional to the product of the H_2 and I_2 concentrations, as expected for a bimolecular reaction, and this tended to exclude consideration of other possible reaction mechanisms. Some experimental inconsistencies with the bimolecular mechanism were noted over the years, but it was not until 1967 that Sullivan⁸ demonstrated conclusively that the bimolecular reaction does *not* occur in the low temperature reaction of hydrogen and iodine, but instead the reaction involves iodine atoms. The

⁷ M. Bodenstein, "Gas Reaktionen in der Chemischen Kinetik. II. Einfluss der Temperatur auf Bildung und Zersetzung von Jodwasserstoff," *Z. Physik. Chem.* **29**, 1899, 295-314; L. S. Kassel, *Kinetics of Homogeneous Gas Reactions*, Chemical Catalog Co., New York, 1932, 144-156.

⁸ J. H. Sullivan, "Mechanism of the 'Bimolecular' Hydrogen-Iodine Reaction," *J. Chem. Phys.* **46**, 1967, 73-78.

reaction mechanism deduced for thermal systems below 600°K was $\text{I}_2 \rightleftharpoons 2\text{I}$, followed by a reaction in which two iodine atoms simultaneously react with a hydrogen molecule, $2\text{I} + \text{H}_2 \rightarrow 2\text{HI}$, or possibly by the reaction sequence $\text{H}_2 + \text{I} + \text{M} \rightarrow \text{H}_2\text{I} + \text{M}$ followed by $\text{H}_2\text{I} + \text{I} \rightarrow 2\text{HI}$. The unusual four center reaction $2\text{I} + \text{H}_2 \rightarrow 2\text{HI}$ has been the subject of several theoretical discussions.

It was found that the reaction mechanism involving iodine atoms gave excellent agreement with the experimental data originally and subsequently used to substantiate the bimolecular reaction mechanism. Thus, after more than half a century of study it was finally concluded that the hydrogen plus iodine reaction was not bimolecular.

A key objective in mass spectrometric studies of elementary reactions is to obtain direct information on the products of reactions and, thus, unequivocally establish the validity of proposed reaction mechanisms. Even in cases where the evidence for a particular reaction mechanism appears overwhelming, it is satisfying to have confirmation by an independent method.

Crossed Molecular Beam Reactions

Crossed molecular beams provide the most direct method for studying elementary gas phase reactions. For many years this field has been almost a private hunting preserve for researchers studying alkali atom reactions. The dominance of alkali systems has been due primarily to the fact that detection of alkali atoms, or molecules containing alkali atoms, with a surface ionization detector is extremely efficient and easily carried out. For other than alkali systems, the problem of beam detection has been a critical factor.

For a long time it has been recognized that the successful integration of a crossed molecular beam system and a high sensitivity mass spectrometer might allow one to study ordinary chemical reactions. The whole matter hinges on the overall system sensitivity, and the discussion becomes rather academic if one cannot detect the reaction products. The study of crossed beam reactions by mass spectrometry⁹ provides an excellent example of the system trade-offs that often have to be made in order to do an experiment.

In assessing the magnitude of the problem faced by the mass spectrometer, it is useful to compare

⁹ S. N. Foner and R. L. Hudson, "Mass Spectrometric Studies of Atom-Molecule Reactions Using High-Intensity Crossed Molecular Beams," *J. Chem. Phys.* **53**, 1970, 4377-4386.

the basic sensitivities of the electron bombardment ionizer used in the mass spectrometer with the surface ionization detector used primarily for alkali atoms. Assume that a beam of molecules of intensity I_p (molecules/cm²sec) is incident on each of these detectors. The ion current i'_p in ions/sec from a surface ionization detector of cross section area A (assuming 100% ionization) is given by

$$i'_p = I_p A \text{ ions/second.} \quad (4)$$

For an electron impact ionizer, the corresponding ion current i_p is given by

$$i_p = I_p i_e \sigma \ell F / (1.60 \times 10^{-19} v) \text{ ions/second,} \quad (5)$$

which can be obtained directly from Eq. (1) by noting that the number density $n = I_p/v$, where v is the average velocity of the molecules. The ratio of the mass spectrometer and surface ionization detector currents is, therefore,

