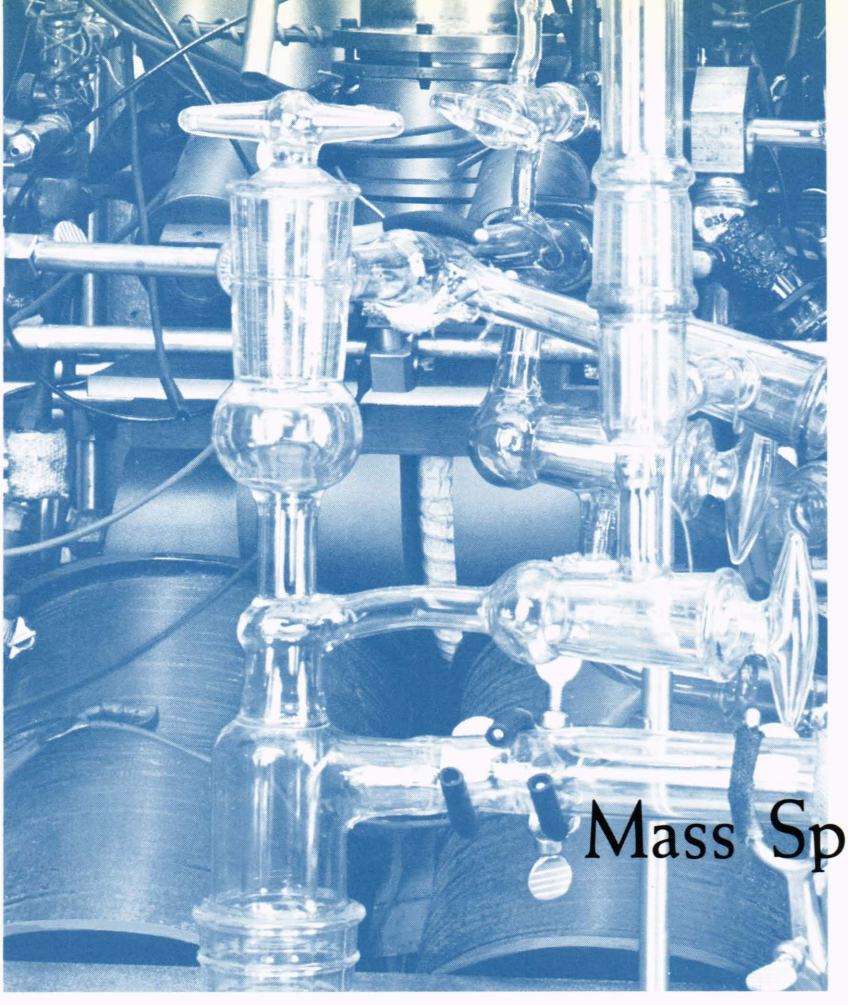

Mass Spectrometry

The study of free radicals by mass spectrometry has been an active area of research at the Applied Physics Laboratory for almost two decades. Scientific interest in these normally short-lived, highly reactive chemical species stems from the fact that most chemical reactions proceed by chain mechanisms involving free radicals as intermediates. Although ordinarily present in quite small concentrations because of their high reactivity, free radicals are responsible for making chemical reactions go, and an understanding of the chemical processes requires identifications of the individual free radicals present in the system and information on the elementary reactions that are occurring.

Of the various analytical techniques that have been used to study gas-phase reactions, mass spectrometry has been developed into a high-sensitivity method having the widest range of application for the detection of free radicals as well as stable constituents. Recently, the scope of mass spectrometric investigations has been successfully extended to include electronically excited atoms, molecules, and free radicals.

In this article we shall discuss general principles and techniques involved in the mass spectrometry of free radicals and metastable molecules, and will present some of the experimental results that have been obtained at APL using these techniques.

General Considerations

A free radical may be defined as a molecular fragment formed by the rupture of a covalent bond in a stable molecule. It is characterized by having one or more unpaired electrons; it is this unsaturated valence condition that is responsible for the chemical reactivity of free radicals. For example, if a molecule of water is dissociated according to the reaction

$$H_2O \rightarrow H + OH,$$

two free radicals are produced, a hydrogen atom and a hydroxyl radical, each possessing an unpaired electron. Historically, atoms have been given special prominence and have often been placed in a separate category. However, in harmony with the general definition of a free radical given above,

S. N. Foner and R. L. Hudson

Short-lived, highly reactive chemical species are being studied by a special mass spectrometer that uses a collision-free molecular beam-sampling system. The information obtained has led to critical insights on the nature of elementary chemical reactions. Recently, the scope of investigation has been extended to include electronically and vibrationally excited components. This article describes the principles and techniques involved in the research, and presents experimental results obtained in studies of exceptional interest.

# of FREE RADICALS and METASTABLE MOLECULES

we shall consider the term free radical to include both atomic and molecular varieties.

The lifetime of a free radical is essentially limited by reaction and, therefore, if isolated in a high-vacuum a free radical would survive indefinitely. On the other hand, an electronically excited component will decay by radiation in a time characteristic of the particular state involved and there is no way to prevent it. Since the transit time of molecules into the ion source of a mass spectrometer is of the order of 10^{-4} sec in a well-designed instrument, only electronic states with highly forbidden radiative decay transitions (i.e., metastable states) can be observed.

It probably comes as no surprise to the reader that a conventional mass spectrometer, designed for analysis of stable chemical compounds, is hardly suited for the study of highly reactive free radicals and metastable molecules. In a conventional instrument, the losses of free radicals in the sampling system are so high that it is almost certain that no interesting radicals would survive to be detected.

