

Ion Cyclotron Resonance and the Determination of Collision Cross Sections*

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It is shown that the ion cyclotron resonance absorption line in weakly ionized gases may be interpreted to obtain e/m ratio, the number, and the collision frequency of the ions. From the observed linewidths, the collision frequencies of several ions are found as a function of pressure and electric field strength. From these data the ion-molecule collision cross section for N_2^+ and Ar^+ in their parent gases are found to be 125 and 140 \AA^2 , respectively, at high E/p and 185 and 215 \AA^2 , respectively, at low E/p . Observed absorption and dispersion line shapes fit closely the Lorentz line shape derived theoretically with the assumption of constant mean free time. The measurement chamber consists of an ion source and drift region in a strong magnetic field within which a transverse rf electric field may be applied. A narrow band, derivative-type system is used to detect the power absorption as a function of frequency.

I. INTRODUCTION

MANY instruments make use of the principle that a charged particle will absorb energy at its cyclotron frequency. Few instruments, however, use this principle to study the low energy interactions characteristic of gaseous electronics. The experimental technique described here was developed to study ion-molecule interactions in a weakly ionized gas at or near thermal energies.¹

The method of producing and detecting ions used is similar to that employed in the omegatron,² especially the version which uses ion cyclotron resonance absorption as the ion detector.³ The main difference is that the ion production region and measurement regions are not separated in the omegatron. In addition, the omegatron is operated under conditions (low pressure, high rf fields, presence of trapping voltage) which do not allow ion-molecule reactions to be studied.

Observations of free-ion cyclotron resonance in a low-density plasma have recently been reported by Buchsbaum.⁴ His measurement technique, however, was intended to study ions in high concentrations and as such would be too insensitive to detect ions in a weakly ionized gas. Many of the complicating factors associated with ion cyclotron resonance in a plasma such as limited penetration of the electric field and the "hybrid resonances" caused by strong ion-electron interactions are not present in a weakly ionized gas. Free-ion cyclotron resonance absorption such as observed by Buchsbaum should not be confused with the rf power absorption in a plasma due to damping of the ion cyclotron wave.⁵ Cyclotron resonance has also been observed for electrons

produced in flames,⁶ and by microwave breakdown in gases,⁷ and by free electrons (and holes) in solids.⁸

The cyclotron resonance absorption mechanism can be described simply as follows. Suppose an ion is placed in a strong magnetic field. It is constrained by this field to move in a helical path, a combination of translation along a field line and a circular motion in a plane perpendicular to the direction of the magnetic field. The motion along the magnetic field is the same as if the field were not present and the circular motion in the plane can be considered independent of its translation along the field lines. It is easily shown that the angular cyclotron frequency, that is, the angular frequency of this circular motion (ω_b) in a magnetic field (B) is equal to eB/m independent of the ion velocity. A N_2^+ ion has a cyclotron frequency, $\omega_b/2\pi$, of 170 kc/sec at 3000 G. The radius of its orbit (\bar{v}/ω_b) is about 0.4 mm at thermal velocities. All ions with the same polarity move with the same sense of rotation.

Suppose now a linearly polarized rf electric field is applied to the region containing the ions, with the direction of the electric field perpendicular to the magnetic field. This linear rf electric field may be considered to be composed of two circularly polarized fields with opposite senses of rotation. If the frequency of the applied field is at the ion cyclotron frequency, the circular component having the same sense of rotation as the ion will cause it to be continuously accelerated until it happens to collide with a neutral molecule or with the walls. This process results in an extraction of energy from the electric field and a corresponding heating of the gas. Since little energy loss occurs unless the applied electric field has a frequency at or near the cyclotron frequency, this absorption is referred to as an ion cyclotron resonance absorption. A small amount of power absorption can occur due to the circular component which has the

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¹ J. R. Graham, Jr., D. P. Malone, and D. C. Wobshell, *Bull. Am. Phys. Soc.* **7**, 69 (1962); **8**, 444 (1963).

² H. Sommer, H. A. Thomas, and J. A. Hipple, *Phys. Rev.* **82**, 697-702, (1951); **76**, 1877 (1949); **78**, 806 (1950); **80**, 487 (1950).

³ N. I. Leont'ev, *Instr. Exptl. Tech. (U.S.S.R.)* **5**, 788 (1961).

⁴ S. J. Buchsbaum, *Bull. Am. Phys. Soc.* **6**, 388 (1961); *Phys. Rev. Letters* **5**, 495 (1960); *Phys. Today* **15**, 32 (1962).

