DR Experiments in the 60 years since the Bates paper

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Abstract. About 60 years have passed since David Bates in a 1950 Physical Review Letter to the Editor first clarified the dissociative recombination mechanism (DR) of molecular ions and provided the conceptual basis for the process that plays an important role in the ionospheres of Earth and other planets, the interstellar medium, and electrical discharges. His visionary (and characteristically “terse”) thumbnail sketch of the DR mechanism only hinted at the subtleties that have kept atomic theorists and experimentalists busy for many years. In my talk, I will focus on experiments on N$_2^+$ recombination, beginning with plasma afterglows, and then move on to the “after”—afterglow period that is now dominated by the powerful storage-ring methods.

1. Introduction
A highly readable personal account of the early (pre-1950s) attempts to explain the fast recombination in the terrestrial ionosphere can be found in a paper written by Bates in 1988 [1]. It became gradually clear to him and others that explaining the ionization loss rates by radiative recombination or formation of negative ions was fraught with insurmountable difficulties and that something radically new was called for.

In the last paragraph of that paper Bates summarizes some of the “bizarre” sequence of events that led to his breakthrough work. (n (e) denotes the electron density)

“The contribution that scientists using radio-soundings have made to our knowledge of recombination in the E-layer is bizarre. If they had correctly deduced that n (e) is greater in the morning than in the afternoon they could not have made any estimate of the recombination coefficient. As it was they erroneously deduced that n (e) is greater in the afternoon than in the morning and deduced a bogus recombination coefficient from the apparent sluggishness of the diurnal variation. This bogus recombination coefficient is about 30 times smaller than the true recombination coefficient but by good fortune is approximately equal to the bogus recombination coefficient from the first microwave measurements of the decay of the electron density in a helium afterglow. Happily it was large enough to alert theorists to the occurrence of a hitherto unknown recombination process (both in the E layer and in the afterglow).”

The “hitherto unknown recombination mechanism”, of course, was the “Dissociative Recombination” that Bates introduced in a brief 1950 Letter to the Editor [2]. His Letter starts off with the sentence: “By the successful exploitation of microwave techniques several groups of workers have recently derived interesting information on the decay of ionization”. A few paragraphs later he says: “The reaction can be thought of as taking place in two stages. As a result of a radiationless
transition an excited molecule, $XY'$ is formed. If this is unstable its constituent may move apart under the influence of their mutual repulsion thereby preventing auto-ionization”.

With these few words, Bates prepared the stage for extensive future theoretical refinements of the DR process, but he also implicitly admits that progress in understanding DR was often guided by, and sometimes forced by experimental evidence, as faulty, ambiguous, and contradictory as it may have been. The discovery of the mechanism of DR was clearly not a product of pure thought! Few theorists paid as close attention to experiments as Bates did, and those who had the good fortune to talk to him in person will recall his often critical and occasionally relentless questions regarding experimental procedures and conclusions.

It is not possible to review 60 years of all experiments on DR in a brief paper. Instead, I will retrace the history of measurements on one particular ion species, $N_2^+$, and while doing so digress occasionally to point out the strengths and limitations of different experimental techniques. I focus on $N_2^+$ not because it is a particularly abundant ionospheric species (which it is not because it is lost also by charge transfer with atomic and molecular oxygen) but because it has been studied extensively by theory and many experimental techniques.

The dissociative recombination of $N_2^+$ in the vibrational ground state has four exoergic product branches:

$$N_2^+ + e^- \rightarrow N(^4S) + N(^4S) + 5.82\text{eV}$$
$$\rightarrow N(^4S) + N(^2D) + 3.44\text{eV}$$
$$\rightarrow N(^4S) + N(^2P) + 2.25\text{eV}$$
$$\rightarrow N(^2D) + N(^2D) + 1.06\text{eV}$$

Experiments and theory are expected to provide the recombination coefficient or cross section, as a function of either temperature or collision energy, and as a function of the $N_2^+$ vibrational state. Knowledge of the overall recombination coefficient often suffices to incorporate recombination in models of planetary ionospheres or other plasmas but one would also like to know the relative branching fractions and the kinetic energies given to the product atoms, which affect the rate of non-thermal escape of $N$ atoms from some planetary atmospheres (e.g. from Mars).

