SCIENCE

Ion Cyclotron Resonance Spectroscopy

Cyclotron double resonance provides a new technique for the study of ion-molecule reaction mechanisms.

John D. Baldeschwieler

The classical motion of charged particles in magnetic and electric fields is the basis for many fundamental experiments and important practical devices. In fact this subject has been so thoroughly sifted that development of a new device based on the same principle as E. O. Lawrence's cyclotron (1) should be uniquely improbable. Ion cyclotron resonance spectroscopy appears to be just such an unlikely development.

The path of a free charged particle in a uniform magnetic field $\mathbf{H}$ is constrained to a circular orbit in a plane normal to $\mathbf{H}$, but is unrestricted parallel to $\mathbf{H}$. This motion can be readily characterized, since the force $\mathbf{F}$ on a charge moving with velocity $\mathbf{v}$ in $\mathbf{H}$ is

$$\mathbf{F} = \frac{q}{c}\mathbf{v} \times \mathbf{H} \qquad (1)$$

where q is the charge of the particle and c is the speed of light. If the charge is initially moving in a plane normal to $\mathbf{H}$, then $\mathbf{F}$ is also in this plane, and normal to the direction of motion. The motion of the particle is thus restricted to a circular orbit such that

$$\frac{mv^2}{r} = \frac{q}{c}vH \qquad (2)$$

The author is professor of physical chemistry at Stanford University, Stanford, California.

where m is the mass of the particle and r is the radius of the orbit. From Eq. 2 it follows that

$$\omega_c = \frac{v}{r} = \frac{qH}{mc} \qquad (3)$$

and

$$r = \frac{mcv}{qH} \qquad (4)$$

where ω_c is the angular frequency or cyclotron frequency of the orbital motion. Equations 3 and 4 show that ω_c, and hence the time required per revolution, is quite independent of the velocity of the particle, whereas the radius of the orbit is directly proportional to v. These relationships are of course familiar as the basis for the cyclotron particle accelerator.

The motion of a swarm of ions with a distribution of velocities in a uniform magnetic field will be characterized by a distribution of orbital radii but a sharp cyclotron frequency ω_c which depends only on q, $\mathbf{H}$, and m. If a pair of parallel plates is placed in the magnetic field, as shown in Fig. 1, then an alternating electric field, $\mathbf{E}(t)$, can be applied normal to $\mathbf{H}$ at frequency ω. When $\omega = \omega_c$, the charged particles absorb energy from the alternating electric field and are accelerated to larger velocities and orbital radii. An absorption of energy from $\mathbf{E}(t)$ must of course be reflected as a

change in the power required from the source of $\mathbf{E}(t)$. The absorption of energy from $\mathbf{E}(t)$ at $\omega = \omega_c$ by a swarm of ions can thus be detected if an oscillator which is extremely sensitive to changes in load is used as the source of $\mathbf{E}(t)$.

The design of a cyclotron resonance spectrometer (2) based on these principles is straightforward. For usual laboratory magnetic fields of from 0 to 15,000 gauss, and particles of mass 1 to 200 atomic mass units, the cyclotron frequencies $\omega_c/2\pi$ from Eq. 3 range from 50 kilocycles per second to 23 megacycles per second. For example, a singly charged argon ion of mass 40 has a frequency of $(\omega_c/2\pi) = 308$ kilocycles per second for a magnetic field of 8000 gauss. This is a convenient frequency range for the operation of the marginal oscillator-detector or Pound-box (3), which has been highly developed for nuclear-magnetic-resonance applications. A marginal oscillator is operated under conditions that are just marginal for continuous oscillation. Under these conditions the level of the oscillator is extremely sensitive to small impedance changes in the resonant circuit. The parallel plates shown in Fig. 1 can be readily incorporated as the capacitive element of the resonant circuit for this oscillator.

A plot of the level of the marginal oscillator as a function of the magnetic field, H, for a fixed oscillator frequency then displays the cyclotron resonance spectrum for a mixture of ions of various masses with a scale linear in mass. For low sample pressures, then, this device is simply a mass spectrometer. It is in fact a rather good mass spectrometer, with a sensitivity of the order of 1 to 10 ions per cubic centimeter and a mass resolution of 1/30,000. However it is not apparent that it has significant advantages over other methods for simply obtaining mass spectra, nor is it apparent that under these conditions the device has any unique properties which will lead to intriguing new applications.

This device becomes interesting when there is a large concentration of neutral

particles in addition to ions in the space between the capacitor plates of Fig. 1. Then the coherent cyclotron motion of all the ions is occasionally interrupted by collisions between ions and neutral molecules. The line width of a cyclotron resonance absorption is determined by the collision frequency at high sample pressures by a mechanism that is analogous to the transverse relaxation time, T_2, of nuclear magnetic resonance or pressure broadening in other spectroscopic techniques. The collision frequency, v_c, depends on the product

$$v_c = \eta v_{rel} \sigma \qquad (5)$$

where η is the number density of neutral species, v_{rel} is the relative ion-neutral velocity, and σ is the ion-neutral collision cross section. The σ's are interesting quantities that are thus available from cyclotron-resonance line-width measurements (4).

When the ions accelerated by $E(t)$ collide with other particles they lose some of their excess energy. A mixture of ions and neutral particles in the presence of H and $E(t)$ then reaches a steady-state condition in which the energy gained by the ions from $E(t)$ between collisions is lost to the neutral molecules in collisions. The average energy of the ions in this steady state will depend on the magnitude of $E(t)$, the collision frequency, and the efficiency of energy transfer upon collision in analogy to the longitudinal relaxation time T_1, of nuclear magnetic resonance. Thus a detailed study of cyclotron-resonance line shapes as a function of $E(t)$ can yield energy-transfer efficiencies for ion-molecule collisions.

Line-Shape Theory

A complete theory of collision-broadened cyclotron-resonance line shapes for a mixture of ions and neutral molecules must of course include consideration of the velocity and spatial distributions of all the particles. This suggests a confrontation with the Boltzmann transport equation (5). Fortunately, the equation of motion for an average particle displays most of the interesting features of this experiment. The equation of motion for a free particle in the presence of $E(t)$ and H is

$$m\frac{d\mathbf{v}}{dt} = q\mathbf{E}(t) + \frac{q}{c}\mathbf{v} \times \mathbf{H} \qquad (6)$$

264

where $q\mathbf{E}(t)$ is the force exerted on the particle by $E(t)$ and $[(q/c)\mathbf{v}] \times \mathbf{H}$ is the force contributed by the motion of the charged particle in H. For a mixture of ions and neutral molecules, this equation can be modified by the addition of a relaxation term so that

$$m\frac{d\bar{\mathbf{v}}}{dt} = q\mathbf{E}(t) + \frac{q}{c}\bar{\mathbf{v}} \times \mathbf{H} - mv_c\bar{\mathbf{v}} \qquad (7)$$

where $\bar{\mathbf{v}}$ is the nonrandom part of the total velocity of an average ion and v_c is an average collision frequency.

The relaxation term in Eq. 7 plays a role that has a striking analogy to the $(1/T_2)$ terms in Bloch's phenomenological equations for nuclear magnetic resonance (6). In fact the analogy between Eq. 7 and Bloch's equations becomes even more apparent when Eq. 7 is given in the form

$$\frac{d\mathbf{J}}{dt} = \gamma\mathbf{E}(t) - \mathbf{J} \times \omega_c + \frac{\mathbf{J}}{\tau} \qquad (8)$$

where $\mathbf{J} = nq\bar{\mathbf{v}}$, n is the number of ions per cubic centimeter, $\gamma = (nq^2/m)$, $\omega_c = (qH/mc)$, and $\tau = (1/v_c)$. Equation 8 can be solved for $\mathbf{J}$ if the linearly polarized electric field

$$\mathbf{E}(t) = E_o \sin \omega t \, \mathbf{i} \qquad (9)$$

is resolved into two counter-rotating circularly polarized components:

$$\mathbf{E}_1(t) = \frac{E_o}{2}\sin \omega t \, \mathbf{i} + \frac{E_o}{2}\cos \omega t \, \mathbf{j} \qquad (10)$$

$$\mathbf{E}_2(t) = \frac{E_o}{2}\sin \omega t \, \mathbf{i} - \frac{E_o}{2}\cos \omega t \, \mathbf{j} \qquad (11)$$

Only the component rotating in the same sense as the cyclotron motion of the ion is of importance in determining the absorption of energy from the electric field as long as $\Delta\omega/\omega_c \ll 1$, where $\Delta\omega$ is a measure of the line width. Equation 8 can then be transformed to a coordinate system rotating with the electric field to yield simple expressions for the absorption and dispersion. The power absorbed from the alternating electric field is given by

$$P(\omega) = \mathbf{J} \cdot \mathbf{E}(t) = \frac{\gamma E_o^2 \tau}{1 + \tau^2(\omega - \omega_c)^2} \qquad (12)$$

Equation 12 suggests that, in the limit of small values for E_o, the collision-broadened cyclotron-resonance line shape should be Lorentzian. The average collision frequency depends, of course, on the relative ion-neutral velocity, as shown in Eq. 8. Thus, for larger values of E_o, τ depends on the

amount of energy absorbed from the alternating field, which in turn depends on $\omega - \omega_c$. For larger values of E_o, then, the line shape will not be Lorentzian. The actual line shape can be calculated by a somewhat tedious but straightforward procedure under the conditions that the field or frequency is varied slowly enough so that the ions are moving under steady-state conditions (5). The line shapes predicted by this procedure are in fact in good general agreement with line shapes observed for N_2 (2) and for rare gases (7), where the collision cross sections are well known.

