5. FREE RADICAL SOURCES

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In the early days of understanding molecular composition, it was known that stable molecules were built up from characteristic parts, which were called radicals. When the bond in a molecule is broken, the components can have a fleeting existence of their own; these fragments are called *free radicals*. For example, water can be broken into two free radicals: a hydroxyl radical, OH, and atomic hydrogen. Free radicals are atoms or molecules which have one or more unpaired electrons; consequently, they have a great propensity to react with other species and have a very short lifetime in most environments. They react with other free radicals or with stable species to form other stable molecules. Much of the interest in free radicals derives from the roles they play as intermediates in chemical reactions.

Free radicals are often created by dissociating stable molecules. In the simplest case, atomic radicals are created by dissociating diatomic gases such as O_2, N_2, H_2, F_2, HCl, or Cl_2; or, if a polyatomic molecule is used, then both atomic and molecular radicals are created, as in dissociating H_2O, NH_3, or CH_4 to produce OH and H, N and H and NH and NH_2, or H and H_2 and C and CH and CH_2 and CH_3, respectively. Dissociation can occur in electrical discharges, by photolysis, in ovens, by laser ablation, and in chemical reactions.

5.1 Electrical Discharges

Much of the progress in the spectroscopy of transient molecules over the last 20 years has depended on the use of electrical discharges (either AC or DC) to generate free radicals, ions, or metastables. Electrical discharges are particularly useful in forming ionic species.

EXPERIMENTAL METHODS IN THE PHYSICAL SCIENCES
Vol. 29B

5.1.1 The Microwave Discharge

A microwave discharge operating at 2450 MHz is one of the most commonly used sources for producing free radicals and ions. This frequency is set aside by international agreement for use in microwave ovens, medical diathermy units, and scientific apparatus. Water and many oils have absorptions at this frequency; hence, it is useful for heating many biological materials. The radiation, with a wavelength of 12.25 cm, permits the construction of conveniently sized microwave cavities for running electrodeless, and hence "clean," discharges.

A review and test of many discharge cavities was made in 1964 [1]. Cavity 5 in that review is still the one most commonly used and is shown in Figure 1. This cavity is a quarter-wavelength coaxial cavity tuned by varying the length of the center electrode (the resonant frequency is not dependent on the diameter of the cavity); it also has a variable coupling adjustment on the coaxial input line. The addition of one-half-wavelength-long metal tubes covering the discharge tube on