2 Afterglow experiments

In the earliest methods to determine the recombination coefficient of $N_2^+$ a brief pulse of microwaves ($f\sim3\text{GHz}$) was admitted to a microwave cavity containing a sealed flask filled with pure nitrogen at pressures of a few Torr and at room temperature. If the microwave pulse is sufficiently intense, gaseous breakdown generates a weakly ionized plasma with initial electron densities around $n_e = 10^9 \text{cm}^{-3}$. Since the Debye length is much smaller than the dimensions of the container the plasma is close to electrically neutral in most of the plasma volume. After the end of the breakdown pulse, the plasma decays by both recombination and ambipolar diffusion to the walls. The first term on the RHS of the electron continuity equation

$$\frac{\partial n_e(t, \vec{r})}{\partial t} = -\alpha n_e^2(t, \vec{r}) + D_n \nabla^2 n_e(t, \vec{r})$$

(2)

describes the local electron loss due to recombination with recombination coefficient $\alpha$, here assumed to be due to a single ion species, while the second term describes ambipolar diffusion losses, again assuming that only one ion species with ambipolar diffusion coefficient $D_n$ is present. If the gas density is sufficiently high, $D_n$ being inversely proportional to density, becomes small and diffusion plays only a minor role during the initial afterglow phase (the “early afterglow”). A commonly used, but not entirely satisfactory, approximation “corrects” for the diffusion loss of electrons by fitting the observed electron density decays to an equation of the form

$$\frac{dn_e(t)}{dt} = -\alpha n_e^2(t) - \frac{D_n n_e}{\Lambda^2}$$

(3)
in which the quantity $\lambda^2$ is the fundamental diffusion length appropriate to the shape and size of the plasma container. Different investigators employ different methods of obtaining recombination coefficients from fits of the observed electron decay to Eq. (3).

2.1 Measuring the electron density decay

There are essentially two experimental methods to measure the electron density decay during the afterglow: Langmuir probes and microwave techniques.

Some of the early experimenters were, perhaps unduly, concerned about the reliability of Langmuir probes and potential perturbations of the plasma by “sticking a wire into it” and drawing electrons out of the plasma. They preferred to use a “probing microwave” to detect the change of the resonant frequency of a microwave cavity due to free electrons. Microwave technology had just been developed and many investigators came from research programs on RADAR development. Somewhat simplified, the macroscopic polarization of the plasma by a microwave with frequency above the plasma frequency causes the dielectric constant of the plasma to become less than unity. Hence, the microwave wavelength exceeds its vacuum value, and, to bring the cavity back into resonance, the microwave frequency has to be increased. The change in frequency can be found by sweeping the probing microwave frequency over a small range and noting the time at which the reflected power goes to zero. The method is highly accurate and relies on well-known textbook physics. However, it returns a “microwave-averaged” electron density, rather than local values and this requires additional but fairly straightforward computations. A second, but minor, problem is that the frequency shift is proportional to the electron density only if the electromagnetic field in the cavity is only slightly perturbed by the plasma. This limits the maximum electron density (at 3GHz) to a few $10^9$ cm$^{-3}$.

Later work, especially in flowing afterglow plasmas, usually employed Langmuir probes to measure $n_e$. It now appears that earlier concerns about Langmuir probes were unwarranted. They are reliable, provided one uses the probes in the electron collecting (rather than ion collecting) mode.