Although obtaining ion-molecule collision parameters from cyclotron resonance spectroscopy is an intriguing proposition, an even more interesting possibility is suggested from the simple form of Eq. 7. There are of course many processes that contribute to the average collision frequency v_c. These include elastic and inelastic collisions between ions and neutral molecules in which the identity of the colliding ion is not changed, and also processes such as charge-transfer and ion-molecule reactions in which the identity of the colliding ion is lost and another ion is formed. If a mixture of ions and neutral molecules of different masses is examined by cyclotron resonance, then an independent equation of motion can be written for each type of ion as long as there are no processes which couple one ionized species with another. However, if an ion-molecule reaction of the general type

$$A^+ + B \rightarrow C^+ + D \qquad (13)$$
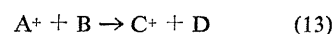
occurs, then the differential equations of motion for A^+ and C^+ are coupled. This coupling occurs in the collision terms which must be expanded to include gain terms in the equation of motion of C^+ that depend on the velocity of A^+, and gain terms in the equation of motion of A^+ that depend on the velocity of C^+. It is possible to calculate the detailed cyclotron-resonance line shapes in the presence of charge-transfer and chemical reactions (5). The resulting formalism is quite analogous to the coupling of the equations of motion of magnetic species by various exchange processes in nuclear-magnetic-resonance and electron-spin-resonance experiments (8).

If the equations of motion of different ionic species are coupled by charge transfer or ion-molecule reactions, it is possible to demonstrate this coupling

by multiple-cyclotron-resonance techniques [9]. Ion-molecule collision cross sections are usually dependent on the relative ion-molecule velocities. Thus, if the velocity of one type of ion is increased by means of a strong radio-frequency electric field $E_2(t)$ at frequency ω_2, then substantial changes will occur in the concentrations and velocities of other ions in equilibrium with the irradiated ion. The consequent changes in cyclotron-resonance line shape and intensity can be observed with a weak radio-frequency field $E_1(t)$ at frequency ω_1. For a mixture of ions and neutral molecules which react according to Eq. 13, $E_2(t)$ can be applied at the cyclotron frequency of species A^+ where $\omega_2 = (qH/m_A c)$. The frequency of collision of A^+ with B depends on the relative velocities of A^+ and B. Heating A^+ with $E_2(t)$ will thus change the rate constant for the reaction, and consequently the number density of C^+ ions. The number density of C^+ ions can be monitored by observing the intensity of the cyclotron resonance signal of C^+ with $E_1(t)$, where $\omega_1 = (qH/m_c c)$.

When the amplitude of $E_2(t)$ is periodically pulsed on and off, the number density of species C^+ and hence the amplitude of $E_1(t)$ also will be modulated at the pulsing frequency. The cyclotron-resonance signal of species C^+ at ω_1 can then be detected with a phase-sensitive detector referenced to the pulsing frequency. The difference between the single and double resonance spectra of species C^+ can then be directly displayed. Pulsed double resonance is a highly specific modulation technique for the cyclotron double-resonance experiment. Only those products that are coupled to the irradiated species by charge transfer or ion-molecule reaction will appear in the pulsed-double-resonance spectrum [9].

Ion cyclotron resonance thus appears to be useful as a technique for the study of ionic collision processes in gases. However, this field is by no means unexplored [10]. One of the most important of these processes is the charge-exchange reaction, in which an electron is transferred between an ion and a neutral molecule [11]. Considerable effort has been invested in both theoretical and experimental studies of these reactions [12]. Most of the experiments, however, have been carried out at ion energies in excess of several electron volts, because of difficulties in controlling low-energy ion beams. The ion-cyclotron-resonance
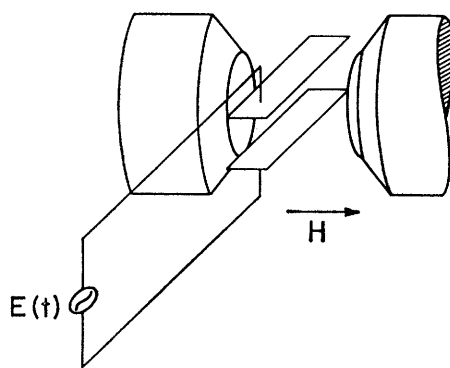
Fig. 1. Orientation of magnetic field **H** and parallel plates such that the radio-frequency electric field **E**(t) can be applied normal to **H** at frequency ω.

technique is best suited for experiments involving ion energies below several electron volts, and thus should find its place as a valuable complement to other available techniques.

Ion-molecule reactions that result in substantial chemical changes have also received increasing attention [13]. Again there are experimental difficulties in studying reactions involving low-energy ions, including the difficulty of identifying the links between the various reactant and product ions when concurrent ion-molecule reactions occur. The ion-cyclotron-resonance technique outlined above should be helpful in establishing the relationships between reactant ions and their corresponding product ions in complex ion-molecule reaction sequences. For example, it is possible to irradiate a specific isotopic species at a fixed frequency ω_2 and obtain a double-resonance spectrum by sweeping the observing frequency ω_1. This experiment indicates all of the product ions that are coupled to a given reactant ion by ion-molecule reactions. It is also possible to observe the cyclotron resonance of a specific isotopic species with a fixed frequency, ω_1, and then sweep the irradiating frequency ω_2. A plot of the intensity of the signal at ω_1 relative to the frequency ω_2 indicates all of the reactant ions that can yield a specific product. This method is reminiscent of various electron-nuclear double-resonance techniques [14].

The most interesting discovery in the development of cyclotron resonance spectroscopy has been the finding that, in addition to displaying the relationships between the reactants and products in complex ion-molecule reaction sequences, the technique also provides information on the reaction mechanisms. Some of the possible applications are discussed later.

Apparatus

The ion cyclotron resonance spectrometer used to obtain the results given in the sections that follow is based on the omegatron of Sommer, Thomas, and Hipple [15]. In an omegatron, resonance is detected when ions starting from a fixed point achieve sufficiently large orbital radii to reach a fixed collector. The spectrometer described here differs from the conventional omegatron principally in that a marginal oscillator-detector is used to supply $E_1(t)$ and to detect resonant power absorption [16]. A block dia-
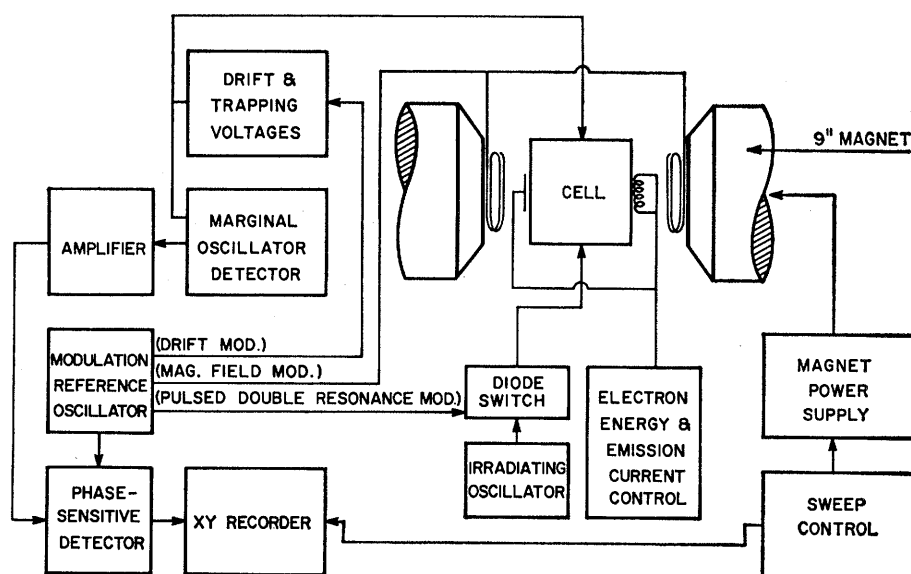

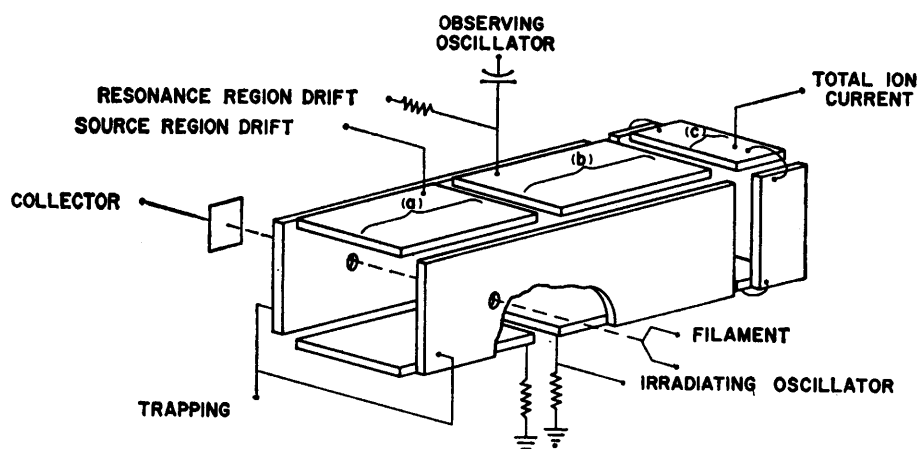Fig. 2. Block diagram of ion-cyclotron resonance spectrometer.

Fig. 3. Cutaway view of cyclotron resonance cell. The electron beam is collinear with the magnetic field. (*a*) Ion source; (*b*) ion analyzer; (*c*) ion collector.

gram of the spectrometer system is shown in Fig. 2. The resonance cell shown in detail in Fig. 3 is located between the pole faces of an electromagnet. This cell supports the pair of parallel plates which form the capacitive element of the parallel resonant circuit of the marginal oscillator-detector. Power absorption in the capacitive element results in a change in the resistive impedance of the resonant circuit, and is reflected by a change in the radio-frequency voltage level of the marginal oscillator. If the magnetic field or various electrostatic voltages are modulated, the radio-frequency level will vary at the modulation fre-

quency when ω_1 equals the cyclotron frequency of an ion in the cell. The output of the marginal oscillator can then be conveniently detected through use of a phase-sensitive detector referenced to the modulation frequency.