In principle, there are two major problems that have to be solved in the mass spectrometry of free radicals: (1) the gas sample must be extracted from the reaction zone and transported into the mass spectrometer without significant loss of reactive intermediates, and (2) a definitive test must be available for distinguishing the free radicals from the stable molecules in the system. It is clear that failure to achieve the first objective, getting the radicals into the instrument, would render all other operations useless. Consequently, considerable effort has gone into designing appropriate gas-

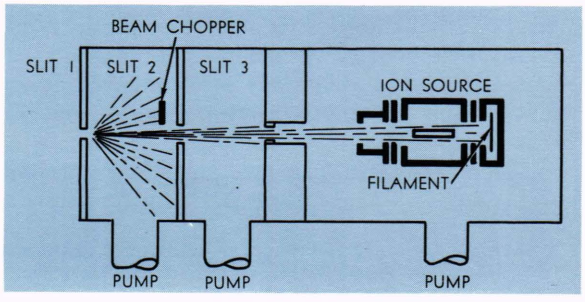

Fig. 1—Schematic diagram of the molecular beam gas-sampling system.

sampling systems. The characterization of a component as a free radical rather than an ionization fragment from a stable molecule is usually a straightforward, although often a time-consuming procedure.

Modulated Molecular Beam Mass Spectrometry

A special mass spectrometer has been designed[1,2] which employs a line-of-sight collision-free molecular beam sampling system shown schematically in Fig. 1. Gas from the reaction zone enters through a small circular aperture (typically 0.01 to 0.03 cm in diameter), designated as Slit 1, in a thin metal plate or a quartz cone ground to a feather edge. Within about 1 microsecond the expansion of the gas has so greatly reduced the density that gas phase reactions have effectively been terminated, and from this time on the molecules are in free flight. Slits 2 and 3 collimate the molecular beam and prevent scattered molecules in the first region from entering the ion source. The three sections of the molecular beam system are separately evacuated by high-speed diffusion pumps, so that typical operating pressures are 10^{-3} Torr (1 Torr = 1 mm-Hg) in the first region, 10^{-5} Torr in the second region, and 10^{-7} Torr in the ion source. The molecular beam system serves the dual function of eliminating losses of free radicals in the sampling system and satisfactorily reducing the gas pressure from the relatively high value in the reactor, which is typically several orders of magnitude higher than allowable in the mass spectrometer ion source, to a convenient operating level.

To discriminate against background interference, the molecular beam is mechanically modulated at about 200 cycles/sec by a vibrating reed beam chopper in the first section of the gas-sampling system. The background consists principally of scattered and reacted input beam molecules which under electron impact may produce ion fragments at the mass numbers corresponding to free radicals. Molecules entering in the beam will bounce around in the ion source region like ping pong balls until they are either pumped out or are removed by reaction. The modulation scheme employed allows one to distinguish clearly between the incoming beam molecules and all other molecules.

In free radical studies, it is particularly important to have a high-sensitivity detection capability. Instead of using a conventional electrometer amplifier for measuring the ion current, which has a noise limit of about 10^{-16} amp, we use an electron multiplier detector and scaling circuits to record the arrival of individual ions (1 ion/sec = 1.6×10^{-19} amp). The sensitivity gained by using an electron multiplier detector instead of a vacuum tube amplifier is about a factor of 1000.

A simplified schematic diagram of the modulated molecular beam mass spectrometer is shown in Fig. 2. Ions produced by electron impact in the ion source are first accelerated to a fixed energy,

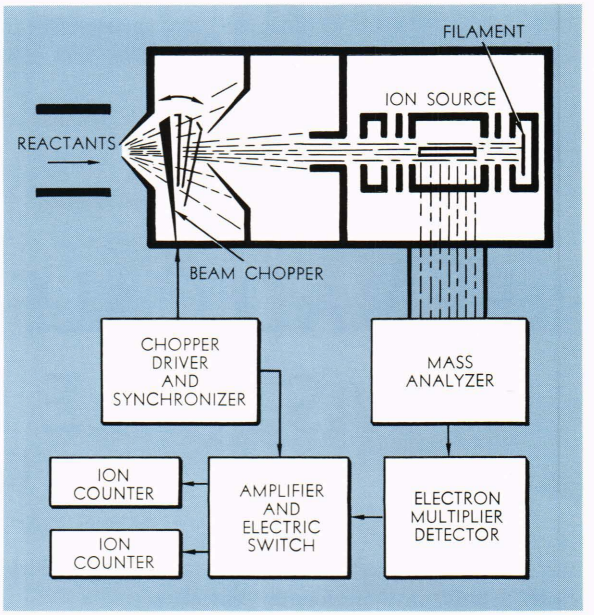

Fig. 2—Simplified schematic diagram of the modulated molecular beam mass spectrometer.

and are then sent through a magnetic sector mass analyzer. On leaving the mass analyzer, the ions are accelerated by a few keV before they strike a 13-stage beryllium-copper electron multiplier detector which has a current gain of about 10^6. An amplifier converts each of the pulses from the electron multiplier into a properly shaped pulse for activating the ion counters. An electronic switch is synchronized with the beam chopper and directs the pulses to one of the ion counters registering counts, N_1, when the beam chopper is open and to the other ion counter registering counts, N_2, when the beam chopper is closed. The difference in the two ion count numbers, $N_1 - N_2$, is the signal due to the molecular beam, while the square root of the sum, $(N_1 + N_2)^{1/2}$ is approximately equal to the standard deviation of the measurement. The effect of the background is essentially to introduce noise

[1] 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.

[2] S. N. Foner and R. L. Hudson, "Mass Spectrometry of the HO_2 Free Radical," *J. Chem. Phys.* **36**, 1962, 2681-2688.

which varies as the square root of the background intensity.