2.2 Afterglows in pure nitrogen

Early afterglow measurements suffered from incomplete knowledge of the “ion chemistry”, which was seriously underdeveloped at that time. The microwave-afterglow measurements of Bryan et al. [3] were carried out in pure N$_2$. The experimenters observed the decay of the electron density and also recorded optical emissions. They concluded that recombination in the early N$_2$ afterglow occurred with coefficients from about $2.3 \times 10^6$ cm$^3$/s at a nitrogen pressure of 6.4 Torr and $6.1 \times 10^6$ cm$^3$/s at 29 Torr. The pressure dependence and the very large recombination coefficient suggest that their plasma contained N$_4^+$ rather than N$_2^+$ ions. They also found rather strong emissions of the second positive band system of N$_2$, which were later shown (Chao and Johnsen [4]) to arise from N$_4^+$ recombination.

The lesson to be learned from this early work is that afterglows in pure molecular gases are difficult to interpret. It is better to use a rare gas (the “carrier” or “buffer” gas) to slow down diffusion and to add only enough of the molecular gas to form the desired ion species. This strategy has been employed ever since. Of course, it helps a great deal to have the extensive data on ion-molecule chemistry that became available in the 1960s! Since one can never be sure that the plasma actually contains the desired species, and no impurities, one adds a mass spectrometer that sample ions from the plasma. Kasner and Biondi [5], then working at the Westinghouse lab in Pittsburgh, used a highly diluted mixture of N$_2$ in neon, added a radio-frequency mass spectrometer to their afterglow apparatus, and were able to establish conditions where N$_2^+$ ions were the dominant species. They observed a remarkably consistent set of N$_2^+$ recombination coefficients of close to $2.8 \times 10^7$ cm$^3$/s at T= 300 K over a significant range of neon and N$_2$ densities. For some unknown reason, the values are somewhat higher than those found in later work but they are essentially correct.

2.3 Measuring the temperature variation

Ionospheric regions can have temperatures in excess of several thousand degrees K. Several methods have been used to measure the variation of recombination coefficients with temperature. One can heat
(or cool) the entire afterglow apparatus to change both the electron and gas temperature. In practice, heating to temperatures above 600 K creates serious technical problems and achieves very little that cannot be done easier by the microwave heating method, to be discussed later.

Kasner, using a modified version of the apparatus as Kasner and Biondi, measured the recombination of N$_2^+$ in the gas temperature range from 205 to 480 K. The 300 K value agreed with that of Kasner and Biondi of $2.8 \times 10^{-7}$ cm$^3$/s, but Kasner [6] did not observe any significant temperature variation. If one accepts the $T^{-0.39}$ variation of $\alpha$ that was found in later work, Kasner’s coefficient at 480 K should have been about smaller by only ~30% than that at 205 K, perhaps too small a change for a reliable determination of the temperature variation.

This does not mean that changing the gas temperature never serves a useful purpose. For instance, cooling the apparatus to temperatures below 300 K is essential for studies involving weakly bound ions (e.g. clusters or weakly bound dimers).

2.4 Microwave heating of electrons

Much higher electron temperatures (up to 10000 K) can be reached by microwave heating of the electrons gas, a technique that was used extensively in stationary afterglows and that has provided data on many important ion species, including N$_2^+$. The basic principles of microwave heating of plasma electrons are well understood and are fairly easy to apply if the transfer of power from the electron gas to the neutral gas involves only elastic collision between electrons and atoms. Electrons, while colliding with gas atoms, absorb power from the microwave field, heat up and, once the steady-state energy has been reached, pass an equal power to the gas atoms. The mean electron energy can be calculated from the power balance. The heating mechanism is sometimes misunderstood: The energy contained in the oscillatory motion of the electrons in the microwave field constitutes only a small fraction of the mean electron energy! The collisional “friction” between electrons and the gas is an essential ingredient. It can be shown that the steady-state electron velocity distribution approaches a Maxwellian in the limit where the microwave frequency is much larger than the electron collision frequency.

