

Letters to the Editor

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Communications

Ion-Cyclotron Double Resonance*

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A CHARGED particle moving in a uniform magnetic field \mathbf{H} describes a circular orbit in a plane perpendicular to \mathbf{H} with an angular frequency or "cyclotron frequency" ω_c . When an alternating electric field $\mathbf{E}(t)$ is applied normal to \mathbf{H} at ω_c , the ions absorb energy from the alternating electric field, and are accelerated to larger velocities and orbital radii.¹ The absorption of energy from $\mathbf{E}(t)$ at the cyclotron resonance frequency can be conveniently detected using a marginal oscillator detector. When the ions accelerated by $\mathbf{E}(t)$ collide with other particles, they lose some of their excess energy. A mixture of ions and neutral molecules in the presence of \mathbf{H} and $\mathbf{E}(t)$ then reaches a steady-state condition in which the energy gained by the ions from $\mathbf{E}(t)$ 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 $\mathbf{E}(t)$, the collision frequency, and the efficiency of energy transfer upon collision. Since the width of a cyclotron-resonance absorption line depends on the number of collisions per unit time, an analysis of cyclotron-resonance line shapes can yield cross sections

and energy-transfer efficiencies for ion-molecule collisions.²

A phenomenological equation similar in form to the Bloch equation for magnetic-resonance absorption³ provides a useful basis for the description of ion-cyclotron-resonance line shapes.⁴ Line shapes derived from this equation of motion are consistent with line shapes for rare-gas ions observed as a function of pressure and $\mathbf{E}(t)$.^{1,5} When a mixture of several ion components as well as neutral species is present in a cyclotron resonance experiment, the equations of motion for each ion in the mixture can be coupled by a variety of interesting processes including charge transfer and chemical reaction. It is possible to calculate the detailed cyclotron-resonance line shapes in the presence of charge transfer⁴ and chemical reactions; the resulting formalism has an intriguing analogy to the coupling of the equations of motion of magnetic species in NMR and *WSR* by various exchange processes.⁶

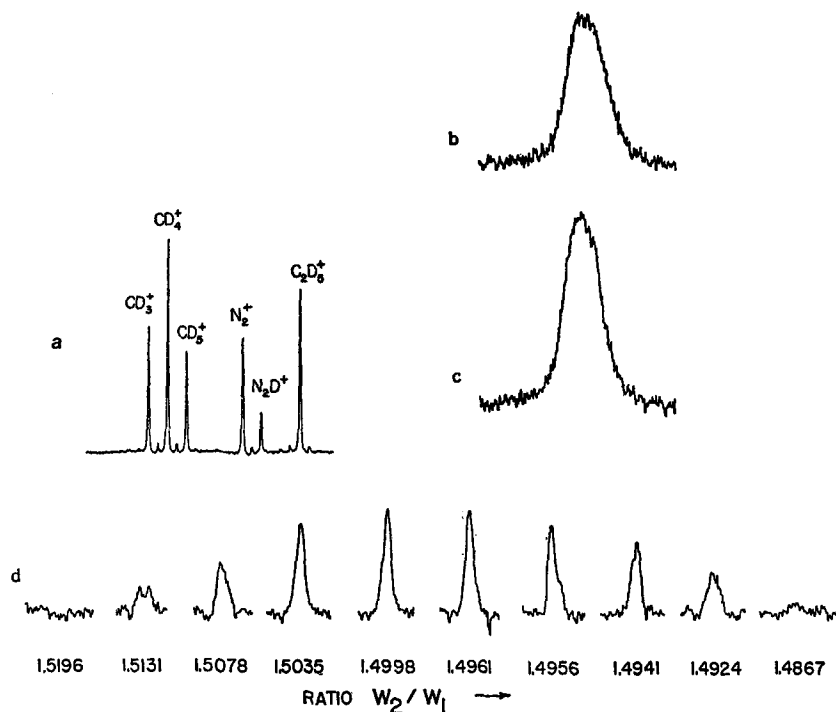
If the equations of motion of different ionic species are coupled by charge transfer or other types of ion-molecule reaction, it should be possible to demonstrate this coupling by multiple-cyclotron-resonance techniques. Ion-molecule collision cross sections are strongly dependent on the relative ion-molecule velocity. Thus, if one type of ion is heated with a strong rf electric field $\mathbf{E}_2(t)$ at frequency ω_2 , then substantial changes should occur in the concentrations and temperatures of other ion components in equilibrium with the irradiated ion. These changes in line shape and intensity can be observed with a weak rf electric field $\mathbf{E}_1(t)$ at frequency ω_1 .