Ion currents as low as 0.01 ion/sec have been measured under favorable conditions with this instrument. Measurements down to the 0.1 ion/sec level are frequently carried out. For orientation purposes it might be noted that at electron energies of 50 to 70 eV used for ordinary chemical analysis an ion current of 0.01 ion/sec corresponds to a partial pressure of about 10^{-16} Torr in the ion source. A pressure of 10^{-16} Torr corresponds to a density of 3 molecules/cm^3 which is comparable to the particle density in interplanetary space, which has been estimated to be about 10 particles/cm^3.

Appearance Potential Measurements

One of the problems that requires careful consideration is how to tell free radicals from stable molecules. In contrast to a free radical selective method, such as electron spin resonance, where only species with unpaired electrons would be observed, mass spectrometry does not possess an inherent means for distinguishing free radicals from stable molecules. One has to do a little detective work. This is the price that has to be paid for having a method which has a universal detection capability for all components in the system. The observation of an ion peak at the charge-to-mass ratio corresponding to that of a radical whose presence is suspected is merely the first step in the detection procedure. Since there is a possibility that the observed ion may have been produced by dissociative ionization of various stable molecules, it is essential to eliminate any ambiguity as to the source of the ion. This is done by measuring *appearance potentials*, which are simply the minimum energies at which particular ions are formed.

Consider the general situation where the radical R is present along with a possible interfering molecule RX. The radical ion R^+ can be produced by the ionization processes:

$$R + e \rightarrow R^+ + 2e \qquad (1)$$

$$RX + e \rightarrow R^+ + X + 2e. \qquad (2)$$

The minimum energy for process (1) is $I(R)$, the ionization potential of the radical R. The appearance potential $A(R^+)$ of the R^+ ion in process (2) is given by

$$A(R^+) \geq I(R) + D(R-X), \qquad (3)$$

where $D(R - X)$ is the R−X bond-dissociation energy, and the inequality in the equation includes the possibility that the fragments may possess excess kinetic and excitation energies. Since bond-dissociation energies are typically of the order of a few electron volts, it is possible, in principle, by using electrons with energies below the appearance potential $A(R^+)$ to detect the presence of very small concentrations of the radical R in the presence of large concentrations of RX molecules. In many cases, it can be shown that excess energy is absent in process (2), in which case Eq. (3) becomes an equality for the determination of the bond-dissociation energy $D(R - X)$ from the measurements of $A(R^+)$ and $I(R)$.

There is a complicating factor in the measurements which arises from the fact that the electron source is a heated filament which emits electrons with a Maxwell-Boltzmann distribution of energies characteristic of the filament temperature. As a consequence, appearance potential curves do not exhibit sharp discontinuities at the nominal energies for onset of ionization, but instead are rounded in the vicinity of the appearance potential and exhibit an exponential tail for energies below the appearance potential. A number of methods having various levels of theoretical sophistication have been developed for analyzing appearance potential curves and assessing the limits of error in measurement. The details are somewhat outside

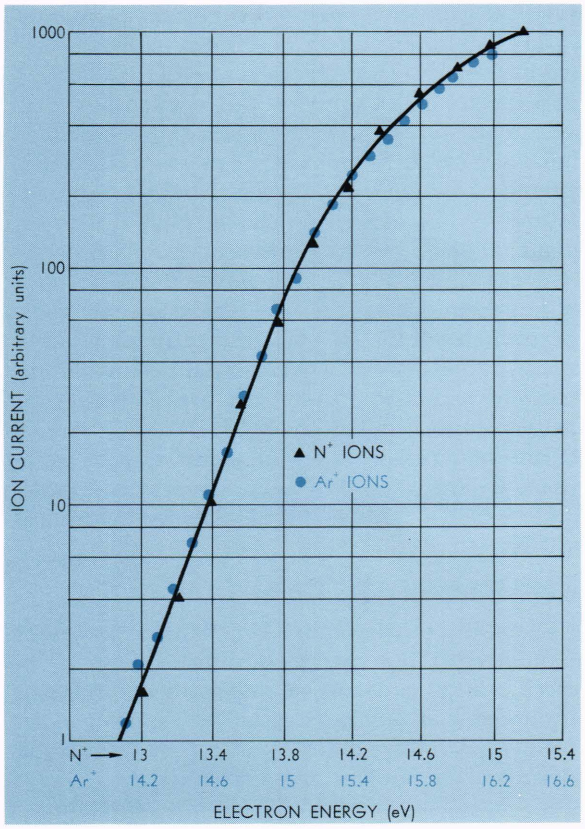

Fig. 3—Nitrogen atom ionization curve with a standardizing argon ionization curve. The ionization potential of the N atom is obtained from the scale shift required to match the curves.

the scope of this article. Suffice it to say that the absolute electron energy scale is established by using a standard gas whose ionization potential is known spectroscopically, usually Ar, Kr or Xe, and the appearance potential of the unknown may be obtained by determining the voltage shift required to bring the two curves into coincidence.

A particularly good example is the case of N atoms obtained from a microwave discharge in nitrogen. The appearance potential curve for N atoms,[3] along with a standardizing curve for argon, is shown in Fig. 3. From the scale shift of 1.20 eV required to match the curves and the spectroscopically known value $I(\mathrm{Ar}) = 15.76$ eV, we obtain the value $I(\mathrm{N}) = 14.56$ eV which is in excellent agreement with the spectroscopic value of 14.54 *eV* for the ionization potential of the nitrogen atom. An example of the determination of the ionization potential of a free radical for which thus far no spectroscopic value is available is the case of the HO_2 free radical produced by an electrical discharge in hydrogen peroxide[2] shown in Fig. 4. The voltage displacement of 4.23 eV required to match the HO_2 and argon ionization curves establishes the ionization potential of HO_2 as $I(HO_2) = 11.53$ eV. The first direct experimental proof of the existence of HO_2 was obtained at APL in 1953 in a mass spectrometric study[4] of the reaction of hydrogen atoms with oxygen molecules and represented one of the early triumphs of the mass spectrometric technique for detecting radicals. In this early experiment, the concentration of HO_2 was only about 0.001%, but was sufficient to establish the existence of HO_2 as a real physical entity. In a more recent, comprehensive study on the mass spectrometry of the HO_2 free radical,[2] much larger concentrations of HO_2 were obtained in various reactions and used to establish precise values for the ionization potential of HO_2 and several thermochemical energies, the most important of which was the value of the bond-dissociation energy $D(\mathrm{H} - \mathrm{O_2}) = 45.9 \pm 2$ kcal/mole for the radical at 0°K.

