GENERAL ATOMIC

DIVISION OF GENERAL DYNAMICS

GA-4322

CHARGE EXCHANGE REACTIONS

by

Wade L. Fite

June 17, 1963

GENERAL ATOMIC

DIVISION OF

GENERAL DYNAMICS

JOHN JAY HOPKINS LABORATORY FOR PURE AND APPLIED SCIENCE

P.O. BOX 608. SAN DIEGO 12. CALIFORNIA

GA-4322

CHARGE EXCHANGE REACTIONS

by

Wade L. Fite

June 17, 1963

CHARGE EXCHANGE REACTIONS

Wade L. Fite
General Atomic Division of General Dynamics Corporation
John Jay Hopkins Laboratory for Pure and Applied Science
San Diego, California

ABSTRACT

This paper reviews the processes wherein the charges on two colliding particles are altered and on the experimental methods used to study these processes. In the high energy range, a comparison is made between the equilibrium beam method of determining neutralization and stripping cross sections and the slow ion detection methods used to study charge transfer. Thermal energy reactions which have been studied using afterglow mass spectrometers are reviewed and the results of various laboratories are compared. After summarizing outstanding problems pertaining to charge exchange reactions, some consideration is given to the effects of these reactions in other mass spectrometer applications.

I. INTRODUCTION

The term "charge exchange" is used somewhat ambiguously in the literature, ranging in meaning from any heavy particle collision process whereby the charge of one of the colliding particles is altered, down to the simple process known increasingly frequently in present-day literature as "charge transfer" or "electron transfer". In this review, major attention will be given to the charge transfer process which can be written down in terms of an ion, A^+, colliding with a heavy neutral particle, B, by

$$A^+ + B \rightarrow A + B^+ + \Delta E \tag{1}$$

where ΔE is the energy defect of the process (which in the simplest case is just the difference between the ionization potentials of A and B).

Viewing this process as a simple electronic transition, the general considerations of quasi-adiabatic theory of Massey[1] for inelastic heavy particle collisions obtain. In brief summary, these considerations hold that at low relative velocities between the colliding particles, the perturbation of the neutral particle by the passing ion changes sufficiently slowly that no electronic transition is excited. In consequence, at low relative velocities, the cross section is small. At the other extreme, that of high initial relative velocity, the time of interaction is sufficiently small that the transition does not occur readily. Intermediate to these extremes, the transition probability and the cross section reach a maximum value which occurs at a relative velocity, v_{max}, given by

$$v_{max} \approx \frac{a|\Delta E|}{h} \tag{2}$$

where h is Planck's constant and a is a length of atomic dimensions. For the case of charge transfer, Hasted[2] has found that a $\cong$ 8A seems to fairly well fit a large number of processes involving singly-charged ion processes.

More detailed theoretical treatment of charge transfer has been carried out by a number of authors, and reviews by Hasted[2] and Bates[3] can be recommended as general background reading. In addition, the fact that a theoretical review is given at this meeting by Donald Rapp[4] justifies directing our attention in this paper to the experimental aspects of charge transfer and other charge changing processes.

II. HIGH ENERGY CHARGE TRANSFER

The basic physical quantity of interest in charge transfer is the cross section as a function of energy. It is evident from Massey's formula (Eq. (2)) that for energy defects of a few ev, the ion energies at which maximum cross sections would be expected are of the order of kev, and most charge transfer measurements have been made with energies of this general magnitude. Customarily the ions have been made in an appropriate ion source, magnetically analyzed, accelerated and then permitted to pass through a gas target. In a simple charge transfer reaction such as (1), there are clearly three signals readily available for experimental use: (a) fast atom signals, (b) fast ion signals, and (c) slow ion signals; all three have been used in different experimental approaches. In most cases of interest, the charge transfer cross section is much larger than the cross section for scattering of the fast particle through an appreciable angle, so that to very good approximation, charge transfer leaves the trajectories of the two colliding heavy particles

unaltered -- only the transfer of an electron from one particle to the other occurs.

A. Fast Particle Detection

One commonly used experimental method is based on an analysis made by Wien[5] over half a century ago. It involves the use of thick gas targets and detection of fast particles. We consider here the simple case where a fast particle can be either neutral or singly ionized.

As an A^+ ion beam enters a gas of particles B at a number density n, electron capture occurs (cross section σ_{10}) and the beam becomes a mixture of fast ions and fast neutrals. The neutrals are subject to electron stripping (cross section σ_{01}), so that if we designate the fraction of fast particles which are ionized as F_1 and the fraction of fast neutrals as F_0, then

$$dF_1/dx = n(\sigma_{01}F_0 - \sigma_{10}F_1) \tag{3}$$

and

$$F_1 + F_0 = 1. \tag{4}$$

If the target is sufficiently thick, dF_1/dx approaches zero and the beam achieves equilibrium fractions of the charge states. From Eqns. (3) and (4) it follows that the equilibrium fraction of the singly charged state is

$$F_{1\infty} = \frac{\sigma_{10}}{\sigma_{01}+\sigma_{10}} \tag{5a}$$

$$F_{0\infty} = \frac{\sigma_{01}}{\sigma_{01}+\sigma_{10}} \tag{5b}$$

and it can be shown that measurement of F_1 and F_0 as a function of the product nx yields the relationships

$$\sigma_{10} = \frac{F_{1\infty}}{nx} \log_e \frac{1-F_{1\infty}}{1-F_1(nx)} \tag{6a}$$

$$\sigma_{01} = \frac{F_{0\infty}}{nx} \log_e \frac{1-F_{0\infty}}{1-F_0(nx)} \tag{6b}$$

Similar relationships can be deduced by analogous arguments for cases where the charge states are more than two in number.

A typical piece of apparatus for measurements of these "electron capture and loss cross sections" is shown in Fig. 1. This is the apparatus of Stier and Barnett[6], who used fast beam detection for the study of collisions between light ions and gases. A beam from an accelerator entered the apparatus from the top and was partially neutralized in the neutralizer. After the mixed beam entered another region of high vacuum, the electrostatic analyzer (No. 1) was used to deflect the remaining charged particles in the fast beam enough so that they would not enter the small aperture in the experimental chamber itself. A fully neutralized beam entered the apparatus. After emergence from the collision chamber, the charged particles in the beam could again be deflected at will by an electrostatic analyzer (No. 6) before the fast particle beam was detected. By varying the pressure in the collision chamber and by proper use of the electrostatic analyzers, all data could be obtained to determine separately the cross sections for the various charge changing processes affecting the fast particle beam.

