Storing ions
for collision studies

A static trap capable of storing ions for many hours—electrons for over a month—bids fair to bring the convenience of the chemist's reagent shelf to the study of ions and their interactions. The trap to store heavy ions developed at the Joint Institute of Laboratory Astrophysics, shown on the cover and in figure 1, is preferable for our work to its older cousin, the laboratory Astrophysics, shown on the front cover of this issue, bids fair to bring the convenience of the chemist's reagent shelf to the study of ions and their interactions.

The adsorption of the recombination of positive ions with electrons. Recombination, an old problem, plays a strong role in the ionization balance; calculations, discussed below, brought the two determinations into harmony.

Volume recombination between electrons and positive ions is often assumed to be the dominant loss mechanism in high-pressure laser discharges. When an external source, such as an electron or uv photon beam, is used to maintain ionization, and the recombination coefficient is lowered, the laser's energy requirement is reduced. The cross section for recombination of H2O+ with electrons has recently been shown to decrease much more rapidly with electron energy than had been thought typical (or even possible) for ions. Arthur Phelps has used this to suggest that the presence of H2O+, or other ions that may behave similarly, could explain some observations of low loss in some plasmas being investigated for laser purposes.

The great number and complexity of molecules observed in interstellar space has led to a variety of proposed models to explain their formation. For a time gas-phase processes were considered too slow, and mechanisms involving formation on grains were considered more applicable. However, recent models, using measured and typical rates for gas-phase reactions, have led to reasonably consistent densities of the observed species. According to a model by Eric Herbst and William Klemperer for dense interstellar clouds, a number of observed neutral molecules result from dissociative recombination (which we shall describe shortly) of electrons and positive ions; these include CH, NH, OH, H2O, NH3, and H2CO. In this model, cosmic rays ionize the ambient neutral particles; the ions in turn undergo various reactions, primarily with the dominant species H and H2, and electron-ion dissociative recombination is often the final step, yielding stable neutral molecules.

The green line in the night sky and in aurorae was attributed as early as 1931 by Joseph Kaplan to dissociative recombination of electrons and O2 ions to give O(S). The green line source. Similarly, the prominent feature in the airglows of Venus and Mars, the Cameron bands of CO, appears to result directly from dissociative recombination of electrons and CO2-. During eclipses, solar flares, and aurorae, when the sun rises and sets, and when there are man-made disturbances in the degree of ionization of the earth's atmosphere, ion densities move with some time constant to new levels. These levels of course strongly influence radio communications, which depend on reflection of radio waves from the ionized layers of the earth's atmosphere; the time for this change is mainly determined by recombination.

Recombination mechanisms

Numerous physical mechanisms lead to recombination; the three two-body processes that normally play a role are illustrated in figure 2. The first of these is dielectronic recombination, in which the electron simply radiates its excess energy, ending up in an excited state of the atom. Since the electron passes the ion in about 10-15 sec, while radiative times are of the order of 10-8 sec, the process has a low probability. Cross sections for it are about 10-26 cm²; they decrease with electron energy E roughly as E. The process has not been measured directly, although radiative recombination data can sometimes be inferred from measurements of the reverse process, photodetachment.

The second mechanism shown is dielectronic recombination. In this process an electron with just the right energy excites an electron of the ion core, and is itself left in a high Rydberg state of the resultant neutral atom. Such multiply excited states lie in the ionization continuum, as shown by the upper black lines in the figure;
Overcoming the limitations of plasma and colliding-beam techniques, the new static trap helps untangle the mechanisms by which positive ions recombine with electrons.

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autoionization can occur, reversing the capture process. However, if the core excited state has a short radiative lifetime, and if the Rydberg state of the captured electron is high enough that interaction with the core electron is small, stabilization by radiation occurs before autoionization takes place. The result is an excited "neutral." This process can have a cross section $10^{-14}$ to $10^{-15}$ cm$^2$. However, because of the resonant nature of this process, the energy range for sizable cross sections is as narrow as a few meV. Dielectronic recombination has been invoked to help account for aspects of the ionization balance of high-temperature plasmas but has not been measured.