⁵ T. H. Stix and R. W. Palladino, *Phys. Fluids* **3**, 641 (1960).

⁶ E. M. Bulewicz, *J. Chem. Phys.* **36**, 385 (1962); K. D. Bayes, D. Kivelson, and S. C. Wong, *ibid.* **37**, 1217 (1962).

⁷ A. D. MacDonald and S. C. Brown, *Phys. Rev.* **75**, 411 (1949). Also see S. C. Brown, *Basic Data of Plasma Physics* (John Wiley & Sons, Inc., New York, 1959), Chap. 5.

⁸ B. Lax and J. G. Mavroides, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 11, p. 261.

opposite sense of rotation. This power loss is the same as though no magnetic field were present except that the effective frequency (as seen by the ion) is twice the applied frequency and the effective field strength due to this component is half that of the linear applied field. This loss mechanism can be neglected if the collision frequency is much less than the cyclotron resonance frequency.

Each species of ion can thus be identified, since it will show an absorption only at its cyclotron frequency. From the intensity of absorption, the number of ions in the chamber can be found. It is also possible to obtain quantitative determinations of collision cross sections through a determination of linewidths. This latter aspect will be emphasized in this paper.

II. COLLISION BROADENED LINES

The dominant ion cyclotron resonance line broadening mechanism is that of collision of the ions with neutral gas molecules. In this section, a derivation of the absorption and dispersion line shapes will be given. The derivation given here proceeds by finding the equation of motion of an average ion in a strong steady magnetic field and under the influence of a perpendicular rf electric field. Since the moving ion corresponds to an electric current, the power absorption and dispersion can be found by forming the product of the ion current density and the electric field intensity.

Let the dc magnetic field (**B**) be in the *z* direction and the electric field (*E*₀ sin ω*t*) be in the *x* direction. The equation of motion for an ion of mass (*m*), a charge (*e*), and a velocity (**v**) undergoing *ν*_{*c*} collisions/sec with molecules of mass (*M*) is

$$m\dot{\mathbf{v}} + \frac{mM}{M+m} \nu_c \mathbf{v} = e[\hat{x}E_0 \sin \omega t + \mathbf{v} \times \mathbf{B}]. \tag{1}$$

The velocity (**v**) may be interpreted as the nonrandom part of the total velocity of an average ion. The second term in Eq. (1) represents the rate of momentum loss of the average ion through collisions with the neutral molecules.⁹ This representation assumes that the scattering is isotropic in the center-of-mass system and that the mean free time between collisions is constant. If these assumptions are not valid this term must be multiplied by a constant factor (usually within a factor of two of unity) and the collision frequency for momentum transfer must be substituted for *ν*_{*c*}. More generally, then, the coefficient multiplying the momentum in the second term of Eq. (1) is not *ν*_{*c*}*M*/(*M*+*m*) but by a constant defined as the "reduced collision frequency" (*ν*₀). This reduced collision frequency is the collision frequency an ion would have if it lost all its nonrandom velocity (in the laboratory system) each collision. For isotropic scattering and constant mean free time, *ν*₀

= *Mν*_{*c*}/(*M*+*m*). Its meaning under other conditions will be discussed later.

Defining the cyclotron resonance frequency, ω_{*b*} ≡ *eB*/*m*, and noting that *B* is the *z* direction, Eq. (1) reduces to

$$\dot{\mathbf{v}} + \nu_0 \mathbf{v} = \hat{x}[(eE_0/m) \sin \omega t + \omega_b v_y] - \hat{y} \omega_b v_x. \tag{2}$$

The steady state component of the ion current due to *n* ions in the *x* direction (*I*_{*x*} = *n**e**v*_{*x*}) has both an in-phase and a quadrature component. The in-phase term gives rise to power absorption and the quadrature gives rise to dispersion. The power absorption (*A*), averaged over time, is given by

$$A(\omega) = \langle EI_x \rangle = \frac{P_0}{1 + [(\omega - \omega_b)/\nu_0]^2} + \frac{P_0}{1 + [(\omega + \omega_b)/\nu_0]^2}, \tag{3}$$

where

$$P_0 = ne^2 E_0^2 / 4m\nu_0. \tag{4}$$

The dispersion (*D*) is

$$D(\omega) = -\frac{P_0 [(\omega - \omega_b)/\nu_0]}{1 + [(\omega_b - \omega)/\nu_0]^2} - \frac{P_0 [(\omega_b + \omega)/\nu_0]}{1 + [(\omega_b + \omega)/\nu_0]^2}. \tag{5}$$