Figure 2 shows some of the results obtained by Stier and Barnett for the case of a fast beam of protons and hydrogen atoms interacting with H_2 (left hand graph) and He (right hand graph). Because the negative hydrogen ion H^- exists, the cross sections σ_{-10} and σ_{0-1} for stripping and forming H^- are shown in addition to the positive ion cross sections.

With regard to the positive ion charge transfer, two features are particularly appropriate to point out. The first is that the electron capture cross sections σ_{10} display peaks as suggested by the near-adiabatic theory arguments and at energies of the order of several kev. In addition, the velocity of the peak for p + H_2 is substantially lower than that for p + He, just as would be expected in view of the energy defects for the processes being about 2 and 11 ev, respectively, again in accordance with Eq. (2). The second point of interest is that the electron capture cross sections near the peak values are as large as or larger than the actual atomic sizes. Clearly the total cross section for electron capture derives its magnitude from electrons transferring from one atom to another when the atoms are substantially separated in distance. Equally obviously, there are many values of impact parameter between the colliding particles that

contribute to the total cross section.

In regard to impact parameter, it is particularly interesting to examine a different type of electron capture and loss experiment, with detection of the fast particles, which has been carried out in recent years by Everhart and his associates[7] at the University of Connecticut. In these experiments a beam of ions is directed at a thin target of gas, and particle detection is made at a few degrees off the axis of the fast beam. From classical mechanics it is clear that a given small range of angle of detection must be associated with a very limited range of impact parameters. Further, it can be shown that the impact parameter must be much smaller than the atomic dimensions. Basically the collisions are those in which the nuclei interact to give the angular deflection, so that the ion passes through the target gas particle; and effectively only one impact parameter is under study at a time.

Everhart and his associates have concentrated their attention on the fractions of emerging fast particles which are in various charge states, and most interesting results, in this case for protons colliding with hydrogen atoms and molecules, are shown in Fig. 3. The oscillatory nature of the probability of neutralization as a function of initial ion energy gains more significance when a plot of the capture probability as a function of inverse velocity is plotted, as is done in Fig. 4. It is seen on this plot that the oscillations are quite regular.

Since the inverse velocity is a measure of the time of interaction of the two colliding particles, Fig. 4 shows that the electron, in the resonant case of p + H collisions, actually oscillates between one proton and the other. Such behavior is predicted by quantum mechanical arguments presented by Firsov,[8] Bates,[9] and other theoreticians.[10] Oscillatory behavior between particles where resonance is not obtained is also predicted and has been studied by the Connecticut group.

The oscillatory behavior is not generally seen in total charge transfer measurements, since a particular oscillatory pattern is associated with a given value of impact parameter, and all impact parameters contribute to the total cross section. The separate oscillatory patterns are thus averaged out.

B. Slow Particle Detection

Experiments which detect the production of slow ions in collisions between fast ions and slow neutrals have perhaps seen more usage for the study of charge transfer. Here there is some ambiguity between charge transfer and ion-impact ionization, both of which yield slow ions; however, the two processes can be separated by virtue of the fact that ionization also yields a slow electron. Hence, in measuring slow particles for studying charge transfer, both electrons and ions must be measured and both the ionization and the charge transfer cross sections are obtained.

The usual experimental arrangement involves taking an analyzed ion beam and passing it through a collision chamber containing a thin target of gas. Either all slow ions are measured (say to a pair of condenser plates such as were used as electrostatic analyzers in Stier and Barnett's apparatus), or mass spectrometric detection of the slow ions can be employed. An alternative method is to run the gas target as a beam and let the ion beam cross the neutral beam.

In either case, in the slow ion detection method where thin targets are used, the cross section is obtained from the formula

$$\frac{dI_B}{dx} = Q \, n_B \, I_A \tag{7}$$

where I_A is the primary current of A^+ ions, $\frac{dI_B}{dx}$ is the current of ions B^+ produced per unit path length of I_A through the gas of number density n_B, and Q is the total cross section for slow ion production (or charge transfer after correction has been made for ionization of B particles by the fast ion beam).

Figure 5 shows a block diagram of a crossed beam experiment for charge transfer measurement, this particular one being selected because it has been used to measure the total cross section for p + H charge transfer,[11,12] which was the case for which data from Everhart were presented to illustrate the oscillatory nature of charge transfer. This apparatus, which was used at General Atomic to study hydrogen atom charge transfer, takes a beam from a furnace source, modulates the beam mechanically, and then crosses it with the fast ion beam. Slow ions are collected either by a total ion collector or in the mass spectrometric detector shown. The modulation is interposed in order to distinguish charge transfer with beam particles as opposed to charge transfer with the background gas in the vacuum chamber. The beam signals are ac at the modulation frequency, and the background gas gives rise to dc signals which can be separated electronically.[13]

Results for p + H charge transfer are given in Fig. 6, and the experimental data are compared with several theoretical calculations for this process. Of particular interest is the absence of a peak in this cross section curve. This is expected, however, because of the fact that the process is fully resonant. Not only is there no energy defect, but the ions, both before and after, are identical -- they are single protons.

Figure 7 shows another total cross section curve, in this case for $H^- + H$ charge transfer, which is also a symmetric process. The purposes in showing this curve are two: first, to illustrate the fact that charge transfer occurs with negative as well as positive ions, and second to illustrate that resonant charge transfer has a cross section depending on energy as

$$Q^{1/2} = A - B \log E.$$

This energy dependence is quite predictable theoretically and the comparison of the prediction of Dalgarno and McDowell[14] is seen to be quantitatively quite satisfactory.