The cyclotron resonance cell shown in Figs. 3 and 4 differs from the omegatron cell (*15*) in several ways. The cyclotron resonance cell, with overall dimensions of $2.54 \times 2.54 \times 12.7$ centimeters, is divided into three sections: an ion source section, an analyzer section, and an ion-collection section. Ions are produced in the source region by means of an electron beam which is accelerated from a filament in a di-

rection parallel to the magnetic field. The source is separated from the analyzer region, to avoid any shift in the resonance frequency due to space charge produced by the electron beam (*17*). Ions are drifted from the source region through the analyzer region by applying static voltages across the top and bottom plates of the cell (*18*). Charged particles in the presence of perpendicular electrostatic and magnetic fields E_D and H move in a cycloidal path with a drift velocity, v_D, equal to (cE_D/H), normal to both E_D and H (*19*). The direction and magnitude of v_D are independent of the mass of the particle and the sign of the charge. The top and bottom plates of the analyzer region form the capacitive element of the resonant circuit of the marginal oscillator. The second radio-frequency electric field for the double-resonance experiments is most conveniently coupled to the bottom plate of the cell with a small resistance. Electrostatic trapping voltages are applied to the side plates in the source and analyzer regions to prevent the ions from escaping from the cell because of their velocity components parallel to H. The top, bottom, and side plates in the ion-collection region are connected in common to an electrometer, to provide a measure of the total ion current.

An obvious method of modulating the cyclotron-resonance-absorption signal for detection is modulation of the density of ions in the analyzer region. This can be easily accomplished at low pressures by modulation of the drift voltage in the source region. Square-wave modulation of the drift voltage in the source region together with phase-sensitive detection, yields directly an absorption-mode line shape. This modulation scheme fails when collisions retard the movement of ions from the source region to the analyzer region and hence destroy the coherence of the ion density with modulation. Modulation of the magnetic field or the frequency of the marginal oscillator is also possible; these schemes yield the first derivative of the absorption line shape. The highly specific double-resonance-modulation scheme is also illustrated in Fig. 2.

The resonance cell is located between the pole faces of a 23-centimeter (9-inch) electromagnet with a gap width of 4.5 centimeters. The cell is enclosed in a bakeable stainless steel vacuum chamber which can be evacuated to a
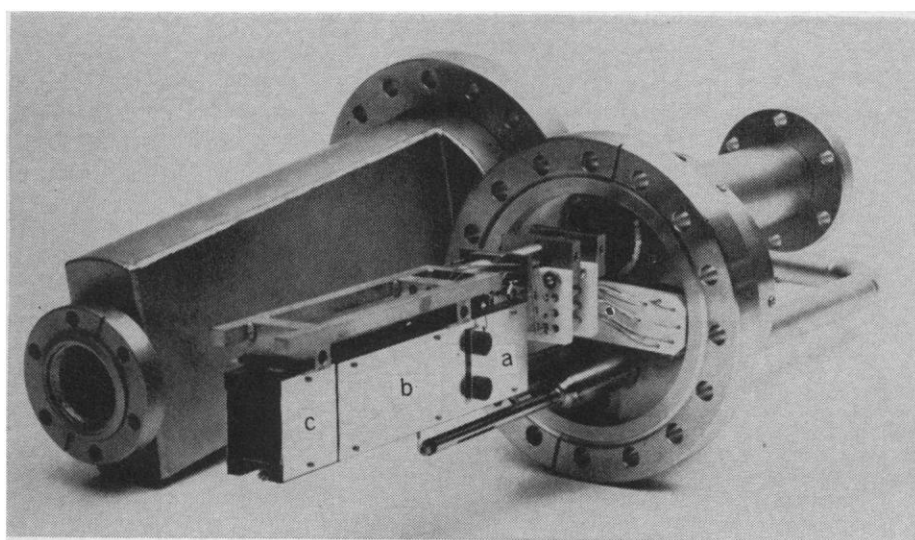

Fig. 4. Typical complete resonance cell. The three sections of the cell (left section of unit in foreground) are, from left to right, (*c*) the ion collector, (*b*) the analyzer, and (*a*) the ion source (see Fig. 3). The fitting on the side of the ion source section is the plate for the ionizing electron beam. The plates and electrical leads are mounted on a plug-in assembly so that cells of different design can be readily interchanged. The complete cell is enclosed in the stainless steel vacuum can shown in background. The small vacuum flange on the left-hand end of the can is fitted with a window, which makes it possible to observe optical emission from the cell. [Photo courtesy of Varian Associates, Palo Alto, California]

pressure of 10^{-8} (1 torr = 1 millimeter of mercury) by means of a getter-ion pump. A gas is introduced into the chamber through a variable leak valve from a sample foreline. The foreline can be evacuated to pressure of 10^{-5} torr by means of a molecular sieve trap and mechanical pump. Most of the variations of inlet systems used with conventional mass spectrometers can also be used with the ion cyclotron resonance spectrometer.

Deuterated Nitrogen Ions

Some of the simplest examples of ion-molecule reactions that can be studied by ion cyclotron double resonance include charge-transfer reactions between isotopic species [7] such as

$$^{3}He^{+} + {}^{4}He \leftrightarrows {}^{3}He + {}^{4}He^{+} \qquad (14)$$

Of perhaps greater interest, however, are ion-molecule reactions which yield unusual chemical products. For example, N_2D^+ can be produced from mixtures of CD_4 and N_2 in a mass-spectrometer ion source [20]. The same species can be readily observed by the cyclotron resonance method. The single-resonance ion cyclotron resonance spectrum of a mixture of CD_4 and N_2 at a total pressure of 2×10^{-5} torr is shown in Fig. 5a [9]. The spectrum is obtained with drift modulation by sweeping the magnetic field from left to right with $\omega_1/2\pi = 285.5$ kilocycles per second. In addition to the molecular ions CD_4^+ and N_2^+, the fragment CD_3^+ and the products of various ion-molecule reactions—CD_5^+, $C_2D_5^+$, and N_2D^+—are apparent. Since both $C_2H_5^+$ and N_2H^+ are mass-29 ions, the use of CD_4 clarifies these assignments. The species CD_5^+ and $C_2D_5^+$ are products of the reactions of methane ions with neutral methane.

$$CD_4^+ + CD_4 \rightarrow CD_5^+ + CD_3 \cdot \qquad (15)$$
$$CD_3^+ + CD_4 \rightarrow C_2D_5^+ + D_2 \qquad (16)$$
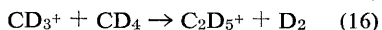
All of the ion-molecule reaction products disappear as the total pressure is reduced. When the ionizing electron energy is reduced below the appearance potential for N_2^+ production, the N_2D^+ product does not disappear. This suggests that the reaction

$$CD_4^+ + N_2 \rightarrow N_2D^+ + CD_3 \cdot \qquad (17)$$
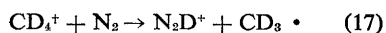
is an important pathway for the production of N_2D^+.

Double resonance effects confirming reaction 17 are shown in Fig. 5, b and c. The N_2D^+ single resonance observed with $\omega_1/2\pi \cong 285.5$ kilocycles per second is shown in Fig. 5b. The N_2D^+ cyclotron resonance observed with strong irradiation of the CD_4^+ ion with $\omega_2/2\pi \cong 425.5$ kilocycles per second is shown in Fig. 5c. Significant changes in the N_2D^+ intensity and line shape occur. A series of field-sweep pulsed-double-resonance spectra of the mixture of CD_4 and N_2 for various fixed values of ω_2/ω_1 is shown in Fig. 5d. A signal from the N_2D^+ product is observed only when the ratio ω_2/ω_1 is very close to the mass ratio of $N_2D^+/CD_4^+ = 1.4968$.

Chloroethylene

The cyclotron resonance spectra obtained for samples of chloroethylene at various pressures with 70-electron-volt electrons are shown in Fig. 6 [21]. The derivative line shapes are characteristic of the magnetic-field modulation scheme. At a pressure of 5×10^{-7} torr, the cyclotron resonance spectrum, shown in Fig. 6a, corresponds closely to

that obtained with a conventional mass spectrometer [22]. Prominent features in this spectrum include peaks arising from the molecule ions $C_2H_3{}^{35}Cl^+$ and $C_2H_3{}^{37}Cl^+$ at mass 62 and mass 64, respectively. The molecular ion is a radical ion formed by electron impact from the neutral molecule minus one electron. Since chlorine in natural abundance consists of two isotopes of mass 35 and mass 37, respectively, a chlorine-containing ion gives rise to two resonances separated by two mass units. Other features in the spectrum include various fragments of the molecular ions, such as $C_2H_3^+$ at mass 27 (formed by loss of $Cl \cdot$ from the molecular ions), $C_2H_2^+$, C_2H^+, Cl^+, HCl^+, CCl^+, and $CHCl^+$.