The first microwave-heated experiments on recombination of rare-gas dimer ions were carried out in pure rare gases. In typical experiments, the plasma container (usually a quartz flask) occupied only part of the microwave cavity (or wave guide) such that the heating microwave field was fairly uniform in the plasma volume. In later work on molecular ions, molecular gases were added to form the desired ion species, and the instruments incorporated mass spectrometers. Now, the afterglow plasma filled the entire cavity, and uniformity of the microwave field became worse. The combined effects of adding molecular gases and non-uniformity of the heating field were not fully understood at the time. It was believed that the heat conductance in the electron gas would suffice to smooth out spatial temperature variations, and that the presence of small traces of molecular gases would not have serious consequences. The problematic nature of these assumptions became apparent in a study of NO$^+$ recombination (Dulaney et al, [7] and Johnsen [8]). I will skip the rather involved details. In essence, microwave heating does not produce a uniform electron temperature and the average electron temperature is reduced significantly by inelastic electron-molecule collisions. The electron velocity distributions are still close to Maxwellian locally, but are not so when averaged over the plasma volume. The effects can be moderate and sometimes negligible (for low concentrations of homonuclear diatomic molecules such as N$_2$), but addition of even small amounts of polar gases like NO, H$_2$O or NH$_3$ drastically reduces microwave heating. This happens because rotational excitation of polar molecules by electrons is an extremely efficient electron cooling mechanism. In extreme cases, ignoring this effect led to the erroneous inference [8] that the recombination coefficients of cluster-ions of the type H$_2$O$^+$ (H$_2$O)$_n$ and NH$_4^+$ (NH$_3$)$_n$ were independent of electron temperature.

Fortunately, the N$_2^+$ measurements by Mehr and Biondi [9] in microwave-heated afterglows were not much affected by the complications just discussed and the results have withstood the test of time. In the range from $T_e = 300$ to 5000 K, the measured recombination coefficients were found to fit the power law
\[ \alpha(N_2^+) = (1.8 \pm 0.4) \times 10^{-7} (T_e / 300)^{-0.39} \text{cm}^3 / \text{s}, \]  

This often quoted benchmark result should still be considered reliable, even though the electron energy distribution probably was not exactly Maxwellian.

2.5 Shock heating to raise the neutral and vibrational temperatures

Higher gas temperatures \( T_{\text{gas}} \) can be reached by employing shock heating of the afterglow plasma. As in the stationary afterglow, a plasma is first generated by a pulse of RF power. Then the plasma is rapidly compressed and heated by a high-pressure driver gas that expands into the shock tube, after a diaphragm bursts that initially separates the two section of the shock tube. At the Mach numbers used in the experiments (up to about 6), translational gas temperatures from 500 K to about 10000 K can be reached. The degree of heating can be calculated from the shock-wave (Rankine-Hugoniot) equations. This experimental method was applied by Hobson and co-workers to several molecular ions, beginning with molecular rare-gas ions. It was found that for \( T_{\text{gas}} > 700 \text{ K} \) the recombination coefficient of \( \text{Ne}_2^{+} \) [10] declined much faster with temperature (as \( \sim T_{\text{gas}}^{-3/2} \)) than the \( T_e \) dependence observed in microwave-heated afterglows. This interesting result agreed rather well with a theoretical prediction by O’Malley that vibrational excitation should reduce the recombination coefficient.

However, when the shock-heating technique was applied to \( \text{N}_2^{+} \) and \( \text{O}_2^{+} \) ions the observed dependence on gas temperature [11] was found to be nearly the same as that on electron temperature found by microwave heating. Hence, the authors suggested that shock heating did not produce a vibrational \( \text{N}_2^{+} \) population in equilibrium with the translational degrees of freedom. Of course, they could equally well have concluded that vibrational excitation has no significant effect on \( \text{N}_2^{+} \) recombination. Later, an improved version of the theory (Cunningham et al [12]) showed that the vibrational effect should be significant only when the probability of auto-ionization subsequent to electron capture is large, and that this is true for \( \text{Ne}_2^{+} \) and other rare-gas dimer ions, but not for \( \text{N}_2^{+} \) and \( \text{O}_2^{+} \).