$$i_p/i'_p = i_e \sigma \ell F / (1.60 \times 10^{-19} v A). \quad (6)$$

There are two important cases to consider: (1) stable molecule detection, for which high electron energy could be used and the ionization cross section could be close to σ_m , the maximum cross section, and (2) free radicals, for which appearance potential measurements at low energy would be used and the ionization cross section would be about two orders of magnitude lower than the maximum cross section. Using the typical values $i_e = 10 \mu\text{A}$, $\ell = 1 \text{ cm}$, $v = 5 \times 10^4 \text{ cm/sec}$, $F = 25\%$, $A = 10^{-2} \text{ cm}^2$, and $\sigma_m = 3 \times 10^{-16} \text{ cm}^2$, we obtain for

Case (1): stable molecules,

$$i_p/i'_p = 10^{-5}. \quad (7)$$

Case (2): free radicals,

$$i_p/i'_p = 10^{-7}. \quad (8)$$

The very low relative sensitivity (factor of 10^7) which is available for free radical experiments as compared to analogous experiments with alkali atoms makes it clear that many experiments easily carried out for alkali beams, such as measurements of differential reactive scattering cross sections, will not be feasible for free radicals formed in ordinary chemical reactions.

To mimic the molecular beam systems used for alkali reactions would court disaster for free radical experiments. What is required is a calculated sacrifice of some sort in order to improve overall system sensitivity. It turns out that the

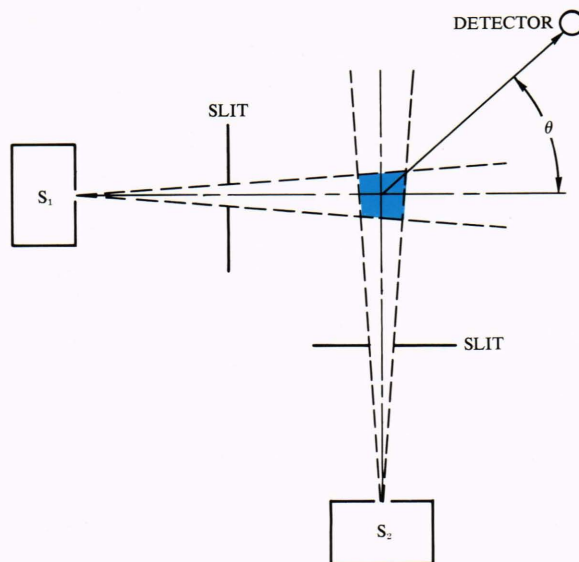


Fig. 10—Geometry of a conventional crossed molecular beam experiment.

parameter that affords the greatest potential gain is the angular resolution of the molecular beams.

Crossed Beam Geometry—The geometry of a typical conventional crossed beam experiment is shown schematically in Fig. 10. Molecular beams from the sources S₁ and S₂ are collimated by slits and intersect in the shaded region. The surface ionization detector is rotatable with respect to the beams and measures reactive scattering as a function of the angle θ .

The high-intensity crossed beam configuration shown in Fig. 11 is obtained by moving the sources very close together and making no attempt at beam collimation. With the large angular divergences of the crossing beams, it is not possible to

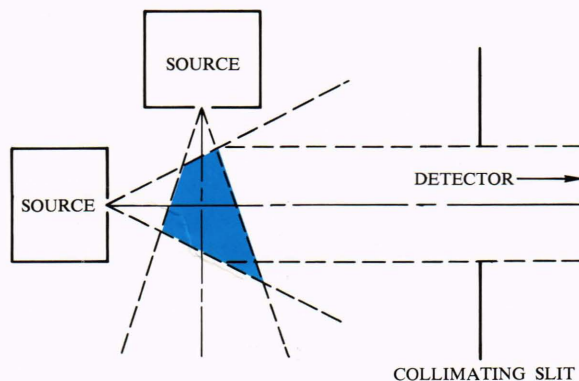


Fig. 11—High intensity crossed molecular beam configuration.

obtain angular information on reactive scattering. The detector observes reaction products from a large range of scattering angles. For a system with the sources placed 1 mm apart, the reaction product beam intensity for the high-intensity arrangement shown in Fig. 11 is about 10,000 times higher than typically obtained with the conventional crossed beam geometry of Fig. 10.