At the higher pressure of 5×10^{-6} torr, numerous reaction products begin to appear in the spectrum, as shown in Fig. 6b. The two chlorine isotopes are very helpful in the identification of the chlorine-containing reaction products. As Fig. 6b indicates, the ion-molecule chemistry of the fragments of chloroethylene is very complex, but there are, nevertheless, some systematic features in this spectrum. For example, there are several sequences of resonances
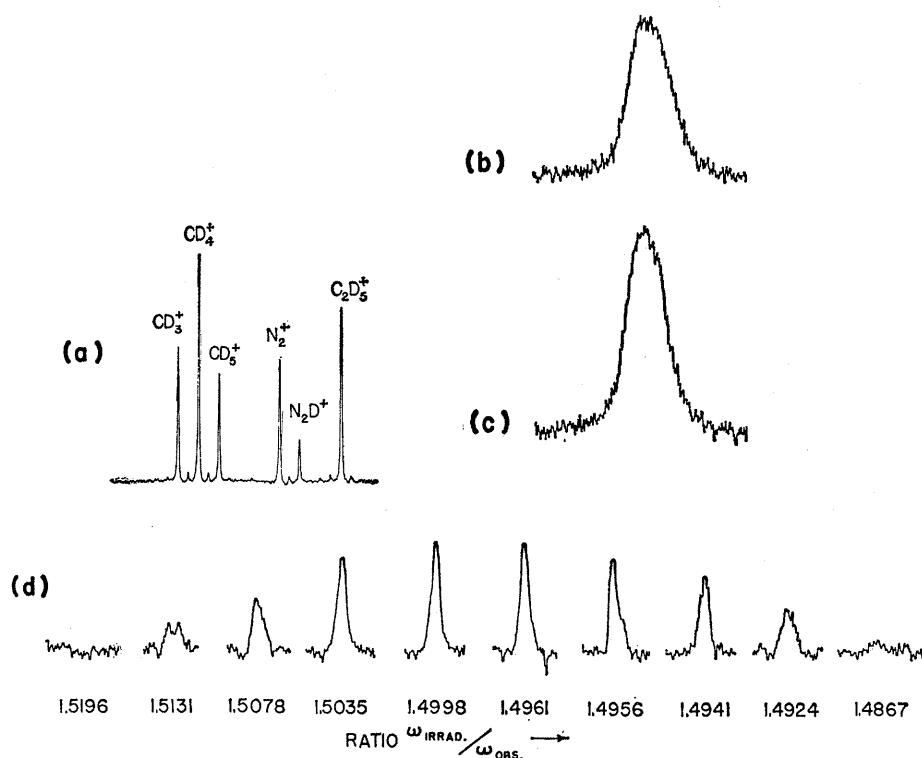

Fig. 5. (a) Single-resonance ion cyclotron resonance spectrum of a mixture of CD_4 and N_2 at a pressure of about 2×10^{-5} torr. (b) Field-sweep single-resonance spectrum of the N_2D^+ peak with expanded scales. (c) Field-sweep double-resonance spectrum of N_2D^+ resonance with continuous irradiation at the CD_4^+ cyclotron resonance frequency. (d) Field-sweep pulsed double-resonance spectra for a series of fixed values of ω_2/ω_1. The mass ratio for $N_2D^+/CD_4^+ = 1.4968$.

separated by 26 mass units. This corresponds to the incorporation of a C_2H_2 group into the reactant ion and suggests the general polymerization reaction

$$A^+ + C_2H_3Cl \rightarrow AC_2H_2^+ + HCl \quad (18)$$
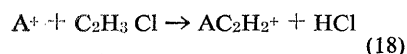
where A^+ is any of a number of ionic species present in the mixture. The product $AC_2H_2^+$ then forms the reactant for another reaction of this type. One such sequence starting with $C_2H_3^+$ includes $C_4H_5^+$, $C_6H_7^+$, and $C_8H_9^+$. Analogous sequences start with the molecular ions $C_2H_3{}^{35}Cl^+_2$ and $C_2H_3{}^{37}Cl^+_2$. Figure 6c shows the chloroethylene cyclotron resonance spectrum at a pressure of 3×10^{-5} torr. At this pressure the intensity of the product ions exceeds that of the ions produced by the initial fragmentation of the neutral molecules by electron impact.

If the ion-molecule reactions of Eq. 18 are indeed responsible for the systematic features of the cyclotron resonance spectrum of chloroethylene, it should be possible to demonstrate the coupling of ions A^+ and $AC_2H_2^+$ by

double resonance. For example, in the first step of the sequence starting with $C_2H_3^+$,

$$C_2H_3^+ + C_2H_3Cl \rightarrow C_4H_5^+ + HCl, \quad (19)$$
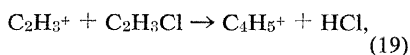
the equations of motion of $C_2H_3^+$ (mass 27) and $C_4H_5^+$ (mass 53) should be coupled. Figure 7a shows the spectrum obtained by fixing the magnetic field and ω_1 at exactly the cyclotron resonance condition for mass 53, and sweeping ω_2 through the low mass range. In addition, ω_2 is periodically pulsed, and ω_1 is detected with a phase-

sensitive detector referenced to the pulsing frequency. In this experiment, a signal appears at ω_1 when ω_2 satisfies the cyclotron resonance condition for mass 27. The equations of motion of $C_2H_3^+$ and $C_4H_5^+$ (mass 27 and mass 53) are indeed coupled, as suggested by Eq. 19. A spurious effect appears at mass 26½, where the irradiating frequency is exactly twice the observing frequency. Figure 7b shows the change in line shape that occurs when the irradiating power is increased by 5 decibels, reminiscent of the effects of exchange on nuclear-magnetic-res-

Table 1. Calculated relative contribution of reactant-ion isotopic species to product-ion double-resonance signal.

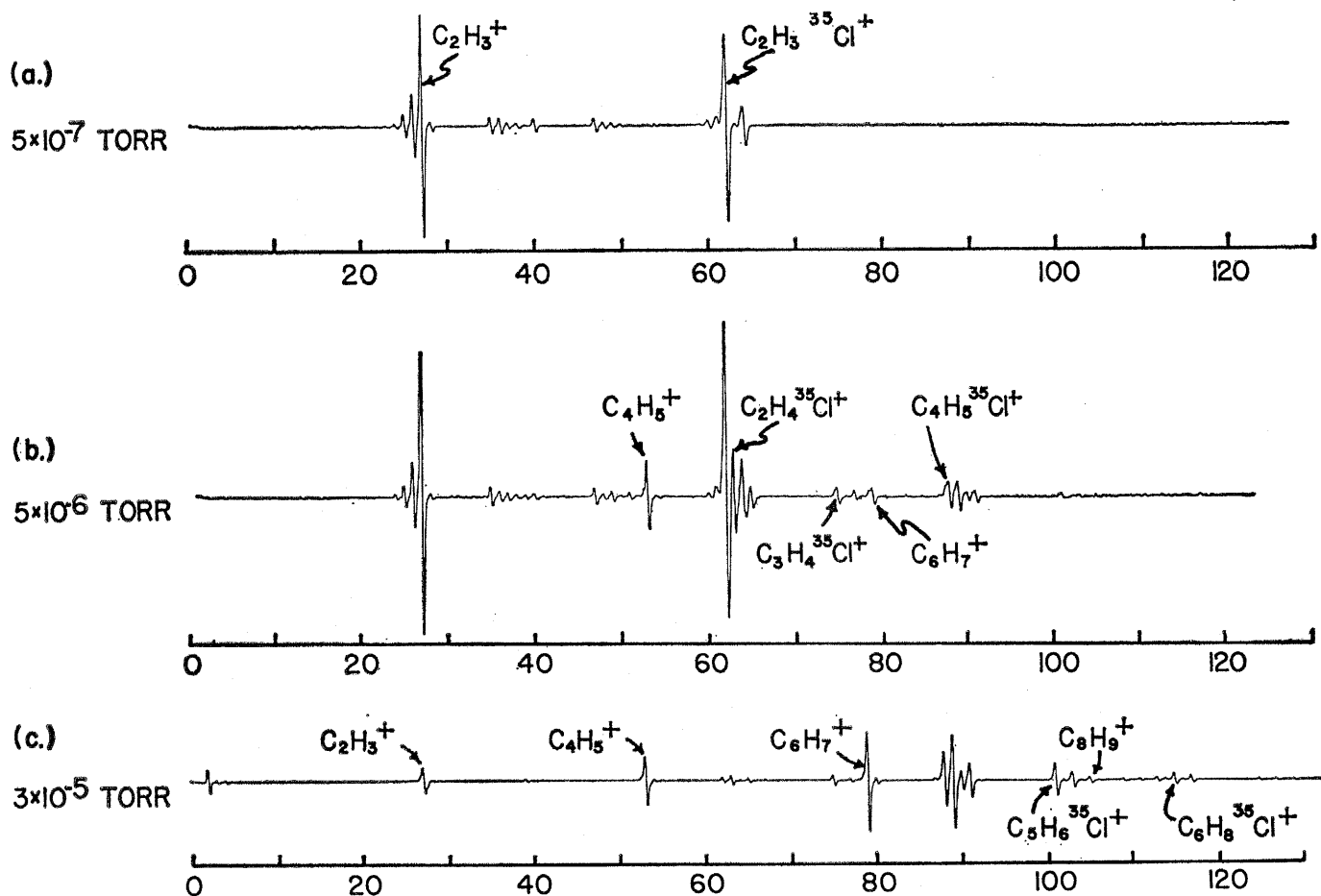| Reaction path	Chlorine isotope in product ion	Chlorine isotope in reactant ion	
		^{35}Cl	^{37}Cl
Either chlorine retained with equal probability	^{35}Cl	0.875	0.125
	^{37}Cl	.375	.625
Chlorine retained from reactant ion	^{35}Cl	1.0	.0
	^{37}Cl	0.0	1.0
Chlorine retained from neutral reactant	^{35}Cl	.75	0.25
	^{37}Cl	.75	.25

Fig. 6. Variation, with pressure, of single-resonance cyclotron resonance spectrum of chloroethylene obtained with 70-electron-volt electrons. For all three pressures, $\omega_1 = 153.0$ kilocycles per second and $E_1 = 0.01$ volt per centimeter. Field modulation gives the derivative line shape. The assignments of some of the prominent resonances are indicated.

onance or electron-spin-resonance line shapes.