Free Radicals in Flames

The study of free radicals in flame reactions is an interesting but extremely difficult area of research. Because of the multiplicity of problems encountered in this work, progress has been slow. However, definitive radical studies have been made on some of the simpler flame systems.

The hydrogen-oxygen flame was examined using a movable burner assembly to position the flame at various distances from the molecular beam entrance slit of the mass spectrometer. H atoms, O atoms, and OH radicals were observed in sufficient abundances to permit mapping of intensity profiles as a function of distance of the burner from the sampling pinhole. In Fig. 5 are shown the ion intensity profiles of the stable components and free radical intermediates for a flame at about 0.1 atmosphere pressure. The free radical measurements were made at sufficiently low electron energies to eliminate contributions caused by dissociative ionization of the stable components. In comparing the curves for stable components and free radicals to obtain concentrations, the adjusted ion intensities in the lower half of Fig. 5 should be multiplied by about a factor of 10 because of the low electron energies used in the radical measurements. The maximum radical concentrations were thus estimated to be of the order of 1%. The composition profiles were highly reproducible, but were complicated by the effects of diffusion, turbulent

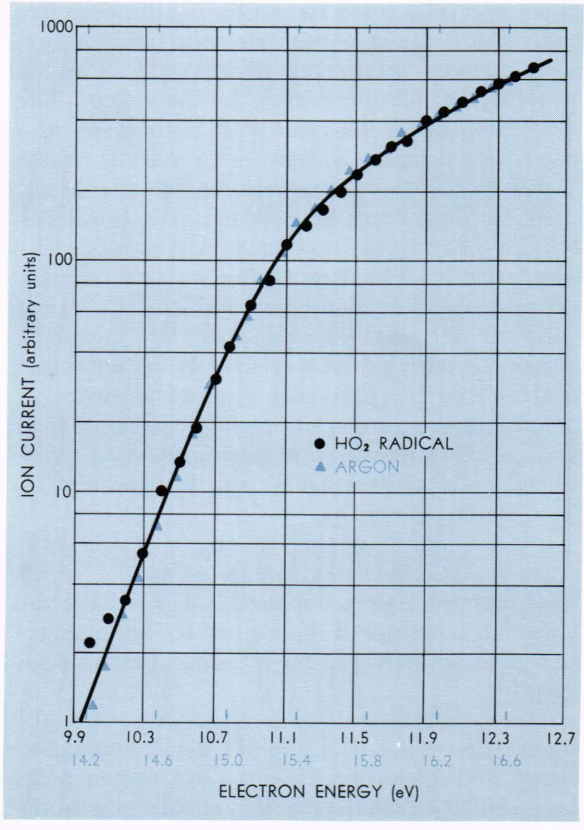

Fig. 4—Determination of the ionization potential of the HO_2 free radical. Voltage scales for HO_2 and the argon standard are indicated on the upper and lower scales, respectively.

[3] 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.

[4] S. N. Foner and R. L. Hudson, "Detection of the HO_2 Radical by Mass Spectrometry," *J. Chem. Phys.* **21**, 1953, 1608-1609.

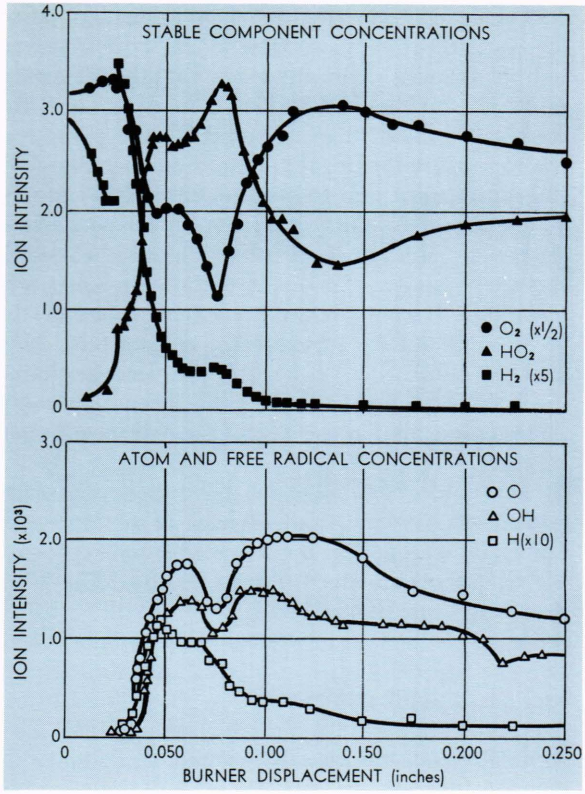

Fig. 5—Ion intensities of stable components and free radicals in a low pressure hydrogen-oxygen flame. The abscissa is the relative displacement of the burner from the molecular beam entrance slit.

gas mixing, and changes in the flame configuration as the burner assembly was displaced.