Only molecular ions are subject to neutralization by the third process, dissociative recombination. For diatomic molecules the internuclear separation $R$ becomes an additional dimension. Again we see excited neutral states lying in the continuum but now, as the energy varies with $R$, they may be below the continuum at large $R$. In this case the excess energy brought in by the electron is carried away as kinetic energy of the dissociating partners. This takes place in $10^{-12}$ to $10^{-13}$ sec, compared to the autoionization time of about $10^{-14}$ sec, so the process can be very efficient; cross sections approach $10^{-13}$ cm$^2$ at low energies. Furthermore, the resonance peak is broad in this case, owing to the range of separations of the original molecular ions. Dissociative recombination is usually the dominant mechanism when molecular gases are present.

When densities become high enough for three-body collisions to be frequent, three-body recombination and third-body enhancement of the above mechanisms takes place. Dissociative recombination may be thought of as a process in which a potential third body is carried around with the ion.

Of the three two-body processes, dissociative recombination$^8$ is the only one that has been measured directly.

Ion trap in which ions have been stored for up to 28 hours. The hyperboloidal molybdenum electrodes consist of two end caps, whose surfaces are partly visible in the photo, and a ring. The structures seen on the left of the electrode assembly are the two electron guns, one a high-resolution trochoidal source and the other on-axis.

Figure 1
Until very recently the only measurements on this process were the determinations of rate coefficients in plasmas (the rate coefficient is equal to the product of cross section and velocity averaged over a Maxwellian velocity distribution.) The most extensive and successful of these experiments have been those of Manfred A. Biondi and his coworkers, whose studies in this field have extended over a 25-year period.

**Plasmas and colliding beams**

In the techniques evolved by the Biondi group, a plasma is generated in a microwave cavity. When the excitation is turned off, one observes the time decays of the densities of electrons (determined from the conductivity) and of mass-selected ion species. A provision for microwave heating of the electrons allows the process to be studied as a function of electron temperature up to a few thousand degrees. The cavity itself can be heated, permitting recombination studies over an ambient temperature range to 450 K. The recombination rates are then computed from the electron- and ion-density decay rates.

Other methods used to obtain rate coefficients include heating a plasma with a traveling shock wave. Pairs of electrostatic probes placed along the shock tube permit the electron density to be observed as a function of distance and hence, time. With this technique, measurements can be made to temperatures of several thousand degrees.

Although the plasma measurements have been successful, the method has some shortcomings: (1) the energy range is limited; (2) the energy resolution is poor, obscuring details and precluding rate calculations for non-Maxwellian distributions; (3) the species one can study are limited; and (4) the internal states are not controllable.

Colliding-beam measurements can overcome the first three of these disadvantages to some degree, with regard to the last, however, the limitations of beams are even more severe than those of plasmas. In these experiments a beam of electrons is made to collide with a beam of ions. One observes the appearance of neutrals, the disappearance of ions or the appearance of photons from excited dissociation fragments. The experiments are difficult, and the only measurements using this technique appear to be those on single-charged deuterium and nitrogen molecular ions, D$_2^-$ and N$_2^-$.

**Two types of traps**

With the trapped-ion technique, the focus of this article, we are able to study the same ions for times ranging to several hours. The limitations of the traditional techniques are overcome, but new limitations appear.

Ion traps depend primarily on an electric saddle potential, illustrated in figure 3. This potential is achieved by machining the electrodes in the shape of hyperboloids of revolution, two end caps and a ring, illustrated in figure 4. Its axis of symmetry will be taken as the $z$-axis of a cylindrical coordinate system. Ions will oscillate in the parabolic well if their position and velocity vectors are along the $z$-axis; otherwise, they will drift out radially.

In the radiofrequency trap the potential is made to change sign before the ion can escape along $r$, then again before it can escape along $z$ and so on. If the amplitude and frequency of the potential are chosen properly, the ion will be trapped. This method of containing ions by alternating electric-field gradients grew out of the work of Wolfgang Paul and his collaborators on electric mass filters. Hans G. Dehmelt reviewed the mechanics of such traps and their application in the rf spectroscopy of ions. Being atomic traps, they have the disadvantage of keeping the ions hot; furthermore, the alternating fields make them unsuitable for studying collisions of the trapped ions with monoenergetic electrons.

In our lab at JILA, we found the static trap to be a better tool for collision studies. To a dc potential of the same configuration as before we add a strong magnetic field. Our trap is thus a passive device, without the undesirable heating effect.