A second and more interesting example of the general polymerization reaction (reaction 18) is initiated by the chloroethylene molecular ion

$$C_2H_3Cl^+ + C_2H_3Cl \rightarrow C_4H_5Cl^+ + HCl \quad (20)$$
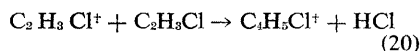
Since chlorine in natural abundance consists of two isotopes, the reactant ions give two resonances, at mass 62 and mass 64, corresponding respectively to the ^{35}Cl and ^{37}Cl ions. Likewise, the product ions give rise to two resonances, at mass 88 and mass 90, corresponding respectively to the ^{35}Cl- and ^{37}Cl-containing products. Now it is possible to display, by double-resonance experiments, which of the reactant isotopic species are coupled to which of the product isotopic species.

The relative importance of the couplings between each of the reactant isotopic species and each of the product isotopic species depends in detail on the reaction mechanism. Suppose the ^{35}Cl-containing product ion at mass 88 is observed while the reactants at mass 62 and mass 64 are irradiated. If it is the chlorine atom in the reactant ion that always is retained in the product ion,

$$C_2H_3Cl^+ + C_2H_3Cl \rightarrow C_4H_5Cl^+ + HCl, \quad (21)$$
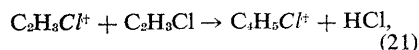
then irradiating the ^{35}Cl-containing reactant at mass 62 should affect the ^{35}Cl-containing product at mass 88. However, irradiating the reactant at mass 64 should have no effect on the product at mass 88. On the other hand, if the chlorine atom from the reactant ion is always eliminated as HCl,

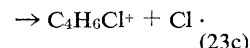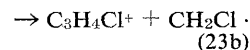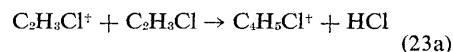$$C_2H_3Cl^+ + C_2H_3Cl \rightarrow C_4H_5Cl^+ + HCl, \quad (22)$$
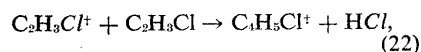
then the result is quite different. Since the chlorine isotope in the reactant ion is immaterial to the product, both the mass-62 and the mass-64 reactant ions will contribute to the mass-88 product, and the relative intensities of the double-resonance effects will depend simply on the number density of the mass-62 reactant relative to that of the mass-64 reactant, or roughly 3:1. If a reaction intermediate is formed from which either chlorine can be eliminated with equal probability, then a statistical argument suggests that the contributions the reactants at mass 62 and mass 64 to the product at mass 88 should be in the ratio of 7:1. The contributions of the reactants at mass 62 and mass 64

to the product at mass 90 for this case should be in the ratio of 3:5. The relative contributions of reactant-ion isotopic species to the product-ion species, as calculated from these simple arguments, are summarized in Table 1.

The results of observing the ^{35}Cl-containing product at mass 88 and irradiating the ^{35}Cl- and ^{37}Cl-containing reactants at mass 62 and mass 64 are illustrated in Fig. 8a. The relative contributions of the mass-62 and mass-64 reactants to the mass-88 product are roughly in the ratio 7:1. When the product at mass 90 is observed and the reactants at mass 62 and mass 64 are irradiated again, the spectrum shown in Fig. 8b is obtained. The finding that the relative contributions of the reactants at mass 62 and mass 64 to the product at mass 90 are roughly in the ratio 3:5 confirms the view that the chlorine atom retained in the product comes with equal probability from either the ionized or the neutral reactant.

It is possible to investigate the reaction of $C_2H_3Cl^+$ with C_2H_3Cl still further by irradiating either isotopic species of the reactant ion at frequency ω_2, modulating ω_2, and then searching the remainder of the spectrum at frequency ω_1 for products which carry the modulation frequency. A product which carries the modulation information must be coupled to $C_2H_3Cl^+$ by an ion molecule reaction. The reaction of $C_2H_3Cl^+$ with C_2H_3Cl in fact can yield three different products:

$$C_2H_3Cl^+ + C_2H_3Cl \rightarrow C_4H_5Cl^+ + HCl \quad (23a)$$
$$\rightarrow C_3H_4Cl^+ + CH_2Cl \cdot \quad (23b)$$
$$\rightarrow C_4H_6Cl^+ + Cl \cdot \quad (23c)$$

In reactions 23b and 23c the chlorine retained in the ionized product again comes with equal probability from either the ionized or the neutral reactant. These results may well encourage some speculation about the reaction mechanism, and the nature of the intermediates.

Alkyl Halide Negative Ions

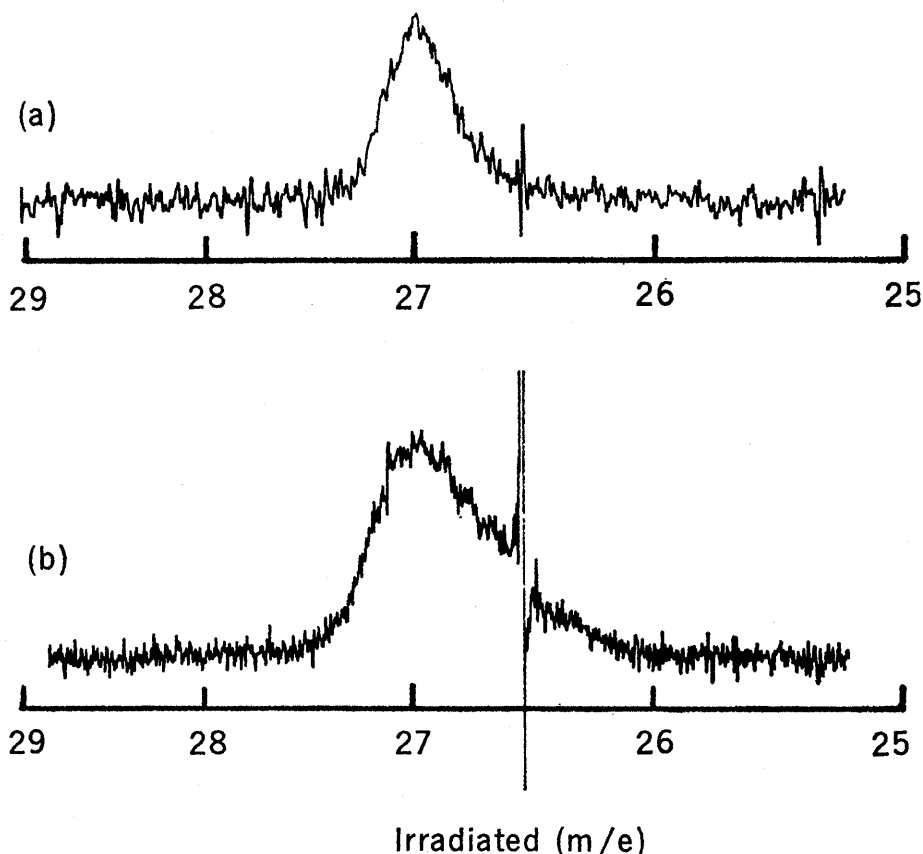The negative ion spectrum of chloroethane obtained with 11-electron-volt electrons is shown in Fig. 9a (23). The

Irradiated (m/e)

Fig. 7. Pulsed double-resonance spectrum of the $m/e = 53$ ($C_4H_5^+$) species with irradiation at the cyclotron frequency of $C_2H_3^+$, where e is the charge of the ion. The irradiating power used in trace b is 5 decibels greater than that used in trace a. The sharp feature at $m/e = 26\frac{1}{2}$ is due to the irradiating oscillator's exciting the first overtone of the marginal oscillator-detector.

only species apparent in the spectrum can be assigned to $^{35}Cl^-$ and $^{37}Cl^-$, probably produced in the pair process *(24)*

$$C_2H_5Cl + e^- \rightarrow C_2H_5^+ + Cl^- + e^- \quad (24)$$
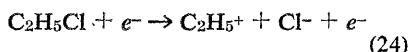
The only obvious multiple-resonance experiment for this mixture is irradiation of $^{35}Cl^-$ and observation of $^{37}Cl^-$. Figure 9b shows the $^{37}Cl^-$ single resonance with expanded scales, and Fig. 9c shows the $^{37}Cl^-$ resonance in the presence of irradiation at the cyclotron resonance frequency of $^{35}Cl^-$. The coupling of $^{35}Cl^-$ with $^{37}Cl^-$ is substantial!