The methane-oxygen flame was also examined in a similar set of experiments. The mass spectra obtained were considerably more complicated than had been anticipated. In fact, it was not even possible to identify all the stable components present. Apparently, what was happening was that a large number of stable compounds of higher mass were being generated in the flame, so that instead of studying just the methane-oxygen reaction we were faced with the general problem of combustion of an assortment of hydrocarbons, a task which we were not prepared to undertake. Stable products readily identified in the reaction were hydrogen, water, acetylene, carbon monoxide, carbon dioxide and diacetylene. Tentative or alternate identifications were made for C_2H_4, CH_3OH, C_2H_6 or HCHO, C_3H_4, C_3H_6 and C_3H_8. The only free radical that was positively identified was CH_3. One of the complications that had to be considered was the possibility that some of the molecules could be in excited states and produce mass spectral patterns that were different from those obtained from unexcited molecules. Under these conditions it was believed that identification of radicals other than methyl would be speculative.

Unstable Hydronitrogen Compounds

Occasionally, the search for a free radical leads to surprising but not unwelcome results. In attempting to generate the imine (NH) free radical by electrical decomposition of hydrazoic acid (HN_3), we accidentally discovered diimide (N_2H_2), the previously unobserved parent molecule of the azo-compounds.[5] To assure ourselves that this was indeed the molecule that had been produced, we also synthesized and studied the deuterated versions of the molecule, N_2HD and N_2D_2. The failure to observe NH can be explained by the rapidity of the highly exothermic reaction

$$NH + HN_3 \rightarrow N_2H_2 + N_2$$

which converts NH radicals into N_2H_2 molecules.

Since hydrazoic acid is an explosive compound, the much safer-to-handle compound hydrazine was investigated as a source of diimide. It was found that diimide could be readily produced by both thermal and electrical decomposition of hydrazine. In addition, decomposition of hydrazine produced the compounds triazene (N_3H_3) and tetrazene (N_4H_4), neither of which had been previously observed, and the free radicals NH_2 and N_2H_3. For a short time, we were in the business of filling in a number of blank spaces in the chemist's table of chemical compounds. From the ionization potentials of the radicals and compounds measured in this study, the following bond-dissociation energies were determined:[5,6] $D(NH_2-H) = 104 \pm 2$ kcal/mole, $D(H_2N-NH_2) = 58 \pm 9$ kcal/mole, $D(H-N_2H_3) = 76 \pm 5$ kcal/mole and $D(HN = NH) = 104 \pm 6$ kcal/mole.

The original target of the investigation, the study of the NH free radical, was not forgotten, and, as will be discussed later, this elusive free radical has finally been detected by mass spectrometry.

Metastable Nitrogen Atoms and Molecules

Microwave (2450 Mc/s) electrical discharges in nitrogen and nitrogen-helium gas mixtures have been used to generate metastable nitrogen atoms and molecules. The gases flowed at high speed through a quartz tube passing through a microwave waveguide. Sampling time was varied by

[5] S. N. Foner and R. L. Hudson, "Diimide-Identification and Study by Mass Spectrometry," *J. Chem. Phys.* **28**, 1958, 719-720.

[6] S. N. Foner and R. L. Hudson, "Mass Spectrometric Detection of Triazene and Tetrazene and Studies of the Free Radicals NH_2 and N_2H_3," *J. Chem. Phys.* **29**, 1958, 442-443.

positioning the waveguide at appropriate distances from the mass spectrometer entrance slit.

In atomic nitrogen there are two long-lived metastable states, $N(^2D)$ and $N(^2P)$, located 2.38 eV and 3.58 eV, respectively, above the $N(^4S)$ ground state. Transitions between these levels are strictly forbidden for dipole radiation, but are allowed to occur with low probability by electric-quadrupole and magnetic-dipole radiation. Calculations give radiative lifetimes of 12 seconds for the $N(^2P)$ state and 9.4×10^4 seconds for the $N(^2D)$ state.

Atomic nitrogen produced by a microwave discharge in N_2 and observed 2 milliseconds after leaving the discharge showed only $N(^4S)$ ground state atoms, with no evidence for metastable N atoms (see Fig. 3). If, however, the gas was studied within 1 millisecond after leaving the discharge, some metastable atoms were observed, indicating that the metastable N atoms were readily deactivated by wall collisions.

The highest concentrations of metastable N atoms were obtained from electrical discharges in helium-nitrogen mixtures with helium in large excess. Figure 6 shows a nitrogen ionization curve for N_2 at 0.016 Torr and He at 2.2 Torr observed within 1 millisecond after leaving the electrical discharge.[3] The ionization potentials for the metastable atoms are indicated by the arrows at the top of the illustration. The dashed curve gives the ion current due to ground state $N(^4S)$ atoms. The synthetic N^+ curve, which fits the experimental data quite well, was calculated using the known spectroscopic energies of the metastable states and assuming that the relative concentrations of the $N(^2D)$ and $N(^2P)$ atoms were, respectively, 17% and 6% of the $N(^4S)$ concentration. In a discharge in pure N_2 the yield of metastable atoms was about 25 times less than in the case of the helium-nitrogen mixture.