Comparison of System Sensitivities—In assessing overall system capabilities, there are factors other than intrinsic detector sensitivity and crossed beam geometry that need to be considered. The main additional factors are atom concentration, reaction cross section, and the ion counting system sensitivity.

While there is no problem in obtaining approximately 100% atoms in alkali beams, high concentrations of atoms, such as H, N, and O, that are used in ordinary chemical reactions are more difficult to achieve and a concentration of 10% has been assumed as typical for a non-alkali source.

The reaction cross section for a typical alkali atom reaction such as $K + Br_2 \rightarrow KBr + Br$ is about $150 \times 10^{-16} \text{ cm}^2$, which is an order of magnitude greater than the hard sphere collision cross section. This is at least an order of magnitude larger than the cross sections for what are usually considered very fast reactions. For purposes of sensitivity estimation it has been assumed that alkali reactions would have cross sections an order of magnitude larger than cross sections for non-alkali reactions.

The modulated molecular beam ion counting system is capable of routinely measuring down to 0.1 ion/sec (and on occasion has carried out measurements as low as 0.01 ion/sec). This turns out to be significantly better than the sensitivities achieved with surface ionization detectors. Under favorable conditions, surface ionization detectors have measured currents down to the order of 10^3 ions/sec with an electrometer amplifier, and to about 10^2 ions/sec with a quadrupole mass analyzer followed by an electron multiplier detector. The system used with the mass spectrometer is, therefore, about 10^3 to 10^4 times better.

The system sensitivity factors have been listed in Table 1. Combining all the factors gives an estimated sensitivity for the crossed beam free radical system which is one to two orders of magnitude lower than for an alkali crossed beam system.

TABLE 1. COMPARISON OF SENSITIVITY FACTORS FOR FREE RADICAL DETECTION VERSUS ALKALI DETECTION IN CROSSED BEAM REACTIONS

Parameter	Factor
Detector sensitivity	10^{-7}
Crossed beam geometry	10^4
Atom concentration	10^{-1}
Reaction cross section	10^{-1}
Ion counting system	10^3 to 10^4
Over-all factor	10^{-2} to 10^{-1}

Experimental Arrangement—The configuration of the crossed beam reactor and mass spectrometer is shown in Fig. 12. Atoms or radicals generated by a 2450 MHz microwave discharge enter on the molecular beam axis of the mass spectrometer through a small aperture in a thin stainless steel plate. A crossed beam of stable molecules effuses from the end of a stainless steel hypodermic needle tube. Reaction products that hap-

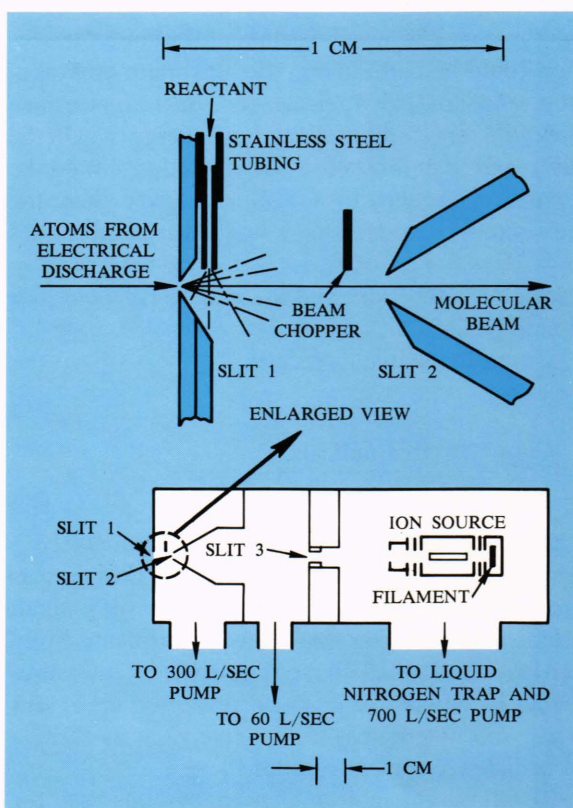


Fig. 12—Schematic diagram of the molecular beam sampling system and mass spectrometer, and an expanded view of the crossed beam reactor, beam chopper, and slit system.

pen to be moving in the proper direction constitute the molecular beam, which is modulated and detected by the mass spectrometer.