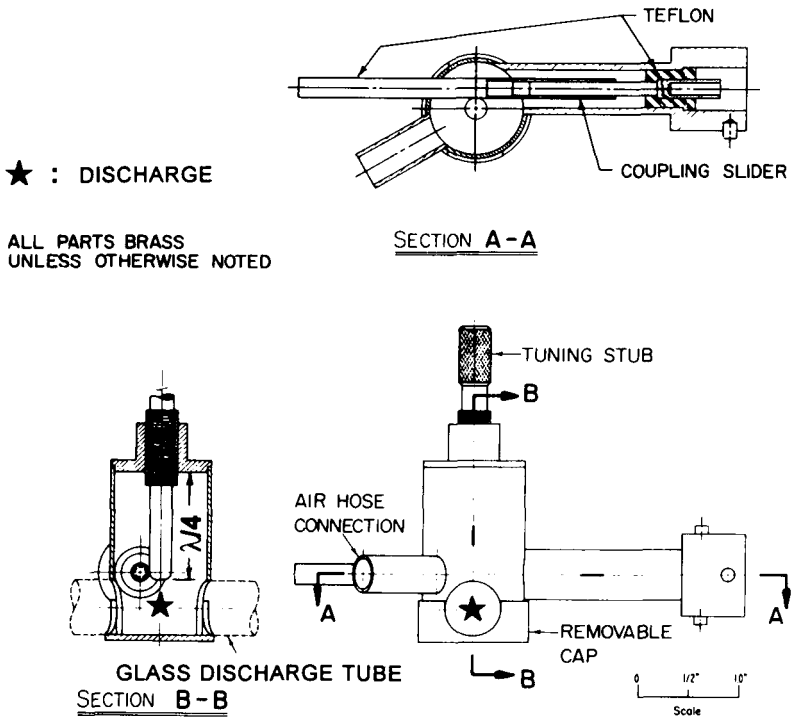

FIG. 1. Quarter-wavelength coaxial cavity operating at 2450 MHz. (Cavity 5 from reference [1].) The discharge location is shown with a star in the lower views.

each side of the cavity prevents radiation from leaking from the cavity [2]. This is very important, for this radiation can produce cataracts [3]. This shielding also dramatically reduces electromagnetic pickup in microwave detectors due to microwave leakage. A high-Q, TMO_{010} cylindrical cavity which operates at high pressures has also been developed [4], but its use is inconvenient because it cannot be removed from the vacuum system without dismantling the system; consequently, it is seldom used.

Cavity 5 was used to produce atomic oxygen from molecular oxygen for the direct measurement of the fine structure frequencies of the three isotopes of atomic oxygen using far infrared laser magnetic resonance [5]. Recently, we have operated a modified microwave discharge cavity with its discharge parallel to a magnetic field for the production of ions [6]. The combination of the discharge and magnetic field produced a considerable increase in the brightness of the discharge, along with a significant pinching and localization of the plasma. Work on this type of plasma is now in progress at the Boulder Laboratories of NIST.

5.1.2 The DC Discharge

A DC electric discharge provides a method for extending the discharge length and generating transient molecules continuously over several meters of path length. Consequently, it is easy to achieve long absorption paths and hence high sensitivity; most other methods of generation, including the RF discharge, produce the species in very confined volumes.

Gaseous electric discharges have been used for a variety of purposes for a very long time, and the principles of their operation are available in many treatises such as reference [7]. The last decade has seen some attempt at characterizing them from the point of view of the formation of both charged and neutral molecules. This has led to the invention of two new discharge configurations: the hollow cathode discharge [8] and the magnetically extended positive column discharge [9].

5.1.2.1 The Conventional DC Discharge. A conventional DC discharge is shown in Figure 2. The concentration of positive ions is greatest in the negative glow region, which is relatively short under normal conditions. Its length is equal to the distance traveled by the high-energy electrons which have been accelerated cross the cathode drop region and is proportional to the electron energy. It is typically a few centimeters long at a pressure of 135 Pa (1 torr). The ions are formed in this region by electron (e) bombardment of neutrals (M):

$$e + \mathrm{M} \rightarrow \mathrm{M}^{+} + 2e.$$

The characteristics of a glow discharge are determined principally by cathode phenomena. In a normal discharge, the voltage across the cathode drop remains

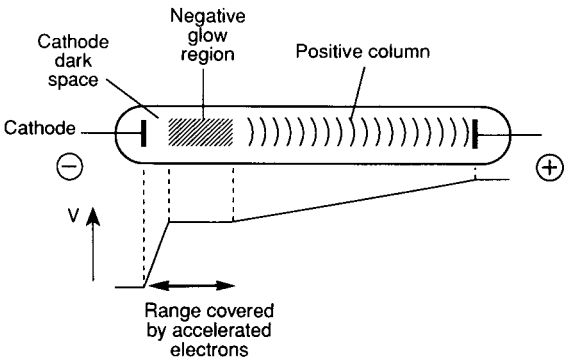

FIG. 2. A diagram showing the different regions in an electric discharge through a low pressure gas. The potential varies nonuniformly through the discharge as shown, the largest fall occurring in the cathode dark space. Positive ions are formed predominantly in the negative glow region.

essentially constant as the current increases; hence, there is a need for a series ballast resistor. At the same time, the cathode area covered by the discharge plasma increases. In the "anomalous discharge," the plasma covers the entire cathode area, and the voltage across the cathode drop rises roughly in proportion to the current. As a result both the energy of the electrons and the distance they travel increase with current. For more details, see Chapter VIII in reference [7].