A reasonable coupling mechanism for ^{35}Cl and ^{37}Cl can be written in the following suggestive way:

$$^{35}Cl^- + \overset{H}{\underset{H}{>}}C - {}^{37}Cl \rightarrow$$

$$^{35}Cl-C\overset{H}{\underset{H}{<}} + {}^{37}Cl^- \quad (25)$$
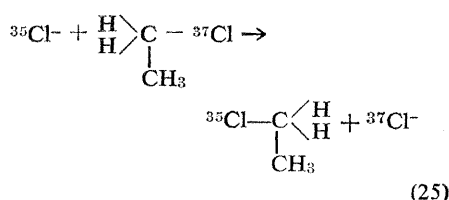
As the translational energy of the $^{35}Cl^-$ ion is increased, the rate of the exchange process first increases, then decreases. The molecular electric dipole
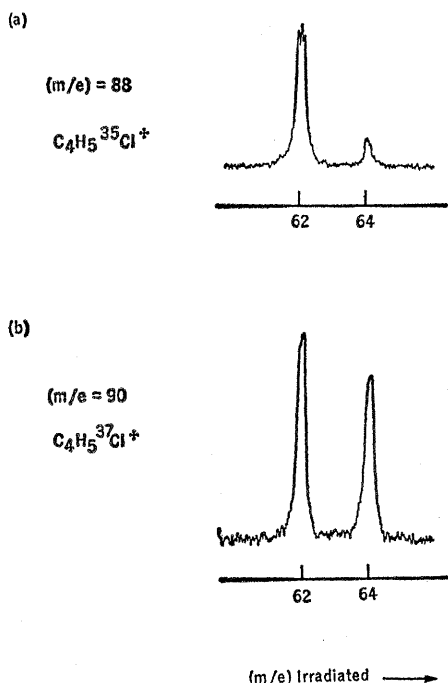
(a)

(m/e) = 88

$C_4H_5{}^{35}Cl^+$

62   64

(b)

(m/e = 90

$C_4H_5{}^{37}Cl^+$

62   64

(m/e) Irradiated ⟶

Fig. 8. Pulsed double-resonance spectra of $C_4H_5Cl^+$ at a pressure of 3×10^{-6} torr and 11-electron-volt electron energy where (a) the ^{35}Cl-containing product at mass 88 is observed and the ^{35}Cl- and ^{37}Cl-containing reactants at mass 62 and mass 64 are irradiated, and where (b) the ^{37}Cl-containing product at mass 90 is observed and the ^{35}Cl- and ^{37}Cl-containing reactants at mass 62 and mass 64 are again irradiated.
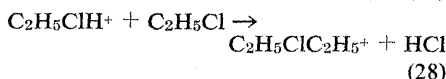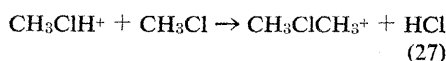
270

moment of C_2H_5Cl would favor backside attack by $^{35}Cl^-$, as suggested in Eq. 25. However, with increasing energy of the $^{35}Cl^-$, the dipolar molecule might not have sufficient time during the collision to reorient in a direction favorable for the displacement with inversion. The analogous displacement with $^{35}Cl^+$ and $^{37}Cl^+$ was not observed. It would be interesting to check the effects of steric factors on this reaction by varying the size and nature of substituents.

Alkyl Halide Positive Ions

The positive ion chemistry of the alkyl halides is very rich. For example, it is readily possible to protonate the alkyl chlorides by reactions such as

$$CH_3Cl^+ + CH_3Cl \rightarrow CH_3ClH^+ + CH_2Cl \cdot \quad (26)$$
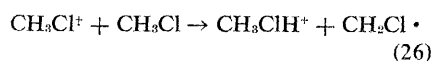
(see *23*). The protonated alkyl chloride then condenses very easily with another neutral alkyl chloride to yield a dialkyl chloronium ion, with the elimination of HCl. For example,

$$CH_3ClH^+ + CH_3Cl \rightarrow CH_3ClCH_3^+ + HCl \quad (27)$$

$$C_2H_5ClH^+ + C_2H_5Cl \rightarrow C_2H_5ClC_2H_5^+ + HCl \quad (28)$$

Although the dialkyl chloronium ions appear unusual at first, they are isoelectronic with the corresponding sulfides. Furthermore, there is some precedent for the appearance of ions of this sort as intermediates in solution reactions *(25)* and as products of rearrangements in unimolecular fragmentation following electron impact *(26)*.
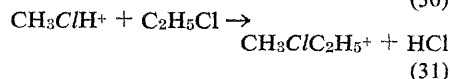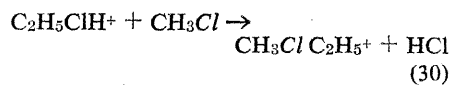
The double-resonance experiments to determine the origin of the chlorine in the ionized products in reactions 27 and 28 yield a surprise. For both reactions, the chlorine in the dialkyl chloronium ion comes with equal probability from either the reactant ion or the neutral reactant. This is not consistent with a hypothetical neucleophilic displacement of the type

$$CH_3Cl + \overset{H}{\underset{H}{>}}C-ClH^+ \rightarrow$$

$$CH_3-Cl-C\overset{H^+}{\underset{H}{<}} + HCl, \quad (29)$$
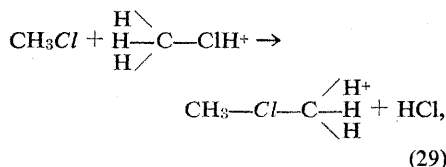
where the chlorine in the chloronium ion must come exclusively from the neutral reactant.

In mixtures of methyl chloride and ethyl chloride, the methyl ethyl chloro-

nium ion can be made by two different routes:

$$C_2H_5ClH^+ + CH_3Cl \rightarrow$$
$$CH_3Cl\,C_2H_5^+ + HCl \quad (30)$$

$$CH_3ClH^+ + C_2H_5Cl \rightarrow$$
$$CH_3ClC_2H_5^+ + HCl \quad (31)$$

In reaction 30, if the ^{37}Cl-containing product ion at mass 81 is observed while the ^{35}Cl- and ^{37}Cl-containing protonated ethyl chloride ions are irradiated, the ratio of the double-resonance signals is found to be 3:1. In reaction 31, if the ^{37}Cl-containing product is observed while the ^{35}Cl- and ^{37}Cl-containing protonated methyl chloride ions are irradiated, the ratio of the double-resonance signals is found to be 0:1. Thus it is evident that, for both of these reactions, the chlorine in the chloronium ion comes exclusively from the methyl-containing reactant. For the mixed chloronium ion, route 30 is consistent with a nucleophilic displacement mechanism:

$$CH_3Cl + \overset{H}{\underset{H}{>}}CClH^+ \rightarrow$$

$$CH_3Cl-C\overset{H^+}{\underset{H}{<}} + HCl \quad (32)$$
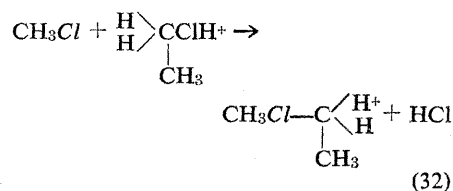
However, for route 31 the wrong chlorine atom is retained and

$$C_2H_5Cl + \overset{H}{\underset{H}{>}}CClH^+ \not\rightarrow$$

$$C_2H_5Cl-C\overset{H^+}{\underset{H}{<}} + HCl. \quad (33)$$
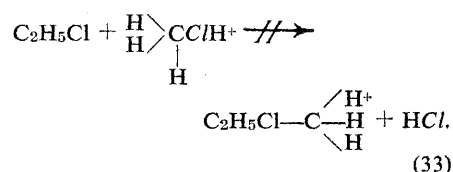
It is of course possible to write other reaction mechanisms that are consistent with the cyclotron resonance data. For example, the reaction might occur via a four-center mechanism, with the proton of the protonated alkyl halide interacting with the chlorine of the neutral molecule at long range. For low relative velocities, the molecules might remain associated for a long enough time for rearrangement to intermediates of the type
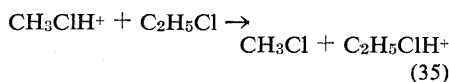
I   II
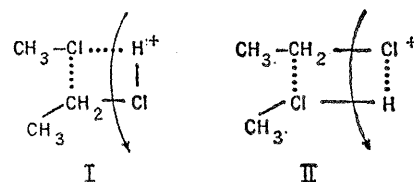
to occur, from which HCl could be eliminated, leaving the chloronium ion. It is then necessary to postulate that the methyl-chlorine bond is stronger than

the ethyl-chlorine bond, in order to get the results of reactions 30 and 31.

The above mechanism suggests that proton transfer reactions should be rapid and should compete with the formation of the dialkyl chloronium ions. Proton transfer reactions between the various methyl and ethyl chloride species can be readily investigated by cyclotron double resonance. The hypothetical reaction

$$C_2H_5ClH^+ + CH_3Cl \rightarrow$$
$$C_2H_5Cl + CH_3ClH^+$$
$$(34)$$
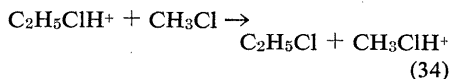
does not occur, while the reverse reaction

$$CH_3ClH^+ + C_2H_5Cl \rightarrow$$
$$CH_3Cl + C_2H_5ClH^+$$
$$(35)$$

proceeds readily. This indicates that the proton affinity of C_2H_5Cl is greater than that of CH_3Cl, and suggests that a scale of relative proton and hydrogen affinities can be readily constructed by means of double-resonance experiments with mixtures of compounds.

The ratios of the double-resonance

signals which were used to determine the origin of the chlorine atom in the product ions in reactions 30 and 31 were obtained in the limit of small amplitudes of the irradiating radio-frequency electric field. The dependence of these ratios on the amplitude of the irradiating field is shown in Fig. 10. For reaction 30, when the ^{37}Cl-containing product is observed with low radio-frequency fields, the ratio of the ^{35}Cl:^{37}Cl double-resonance signals is found to be 3:1. This ratio is practically independent of the amplitude of the irradiating field, as shown in Fig. 10, top. For reaction 31, when the ^{37}Cl-containing product is observed with low radio-frequency fields, the ratio of the double resonance signals is found to be 0:1. As shown in Fig. 10 (bottom), this ratio is strongly dependent on the amplitude of the irradiating radio-frequency field.