These two cases represent an extremely simple situation where the process is fully resonant. We have seen in the data of Stier and Barnett the case of two non-resonant processes, $p + H_2$ and $p + He$. Yet, a third general case in charge transfer is that of "accidental resonance", by which it is meant that the energy defect is zero but the two ions are not chemically identical. Considerable interest accrues to these cases and in passing it is of interest to consider Fig. 8. This figure[15] shows two resonant cases, $H^+ + H \to H + H^+$ and $O^+ + O \to O + O^+$, and two accidentally resonant cases, $O^+ + H \to O + H^+$ and $He^{++} + H \to He^+(n=2) + H$. It is seen that over the energy range examined the $O^+ + H$ charge transfer appears to be resonant but that the $He^{++} + H$ process does not, despite the fact that $He^+(n=2)$ and H have identical ionization potentials. The important point in connection with accidental resonance is that the effective energy defect is not necessarily the infinite separation energy defect; that the effective energy defect should be thought of as the difference in energy between the two quasi-molecular states at the internuclear separation at which the charge transfer actually occurs. Illustrating this point, as the He^{++} and H approach, forming a quasi $(He^{++}H)$ molecule, polarization of the H by the He^{++} makes a weakly attractive force between the two. As the two separate after the charge transfer, coulomb repulsion in the quasi (He^+H^+) molecule is operative. The potential energy which has to be added at the separation at which the electron transfer takes place can be thought of as the effective energy defect, which, in the case of $He^{++} + H$ charge transfer is of the order of 7 ev. By similar arguments, one would expect that at very low energies the $O^+ + H$ charge transfer might no longer appear resonant. The differences in the polarizabilities of the H and O atoms would introduce a small energy defect at separations at which the electron transfer could occur and at the lowest relative velocities there would be insufficient perturbation to excite the electronic transition over this small energy defect.

The cases which have received the major experimental attention are those involving no resonance whatever. Reviews such as are given in references 2, 16, 17, and 18 and a compilation of charge transfer cross section measurements assembled by O. Heinz and E. J. Feinler[19] summarize excellently almost all of the results which were obtained up to about 1960. Generally speaking, the non-resonant charge transfer results are rather similar to those given in Fig. 2 and in Fig. 9 and extend to lower energies the results for $H^+ + H_2$ charge transfer.

Figure 9 is also presented here for a second reason -- to illustrate some of the remaining problems in higher energy charge transfer measurement. This figure treats the inverse processes, $p + H_2 \rightleftarrows H + H_2^+$. One would expect on the basis of detailed balancing that these two processes would have similar cross section curves when plotted as a function of relative velocity. Although Fig. 9 is a plot on the basis of energy rather than velocity, it is clear that the data of Fite, Brackmann, and Snow[11] on $H_2^+ + H$ give much larger cross sections at lower energies than would be expected. Presumably the differences arise because of uncertainty of the actual states of both the reactants and the products. In the forward reaction, for example, the state of the H_2^+ is unknown, although at these low energies the H must almost certainly be in the groundstate. In the inverse reaction there is no assurance that the H_2^+ from the ion source used gave these ions in the same states as were produced in the forward reaction. Likewise there is no assurance that the resulting H_2 in the inverse reaction was in the groundstate, although the H_2 reactant in the forward reaction certainly was.

What is being said here basically is that if we are to retain our present conceptions of the charge transfer process, it is necessary to ascribe discrepancies such as are evident in Fig. 9 to uncertainty as to the internal energy states of the particles participating in the charge transfer collision.

Perhaps the point can be further illustrated by reference to Fig. 10, which compares the results of various laboratories on the charge transfer between N_2^+ ions and N_2. While

the same overall features of the cross section curve are forthcoming from the various data, there are serious discrepancies in the results -- far greater than differences in carefulness would seem to warrant. It is fairly obvious to hypothesize that much of the difference between the results lies in the fact that the various laboratories used different sources of the N_2^+ ions and that the populations of the ion states differed from laboratory to laboratory. Some evidence is already being gathered in various laboratories to support this hypothesis. Utterback,[20] for example, has recently examined charge transfer of O_2^+ on N_2 using a controlled electron bombardment source for the O_2 and has found that the charge transfer cross section curve at low ion energies depends strongly on the electron energy used to produce the O_2^+ ions. Presumably such shifts in the charge transfer curve could arise only from differences in population of states of the O_2^+ ions produced by electrons of different energies. Similar experiments have been carried out in other laboratories, and indeed the discussion of J. W. McGowan[21] at this meeting bears very strongly on this point. Clearly, further investigation of the effects of initial ion states in charge transfer collisions will constitute a major direction for research in heavy particle collisions in the immediate future.

In addition to concern with initial states of the reactants, another rather recent direction for charge transfer collision experimentation involves determination of the final states of products. In these researches, detection of excited products has been made spectroscopically for the most part. Kistemaker and his associates[22] have used a grating spectrometer in conjunction with otherwise conventional apparatus to detect the states of both neutral and ionic products in heavy particle collisions, and similar experiments involving excitation of the Balmer series when using hydrogenic ions have been carried out at the University of Arkansas. Experiments by Dunn, Geballe, and Pretzer[23] have used iodine-vapor-filled photon counters[24] to detect Lyman-α production in collisions of protons with various gases, and experiments to study both charge transfer and excitation into both the 2S and 2P states in collisions of protons and atomic hydrogen are now under way using crossed beam techniques at General Atomic. Perhaps this last case will be of particular value in comparing experiment with the theory of charge transfer into excited states, for the p + H collisions have received the most detailed theoretical treatment.

Unquestionably, in the area of high energy charge transfer, the role of internal energy in the reactants and the products is the major enigma at present.

III. LOW ENERGY CHARGE EXCHANGE

Experiments on charge changing collisions which employ ion beams begin to fail as the energy of the colliding particles is reduced, primarily because of space charge effects which limit ion currents and generate serious sensitivity and signal-to-noise problems. In combination with this fundamental problem, such practical problems as imperfections in ion-optical systems and the fairly broad energy spreads associated with most ion sources make the experimental approaches using ion beam techniques highly unattractive at energies less than a few ev.

In order to reach the thermal energy range, where heavy particle collision data are needed for several important applications, other experimental techniques must be employed. One of these, which has seen a great amount of service for several decades, involves the measurement of mobilities of positive ions in gases in drift tube experiments. Actually the measured mobility can be related only to a total collision cross section, it has long been known that the mobilities of ions in their parent gases are substantially lower than in other gases. This observation has been explained in terms of resonant charge transfer, for which the cross section is not only large but also always produces an ion starting from rest after the collision. For resonant and near resonant charge transfer, mobility measurement continues to offer an excellent experimental method.

An entirely different technique which has seen service in at least three laboratories[25, 26, 27] involves the mass-spectrometric monitoring of afterglows. In this technique, a mixture of gases is placed in a confined volume and this mixture is then weakly ionized by a pulse of rf power or other means. After cessation of the pulse, the positive ions are fairly representative of the gases placed in the afterglow volume. As time elapses, however, the ions undergo collisions with the neutral gas molecules and both ion-atom interchange and charge exchange occur to effect a change in the relative populations of the ions. Placing a small aperture in the afterglow chamber allows the ions diffusing to the walls to be extracted, accelerated, and mass analyzed. The analyzed ion currents which are observed then indicate the different ion-neutral collision processes which are occurring in the afterglow, and the time histories of the detected ion currents give an index to the rates at which the processes proceed.