The magnetic field is in the $z$-direction. Now, when an axially oscillating ion starts to escape along $r$, it is turned back in a cyclotron orbit. The ions see crossed electric and magnetic fields and therefore they will precess, in $E \times B$ drift about the $z$-axis. The ions thus execute harmonic motion in the parabolic well along $z$, cyclotron motion in the equatorial plane and precession about the $z$-axis. In the absence of collisions they will be trapped indefinitely.

Tracing the history of the development of the static ion trap is difficult, as there are many references to unpublished work. The basic configuration is that used by Frans M. Penning in the study of discharges. Solutions to the equations of motion were published by J. Byrne and Peter S. Farago, who cite unpublished work of Otto R. Frisch (1954), Felix Bloch (1953) and Robert H. Dicke (1965). Dehmelt has reviewed the technique and noted his own unpublished work (1960). The demonstration of the long trapping times that are achievable with this trap, however, awaited the work of Dehmelt and Walls, who reported trapping times for electrons of about $3 \times 10^8$ sec, or five weeks! Of comparable importance was their demonstration of a nondestructive bolometric technique usable with the trap.

While the dc trap is not suitable for some kinds of ion spectroscopy because of the Zeeman splittings associated with its large magnetic fields, it appears to be ideally suited for collision studies. This is because, first, the passive nature of the trap allows the
ions to be cooled enough for energy resolutions as low as tens of meV; second, the long lifetimes create the possibility of preparing the ions in the desired state, and third, it allows us to make repeated nondestructive measurements of the numbers of the ion species present. Let us examine the trapping scheme and its realization in more detail.

Figure 4 shows a cross-sectional view of a dc ion trap with a block diagram of the associated detection system. The trap electrodes form equipotential surfaces given by

\[ V = V_0 (r^2 - 2z^2)/(a^2 + 2z^2) \]  

where \( r \) is the equatorial diameter of the ring, \( 2b \) is the axial distance between the end caps and \( V_0 \) is the potential applied to the ring electrode with respect to the end-cap electrodes.

The dimensions of our trap are \( 2a = 1.25 \) cm and \( 2b = 0.76 \) cm.

Ions can be introduced into traps by a variety of means, including photoionization, colliding ion beams and collisions of an ion beam with the residual gas; the most common way is by electron impact on a selected gas within the trap.

The axial motion of the ions in the trap consists of harmonic oscillation at the frequency

\[ \nu = (aqV/\sqrt{2m})/(a^2 + 2z^2)^{1/2} \]  

where \( q/m \) is the charge-to-mass ratio of the ions. As noted above, the ions also move in small circles at a frequency \( \nu_c \) equal to the third motion, the centers of the circles precess about the \( z \)-axis at angular frequency \( \nu_m \), which is related to the others through

\[ 2\nu_b = 2\nu_c + \nu_m = 0 \]

Because of the parabolic potentials and the assumed uniformity of the magnetic field, the motions are harmonic and the frequencies are independent of energy and position. For \( \nu_b \), with potential \( V_0 = -1 \) V and \( B = 1.15 \) Tesla (1 T = 10^4 gauss), these are \( \nu_c = 552 \) kHz, \( \nu_z = 67 \) kHz and \( \nu_m = 4.1 \) kHz.

Storage times and ion temperatures

The conditions for long-term ion storage are that the cyclotron radius be much smaller than \( a \), that the radial magnetic force \( Bq\nu_c \) be larger than the radial electric force \( qE \), and that the magnetic and electric fields be cylindrically symmetrical, with coinciding axes. When these conditions are satisfied, the loss of ions is due solely to collisions with the background gas.

The losses due only to diffusion induced by elastic scattering can be studied by measuring lifetimes of ions that do not react with the background gas. We have already noted the figure \((3 \times 10^8 \) sec\) of Dehmelt and Walls for trapping times of electrons. Measurements on \( \text{NH}_3^+ \) with \( B = 1.15 \) T, \( V_0 = 1.8 \) V, and a background pressure of about \( 1 \times 10^{-10} \) torr, presumably mostly hydrogen, yield lifetimes of about \( 10^6 \) sec (28 hours). Both indicate that diffusion effects can be made small in attainable vacuum. Typically, however, lifetimes are determined by such reactions with the background gas as charge transfer, clustering and ion-atom interchange, which lead to the more common lifetimes of about \( 10^4 \) sec (17 minutes).