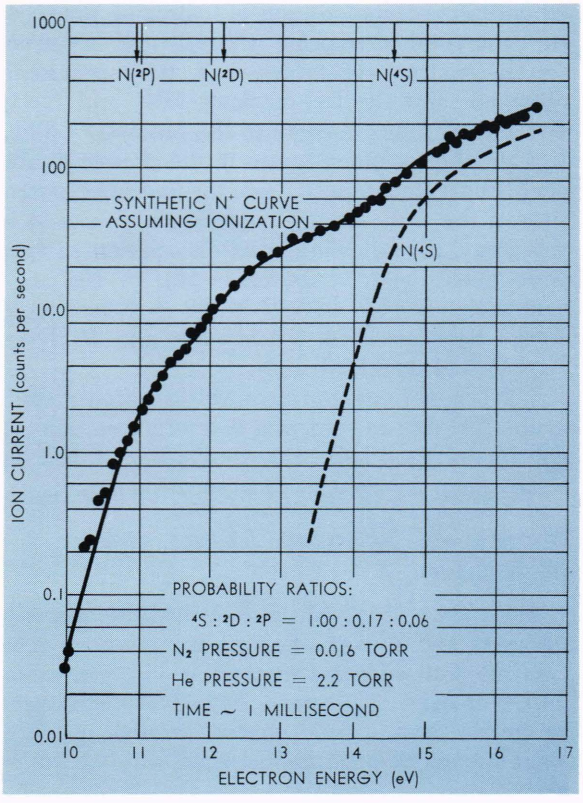

Fig. 6—$N(^4S)$, $N(^2D)$, *and* N (^2P) atoms from an electrical discharge in a helium-nitrogen mixture. The synthetic N^+ curve was theoretically calculated assuming ionization onsets at the spectroscopically known ionization potentials of the atoms.

Metastable N_2 molecules have been observed both in the presence and absence of metastable N atoms, indicating that the metastable molecules are less readily deactivated by wall collisions. The situation in the case of metastable N_2 molecules is much more involved than in the case of N atoms. What one has to deal with is a mixture of vibrationally excited ground-state molecules, electronically excited molecules, and molecules that are both electronically and vibrationally excited. The ionization curves obtained are complex and do not exhibit resolved structure. It has been established that a substantial fraction of the N_2 molecules are in the $A^3\Sigma_u^-$ electronic state, which is 6.169 eV above the ground state, and that a number of vibrationally excited levels of this state are populated. In recent studies, excitation energies to about 9 eV have been observed, indicating that two higher energy electronic states may be populated by the discharge.

Pulsed Electrical Discharges

A very recent development is the use of short-duration pulsed electrical discharges in high-speed gas streams to generate chemical intermediates which are very difficult to obtain by other means.[7] The high peak power available in the discharge is conducive for the generation of various non-equilibrium products.

The volume of gas subjected to the discharge was limited by the configuration of the electrodes to about 0.01 cc in the experiments to be reported. To reduce losses of unstable species, the gas-sampling time was reduced by having the discharge take place within a few mm of the molecular beam entrance slit.

Extremely short-duration electrical discharges

[7] S. N. Foner and R. L. Hudson, "Mass Spectrometry of Free Radicals and Vibronically Excited Molecules Produced by Pulsed Electrical Discharges," *J. Chem. Phys.*, 1966 (in press).

have been very useful in diagnostic studies of the gas-sampling system. An example of one of the shortest pulses used is shown in Fig. 7. The pulse has a half-width of 0.035 μsec, a full-width of about 0.07 μsec, and a peak current value of 15 amperes. The breakdown voltage in this experiment, a N_2-He mixture at 5 Torr, was approximately 3 kV, so that the peak power was of the order of 45 kW. The gas heating rates attained with these short pulses are surprisingly high. If all the available energy

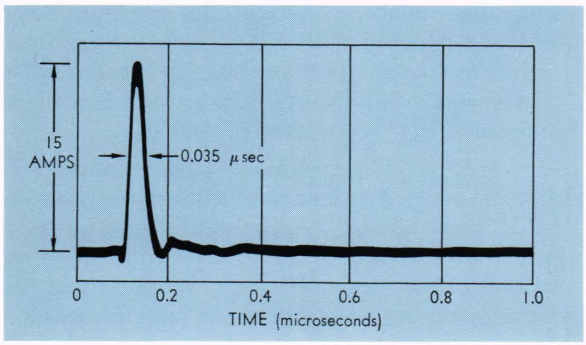

Fig. 7—Oscillogram trace of a short-duration electrical discharge pulse.

went into heating the gas, the average heating rate would be 30 billion deg/sec and the gas would have a temperature of about 2000°C at the end of the 0.07 μsec pulse. Since some energy goes into dissociation, excitation, and ionization of the molecules, and a substantial amount is diverted into heating the electrodes, the actual heating rate is lower than the calculated maximum value. In the particular example illustrated in Fig. 7, the heating rate was found to be about 10 billion deg/sec (one-third of the theoretical maximum rate), which is still an impressive figure.

Ordinarily, one is interested in obtaining the highest possible production of radicals and excited molecules. For this purpose, longer pulses (typically some tens of μsec in duration) at lower current have been found to be more effective than the extremely short-duration pulses, principally because the integrated energy per pulse is much higher.

When using pulsed electrical discharges, a different mode of molecular beam modulation is used than is employed in the case of sampling a steady gaseous source of radicals. Modulation is produced by the periodic pulsing of the electrical discharge rather than by mechanical chopping of the beam. Also, an order of magnitude higher modulation frequency is used, typically 2kc/s in the experiments to be described. Special circuits have been developed for triggering the pulsed discharge and accurately synchronizing the ion counting circuits for recording the molecular beam signal and the background. The ion counters integrate the signals over many pulses. For strong signals, integration is carried out for 10 seconds, or 20,000 pulses. Weak signals require longer integration times in order to reduce statistical fluctuations. With pulsed discharges, ion currents as low as 0.2 ion/sec have been measured without difficulty, corresponding to the generation of a single ion count in 10,000 electrical discharge pulses.

Ultra-short Pulse Generation of N Atoms

An extremely short-duration discharge pulse is an effective device for instantaneous generation of radicals. We have used pulse-generated nitrogen atoms to study the dynamics of the molecular beam sampling system and to measure the effective temperature of the heated atoms.