Figure 11 shows a diagram of such an experiment, this being one in use at General Atomic.[26] The apparatus is basically a bakeable, 60° magnetic sector mass spectrometer whose source is an afterglow chamber rather than a conventional electron bombardment source. Gas is introduced into the chamber at the right and it is excited either by a pulse of rf

power or by a pulse of electrons from the General Atomic Linear Electron Accelerator (40 mev). Ions then leave the afterglow chamber through the pinhole and are accelerated and focussed by the ion lenses. Not shown in the figure is a small electron gun placed just outside the afterglow chamber which can be used to electron-impact-ionize neutral gas escaping through the pinhole. By use of this gun, the partial pressures of gases in the afterglow chamber can be determined. The time constant of the electron multiplier used to detect the analyzed ions and its associated circuitry was made less than 1 microsecond so that quite rapid reactions can be followed with the instrument.

Figure 12 shows an overlap of oscilloscope traces observed with a 100:1 mixture of $N_2:O_2$ where the excitation was provided by a pulse of relativistic electrons from the linear accelerator. No other ions in significant quantities were observed. This figure would seem to indicate that the two major processes occurring in the afterglow are the ion-atom interchange process, $N^+ + O_2 \rightarrow NO^+ + O$, and the charge exchange process, $N_2^+ + O_2 \rightarrow N_2 + O_2^+$. Both processes appear to have very similar rates.

Before discussing further the experimental methods and results, it is appropriate to digress briefly to emphasize that in this section the words "charge exchange" rather than "charge transfer" are being used. It is to be noted that in the $N_2^+ + O_2$ process given above, the infinite separation energy defect for the groundstates is about 3 ev. Recalling that where there is an energy defect a sharp perturbation is required to effect an electronic transition, and that at thermal velocities the relative motions of the particles are insufficient to produce a sharp perturbation, it would seem that the $N_2^+ + O_2$ process yielding O_2^+ cannot be "charge transfer" in the sense of a collision-induced electronic transition if all particles are in or near their groundstates.

There is a certain appeal to considering the process yielding O_2^+ in the afterglow to be one of accidentally resonant charge transfer where the states of the resulting O_2^+ and N_2 are excited so as to make the effective energy defect be zero. While this interpretation would preserve the concept of the process still being one of "charge transfer", considerations of the type applied by Bates and Lynn[26] to the case of accidental resonance as opposed to true resonance in charge transfer between atoms would lead one to question this interpretation.

It would appear to this reviewer that perhaps the basic physics of thermal processes such as those that lead to O_2^+ production in collisions between N_2^+ and O_2 is not yet properly identified. It is in deference to this opinion that the whole question about the physics involved will be begged by continuing to use in this section the general term "charge exchange" rather than the more specific "charge transfer".

Returning to the matter of results from afterglow mass spectrometer experiments, there have been two methods used to obtain rate coefficients from ion history curves such as are shown in Fig. 12. In the first method, attention is directed toward the rate of decay of a single primary ion, after it has been determined that only one type of secondary ion appears to be associated with the loss of the primary ion (e.g., in the case of the charge exchange results of Fig. 12, it appears that O_2^+ only is generated by decaying N_2^+, so attention would focus on the decay of N_2^+). After the plasma density has dropped to where electron-ion recombination can be neglected, the total decay of the primary ion arises both through collisions in the gas phase under study, with a reaction rate k, and through ambipolar diffusion to the walls of the entire plasma. Thus the overall exponential decay rate, Z, can be expressed as

$$Z = \frac{D_a}{\Lambda^2} + kp_2 \tag{8}$$

where D_a is the ambipolar diffusion coefficient of the primary ion, Λ is the diffusion length for the afterglow chamber (usually taken to be the fundamental mode when observations are limited to late times in the afterglow) and p_2 is the partial pressure of the neutral gas with which the primary ions interact to produce the secondary ions. If p_2 is very much smaller than the total gas pressure, then variations in p_2 should not affect the total pressure appreciably nor the ambipolar diffusion coefficient. Thus, by varying p_2 and observing Z, a linear plot should be obtained, the slope of which is the rate constant, with the intercept being the diffusion term.

The second method for handling data avoids the explicit consideration of ambipolar diffusion by studying the ratio of secondary to primary ion currents as a function of time. It can be shown[26] that the ratio, R, of number densities of secondary to primary ions at any point in the plasma is given by

$$\frac{\partial R}{\partial t} = \left[(\alpha_1 - \alpha_2) n_e + \left(D_2 \frac{\nabla^2 N_2}{N_2} - D_1 \frac{\nabla^2 N_1}{N_1} \right) \right] R + kp_2(1+R) \tag{9}$$

for a case where a single primary is producing a single secondary ion, where α_1 is the

electron-ion recombination coefficient, D_1 is the ambipolar diffusion coefficient, and N_1 is the ion density of the i-th species, and n_e is the electron density. Assuming that the measured ion currents are proportional to the ion densities in the vicinity of the aperture through which the ions leave the afterglow chamber, then the ratio of measured currents should obey the same expression. If the primary and secondary ions are similar in mass, charge, number of atoms, etc., it is reasonable to expect that the differences appearing in the first term in Eq. (9) would make the entire first term small. Even if it is not small, however, it becomes unimportant if one interests himself in small times where R is small and $\frac{dR}{dt} \sim kp_2$.

By using the second method of data analysis on the process in Fig. 12, the rates obtained by Fite et al[26] are about 2×10^{-10} cm³sec⁻¹ for $N_2^+ + O_2$ charge exchange and about 5×10^{-10} cm³sec⁻¹ for $N^+ + O_2 \rightarrow NO^+ + O$.

To the present time, only one process has been examined by as many as three different groups of investigators using afterglow mass spectrometry. This process is $O^+ + O_2 \rightarrow O + O_2^+$. (Since none of the three groups used isotopic labeling, whether the process is charge exchange or ion-atom interchange is a moot question.)

Dickinson and Sayers[25] at Birmingham studied the decay of the O^+ ions in collisions with O_2 using an afterglow of a pulsed rf discharge in helium-oxygen mixtures and a rf mass spectrometer of the linear accelerator type. Langstroth and Hasted[27] at University College London did a similar experiment using similar equipment, although they excited the afterglow by a pulsed dc discharge. They too used the first method of data analysis. Both the first and second types of data analysis were applied to more recent experiments at General Atomic which used both He and Ne as buffer gases.