Crossed Beam Experiments—A variety of elementary atom-molecule reactions have been studied with high-intensity crossed molecular beams. Free radicals and unstable molecules have been observed in reactions of H, O, and Cl atoms with a number of compounds.⁹ Ionization potentials of the free radicals and unstable molecules have been measured and used to determine bond dissociation energies and heats of formation.

An interesting example of a reaction studied by crossed beams is the reaction of hydrogen atoms with nitrogen dioxide. The reaction



is very fast and is often used as a titration reaction to determine H atom concentrations. What makes the reaction of exceptional interest is that all four reaction participants can be readily observed by the spectrometer. Direct confirmatory observation of the reaction mechanism obviously would be a useful contribution, particularly when one recalls the traumatic experience of the "bimolecular" hydrogen-iodine reaction.

In the experiment, a constant supply of H atoms from a microwave discharge interacted with a

variable intensity of NO₂ in the cross beam. The ion currents for the OH and NO radicals are plotted as a function of NO₂ input in Fig. 13. The first thing to note is that OH and NO are, indeed, the products of the reaction. Next, the yields of the reaction products, within experimental error, show a linear dependence on NO₂ input, as expected for a bimolecular reaction. The reaction mechanism is, therefore, confirmed to be $\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$.

Summary

Mass spectrometry of transient species has been discussed from a fundamental viewpoint. The low concentrations and ease of destruction of transient species place stringent requirements on the gas sampling system and on the analytical technique. It was shown that considerable enhancement in the detection and identification of transients, such as free radicals and electronically excited molecules, can be obtained by employing low energy electron bombardment, a modulated molecular beam sampling system, and ion counting.

A high sensitivity mass spectrometer incorporating these features has been described. A variety of experiments involving measurements of free radicals at low concentrations have been carried out with this instrument.

One of the current areas of investigation by high sensitivity mass spectrometry is the study of elementary gas phase reactions. Crossed molecular beams provide the most direct means for studying these reactions. Beam detection in these systems is a critical factor and, until recently, experiments had been restricted to studies of alkali systems. By making a number of calculated system trade-offs, it has been possible to successfully integrate a crossed molecular beam system with a mass spectrometer to study ordinary chemical reactions. Free radicals have been observed in a variety of elementary reactions involving H, O, and Cl atoms and a number of chemical reaction mechanisms have been confirmed. In addition, some interesting reactions have been investigated in which unexpected reaction products were observed.

The potential applications of high sensitivity mass spectrometry of transient species cover a broad spectrum. One of the areas is the detection of small concentrations of atmospheric pollutants that may escape detection by other techniques.

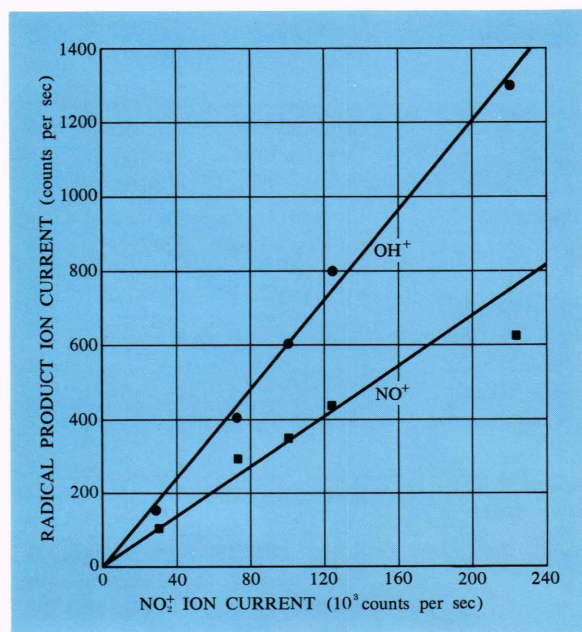


Fig. 13—Reaction of hydrogen atoms with nitrogen dioxide. The OH and NO radicals produced are shown as a function of NO₂ crossed beam input.