In the collision of a protonated ethyl chloride ion with a neutral methyl chloride, there is only one important set of products, since reaction 34 does not occur. Although the cross section for reaction 30 decreases with increasing

translational energy of the $C_2H_5ClH^+$ reactant, the isotopic specificity of the double-resonance experiment is not affected. However, in the collision of a protonated methyl chloride ion with a neutral ethyl chloride, there are two competing product channels:

$$CH_3ClH^+ + C_2H_5Cl \rightarrow$$
$$CH_3ClC_2H_5^+ + HCl$$
$$(31)$$
$$\rightarrow CH_3Cl + C_2H_5ClH^+$$
$$(35)$$
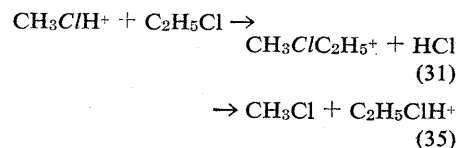
The dependence of the rates of these two competing reactions on the translational energy of the CH_3ClH^+ ion should be quite different. If the four-center intermediate suggested by structure II is a reasonable possibility, then reaction 31 should be favored at low reactant energies. The production of $CH_3ClC_2H_5^+$ requires that the intermediate stay together for a time sufficiently long for the required rearrangements to occur prior to elimination of HCl. However, reaction 35 might be described as a stripping reaction. In a high-energy collision, the light proton can be stripped from the CH_3ClH^+ ion
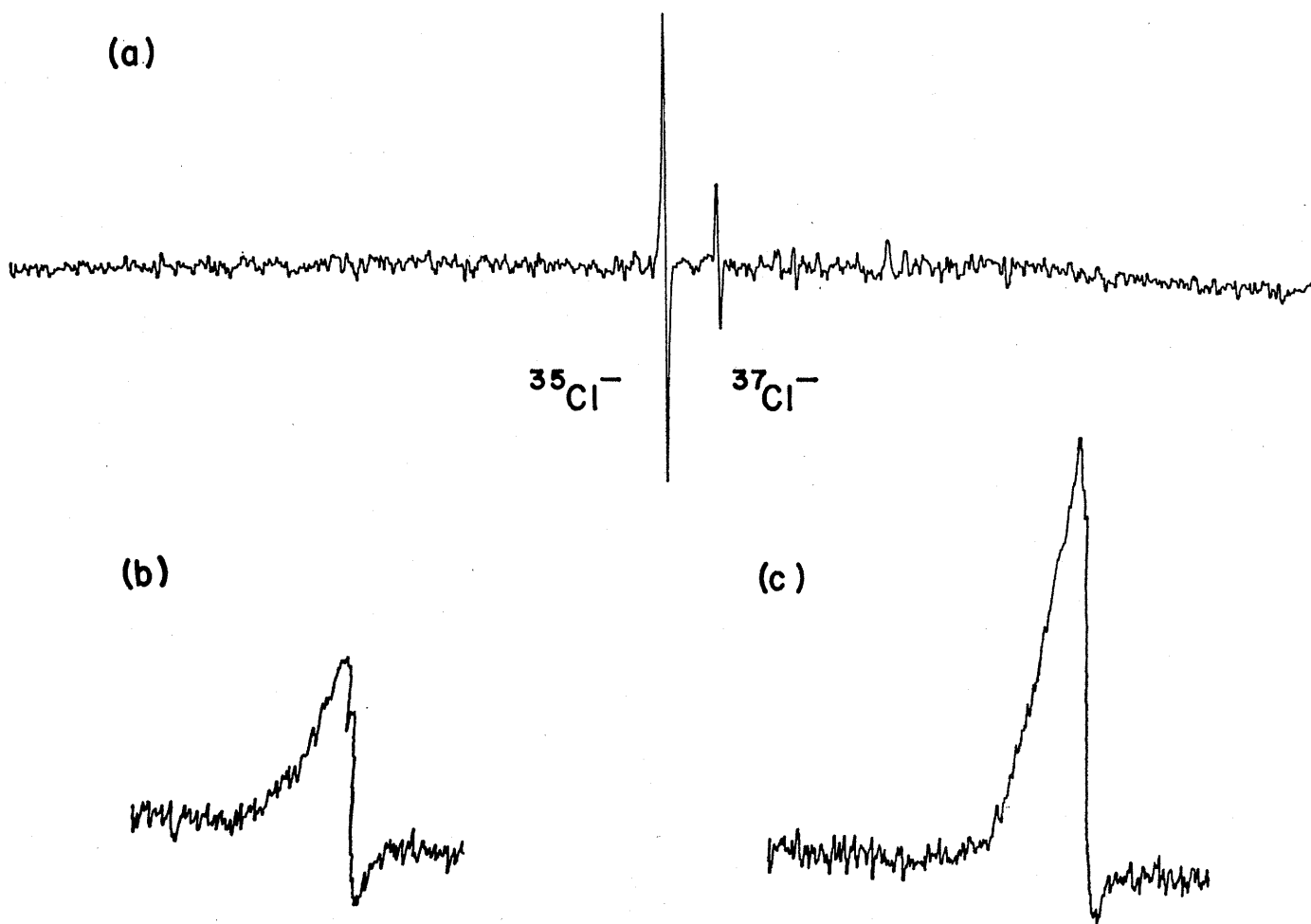
(a)

(b)

(c)

$^{35}Cl^-$ $^{37}Cl^-$

Fig. 9. (a) Negative ion-cyclotron resonance spectrum of chloroethane obtained with 11-electron-volt electrons; (b) $^{37}Cl^-$ single resonance signal with expanded scales; (c) $^{37}Cl^-$ signal observed with simultaneous irradiation at the $^{35}Cl^-$ resonance frequency.
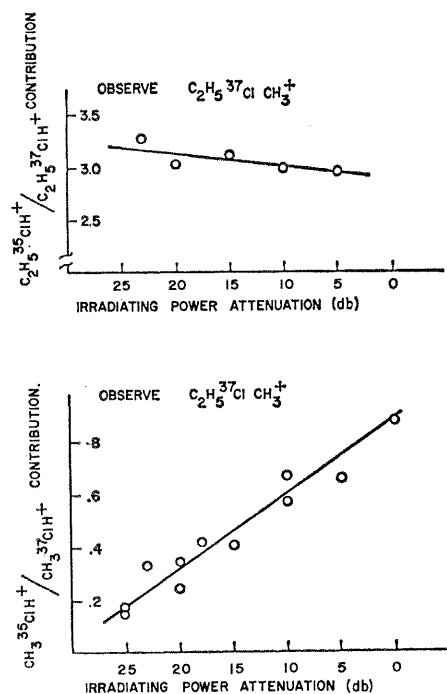
Fig. 10. Variation with irradiating power of the relative contributions of ^{35}Cl- and ^{37}Cl-containing reactant ions to the double-resonance signal of the ^{37}Cl-containing product ion for (top) reaction 30 ($C_2H_5ClH^+$ + $CH_3Cl \rightarrow CH_3ClC_2H_5^+$ + HCl) and (bottom) reaction 31 (CH_3ClH^+ + $C_2H_5Cl \rightarrow CH_3ClC_2H_5^+$ + HCl).

by a C_2H_5Cl molecule, while the massive parts of the ion continue past the target molecule in a trajectory that is practically unchanged. Reaction 35 thus should be favored over reaction 31 with increasing translational energy of the CH_3ClH^+ ion.

The stripping reaction (reaction 35) of course can transfer some translational energy to the product $C_2H_5ClH^+$, and this ion can react with another neutral CH_3Cl molecule to form the methyl-ethyl chloronium ion:

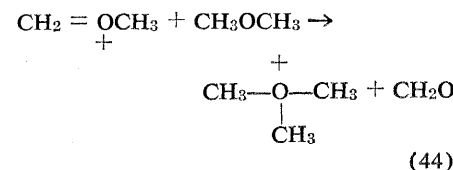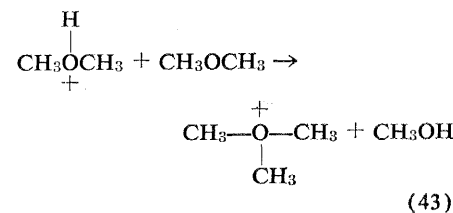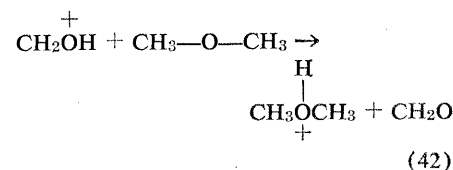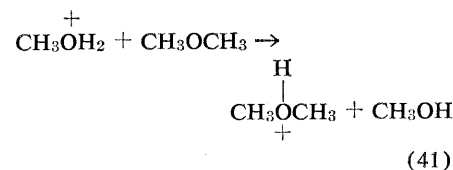$$CH_3ClH^+ + C_2H_5Cl \rightarrow$$
$$CH_3Cl + C_2H_5ClH^+,$$
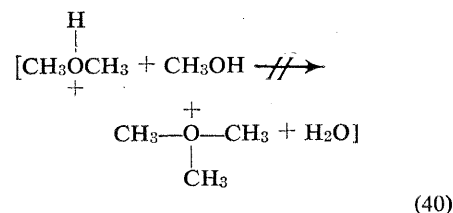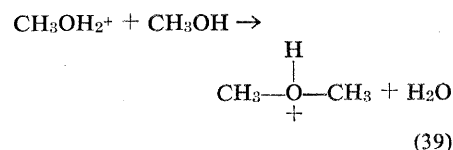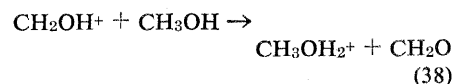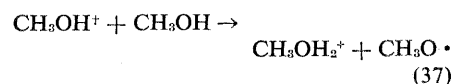$$C_2H_5ClH^+ + CH_3Cl \rightarrow$$
$$CH_3ClC_2H_5^+ + HCl \quad (36)$$
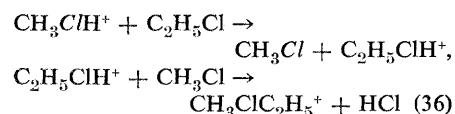
These two steps provide a sequence whereby irradiation of either isotopic component of the CH_3ClH^+ resonance will affect the intensities of the $CH_3ClC_2H_5^+$ resonances. However, the ratio of the isotopic double-resonance experiments should now be quite different from that for the single-step path of reaction 31. In the limit that reaction path 36 provides the dominant change in the $CH_3ClC_2H_5^+$ concentration when CH_3ClH^+ is irradiated, the ratio of the contributions of the ^{35}Cl-containing and ^{37}Cl-containing reactants to the ^{37}Cl-containing product should reach 3:1.