The rather poor state of reliability of afterglow mass spectrometry as a means to obtain thermal energy reaction coefficients is indicated by the results of the three laboratories. Dickinson and Sayers' value, 2.5×10^{-11} cm³sec⁻¹, is in marked conflict with Langstroth and Hasted's 1.2×10^{-12} cm³sec⁻¹. The General Atomic group's range of values presently lies between 4 and 8×10^{-11} cm³sec⁻¹, depending on experimental conditions.

The origin of these very large discrepancies in the rate constant for $O^+ + O_2 \rightarrow O + O_2^+$ is not clear. Since there were no obvious errors made in any of the investigations, it seems likely that the many unassessed complexities of the experimental technique itself are responsible in some way. Particularly suspect are such purely plasma phenomena as plasma potential variations and ion sheath formation and decay in the vicinity of the ion extraction aperture. Clearly, other experimental methods are urgently needed to study energy charge exchange processes -- methods which avoid the problems of extracting an ion from an afterglow.

Among the possible techniques to accomplish this are those of ion cyclotron resonance coupled with afterglows. Recent experiments of Wobschall, Graham, and Malone[29] have used ion cyclotron resonance in weakly ionized gases to determine collision frequencies from the absorption line shapes. While these experiments to date relate more closely to mobility measurements, they would seem to offer a particularly interesting possibility in regard to charge exchange collisions between non-identical species as well.

IV. CHARGE EXCHANGE AND MASS SPECTROMETRY

In light of the nature of this topical conference, it seems appropriate to conclude with some brief reference to the relations between charge exchange generally and mass spectrometry.

Clearly, the first relation is that the techniques of mass spectrometry have been widely employed in the experiments on charge transfer. Mass-spectrometric methods produce and analyze the fast beams in the higher energy experiments, and mass spectrometers are used to detect the slow ions produced in the heavy particle collision. It has been mass spectrometers which have been used to study ion decay in thermal plasmas up to the present. There is every indication that whatever form charge exchange research takes in the future, mass spectrometers of one form or another will be the major instrumental components.

Perhaps a little less obvious are the consequences of charge transfer research to more conventional mass spectrometry, however. It would seem clear that the analytical chemist should concern himself with charge transfer in the tube of his analyzer. Resonant charge transfer cross sections become large at typical mass spectrometer ion energies, and the danger of losing certain ions between the source and the detector is a very real one in some analytical mass spectrometers. Since the charge transfer cross section will depend strongly on the ion species in any given residual gas, the ion populations arriving at the detector may not be the same as those leaving the source, particularly if the vacuum in the analyzer is not the best.

Another consequence of charge transfer research of some potential interest for analytical mass spectrometry comes from the afterglow mass spectrometry experiments. In particular, the mass spectrum late in the afterglow is very rich in secondary ions as compared with primary ions. If the primary ion can exchange charge with an impurity to produce a secondary ion, then the long time that an afterglow is held permits a considerable amplification of secondary ion signal relative to the primary ion signals. As a case in point in helium of the "spectroscopically pure" classification; i.e., less than 50 ppm impurity both by manufacturer's claim and conventional mass analysis, it is found that after about 2 milliseconds in the afterglow, the major ion present is Ne^+. Also in helium, unmeasurably small concentrations of CO are indicated in the afterglow spectrum by the appearance of C^+, probably formed by dissociative charge exchange. Indeed it would appear that where a given charge exchange cross section is large for a primary ion and an impurity neutral, the time in the afterglow permits the ions to seek out the impurities and ionize a very high fraction of them. It seems probable that charge exchange can be used to provide ultra-sensitive detection of certain impurities in certain gases.

REFERENCES

1. H. S. W. Massey, Rep. Progr. Phys. 12, 249 (1949).

2. J. B. Hasted, "Inelastic Collisions between Atomic Systems", Advances in Electronics and Electron Physics, Vol. 13 (Academic Press, New York, 1960).

3. D. R. Bates, "Theoretical Treatment of Collisions between Atomic Systems", Chapter 14 in Atomic and Molecular Processes, D. R. Bates, ed., (Academic Press, New York, 1962).

4. D. Rapp, Proceedings of this conference.

5. W. Wien, Ann. Physik 27, 1025 (1908).

6. P. M. Stier and C. F. Barnett, Phys. Rev. 103, 896 (1956).

7. G. J. Lockwood and E. Everhart, Phys. Rev. 125, 567 (1962); F. P. Ziemba, G. J. Lockwood, G. H. Morgan, and E. Everhart, Phys. Rev. 119, 1552 (1960).

8. O. B. Firsov, Zh. Eksper. i. Teor. Fiz. USSR, 21, 1001 (1951).

9. D. R. Bates, H. S. W. Massey, and A. L. Stewart, Proc. Roy. Soc. A216, 437 (1953).

10. D. Rapp and R. E. Francis, J. Chem. Phys. 37, 2631 (1962).

11. W. L. Fite, R. T. Brackmann, and W. R. Snow, Phys. Rev. 112, 1161 (1958).

12. W. L. Fite, R. F. Stebbings, D. G. Hummer, and R. T. Brackmann, Phys. Rev. 119, 663 (1960).

13. W. L. Fite and R. T. Brackmann, Phys. Rev. 112, 1141 (1958).

14. A. Dalgarno and M. R. C. McDowell, Proc. Phys. Soc. Lond. A69, 463 (1959).

15. W. L. Fite, A. C. H. Smith, and R. F. Stebbings, Proc. Roy. Soc. Lond. A268, 527 (1962).

16. H. S. W. Massey and E. H. S. Burhop, Electronic and Ionic Impact Phenomena, Ch. VIII (Oxford University Press, 1962).

17. J. B. Hasted, "Charge Transfer and Collisional Detachment", Chapter 18 in Atomic and Molecular Processes, D. R. Bates, ed., (Academic Press, New York, 1962).

18. S. K. Allison and M. Garcia-Munoz, "Electron Capture and Loss at High Energies", Chapter 19 in Atomic and Molecular Processes, D. R. Bates, ed., (Academic Press, New York, 1962).

19. O. Heinz and E. J. Feinler, "Tabulation of Atomic and Molecular Charge-Transfer Cross Sections", Stanford Research Institute Report, Interim Technical Report No. 1, SRI Project No. SU-2853 (1961).