If the lines are narrow (ω_{*b*} ≫ *ν*₀), as they are for most cases of interest, the second term of Eqs. (3) and (5) can be neglected. Equation (3) then takes the form of the usual Lorentzian line shape. For this line shape, the half-width at half-maximum (Δω_{1/2}) is simply related to the reduced collision frequency (*ν*₀) by

$$\nu_0 = \Delta\omega_{1/2}. \tag{6}$$

The total number of ions (*n*) within the volume in which the electric field is applied is given by

$$n = \frac{m\nu_0 P_0}{e^2 (E_0/2)^2}, \tag{7}$$

where *P*₀ is the peak power absorption at ω = ω_{*b*}.

In Figs. 1 and 2, the line shapes predicted by Eqs. (3) and (5) (solid lines) are fitted to experimentally observed data points. These experimental lines were obtained by numerically integrating the recorder curves

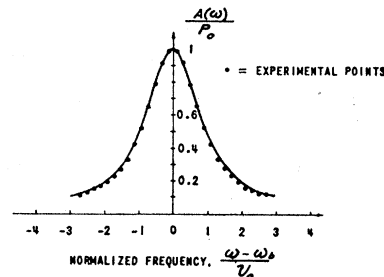
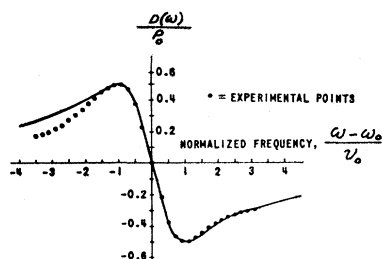


FIG. 1. Ion cyclotron resonance absorption line. Data points were found by integrating the points indicated in Fig. 5 and normalizing. Solid line is theoretical shape as predicted by Eq. (3).

⁹ L. G. H. Huxley, Australian J. Phys. 13, 718 (1960).

FIG. 2. Ion cyclotron resonance dispersion line. Data points were found by integrating the points indicated in Fig. 6 and normalizing. Solid line is theoretical shape predicted by Eq. (5).



which, as will be discussed in Sec. III, correspond to the derivative of the absorption and dispersion lines. It can be seen that the observed points can be fitted to the Lorentz line shape fairly well. Small deviations from the Lorentz line shape can be accounted for by systematic equipment error.

A derivation of the collision broadened electron cyclotron resonance line shapes has been given by Kelly, Margenau, and Brown.¹⁰ Their results are the same as those derived here if the collision frequency in their formulas is replaced by the reduced collision frequency (ν_0). Not only is their derivation somewhat more rigorous than that given here but they have derived the line shape assuming constant mean free path and a $1/\nu$ cross section, as well as constant mean free time. They found that the line shapes near the region of peak absorption are much the same with these different assumptions.

From the preceding discussion, it can be seen that the observation of lines that can be closely fitted to the Lorentz line shape does not necessarily imply that the assumption of constant mean free time is valid. Very precise shape determinations would be needed to prove this point. But the assumption of constant mean free time is not critical to the approximate discussion given here. By fitting the observed line by a Lorentz shape, the best (constant) value of ν_0 given by Eq. (2) is chosen. Thus, ν_0 is an effective, momentum-weighted, constant mean-free-time collision frequency in the laboratory system and is as well defined as other types of collision frequencies.

There are, of course, line broadening mechanisms other than the elastic collision of ions with neutral molecules. Collisions of the ions with the walls are important, especially at lower pressures. The effects of collisions with the walls can be reduced by proper equipment design (Sec. III) or taken into account during data reduction (Sec. IV). If molecules with which the ions can react chemically are present in high concentrations, it may be possible for these inelastic collisions to affect the total collision frequency. Relatively few reactions however are fast enough to have an appreciable effect. Collisions with electrons or other ions

have a negligible effect on the total collision frequency if the gas is weakly ionized. A strong space charge, however, can shift the ion cyclotron resonance frequency³ or, if it is nonuniform, broaden the line. The ion and electron concentrations actually used were too low to expect an appreciable effect. Line broadening due to magnetic field inhomogeneities was negligible for these experiments.