Suppose at time $t = 0$, we suddenly generated at the entrance slit of the molecular beam system a burst of molecules having the usual Maxwellian velocity distribution, that is, the number of molecules in the velocity interval v to $v + dv$ is proportional to $v^2 \exp(-v^2/\alpha^2)dv$, where $\alpha = \sqrt{2kT/m}$ is the most probable velocity, k is the Boltzmann constant, m is the mass of the molecule, and T is the gas temperature. The molecules will spread out as they travel toward the ion source, the higher velocity molecules arriving at the ion source ahead of the slower ones. The molecular beam density $N(t)$ in the ion source (which is proportional to the ion current that is measured by the mass spectrometer) as a function of time t can be written as

$$N(t)\,dt = \frac{2\Delta I_0 s^3}{\alpha^4 t^4}\left[\exp\left(-\frac{s^2}{\alpha^2 t^2}\right)\right]dt, \qquad (4)$$

where I_0 is the molecular beam intensity for a steady source, Δ is the time duration of the pulse, and s is the distance from the entrance slit to the ion source, which in the case of our instrument is 10 cm. The equation can be transformed into a simpler form by measuring time in units of s/α, the travel time of a molecule having the most probable velocity, by using the variable $\mathbf{T} = \frac{\alpha}{s}t$ and normalizing the beam density to the total number of molecules N_0 in the pulse. The reduced equation for the beam density becomes

$$N(\mathbf{T})\,d\mathbf{T} = \frac{4N_0}{\sqrt{\pi}}\frac{1}{\mathbf{T}^4}\left[\exp\left(-\frac{1}{\mathbf{T}^2}\right)\right]d\mathbf{T}. \qquad (5)$$

The ion intensity for nitrogen atoms as a function of time from a very short (0.035 μsec half-width) pulse discharge in a mixture of nitrogen and helium is shown in Fig. 8. The experimental points were fitted with theoretical curves in accord-

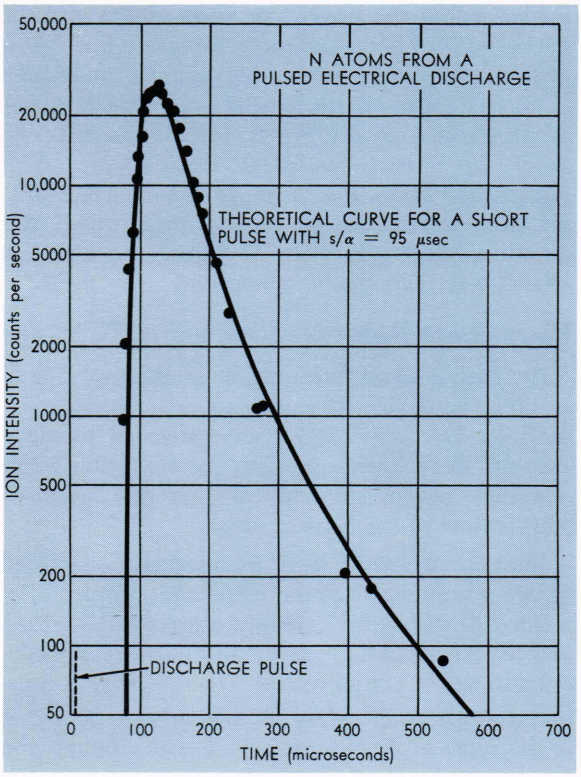

Fig. 8—Nitrogen atoms from an extremely short-duration electrical discharge. The theoretical curve is drawn for s/α, the transit time for a molecule having the most probable velocity, equal to 95 μsec.

ance with Eq. (5), using two arbitrary parameters: the molecular beam transit time s/α, which is essentially a scaling factor for the time variable, and a shift in reference time corresponding to the effective time delay for molecules to enter the molecular beam. The theoretical curve which has been fitted to the data was calculated with s/α = 95 μsec and a sampling-time delay of 44 μsec. From the molecular beam transit time s/α = 95 μsec, one obtains an effective temperature of 930°K for the N atoms. The temperature rise of 630°C is about one-third of the calculated maximum rise of 2000°C discussed earlier. Although the theoretical curve in Fig. 8 fits the data satisfactorily, an even better fit can be obtained if one considers the fact that the discharge is not an instantaneous point source of atoms but has a finite spatial extent and it requires about 20 μsec for the gas to be swept out. A detailed analysis shows that the gas-sampling time is about 33 μsec, or about one-third of the molecular beam transit time.

NH Free Radical

The NH free radical has been an unusually difficult radical to study by mass spectrometry. As has been discussed in the section on Unstable Hydronitrogen Compounds, efforts to obtain this radical from thermal and electrical decompositions of hydrazoic acid and hydrazine, as well as ammonia, were unsuccessful, although associated radicals were readily observed and unstable compounds were discovered. This was a rather embarrassing situation for the mass spectrometric method of radical detection, because the NH radical was being observed in similar systems by optical spectroscopy. It turns out that there are a number of technical problems, such as interference from other ions that fall on top of the NH mass, which seriously degrade the sensitivity of the mass spectrometer for NH detection, and, therefore, larger concentrations are needed than for most other radicals.

It was found that a pulsed electrical discharge in ammonia would produce significant concentrations of NH free radicals.[7] As a bonus, perhaps as a reward for persisting in the labyrinthine chase for this radical, we found NH radicals not only in the ground state, but also in an excited electronic state. The appearance potential curve for the NH radical is shown in Fig. 9. The appearance potential curve is a superposition of two curves, corresponding to ionization of NH in the $X\,^3\Sigma^-$ ground state