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. Of perhaps greater interest, however, are ion-molecule reactions which produce unusual chemical species. Shannon and Harrison⁷ have shown for example that species such as N_2D^+ can be produced from mixtures of CD_4 and N_2 in a mass-spectrometer ion source. These same species can be readily observed with the cyclotron-resonance technique.

The single-resonance ion-cyclotron spectrum of a mixture of CD_4 and N_2 is shown in Fig. 1(a). In addition to the parent ions CD_4^+ , N_2^+ , the fragment CD_3^+ and the products of various ion-molecule reactions CD_6^+ , N_2D^+ , and C_2D_6^+ are apparent. These reaction products disappear as the total pressure is reduced. However, N_2D^+ does not disappear even when the ionizing electron energy is reduced below the threshold for N_2^+ production. This suggests that the reaction $\text{N}_2 + \text{CD}_4^+ \rightarrow \text{N}_2\text{D}^+ + \text{CD}_3$ is important for the production of N_2D^+ .

A double-resonance effect for this reaction is illustrated in Figs. 1(b) and 1(c). The N_2D^+ single resonance observed with $\omega_1 \cong 285.5$ kc/sec is shown in Fig. 1(b). The N_2D^+ cyclotron resonance observed with

FIG. 1. (a) Single-resonance ion-cyclotron resonance spectrum of a mixture of CD_4 and N_2 at about 2×10^{-5} torr obtained by sweeping the magnetic field with field increasing from left to right and $\omega_1 = 285.5$ kc/sec. The linewidths (full width at half-height) are about 20 G. (b) Field-sweep single-resonance spectrum of the N_2D^+ peak with expanded scales. (c) Field-sweep double-resonance spectrum of the N_2D^+ resonance with continuous irradiation at the CD_4^+ cyclotron-resonance frequency, where $\omega_1 \cong 285.5$ and $\omega_2 \cong 425.5$ kc/sec. (d) Field-sweep pulsed-cyclotron double-resonance spectra for a series of fixed values of ω_2/ω_1 . The magnetic field increases from left to right for each trace. The mass ratio of $N_2D^+/CD_4^+ = 1.4968$.



strong irradiation of the CD_4^+ ion with $\omega_2 \cong 425.5$ kc/sec is shown in Fig. 1(c). Significant changes in the N_2D^+ intensity and line shape occur.

If E_2 is periodically pulsed and the signal at ω_1 is detected with a phase detector referenced to the pulsing frequency, then the difference between the single- and double-resonance spectra is directly displayed. Only those products that are coupled to the irradiated species by chemical reaction will appear in the pulsed double-resonance spectrum. A series of field sweep spectra of the CD_4 - N_2 mixture for various fixed values of ω_2/ω_1 is shown in Fig. 1(d). 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 $N_2D^+/CD_4^+ = 1.4968$.

It is evident that ion-cyclotron resonance has practical interest as a technique for the direct study of ion-molecule reactions and that multiple-resonance methods will be very useful in identifying specific ion-molecule reactions in complex mixtures.

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Electric Dipole Moment for First- and Second-Row Diatomic Hydride Molecules, AH^*

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THE electronic dipole moments μ have been calculated for the ground electronic states of LiH, BeH, BH, CH, NH, OH, and HF of the first-row and NaH, MgH, AlH, SiH, PH, SH, and HCl of the second-row diatomic hydride molecules. These results are based on Hartree-Fock-Roothaan wavefunctions in which the molecular orbitals $\varphi_{i\lambda\alpha}$ are believed to be identical to the Hartree-Fock molecular orbitals to probably three decimal places. The wavefunctions employed and a discussion of their quality are presented in forthcoming papers.¹ The electronic configurations, $R_e(\text{exptl})$ values, and the calculated dipole moments (also shown in Fig. 1) are given in Table I. Experimental values are known for only five of these molecules, and they are also given in Table I.

The good agreement of the calculated dipole moments with the five experimental values is encouraging. In each case the calculated values are larger in absolute