III. THE ION CYCLOTRON RESONANCE SPECTROMETER

Central to the success of the ion cyclotron resonance absorption technique is the design of the spectrometer. One of the most important requirements is that the mean free path of the ion be sufficiently long so that the ion makes a number of revolutions before colliding. If this is not done, the line will become too broad to observe. For good mass resolution, the line width $\Delta\omega_{1/2}$ should be of the order of $3 \times 10^{-3}\omega_b$ but if little resolution is required, a width as high as $0.3\omega_b$ can be tolerated. For a given ion, in the region where pressure broadening dominates, the relative line width, $(\Delta\omega_{1/2}/\omega_b)$, is set by the ratio of pressure to the magnetic field strength. If the pressure is low, the mean free path is limited by the length of the chamber along the magnetic field lines. The design procedure is to pick a chamber length much longer than the mean free path at the desired operating pressure and then to set the magnetic field high enough to obtain the desired resolution. In most cases, high resolution can be achieved only by using a long, high field solenoid but moderate resolution is possible using a standard electromagnet.

Figure 3 shows schematically the measurement chamber together with the ion source. This part of the apparatus was placed in a vacuum chamber between the pole pieces of an electromagnet (3300 G, 4-in. diam, 2-in. gap). It was oriented so that the electron beam, after passing through the entrance hole, followed the lines of force into the electron collector. Many of the ions which are created along the electron path can diffuse around the electron collector tube into the measurement chamber. Electron diffusion around this obstacle is much smaller because the diffusion is transverse to the mag-

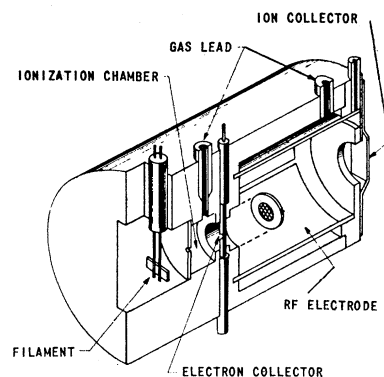


FIG. 3. Sketch of measurement chamber. Apparatus was placed in vacuum vessel between the pole pieces of an electromagnet.

¹⁰ D. C. Kelly, Margenau, and S. C. Brown, *Phys. Rev.* **108**, 1367 (1957). Also see F. C. Fehsenfeld, L. R. Megill, and F. R. Dippleman, *Bull. Am. Phys. Soc.* **8**, 444 (1963).

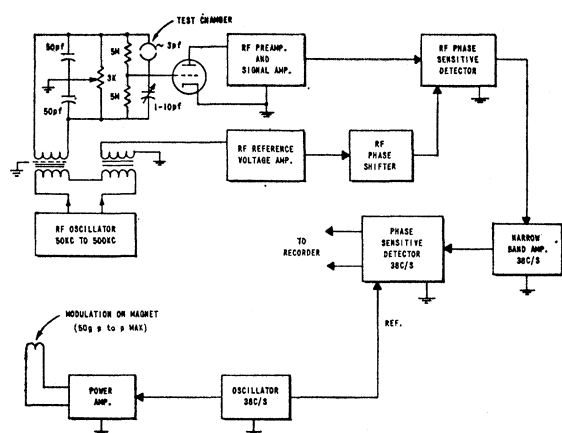


FIG. 4. Block diagram of derivative detection system.

netic field. It is estimated that the electron concentration in the measurement chamber is one or two orders of magnitude less than the ion concentration. Although the performance of this ion source is adequate for the present study, it would not be satisfactory for any studies where recombination or electron attachment reactions are important.

The measurement chamber consists of a quartz tube (2 cm long, 2-cm diam) with two gold electrodes shadowed on the inside. The rf electric field produced by these electrodes is nearly uniform near the axis of the tube. The ion collector electrode is located at the end of the chamber. Before a run it is operated with a negative potential and used to monitor the ion current. During a run it is operated at a positive potential so that the electron concentration in the measurement chamber does not build up. A suppressor screen (not shown in Fig. 3) operated at +15 V and located between the filament and entrance hole was used to reduce space charge.

The method of detecting the power absorption is basically the same as the method used in the derivative-type nuclear magnetic spectrometer and the electron cyclotron resonance spectrometer used for solid state studies.⁸ A block diagram of the electronics is shown in Fig. 4. The rf electrodes in the measuring chamber form one arm of an rf bridge. Any unbalance of this bridge is amplified and detected by the rf phase sensitive detector. This detector can be adjusted to respond to either

the absorption or dispersion signal by changing the phase of reference voltage. The audio frequency signal from this rf phase sensitive detector is further amplified and detected by a second phase sensitive detector synchronized with the modulation frequency. The output on the second detector is displayed on a time base recorder. Since the frequency is being swept with time, the recorder displays the derivative of the power absorption or dispersion as a function of frequency. Frequency sweep rather than magnetic field sweep was used because the diffusion of ions into the measurement chamber was sensitive to the magnetic field.