20. N. G. Utterback, private communication, 1962.

21. J. W. McGowan, Proceedings of this conference.

22. T. J. M. Sluyters, E. de Haas, and J. Kistemaker, Physics 25, 1376 (1959).

23. G. H. Dunn, R. Geballe, and D. Pretzer, Phys. Rev. 128, 2200 (1962).

24. W. L. Fite, R. T. Brackmann, and K. E. Hagen, Rev. Sci. Instr. 29, 125 (1958).

25. P. H. G. Dickinson and J. Sayers, Proc. Phys. Soc. Lond. 76, 137 (1960).

26. W. L. Fite, J. A. Rutherford, W. R. Snow, and V. A. J. van Lint, General Discussions of the Faraday Society 33, 264 (1962).

27. G. F. O. Langstroth and J. B. Hasted, General Discussions of the Faraday Society 33, 298 (1962).

28. D. R. Bates and N. Lynn, Proc. Roy. Soc. A253, 141 (1959).

29. D. Wobschall, J. R. Graham, Jr., and D. P. Malone, Paper No. F-6, 15th Annual Gaseous Electronics Conference, Boulder, Colorado, October, 1962.
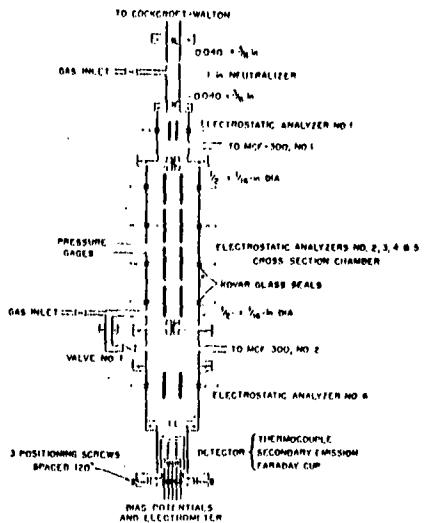
Fig. 1--Schematic diagram of the apparatus of Stier and Barnett[6] for the measurement of electron capture and loss cross sections using fast particle detection
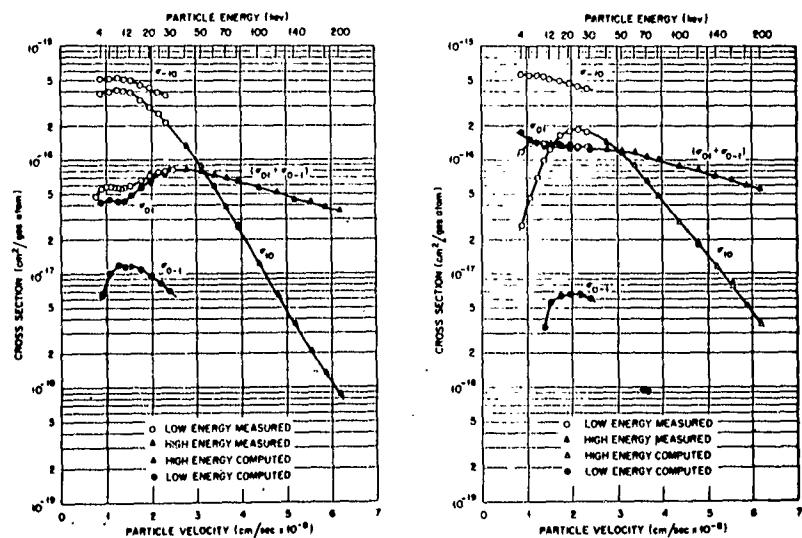
Fig. 2--Cross sections for electron capture by protons (σ_{10}), electron loss by fast hydrogen atoms (σ_{01}), electron capture by H atoms to form H⁻ ions ($\sigma_{0,-1}$), and electron loss from H⁻ ($\sigma_{-1,0}$) in target gases of H_2 (left side) and He. In the H_2 data the given cross sections should be multiplied by 2 to obtain the cross section for a target H_2 molecule
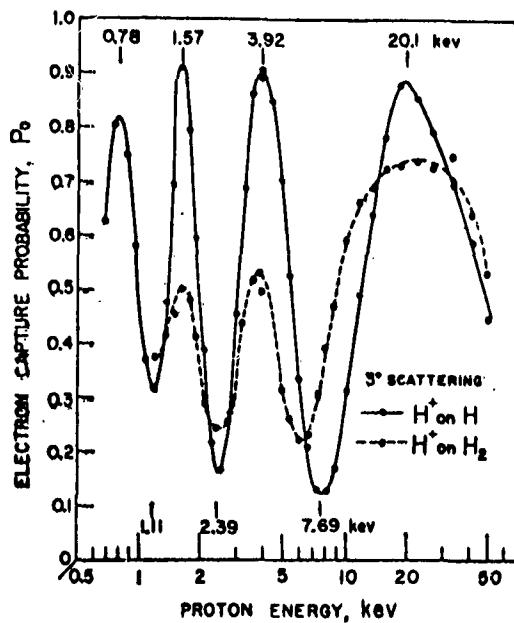
Fig. 3--Electron capture probability of protons in collision with hydrogen atoms, where the collisions are sufficiently "hard" to deflect the past particles through 5°. These data are from Lockwood and Everhart[7]