These trapping times are long enough that most excited ions will have relaxed to the ground state. Notable exceptions are homonuclear molecular ions with vibrational modes that have lifetimes of about \( 10^5 \) sec (4 months). The ion-storage times are long enough to suggest future experiments in which the ions are pumped to excited states by means of a suitable form of radiation.

Coulomb collisions between trapped ions establish a Maxwellian distribution of kinetic energies in a time \( \tau_c \) varying as \( T_i^3 \cdot 3m^{1/2}/nZ^2 \) approximately.18 For ion temperature \( T_i = 300 \) K, ion mass \( m = 30 \) amu, ion density \( n = 10^6 \) ions/cm^3, and valence \( Z = q/e = 1 \), \( \tau_c \) is about 0.02 sec. Because the trapping times are so much longer than \( \tau_c \), one can speak of an ion gas at a definite temperature \( T_i \), and use the nondestructive detection technique described below.

The oscillatory axial motion of the ions causes an alternating image current to flow from one end cap to the other. If a resistor, \( R \), is inserted in this current path, the Joule heating losses will cause the ions to approach the noise temperature of the resistor, with a time constant, assuming no other external coupling to the ion motion, of about \( 8m_b^2/\pi^2R \). The collective motion of \( N_i \) ions is damped \( N_i \) times as fast. Note that this process can be used either to heat or to cool the ions. Evaporation, that is, escape of fast ions from the trap, will also cool the ions sufficiently to a mean energy of about one-tenth of the well depth, but there are not enough ions high in the tail of the distribution to have much effect beyond this. One might think of using collisions with the background gas as a cooling mechanism; however, these collisions would also cause an unwanted loss of ions by radial diffusion.

Nondestructive ion detection

The ions may be detected without loss by measuring the noise power in the image currents to one end cap of the trap. The very broad-band heterodyne detection circuit shown in figure 4 allows nondestructive detection of charged particles ranging from electrons to ions of several hundred amu. Individual ion species are manifest as peaks in the noise-power spectrum at the ions' axial oscillation frequency, given by equation 2.

The area under the peak is proportional to ion number multiplied by temperature, \( N_i T_i \). Under conditions in which \( N_i \) is kept constant, one can investigate processes that raise the kinetic temperature of the ions. For ex-
ample, introducing power at the cyclotron frequency raises the ion temperature, which appears as an increase in the area of the noise-power peak. Similar heating of internal degrees of freedom that couple to the ionic center-of-mass motion can also be so detected.17,19 Resonant cyclotron heating is used to measure ion q/m ratios with a resolution of about two parts in 10^4; it has been used, for example, to distinguish between H_2O^- (m = 18.020 amu) and NH_4^+ (m = 18.044 amu).

On the other hand, when T_i is constant, one can study processes in which N_i changes. The wideband, nondestructive nature of the detection technique makes it possible to measure N_i repeatedly for each ion species of interest, and so keep track of both primary and competing processes. At this point we can see why this technique is so suitable for the study of ion recombination: The goal here is to find the decrease in ion number brought about by the introduction of electrons, while ion temperature remains constant.

The space charge limits the number of ions that can be stored in a trap for the cited dimensions and a well depth of 1 V the maximum is about 3 \times 10^8 ions. In recombination studies the need for a well defined interaction energy between electrons and stored ions reduces the useful radial extent of the trap; correspondingly, the maximum number of stored ions is reduced to about 10^8 at a density of about 10^7 ions per cubic centimeter.

Performing the experiment

Implementation of the storage technique described for the study of electron recombination with ions is relatively straightforward, once the trap and detector are operating properly. Electrons from either of two attached guns pass through a hole in the center of one end cap into the cavity, then through a collinear hole in the opposite end cap, finally to be absorbed by an electron collector at the far end. One electron gun, consisting simply of a cathode and series of apertures along the z-axis, provides an electron beam having an energy spread with full width at half maximum of about 120 meV. The other gun, similar to the trochoidal gun described by Aleksandar Stamatović and George S. Schultz, uses E \times B drift to disperse the electron velocities. With this gun, we have achieved an FWHM resolution of about 35 meV.