Figures 5 and 6 show selected recorder curves of the absorption and dispersion, respectively. These data have been normalized and corrected for the frequency response of the equipment. The solid line in Fig. 5 is the derivative of the Lorentz line shape [Eq. (3)] matched to the peaks of the experimental derivative curves. Similarly, the solid line of Fig. 6 is the derivative of Eq. (5) matched to the cross over points of the observed curves. The experimental curves in Figs. 5 and 6 were integrated numerically to obtain the curves presented in Figs. 1 and 2. Line widths were found by measuring the peak-to-peak frequency separation of the observed absorption derivative curves and multiplying by $\pi\sqrt{3}$, which is the ratio of the half-width (in angular frequency) at half maximum for the Lorentz line shape to the distance between the points of maximum slope.

An attempt was made to check the magnitude of the power absorption, that is, the factor P_0 in Eq. (4). Unfortunately, the ion concentrations could not be accurately determined from the ion current, so P_0 was verified only to within an order of magnitude. It is estimated that the minimum detectable number of ions is about 10^3 , corresponding to a concentration of about 10^8 ions/cc in this apparatus. Most measurements were taken at concentrations which were about 100 times higher. It is felt that considerably lower ion concentrations can be detected with a larger measurement chamber, particularly if high values of E_0 can be tolerated.

It was found that it was necessary to outgas the measurement chamber only to 10^{-4} to 10^{-5} Torr. If this was not done, the line intensities and symmetries were affected, but the linewidths were only slightly affected. The ion cyclotron resonance method therefore appears to be quite insensitive to impurities, at least in this instance. Most gaseous electronics experiments require much better initial vacuums even though they are

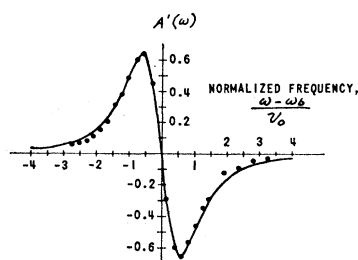


FIG. 5. Absorption line derivative trace. This recorder trace of the derivative of the absorption line and the trace of Fig. 6 have been redrawn to compensate for equipment errors.

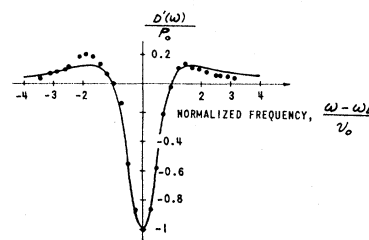


FIG. 6. Dispersion line derivative trace.

usually carried on at higher pressures. In this experiment, reactions with impurities (e.g., charge exchange) will reduce the number of desired ions; however, these reactions will not appreciably affect the collision frequency of the ions unless the impurity concentration approaches that of the desired neutral gas molecules. Actually, an ion suffers at most 10 to 100 collisions before it hits the wall and so has little chance to react with impurities.

Design and construction details of the equipment have not been given here although the equipment is novel enough to warrant this. Rather it is intended that the details of an improved apparatus now under construction be published when completed.¹¹

IV. ION-MOLECULE COLLISION CROSS SECTIONS

It has been shown in Sec. II that the collision frequency can be found from line width measurements. In this section the measured reduced collision frequency (ν_0) for several ions as a function of pressure will be given and the results used to calculate the ion-molecule collision cross section (σ).¹²

The collision cross section is related to the collision frequency (ν_c) by the formula

$$\nu_c = N\sigma\bar{g} = N\sigma\bar{c}(1+m/M)^{1/2}, \quad (8)$$

where \bar{g} is the average speed of the ions with respect to the molecules, \bar{c} is the average speed of the molecules, and N is the number of molecules per cm³. The relation between \bar{g} and \bar{c} given above holds only if the ions are in thermal equilibrium with the molecules.¹³ In terms of

TABLE I. Collision cross sections for ions in their parent gases (\AA^2).