In hindsight, it appears that in the \( \text{Ne}_2^{+} \) shock-tube experiment vibrational equilibration of the ions was approached rapidly, presumably as a result \( \text{Ne}_2^{+} + \text{Ne} \rightarrow \text{Ne} + \text{Ne}_2^{+} \) ion-atom interchange, and that recombination of \( \text{Ne}_2^{+} \) actually is reduced by vibrational excitation. However, no firm conclusion can be reached for \( \text{N}_2^{+} \) and \( \text{O}_2^{+} \) since the degree of thermal vibrational excitation in these experiments was not known. Probably, some vibrationally excited ions were produced during the discharge phase and persisted during the afterglow.

The shock tube technique provides a clean way to heat the gas to high temperatures, but is has the practical problem that after each experimental cycle the tube has to be partially disassembled to replace the diaphragm and then has to be pumped out again for the next cycle. Hence, data collecting is painfully slow and that may have contributed to the demise of this method. I will now turn to an interesting experiment in which the \( \text{N}_2^{+} \) vibrational excitation was actually measured.

2.6 Laser induced fluorescence determination of the effect of \( \text{N}_2^{+} \) vibrational excitation

The high density of recombining ions in an afterglow makes it possible to measure their concentrations by laser-induced fluorescence (LIF). Zipf [13], in a pioneering but unfortunately not definitive experiment, applied LIF to the first negative band system of \( \text{N}_2^{+} \) and determined the rate at which \( \text{N}_2^{+} \) ions in \( v = 0, 1, 2 \) vibrational states decay in an \( \text{N}_2^{+} - \text{Ne} \) afterglow at 300 K. The initial vibrational excitation occurs during the discharge, mainly by Penning ionization by neon metastables. Typically, the \( v=1 \) and \( v=2 \) ions had concentrations of \( \sim 1\% \) or \( \sim 0.1 \% \), respectively, of that of \( v=0 \) ions. Zipf found that the decay rates of the \( v=0, 1, 2 \) ions depended only very weakly on vibrational state, combined his results with the \( T_e \) dependence found by Mehr and Biondi and expressed the variation of the recombination coefficient with vibrational and electron temperature by a power law:

\[ \alpha(N_2^+) = (2.2) \times 10^{-7} (T_e / 300)^{-0.39} (T_{\text{int}} / 300)^{0.04} \text{cm}^3 / \text{s} \]  

Obviously, such a formula is very useful for ionospheric models and it was accepted for some time until Johnsen [8] pointed out an unexpected complication in the interpretation of the experiment. The
problem is that vibrational excited $N_2^+$ ions are quenched rapidly by charge transfer with neutral $N_2$ and could not have persisted in the afterglow as long as Zipf had observed and if, as he had assumed, the neutral $N_2$ in the gas mixture was vibrationally cold. In reality, the neutral $N_2$ must have been excited during the discharge to a vibrational temperature of about 1500 K such that rapid back-and-forth ion-neutral charge transfer kept the $N_2^+$ ions in vibrational equilibrium with the hot $N_2$. The only conclusion that can be drawn is that an $N_2^+$ population with a vibrational temperature of $\sim$1500 K recombines with nearly the same recombination coefficient as the majority $v=0$ ions. The measurements do not exclude the (however unlikely) possibility that the $v=1$ and $v=2$ minority ions recombine very slowly or not at all, but they do exclude the possibility that the majority $v=0$ ions recombine much more slowly than $v=1$ and $v=0$ ions. A more complete analysis of Zipf’s and other experiments is given in a paper by Bates and Mitchell [14]. Even though Zipf’s conclusions and formula (5) do not follow from his experiment, later work has confirmed that vibrational excitation has only a minor effect on $N_2^+$ recombination.