Ions are formed by electron bombardment of gas introduced into the system at pressures typically about 3 \times 10^{-10} torr; the gas is then pumped out to 1 \times 10^{-10} torr. Some of the ions studied are the product of the reaction of a primary ion with the background gas. For example, H_3O^+, an ion important in the ionosphere, interstellar space and some gas lasers, is formed from H_2O^- by reacting with H_2O and other gases. After the ions are formed, we allow them to cool by coupling to an external resistor, as described above. The well depth, V_0, is then cut in half, and the ions cool further by evaporation to a mean energy, in the axial motion, of about 15 meV.

After cooling, the natural decay period r_n, due to interactions with the background gas, is established by observing the area under the noise power peak as a function of time. We then introduce electrons of selected energy for a measured time t, long enough to give a measurable ion loss, after which the natural decay is again observed. Figure 5 shows this measurement sequence for a recombination measurement on NO^+ at an electron energy of 45 meV. This process is repeated at specific electron energies, and the cross section \sigma at each energy is calculated from the expression

\[ \sigma = \frac{r_n}{t} \left( \ln \frac{N_1}{N_2} \right) \]

where \nu_e is the electron current, N_1 and N_2 are respectively the numbers of ions before and after introducing the electrons and A is a geometric quantity depending on the overlap of the electron beam with the ion cloud.

All the quantities in equation 3 except A are readily measured. In a simple model, A is just the area of the ion cloud seen by the electron beam. This quantity can be estimated, although not closer than a factor of two or three. A more precise procedure is to determine A by measuring the other quantities for a process of known cross section. The process chosen for this calibration is the recombination of electrons with O_2^+. However, instead of \sigma, only the recombination rate coefficient

\[ \sigma = \int_0^\infty \sigma(\nu) F(\nu) d\nu \]

is known. This quantity has been measured, with consistent results, by a number of investigators. Since \sigma is known to within a factor A from the ion-trap measurements and equation 3, \sigma/A can be calculated. Comparison to the known value of A yields A. We have recently developed a method for the direct measurement of A, and have built the apparatus for it.

An example of results of a recombination cross-section measurement is shown in figure 6 for NO^+ Rate coefficients calculated from these experiments are in good agreement with afterglow measurements, but we have obtained them to much higher temperatures. The slope changes in the cross-section versus electron-energy plot indicate the importance of several repulsive levels of excited NO—the final states of the recombination process. We have made similar measurements for O_2^-, H_3O^+, NH_4^+, N_2H^+, and HCO^-.

Limitations and prospects

Recombination studies with the trapped-ion technique are revealing de-
tails that will help guide efforts to explain recombination cross sections theoretically. The technique provides a hitherto unavailable means of obtaining rate coefficients in practical plasmas, where the energy distribution of electrons is often other than Maxwellian. Ion storage extends the accessible energy range; it also provides an environment in which one can define more accurately the distribution of the internal states of the reacting ions.

The two main limitations of the technique applied to recombination are the limited storage times imposed by reactions of ions with background gas molecules, and the uncertainties attendant upon the indirect measurement of A.

We have mentioned the work of Dehmelt and coworkers on electrons\(^{17,18,22}\) and described our work on ion recombination.\(^{21}\) At least two other groups have also used dc ion techniques successfully. Michael D. McGuire and E. Norvel Fortson\(^{23,24}\) have studied elastic, inelastic and spin-dependent collisions of stored electrons with selected atoms and molecules. Michael H. Prior\(^{25}\) and Prior and Howard A. Shugart\(^{26}\) have trapped ions for times of the order of 10 ms and the metastable He\(^{+}\) (2S) and Li\(^{+}\) (2S) lifetimes.

What about spectroscopic investigations? We have seen that, while some are possible with dc ion traps, others are better suited for study with rf traps.\(^{20}\) On the other hand, studies on recombination and lifetimes, photoionization, photodissociation, ion-molecule reactions, electron-impact ionization and dissociation, and negative ions all appear to lend themselves to attack with nondestructive bolometric detection, are to this warehouseful of problems, we anticipate a future of increasing use for this new tool.

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References