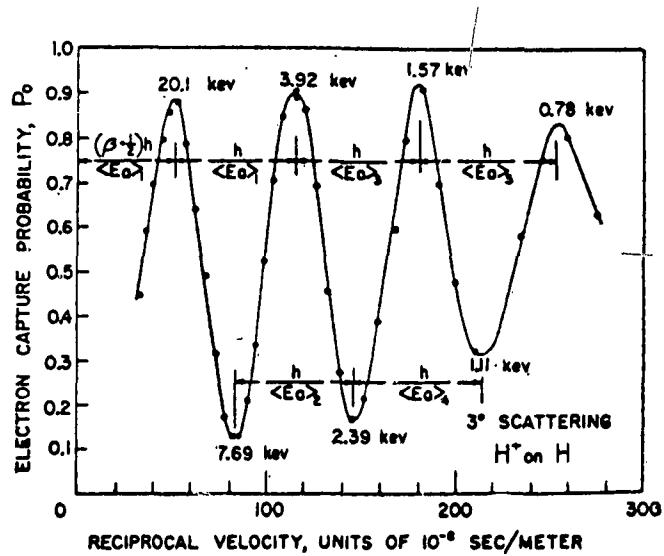
Fig. 4--The: results of Fig. 3 replotted to show capture probability as a function of inverse relative velocity of the colliding particles. The regularity of the oscillatory pattern is to be noted
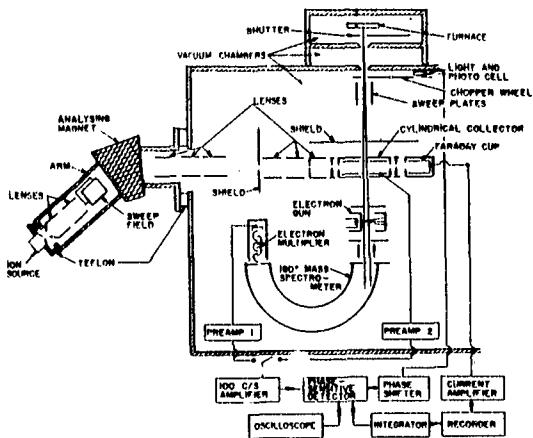
Fig. 5--Modulated crossed beam experiment of Fite
et al[12] for the measurement of the total charge
transfer cross section in collisions of protons and
hydrogen atoms
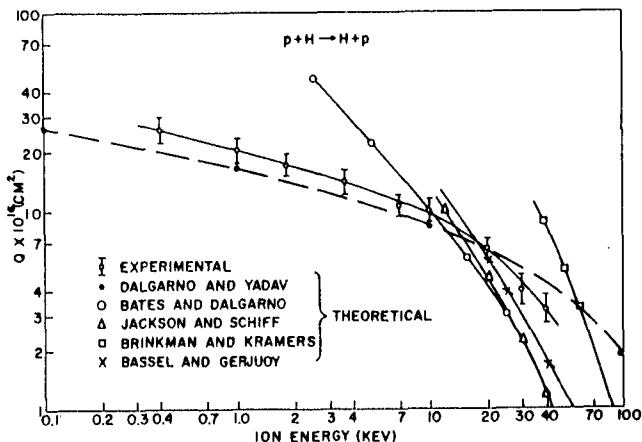
Fig. 6--Total cross section for charge transfer in
proton-hydrogen atom collisions comparing experimental
results[12] with several theoretical calculations. The
calculation of H. C. Brinkman and H. A. Kramers (Proc.
Acad. Sci. Amsterdam 33, 973 1930) uses the simplest
Born approximation. Modified Born calculations are
shown in the curves of D. R. Bates and A. Dalgarno
(Proc. Phys. Soc. Lond. A66, 972 1953) and J. D.
Jackson and H. Schiff (Phys. Rev. 89, 359 1953). The
calculation of R. H. Bassel and E. Gerjuoy (Phys. Rev.
117, 749 1960) employs a distorted wave approximation.
The perturbed stationary state calculations of A.
Dalgarno and H. N. Yadav (Proc. Phys. Soc. Lond. A66,
173 1953) differ substantially from the other approxi-
mations used and treats the entire collision in terms
of an H_2^+ molecular ion model in which internuclear
separation varies
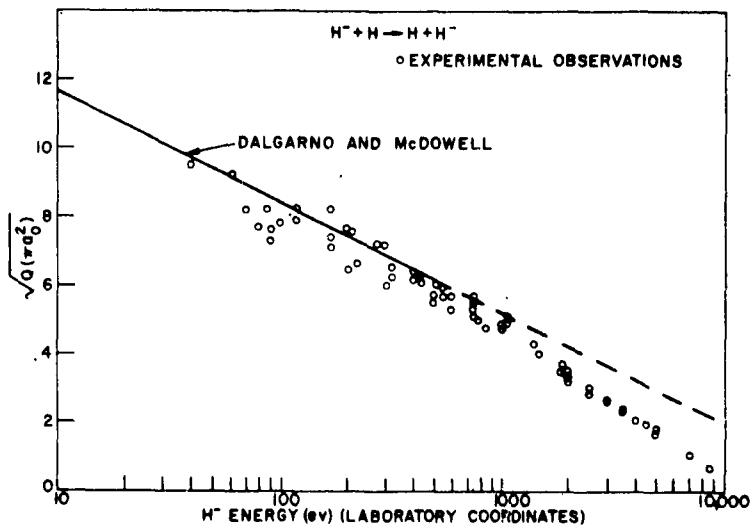
Fig. 7--Cross section for charge transfer between H⁻ and H atoms compared with the perturbed stationary state calculation of Dalgarno and McDowell[14]
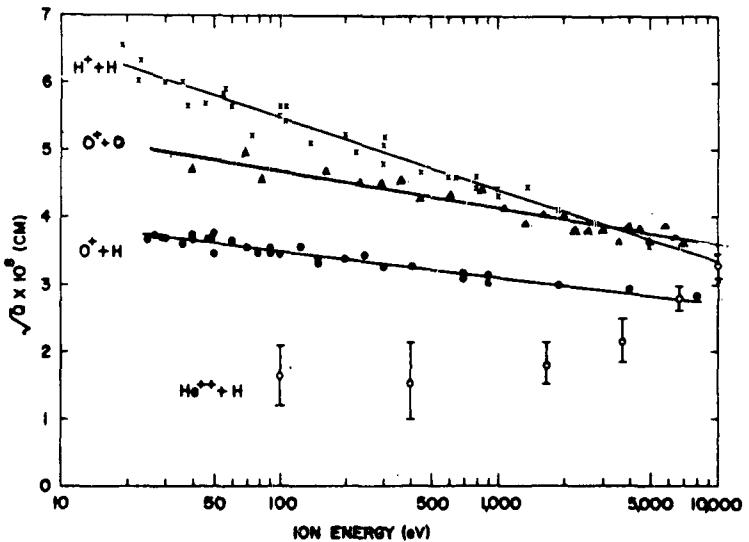