There were some further “twists and turns” in the history of $N_2^+$ ($v$) recombination. Model analyses of satellite ionospheric data seemed to imply that $N_2^+$ in $v=0$ recombined much more slowly than in $v=1$ and $v=2$. I will discuss them only briefly.

2.7 The “great afterglow in the sky”.

During the 1970s extensive data on the ionospheric composition became available and computational models were developed that combined both laboratory and observational data. Obviously, ionospheric models are very valuable tools but their limitations were sometimes disregarded and apparent discrepancies were “resolved” by adjusting, for instance, recombination rates to fit the model. In one example, the modeling of Atmosphere Explorer data by Orsini et al [15] led to the inference that vibrationally excited $N_2^+$ should recombine much more rapidly (DR coefficients $>10^{-6}$ cm$^3$/s) than $v=0$ ions, which, as Biondi [16] quickly pointed out, contradicts both the basic physics of DR and available laboratory data. The ensuing controversy was eventually resolved in favor of the laboratory data when Breig et al [17] included in the model a previously ignored fast charge transfer reaction of metastable $O^+$ ($^3\text{D}$) with $N_2$. The details are not very important in this context. The positive aspect is that seeming discrepancies, if properly diagnosed, often lead to new insights.

3. Merged beam and storage-ring measurements

The foregoing discussions make it clear that the plasma environment in afterglow studies of recombination introduces some “interesting complications”. One would like to be able to observe purely binary recombination between ions and electrons with well-defined relative velocity in an otherwise “empty universe”. This “theorists’ view” of recombination is closely approached in merged-beam and storage-ring methods, but the conceptual simplicity comes at a high cost and requires large-scale facilities.

The original single-pass merged-beam method developed at the University of Western Ontario [10] and storage-rings have in common that recombination of ions and electrons takes place between coaxial ion and electron beams of nearly the same velocity. In a single-pass merged beam the ion beam passes through the electron target beam once and is then discarded; in a storage ring the ions circulate in the ring and pass through the interaction region many times. Except in cases where the ions under study are “expensive” to make, it is not the recycling of ions in storage rings that makes them preferable but the fact that the longer storage time (up to 10 seconds) in a ring removes all instance infrared active vibrationally excited ions. The relative velocity between the two beams can be made very small and the velocity spread in the electron target gas is greatly reduced by accelerating the (initially “hot”) electrons to a high velocity that closely matches that of the ions. In part, the narrowing of the electron velocity distribution in the direction of the beam (but not transverse to it) is a kinematic effect that follows from the classical equations of motion. In the single pass merged-beam apparatus, further improvements in the energy resolution were made by using trochoidal analyzers to merge electron and ion beams. Storage rings employ “electron coolers” in which the electrons are
cooled by expansion in a magnetic guiding field. The coolers also cool the ion beam by a “friction” effect and reduce the diameter of the ion beam.

In the merged-beam techniques recombination events are detected by counting their products using an energy sensitive barrier detector. The technique has the advantage that product branching fractions and the kinetic energies released by recombination can be determined with high accuracy. Afterglow experiments can provide complementary information on branching fractions by detecting products via laser induced fluorescence of emission spectroscopy, but with few exceptions (e.g. Doppler broadening of emission lines) the kinetic energy of fragments cannot be determined.

3.1 Merged beam data on N\textsubscript{2}\textsuperscript{+}
recombination

The first merged-beam measurements on N\textsubscript{2}\textsuperscript{+} (Mul and McGowan [18]) yielded recombination cross sections up to an energy of 1eV that declined with energy as $E^{-1}$, equivalent to a $T_e^{0.5}$ dependence of the thermal rate coefficient, somewhat faster than the $T_e^{0.39}$ dependence observed by Mehr and Biondi [9] in a microwave heated afterglow. The absolute values at 300 K agreed to about 30%. Mul and McGowan state that the ions may have been vibrationally excited. A later repletion of the merged-beam experiment (Noren et al [19] employed two different ions sources and led to the puzzling conclusion that N\textsubscript{2}\textsuperscript{+} (v=0) recombines much more slowly (by a factor of 5) than the afterglow value. As Bates and Mitchell [14] discuss in a later joint paper, this experimental result is incompatible with both theory and other experiments, but the precise cause of the discrepancy remains unclear.