Ion	Ion cyclotron resonance		Dc mobility	
	Low E/p	High E/p	Low E/p	High E/p
N_2^+	185 ± 30	125 ± 30	...	123
Ar^+	215 ± 40	140 ± 40	194	134
O_2^+	150^a	$70^a \pm 30$	154	79

^a Tentative data.

the reduced collision frequency (ν_0), the cross section is given by

$$\sigma = \nu_0(1+M/m)^{1/2}/N\bar{c}. \quad (9)$$

For thermal ions in their parent gases ($m=M$) at 300°K,

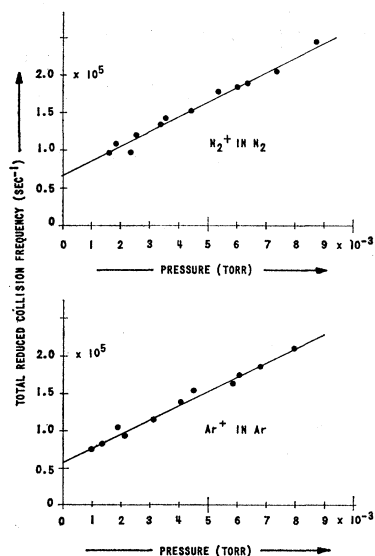
$$\sigma = 1.75 \times 10^{-6} m^{1/2} (\nu_0/p), \quad (10)$$

where p is the pressure in Torr, m is in atomic mass units, ν_0 is in sec⁻¹, and σ is in \AA^2 .

Figure 7 shows a plot of "total reduced collision frequency" of several ions in thermal equilibrium with their parent gases as a function of pressure. The "total reduced collision frequency" includes the effects of collisions of the ions with the walls. This gives rise to a "zero pressure line width" approximately equal to $2\bar{c}/L$, where L is the length of the measurement chamber. It is assumed that the contribution of the zero pressure line width is linearly additive, a characteristic of Lorentz lines.¹⁴ Thus, the slope of the lines in Fig. 7, rather than the absolute value of the collision frequency, is of fundamental significance. By substituting these slopes into Eq. (10), "low E/p " cross sections listed in Table I were found.

Thus far, it has been assumed that the electric field, or more precisely E/p , is so small that the energy gained between collisions is much less than kT . Actually, E/p was not particularly small, nor was it constant in any of these experiments. It is desirable, therefore, to consider the variation of collision frequency with E/p in order to justify the procedure used to determine the cross sections at low E/p . More important, it is possible to determine the cross sections at high E/p also. Figure 8 illustrates the variation of total collision frequency of

FIG. 7. Total collision frequency as a function of pressure for several ions. The total collision frequency is equal to the observed line-width as explained in the text. The slopes were used to calculate the cross sections at low E/p . The range of E/p is from 5 to 50 V-cm⁻¹-Torr⁻¹.



¹¹ This equipment has been built and has confirmed most of the results given here.

¹² The symbol for the cross section (σ) should not be confused with the impact parameter $(\sigma/\pi)^{1/2}$.

¹³ S. Chapman and T. G. Cowing, *Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, New York, 1952),

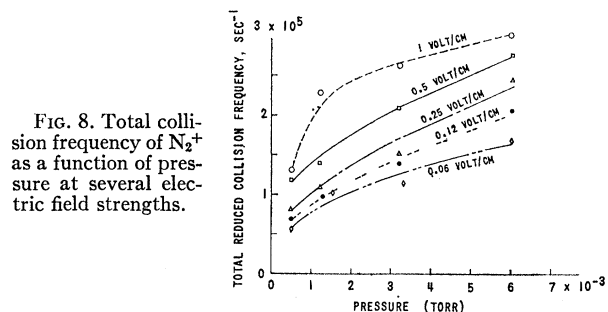


FIG. 8. Total collision frequency of N_2^+ as a function of pressure at several electric field strengths.

2nd ed.; or see E. A. Guggenheim, *Elements of the Kinetic Theory of Gases* (Pergamon Press Inc., New York, 1960).

¹⁴ D. G. Hughes and D. K. C. MacDonald, Proc. Phys. Soc. (London) 78, 75 (1961).

N_2^+ in N_2 with pressure at various electric field strengths. In order to analyze these data, however, it is necessary to draw upon the results of dc mobility experiments and theory. The mobility (μ) is related to the collision frequency by the formula^{9,15}

$$\mu = e(M+m)/v_e M m = e/mv_0. \quad (11)$$

This relation, like the derivation in Sec. II, assumes constant mean free time between collisions and should be valid at arbitrary E/p .