A DC discharge 4 m long was used to create atomic oxygen [10] for the accurate measurement of its fine structure spectrum in a tunable far infrared spectrometer.

5.1.2.2 Hollow Cathode Discharge Cell. The principle of the hollow cathode discharge is to wrap the cathode around as much of the discharge volume as possible, thereby increasing the extent of the negative glow region and hence the number of ions formed in the discharge. Van den Heuvel and Dymanus published an effective design [8] which has since been copied by many other groups. It is shown in Figure 3. The discharge is struck between the hollow cathode and an anode positioned at the end of a perpendicular glass side arm in the center of the main tube, as is shown in Figure 3. Stable operation is possible over a large range of currents and pressures. The positive column is confined to the glass insert between anode and cathode only, and the negative glow is concentrated along the axis of the cathode tube. A few millimeters from the wall, the glow changes from the cathode dark space to the negative glow which extends along the axis of the tube. The length of the glow is directly related to the voltage applied to the anode. The cathode is cooled efficiently by a slow flow of liquid nitrogen through a helical copper tube soldered around the cathode tube.

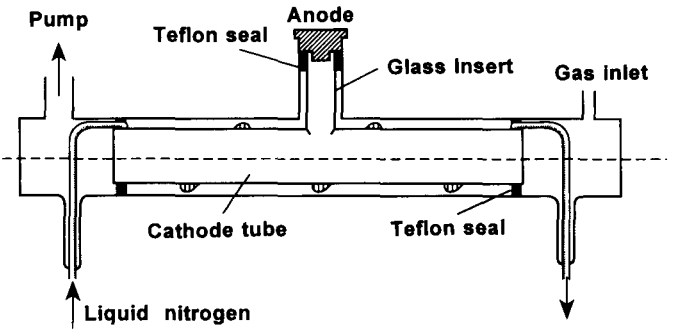

FIG. 3. A hollow cathode discharge cell for the generation of positive ions, after the design of van den Heuvel and Dymanus [8]. The copper cathode first inside a glass cell and is cooled by flowing nitrogen through a spiral tube soldered to its outside surface.

This cell was used in Dymanus's group [11] to produce NH^+ to observe the first rotational transition of that ion.

5.1.2.3 Magnetic Field Enhancement of the Negative Glow Region. In a conventional DC discharge tube (Figure 2), the electrons which are accelerated through the cathode gap spread out; consequently, many are lost through collisions with the wall of the tube. The distance which they travel down the discharge tube is therefore much less than it might otherwise be. The length of the negative glow can be extended by the application of a longitudinal magnetic field [12]. De Lucia and his group at Duke University exploited this observation to achieve dramatic increases in the signals recorded from ions formed in a discharge [9]. Using a solenoid magnet around their discharge tube, they achieved magnetic field strengths of several tens of milliteslas. Fields of this magnitude are sufficient to confine electrons with several hundred volts of transverse energy to a cyclotron radius of the order of 1 cm, roughly the cross-section of the discharge probed by the laser beam. The discharge can be forced to run in the anomalous mode described in Section 5.1 by restricting the size of the electrodes. The increase in positive ion concentration achieved in this way is about 100-fold.

The group of Destombes *et al.* [13] used this type of discharge to produce the ion complex ArH_3^+ and measure its millimeter-wave spectrum.