3.2 Flowing afterglow data N\textsubscript{2}\textsuperscript{+} recombination.

As has been discussed before, exposing molecular gases to an intense discharge in stationary afterglows containing N\textsubscript{2} creates a reservoir of vibrationally hot molecules that keep the ions hot during the afterglow. The flowing afterglow technique gets around this problem by separating the discharge region from the recombination region. Since the N\textsubscript{2} downstream from the N\textsubscript{2} inlet is cold, charge transfer with N\textsubscript{2} now reduces the N\textsubscript{2}\textsuperscript{+} vibrational state to v=0 and one measures the recombination of this ion. Two such experiments have been performed. The 300 K rate coefficients were found to be $2.6 \times 10^{-7}$ cm\textsuperscript{3}/s (Canosa et al [20]) and $2.0 \times 10^{-7}$ cm\textsuperscript{3}/s (Geoghegan and Smith [21]) in reasonable agreement with the Mehr and Biondi value.

3.3 Storage-ring data on N\textsubscript{2}\textsuperscript{+} recombination

Storage rings are currently the method of choice for recombination studies and really deserve a more extended discussion of their outstanding capabilities than can be given in this brief historical review. The results obtained by this technique have been quite consistent over the years and the N\textsubscript{2}\textsuperscript{+} measurements by Peterson et al [22] are no exception. Converted to a thermal rate coefficient, the result (for a vibrational distribution of 46% in v=0, 27% in v=1) can be expressed as

$$\alpha(N\textsubscript{2}\textsuperscript{+}) = (1.75 \pm 0.09) \times 10^{-7} \left( T_e / 300 \right)^{0.30} \text{cm}^3 / \text{s}$$

which is essentially the same as that given by Mehr and Biondi, except that the temperature exponent is slightly smaller. The storage ring measurements employed two different ion sources that produce N\textsubscript{2}\textsuperscript{+} ions with different vibrational populations. Both gave nearly the same recombination cross sections. The authors also determined the product fractions for three of the branches listed in Eq. (1). At a collision energy of zero and for v=0 ions, the fractions were found to be 37%, 11%, and 52% for N(\textsuperscript{4}S) + N(\textsuperscript{2}D), N(\textsuperscript{4}S) + N(\textsuperscript{2}P),and N(\textsuperscript{2}D) + N(\textsuperscript{2}D), respectively.

3.4 Comparison with theoretical results

The extensive theoretical work by Guberman on N\textsubscript{2}\textsuperscript{+} recombination largely supports the observed of the recombination rate but his theoretical result [23] indicates a somewhat stronger dependence on vibrational state and the theoretical branching fraction [24] for the N(\textsuperscript{4}S ) + N(\textsuperscript{2}D) product channel is considerably larger than was observed by Peterson et al [22].
4. Conclusions

Peterson et al [22] sum up the long history of N$_2^+$ recombination measurements by saying “We note that surprisingly good agreement is found between all reported experiments on N$_2^+$, using different techniques, and undoubtedly with a variation in vibrational composition. This can now be rationalized, since the DR rates from our two ion sources with markedly different vibrational populations were about the same”.

My quick tour through the history was intended to review the different experimental approaches using N$_2^+$ as an example. In this case, the story indeed has a “happy ending”, at least as far as experiments are concerned, but one should not necessarily assume that the same is true for other ion species. Differences in vibrational distributions are not the only cause of discrepancies between measurements and I still believe that recombination of ions in plasmas can involve additional mechanisms that are not present in the rarefied environment of beam experiments. But the “bogus” era of DR studies certainly has clearly come to an end!

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