Consider first the functional form of the variation of collision frequency with E/p . The mobility of many ions has been found empirically to obey the relation; $\mu/\mu' = (1+AE/p)^{-1/2}$, where μ' is the mobility at $E/p=0$ and A is an empirical constant.¹⁶ Although more precise mobility measurements reveal a more complicated variation, this relation is accurate enough for the data to be analyzed here. Using Eqs. (11) and (12), the collision frequency may be approximated by

$$v_0 \simeq v_0'(1+AE/2p), \quad AE/2p \ll 1, \quad (12)$$

where v_0' is the reduced collision frequency at $E/p=0$. Notice that the second term on the right side of Eq. (12) gives an intercept rather than a change in slope on a graph of v_0 against p such as Fig. 7 or 8. Thus if E , rather than E/p , is held constant on such a graph, the slope ($\Delta v_0/\Delta p$) is automatically extrapolated to $E/p=0$.

The empirical relation represented by Eq. (12) while useful in analyzing the extrapolation procedure, does not allow one to compute the cross section at high E/p . An exact theory of the variation of linewidth (or collision frequency) with electric field is unavailable and only a very approximate theory will be given here. Wannier^{17,15} has derived theoretically a relation between drift velocity and E/p at high E/p assuming constant mean free path. For hard sphere interactions, the drift

velocity of ions in their parent gases is equal to $1.147(a\lambda_0)^{1/2}$, where $\lambda_0=1/N\sigma$ is the center-of-mass mean free path and $a=eE/m$ is the acceleration of the ion. In terms of the collision frequency [using Eq. (11)]:

$$v_0 = 1.53 \times 10^{+6} (E p \sigma / m)^{1/2} + v_0'. \quad (13)$$

Here the peak effective field (E) is in V/cm, the gas pressure (at 300°K) is in Torr, the mass (m) is in atomic units, and the cross section (σ) in Å².

The effective electric field (E) must be taken as half of the peak amplitude of the applied rf field (E_0) because only one circularly polarized component is effective in accelerating the ion. Actually, the effective value of electric field (E) varies over the absorption line and, consequently, the line is no longer Lorentzian. However, it happens that the points of maximum slope occur at about the same value of ω as if the E (and v_0) were constant and had the same value as at $\omega=\omega_0$ (i.e., $E=E_0/2$). Thus, v_0 can be found from the peaks at the derivative curves (e.g., Fig. 5) using the same procedure as previously given.

As Fig. 9 shows, the observed collision frequency does increase as $E^{1/2}$ at high E/p if the pressure is held constant. As before, only the slopes of the lines are significant. These slopes are also proportional to $p^{1/2}$ at higher pressures. If, however, the pressure is so low that the mean free path is longer than the chamber length, Eq. (13) is no longer valid, nor is the quantity E/p meaningful. The average ion apparently must collide with the molecules at least two or three times before its random energy approaches the value it would have after many collisions. Figure 10 illustrates this point. Here the slopes taken from Fig. 9 are plotted against $p^{1/2}$. Only at higher pressures do these slopes approach a straight line as Eq. (13) predicts. This asymptotic straight line is assumed to have a slope of $1.53 \times 10^{+6} (\sigma/m)^{1/2}$. It is from data similar to this that the high E/p cross sections were calculated.

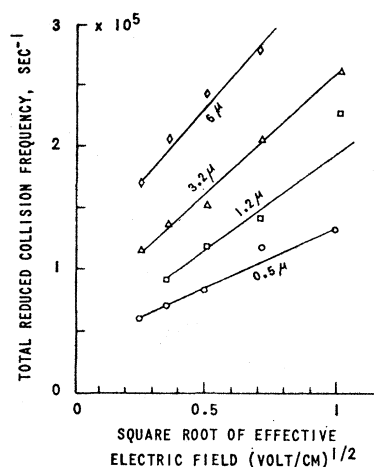


FIG. 9. Total collision frequency of N_2^+ as a function of the square root of the effective electric field at several pressures. The effective field (E) is half of the peak amplitude of the applied rf electric field (E_0).

V. DISCUSSION

It is informative to compare the cross sections determined by ion cyclotron resonance with those found by dc mobility measurements.¹⁸⁻²¹ Although the ion cyclo-

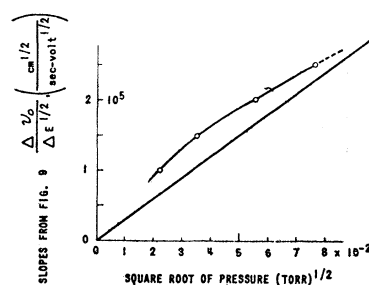


FIG. 10. Slopes from Fig. 9 plotted against the square root of pressure. The slope of the asymptotic straight line was used to compute the collision cross section at high E/p .