5.2 Photolysis

The photolytic generation of free radicals with UV flash lamps has been used for a long time. It provided the basis for a large number of papers for electronic spectroscopy in the 1950s, the technique being referred to as flash photolysis [14]. However, the concentrations of transient species generated in this way were

not high enough to permit the detection of rotational or vibrational spectra. Now the situation has been changed with the availability of high-power excimer lasers. It is usual to photolyze the stable parent molecule in the bulk phase. For example, the methyl radical can be generated efficiently by the photolysis of CH_3I [15]:

$$CH_3I + h\nu \rightarrow CH_3 + I.$$

Radicals and even ions have also been formed by photolysis or photoionization of a stable precursor seeded into a rare gas free-jet expansion [16] (to be described later). The molecules are thereby generated cold, considerably simplifying the resultant spectrum.

5.3 Chemical Formation

Free radicals are produced in electrical discharges from reactions between the reactive species produced in the dissociation. They can also be produced downstream from the discharge when one of the neutral reactive species reacts with another reactant. Most methods of generating transient molecules involve flow systems in which streams of gas are pumped continously through tubes. In the discharge/flow system, two such streams of gases are mixed in a reaction zone to generate the molecule of interest. The principle behind these reactions in the gas phase is to generate a reactive species A that is relatively easy to handle, such as an atom, and to react it with a parent molecule BR to form the free radical of interest, ideally in a fast single-step process:

$$A + BR \rightarrow R + AB.$$

A diagram of the production scheme is shown in Figure 4. Although the

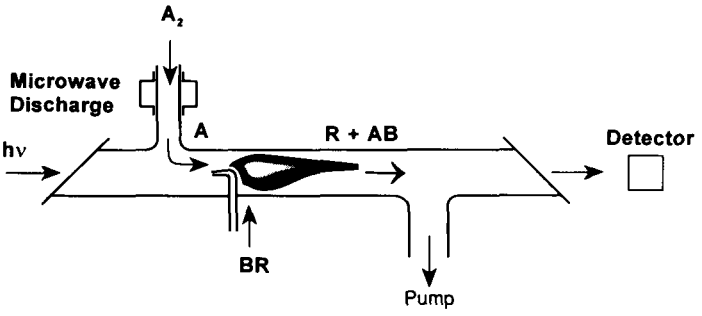

FIG. 4. A schematic diagram of the discharge/flow apparatus for the generation of short-lived molecules. The products of a discharge through flowing gas, producing A, are mixed with a continous flow of a secondary gas BR and react downstream to generate the desired product.

discharge can be operated DC (or at low AC frequencies), it is preferable to use either an RF or a microwave discharge because these do not require electrodes within the gaseous volume (electrodes provide very efficient sites for the removal of transient molecules). An example of the use of this method is the production of the HCO radical [17]:

$$F + H_2CO \rightarrow HCO + HF,$$

where the fluorine atoms are formed by discharging CF_4 or 10% F_2 in helium (the second source produces significantly more fluorine atoms) and reacting them with formaldehyde.

5.4 Laser Ablation

This method is used to vaporize less volatile materials, such as metals. Radiation from a powerful, pulsed laser (either a Nd:YAG or an excimer laser) is focused onto a solid sample. The material is thereby vaporized, often to form a gas plasma above the surface of the solid. The atoms or molecules in the gas phase then react with a secondary species to form the desired product, for example [18]:

$$2Al + N_2O \rightarrow Al_2O + N_2.$$

This method for the formation of transient species is routinely used in conjunction with supersonic nozzle expansion to form the species for observation at low rotational and vibrational temperatures [16]. Often the solid surface needs to be fresh if the material is to be vaporized efficiently. In these circumstances, the material is constructed in the form of a rod which is then slowly rotated to present a new surface for each pulse of laser light. The choice of wavelength of laser light depends on the material to be ablated; this technique is still somewhat of a "black art."

5.5 Thermal Generation

At first glance, the use of high temperatures to generate molecules for the study of their infrared spectra, does not look like a promising approach, because a furnace is a strong source of blackbody radiation. However, a laser beam is easy to collimate, so spatial separation of signal beam and furnace background can easily be achieved. Several groups have recorded infrared spectra of transient molecules by generating them in a furnace [19, 20], and Jones and his group at Ulm University have exploited this technique in studying a whole series of diatomic hydride molecules [21]. Their apparatus is shown schematically in Figure 5.