Fig. 8--Cross sections for the symmetrically resonant charge transfer collisions between H^+ and H, and between O^+ and O. The accidentally resonant process between O^+ and H is seen to display the characteristics of resonant charge transfer over the energy range in this figure, but the process $He^{++} + H \rightarrow He^+ (n=2) + H^+$ does not. The data are from reference 15
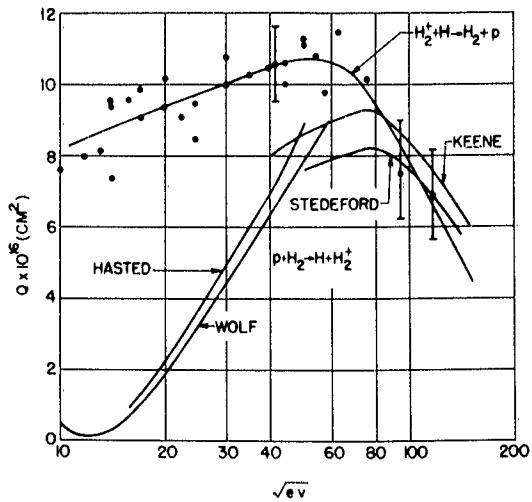
Fig. 9--Data[11] comparing the inverse charge transfer processes

$$H^+ + H_2 \rightleftharpoons H + H_2^+$$
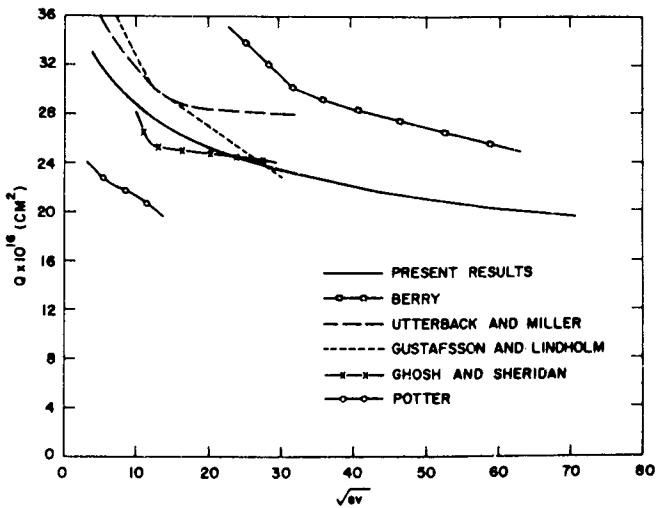
Fig. 10--Comparison of data for the charge transfer process between N_2^+ and N_2. Curves shown are from R. F. Potter (J. Chem. Phys. 22, 974 1954); S. N. Ghosh and W. F. Sheridan (J. Chem. Phys. 27, 1436 1957); E. Gustafsson and E. Lindholm (Arkiv Fysik, 18, 219 1961); N. G. Utterback and G. H. Miller (Rev. Sci. Instr. 32, 1101 1961); and H. W. Berry (Phys. Rev. 74, 848 1948). The "present results" are those of R. F. Stebbings, B. R. Turner and A. C. H. Smith (J. Chem. Phys. 38, 2277 1963)
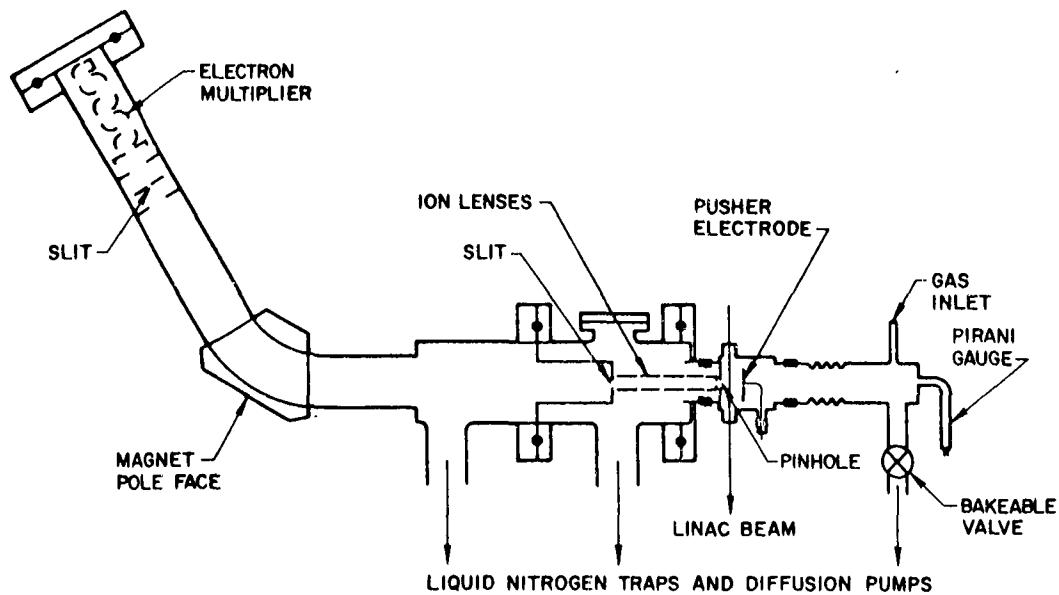
Fig. 11--Afterglow mass spectrometer used by Fite et al[26]
to study thermal-energy charge exchange and ion-atom inter-
change collisions
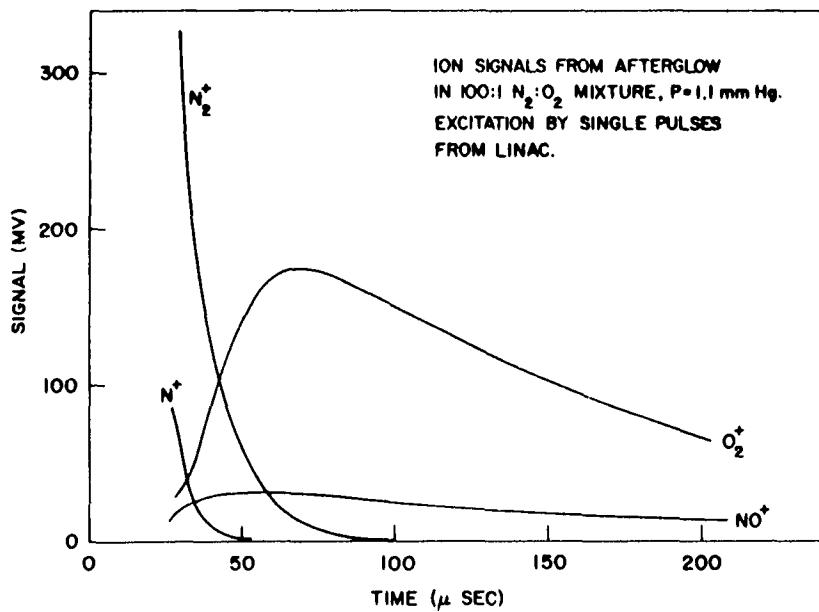
Fig. 12--Overlay of oscilloscope traces in an afterglow mass
spectrometer experiment in a 100:1 $N_2:O_2$ gas mixture. Data
are from reference 26