¹⁵ W. P. Allis, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 21, especially pp. 423-426.

¹⁶ L. S. Frost, *Phys. Rev.* **105**, 354 (1957).

¹⁷ G. H. Wannier, *Phys. Rev.* **83**, 281 (1951). Also see G. Wannier and J. A. Hornbeck, *ibid.* **82**, 458 (1951).

¹⁸ J. A. Hornbeck, *Phys. Rev.* **83**, 374 (1951); **84**, 615 (1951).

¹⁹ R. N. Varney, *Phys. Rev.* **89**, 708 (1953); F. R. Kovar, D. C. Beatty, and R. N. Varney, *ibid.* **107**, 1490 (1957).

²⁰ M. A. Biondi and L. M. Chanin, *Phys. Rev.* **94**, 910 (1954); **106**, 473 (1957).

²¹ E. C. Beatty, in *Proceedings of the Fifth International Con-*

tron resonance and dc mobility methods of determination of cross sections differ in experimental technique, both methods are basically similar in that both measure drift velocity. Equation (11) can be used to relate fairly accurately the dc mobility and the reduced collision frequency [as found from the ion cyclotron resonance line width according to Eq. (6)] even though, in fact, the mean free time is not constant. This is because the consistent assumption of constant mean free time is made in the derivation of both Eqs. (3) and (11). Thus, the cross sections determined by these two methods should agree; if they do not, the difficulty should lie in the experiments rather than the theory. Langevin's formula²² together with Eq. (11), for example, should predict the cyclotron resonance linewidth almost as accurately as it does the mobility.

Table I shows the cross sections found from ion cyclotron resonance compared with those determined by mobility studies. The high E/p cross sections given by Varney and Hornbeck are "hard sphere" cross sections which are presumably due to charge exchange. The low E/p cross sections are larger because of polarization effects. They were computed from the published "zero field" mobilities^{19,21} using Eqs. (11) and (8). As Table I indicates, the agreement between the dc mobility and ion cyclotron resonance cross sections is well within experimental error. These cross sections should not be given too literal an interpretation in terms of a hard sphere radius, not only because velocity dependent polarization forces are present at low E/p , but because the assumption of constant mean free time may not be correct.

ference on Ionisation Phenomenon in Gases, Munich, 1962 (North-Holland Publishing Company, Amsterdam, 1962), p. 183; *Phys. Rev.* **104**, 17 (1956).

²² For a discussion of Langevin's equation, see L. B. Loeb, *Basic Process of Gaseous Electronics* (University of California Press, Berkeley, 1955). Langevin's equation predicts, in the limit of hard sphere interactions, that $\mu = 0.75e(M+m)/Mmv_e$ and, thus, our "hard sphere" cross sections would be about 25% too high.

The results for N_2^+ at low E/p are particularly interesting. Varney was able to determine the cross section of N_2^+ only at high E/p because N_4^+ predominated at low E/p . In our experiments, N_4^+ ions were not present in appreciable amounts because the total number of collisions was too small, but even if they were present, the inherent mass resolution would allow cross sections of each ion to be determined independently. Clusters and reactions with impurities likewise would have little effect on the ion cyclotron resonance results. The equivalent "zero field" mobility for N_2^+ is $1.85 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$, in reasonable agreement with the theoretical value predicted by Langevin's formula ($2.17 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$), as calculated by Varney.¹⁹

The good agreement between the cross sections determined here at both high and low E/p and those found from dc mobility studies confirms the line width theory developed here and, to some extent, the dc mobility theory and experiments. It is important to realize that, since the ions reported here are definitely identified through their e/m ratio, the identities of many ions studied by dc mobility methods are likewise confirmed.

Unfortunately, the data reduction technique which must be used to eliminate the effect of "zero pressure broadening" does not allow one to plot the collision frequency or cross section density as a function of E/p . This is not an inherent limitation of the ion cyclotron resonance method, but a consequence of the undesirably short measurement chamber. On the contrary, it is felt that an instrument capable of measuring collision frequencies with a precision of 1% and at values of E/p several orders of magnitude lower than employed here would be quite feasible.

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