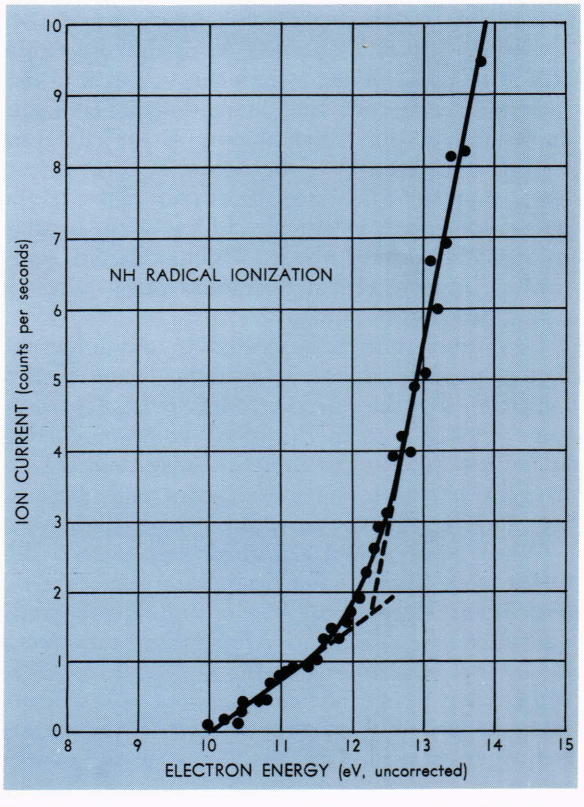

Fig. 9—Appearance potential curve for NH free radicals from a pulsed discharge in ammonia.

and NH in the $a\ ^1\Delta$ excited state. The excited state NH radicals, which have a lower ionization potential than the ground state NH radicals, are responsible for the lower part of the ionization curve. It was estimated that about 22% of the NH radicals were in the excited electronic state. Direct measurement of the ionization potential of NH in the ground state gave the value $I(NH) = 13.1$ eV. This value is in good agreement with previously indirectly derived estimates for the ionization potential of this radical.

Methylene Free Radical

For several years, an unusually large discrepancy has existed between the mass spectrometric value for the ionization potential of the methylene (CH_2) free radical and the value determined by optical spectroscopy. The mass spectrometric measurement with highest claimed precision, 11.82 eV, differed from the spectroscopic value,[8] 10.396 eV, by 28 times the estimated limits of experimental error. What added some confusion to the controversy was the failure of a recent attempt to remeasure the ionization potential by mass spectrometry because the investigators could not find any CH_2 radicals when they attempted to repeat the earlier experiments.

To resolve this situation, an effort was made to generate CH_2 radicals by short-duration pulsed electrical discharges. It was found that a discharge in a methane-helium mixture produced significant concentrations of CH_2 radicals, along with large amounts of CH_3 radicals and a small but measurable amount of CH radicals.[9] To check on possible systematic errors, the ionization potential of CH_3 was measured in this study and found to be in excellent agreement with the known spectroscopic value.

The ionization curve for the CH_2 radical is shown in Fig. 10. The argon ionization curve, used as an energy standard, has been scale shifted by 5.43 eV to match the CH_2 radical ionization curve. From the spectroscopically known value $I(Ar) = 15.76$ eV and the 5.43 eV scale shift, the ionization potential is determined to be $I(CH_2) = 10.33 \pm 0.1$ eV. The electron impact value measured in this experiment is in good agreement with the spectroscopic value, thereby removing the large disagreement that previously had existed between the mass spectrometric and optical spectroscopic measurements. It has not been possible to isolate the sources of difficulty in the earlier mass spectrometric studies.

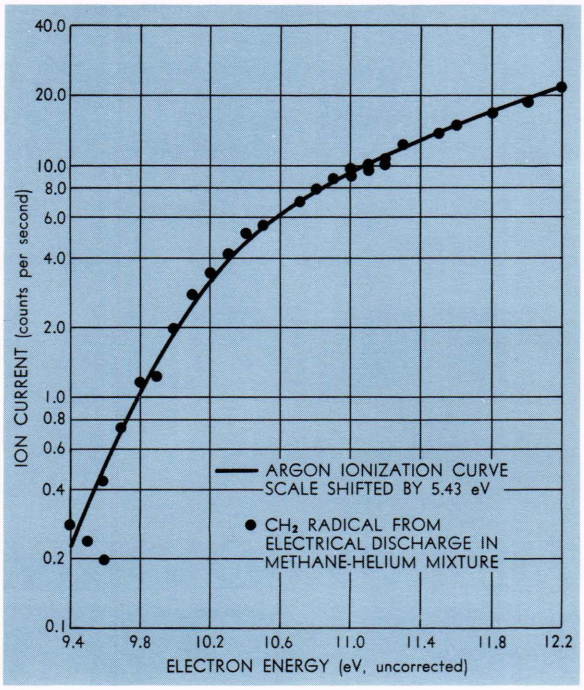

Fig. 10—Ionization curve for the CH_2 free radical from a pulsed electrical discharge. Argon ionization is used to standardize the electron energy scale.

Summary

Mass spectrometric studies have been carried out on a wide range of highly reactive transient chemical species. The unambiguous identifications of free radicals in gas phase reactions and determinations of their energies have served to crystallize and refine our concepts of the reaction mechanisms involved. In some instances, an unsuccessful search for an expected free radical has led to the unexpected discovery of new chemical compounds. The extension of the scope of mass spectrometric investigations of free radicals to include electronically and vibrationally excited components represents a significant technical advance. Short-duration pulsed electrical discharges in high-speed gas streams have been successfully employed to generate and study certain free radicals, such as NH and CH_2, which had been difficult to obtain by other techniques. A recent result has been the resolution of a controversy over the ionization potential of the methylene free radical. The study of highly reactive free radicals and metastable molecules remains a challenging area for scientific exploration.

[8] G. Herzberg, "The Ionization Potential of CH_2," *Can. J. Phys.* **39**, 1961, 1511-1513.

[9] S. N. Foner and R. L. Hudson, "The Ionization Potential of the CH_2 Free Radical by Mass Spectrometry," *J. Chem. Phys.*, 1966 (in press).