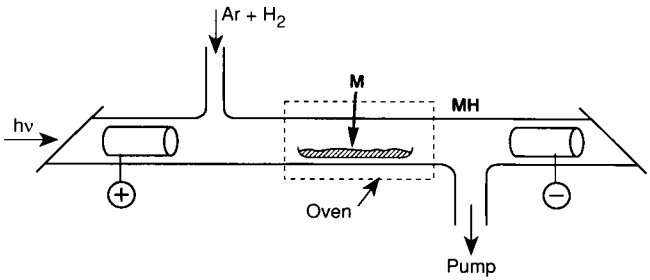

FIG. 5. Apparatus for the generation of metal hydrides by flowing discharged H_2 over metal heated in a furnace indicated by the dashed outline.

The cell is made of an aluminum oxide ceramic body and has two cylindrical water-cooled stainless steel electrodes fitted coaxially to the ends of the tube. The cell is placed inside a furnace capable of producing temperatures up to 1300°C. A suitable metal, M, is placed in the center of the cell in a ceramic boat, and the cell is filled with a 20% mixture of hydrogen in helium at a total pressure of 506 Pa (5 mbar). The gas is discharged to generate hydrogen atoms which combine with the hot metal to produce MH. The technique works particularly well for the more volatile metals for which significant vapor pressure can be generated.

5.6 Supersonic Expansion

Supersonic expansion is not necessarily a way of creating free radicals, but rather a method of cooling the molecules and isolating them for spectroscopic investigation. However, new, weakly bound complexes including free radicals can be formed in this way. When a gas is forced through a small hole from a high- to a low-pressure region, a diverging jet of molecules for which the equipartition of energy is no longer applicable is formed. The translational velocity of the molecules is increased at the expense of the internal (vibrational and rotational) degrees of freedom [16]. With low vibrational "temperatures," it is possible to form and maintain weakly bound complexes such as van der Waals molecules [22]. Much work has been done in the past 5 years on the infrared spectroscopy of such species [23, 24], using an apparatus like that shown in Figure 6.

The compound from which the complex is to be formed is seeded into an inert gas carried at moderately high pressures, 100 kPa (1 atm), and the whole is expanded through a pulsed nozzle into a high-vacuum region. The region just in front of the nozzle (where the complexes are formed) is sampled with a beam from an infrared laser. The laser absorption is enhanced by the use of a multipass

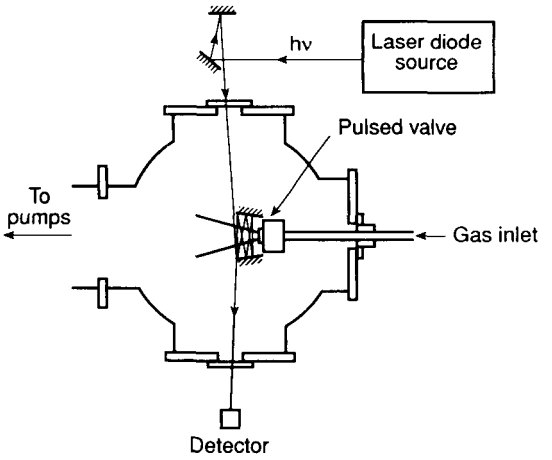

FIG. 6. Apparatus for the study of infrared spectra of van der Waals molecules, formed by supersonic expansion of the component gases through a pulsed nozzle. The system of tilted plane mirrors causes the laser beam to make several passes through the sample, thereby increasing the absorption.

system; the plane mirrors are not parallel, so successive reflections of the beam "walk" toward the nozzle and then out again. Greater path lengths and hence sensitivity can be achieved by using a slit nozzle [25]. The slit nozzle was used very effectively in the study of $(HCl)_2$ [26].

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