For translationally cool CH_3ClH^+, $CH_3ClC_2H_5^+$ is formed by way of reaction 31, whereas, for hot CH_3ClH^+ ions, the two-step stripping condensation sequence is probably favored.

The ion molecule chemistry of the alkyl halides is extremely rich; variation of the halide-atom and alkyl groups shows that this chemistry has many systematic features, as might be expected (23). Since tables of proton and hydrogen affinities can be readily constructed from double-resonance studies of mixtures of the halides, reactions can then be chosen for distinguishing, for example, between primary, secondary, and tertiary substituents.

The ion molecule chemistry of the alcohols is analogous to that of the alkyl halides. Some typical reactions are listed below.

$$CH_3OH^+ + CH_3OH \rightarrow$$
$$CH_3OH_2^+ + CH_3O \cdot \quad (37)$$

$$CH_2OH^+ + CH_3OH \rightarrow$$
$$CH_3OH_2^+ + CH_2O \quad (38)$$

$$CH_3OH_2^+ + CH_3OH \rightarrow$$
$$CH_3\overset{\overset{H}{|}}{\underset{+}{O}}CH_3 + H_2O \quad (39)$$

$$[CH_3\overset{\overset{H}{|}}{\underset{+}{O}}CH_3 + CH_3OH \not\rightarrow$$
$$CH_3\overset{+}{\underset{\underset{CH_3}{|}}{O}}CH_3 + H_2O] \quad (40)$$

$$CH_3\overset{+}{O}H_2 + CH_3OCH_3 \rightarrow$$
$$CH_3\overset{\overset{H}{|}}{\underset{+}{O}}CH_3 + CH_3OH \quad (41)$$

$$CH_2\overset{+}{O}H + CH_3\text{---}O\text{---}CH_3 \rightarrow$$
$$CH_3\overset{\overset{H}{|}}{\underset{+}{O}}CH_3 + CH_2O \quad (42)$$

$$CH_3\overset{\overset{H}{|}}{\underset{\overset{+}{.}}{O}}CH_3 + CH_3OCH_3 \rightarrow$$
$$CH_3\text{---}\overset{+}{\underset{\underset{CH_3}{|}}{O}}\text{---}CH_3 + CH_3OH \quad (43)$$

$$CH_2 = \overset{+}{O}CH_3 + CH_3OCH_3 \rightarrow$$
$$CH_3\text{---}\overset{+}{\underset{\underset{CH_3}{|}}{O}}\text{---}CH_3 + CH_2O \quad (44)$$

It is interesting to note that, although the trimethyl oxonium ion cannot be produced via reaction 40, it is readily synthesized by reactions 43 or 44 when dimethyl ether is used.
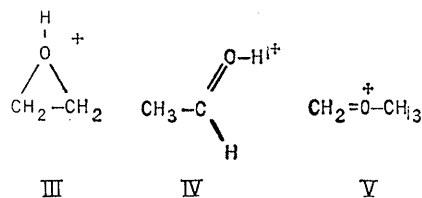
Summary

Ion cyclotron resonance spectroscopy yields information on many aspects of ion-molecule chemistry. The method is ideally suited for experiments involving ion energies below several electron volts, and hence provides a valuable complement to other techniques (27). Cyclotron double resonance is uniquely suitable for establishing relationships between reactant ions and their product ions in complex ion-molecule reaction sequences. The double-resonance experiments with isotopic species yield information on reaction mechanisms and the nature of intermediate species.

Ion-molecule reactions which occur at low energies are quite sensitive to the nature of functional groups and the details of molecular structure (28). Reactions of ions or neutral molecules with specific reagents in the cyclotron spectrometer can thus be used to characterize unknown species. Once the systematic ion-molecule chemistry of useful reagents has been worked out, it should be possible to proceed in a manner directly analogous to classical chemical methods. Suppose, for example, that reagents A^+, B^+, C^+, and D^+ each have characteristic reactions with different functional groups. Then these reagents can all be mixed with an unknown neutral species, X, and each of the reactions, $X + A^+ \rightarrow ?$, $X + B^+ \rightarrow ?$, ... can be examined. In contrast to solution chemistry, all the reagents can be added simultaneously to the unknown, since each of the specific reactions can be examined by cyclotron double resonance. The reactions which occur, the species synthesized, and the products of degradation then characterize X.

The same methodology can be applied to characterize an unknown ionic species X^+, through use of neutral reagents A, B, C, and D. For example, proton transfer reactions to neutral species have been applied in studying ions of mass 45 produced from various sources (29). The order of the proton affinities of the neutral reagent molecules are as follows: $NH_3 >$ isobutylene $>$ propene. Ions of mass 45 can be produced by the protonation of

ethylene oxide (see structure III), the protonation of acetaldehyde (see structure IV), and the fragmentation of dimethyl ether (see structure V). Those ions might be expected to have, respectively, the three structures:

$$\underset{\text{III}}{\underset{\text{CH}_2-\text{CH}_2}{\overset{\overset{\displaystyle +}{\overset{\displaystyle O}{\diagdown}}}{}}} \qquad \underset{\text{IV}}{\underset{\overset{|}{\text{H}}}{\overset{\overset{\displaystyle O-H}{\parallel}}{\text{CH}_3-\text{C}}}} \qquad \underset{\text{V}}{\overset{+}{\text{CH}_2=\overset{}{\text{O}}-\text{CH}_3}}$$

Proton transfer from the mass-45 ions from sources III and IV to NH_3 and to isobutylene occurs readily, but not proton transfer to propene. For the ion from source V, proton transfer to NH_3 occurs, but not proton transfer to isobutylene or propene. Thus the proton transfer reactions to various neutral reagents demonstrate that the mass-45 ions from the various sources are different. This example is only a rudimentary version of an approach to the characterization of unusual ionic species; more sophisticated applications can follow when the systematic chemistry of more reagents is available. This approach should be ideal for comparing nonclassical carbonium ions produced by different routes. Some very interesting ionic species are produced by rearrangements in the fragmentation of molecules, following electron impact. Such molecular rearrangements frequently result in the fragmentation of an ion radical to another ion radical with the elimination of a small neutral species (30). It should be possible to run these reactions in reverse to check the postulated mechanisms.

An interesting result of the systematic study of proton transfer to various functional groups is the finding that the proton affinity of various amines and pyridine is extremely high (31). Species such as VI and VII:

$$\underset{\text{VI}}{\text{RNH}_3{}^+} \qquad \underset{\text{VII}}{\overset{+}{\text{HN}}\text{—}\langle\text{ }\rangle}$$
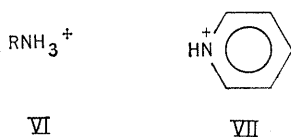
might be expected to be very stable; they are in fact so stable that they are unreactive with respect to subsequent chemistry at the charge center. Thus, if there are other functional groups on the ion, the important reactions should occur at these functional groups. It should be possible to design species for which the presence of the charge has little influence on the reactivity

19 JANUARY 1968

of a neutral functional group. In this case the charge functions simply as an inert label which makes the study of neutral-neutral reactions accessible by cyclotron resonance:

$$\overset{+}{\text{HN}}\langle\text{ }\rangle\text{—R}+\text{R}'\longrightarrow\overset{+}{\text{HN}}\langle\text{ }\rangle\text{—R}''+\text{R}''' \qquad (45)$$
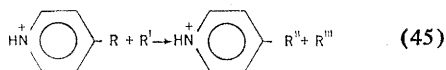
Various routes for development of the basic technique also appear to be very promising. Echo phenomena following sequences of pulsed excitation have been observed in electron cyclotron resonance (32). Analogous transient phenomena should also occur in ion cyclotron resonances (33). Pulsed-cyclotron-resonance techniques of course have intriguing analogies to nuclear-magnetic-resonance spin-echo experiments (34) and may be the technique of choice for making accurate measurements of ion-molecule-reaction cross sections as a function of energy for low ion energies.

Finally, many ion-molecule reactions yield products in excited electronic states (35). For example, the reaction

$$N_2{}^+ + CO \rightarrow N_2 + CO^+ \qquad (46)$$
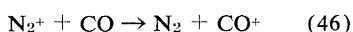
has been studied by beam techniques (36). A straightforward procedure is to observe optical emission from the cyclotron spectrometer by placing a window at the end of the cyclotron cell (37). The emission can be analyzed with a crude set of optical filters, or with a high-speed spectrograph. Optical emission from the cyclotron cell can of course originate from many sources. The radiation from a specific excited product ion can be selected by a radio-frequency-optical double-resonance experiment. If, in the general reaction

$$A^+ + B \rightarrow {}^*C^+ + D, \qquad (47)$$
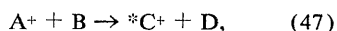
ion A^+ is irradiated at its cyclotron resonance frequency, the number density of optical emitters $^*C^+$ is changed. If the irradiating frequency is modulated, then the number of optical emitters will be modulated, so that the intensity of emission from $^*C^+$ will also be modulated. When the optical emission from $^*C^+$ is analyzed in a spectrograph with a photoelectric cell, the output of the photoelectric cell can be detected with a phase-sensitive detector referenced to the modulation frequency. This highly specific modulation-detection scheme should discriminate against other sources of light in the cyclotron cell.

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