A Personal History of the Early Development of the Flowing Afterglow Technique for Ion-Molecule Reaction Studies

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A personal perspective of the historical development of the flowing afterglow (FA) technique for measuring thermal energy ion-molecule reaction rate constants is presented. The technique was developed in the period starting in late 1962 in what was then the National Bureau of Standards in Boulder, Colorado. The motivation was primarily to obtain a quantitative understanding of the ion chemistry of the terrestrial ionosphere, a program that was substantially achieved. The thermal energy measurements were extended in temperature from 300 K to a range of 80 K-900 K and subsequently to a center-of-mass kinetic energy range up to ~ 2 eV with the introduction of a drift tube into the FA.

The chemical versatility, in regard to both the ion and the neutral reactants measured, remains unequaled and FA systems are currently in widespread use around the world for a variety of chemical research programs. (*J Am Soc Mass Spectrom* 1992, 3, 479-486)

A n account of the early development of the flowing afterglow (FA) technique for ion-molecule reaction studies during the past almost 30 years may have some general historical interest for mass spectroscopists and ion-molecule chemists and physicists. I welcomed this opportunity to write such an account from my personal perspective. This is a congenial endeavor for me at this time when I have recently switched my own research interests away from ion chemistry largely to environmental matters, such as chemical aspects of the "greenhouse" effect. I remain in contact with my two collaborators in the development of the FA technique, Art Schmeltekopf and Fred Fehsenfeld, both of whom switched their research efforts to neutral atmospheric chemical problems many years ago (again becoming leaders in their fields). I have also maintained close ties, including several recent collaborations, with a number of active practitioners in the field, some of them alumni of our Laboratory, and I have prevailed on many of these participants in the FA saga to help correct my memory lapses and errors of commission and omission. The defects remaining are entirely my own responsibility.

This is not in any sense a comprehensive survey or review of the by-now very widely spread field of flow tube studies of ion-molecule reactions. The monu-mental comprehensive effort of Susan Graul and Bob Squires [1] will serve that purpose beautifully for a long time to come.

The invention of the FA was, like much of science, more a matter of serendipity than of judiciously calculated planning. The story for me began when, frustrated with the dual demands of research and a nine-hour teaching load, I chose to concentrate on the former and left a tenured faculty position in Physics at the University of Texas, Austin, for a position in the Upper Atmosphere and Space Physics Division of the National Bureau of Standards (NBS) in Boulder in 1962. This opportunity was arranged for me by a close friend, the late II. P. Broida, a senior scientist in NBS Washington at that time, and one of the world's leading spectroscopists and atomic physicists. I was offered the opportunity to create a laboratory aeronomy program in support of the NBS mission in radio propagation. It was my exceptionally good fortune at that time to have two extraordinarily able graduate students at Texas, Art Schmeltekopf and Fred Fehsenfeld, who joined me in this new endeavor in Boulder. We called the new group the Atmospheric Collision Processes Group.

We soon learned that the subject of atmospheric ion chemistry was in a primitive state. Satellite- and rocket-borne mass spectrometers were obtaining atmospheric ion composition data, but none of the relevant ion-neutral chemistry was understood. Art, Fred, and I had had a brief and informal introduction to ion-molecule chemistry shortly before this on the

occasion of a visit to the University of Texas by Joe Franklin from Rice and found the subject to be one of considerable interest.

The standard technique for measuring ion-molecule reactions at that time utilized conventional mass spectrometers with specially designed ion sources that served as reaction chambers, the familiar technique used with such great success by Joe Franklin, Frank Field, Fred Lampe, Burnaby Munson, and others. This technique was far too limited in chemical versatility to contribute significantly to atmospheric ion chemistry. The reasons for this must be readily apparent to this audience.

Another approach, pioneered by Jim Sayers and John Hasted in England, and by Wade Fite, Larry Puckett, Carl Lineberger, Fred Biondi, and Art Phelps in the United States, was the stationary afterglow (SA) in which a gas mixture in a bulb was subjected to an ionizing pulse and the ion composition was monitored at the wall as a function of time after the cessation of ionization, the ion composition varying in time due to ion reactions with the neutrals. The lack of chemical versatility of this approach is also evident. In addition, there were problems associated with unknown states of the ions and even the neutral reactants, both of which had been subjected to a discharge. The few ionospherically relevant measurements available from SAs in 1964 on common reactions were in order of magnitude disagreement, e.g., the reactions between O^+ and N_2 and between O^+ and O_2. In brief, the situation in 1962 was that no single atmospheric ion-molecule reaction rate constant was unambiguously determined!

Our initial plan was to utilize an SA with the hope of overpowering the situation with diagnostic capabilities. While waiting for the arrival of the parts we had ordered, as well as the completion of our new laboratory space, Art spent one month at NBS in Washington with Herb Broida doing optical spectroscopy on the original "flowing afterglow," a glass tube of about 10 cm diameter and 1 meter length, exhausted by very large Roots Blower pumps. An electrodeless microwave discharge was initiated at a constriction in the tube. The light emission downstream in the fast flow, i.e., the "afterglow," was examined spectroscopically [2]. The gas flow speed was on the order of 10,000 cm/sec, about one tenth of sound speed. Upon Art's return to Boulder he was anxious to have such a spectroscopic light source in the lab, for aesthetic as well as scientific reasons. Afterglows in glass tubes are colorful and interesting as well as effective places to do atomic and molecular physics and chemistry. We quickly realized that the light emission from the He afterglow must be due to electron-ion recombination, specifically the collisional-radiative process described shortly before (1962) by Bates et al. [3]. Ergo, ions must exist in the afterglow, and hence the possibility of studying ion chemistry in such a tube was suggested. Our expectation was that the FA might be

useful in a qualitative survey fashion for determining suitable conditions for the operation of our ultrahigh vacuum SA under construction. SA experiments are necessarily tedious and time consuming. The very first time the FA was turned on, however, we realized that we had a very useful tool on our hands. (Indeed, the SA was never turned on!) Our first He flowing afterglow was not spectroscopically pure, unsurprisingly. A glass tube had been connected to a pumping port with O-rings, etc. The characteristic blue nitrogen emission spectrum was a clear indication of an air leak, and there was a large N^+ signal in the quadrupole mass spectrometer (which was homemade because they were not commercially available at the time). There was also an O^+ signal and lesser N_2^+ and O_2^+ signals. The N^+ signal was by far the largest, over four times larger than the oxygen ion signals, and it was therefore clear that the dissociative ionization of N_2 by He^+ was very fast. This had an important geophysical consequence that we immediately recognized.

David Bates and Tom Patterson [4] had very recently (1962) published a paper theorizing that the mysterious escape of He from the Earth's atmosphere might be due to the very exothermic reaction of He^+ with O_2, invoking a mechanism giving the light He atom sufficient energy (2.4 eV) to escape the Earth's gravitational field. This followed a finding by Nicolet that the rate of photoionization of He in the Earth's atmosphere was equal to the He loss required to yield a steady state. This *assumed* that He ions would not react with N_2. The first FA experiment showed clearly that this was not the case! This, of course, got us off to an exciting start in "Flowing Afterglowery" [5]; but of more substantial importance, we quickly learned that we could get rather good rate constants from a very simple hydrodynamic flow analysis. This was established by comparing our measured rate constants for the reaction of He^+ with N_2 and O_2 with those that had been measured by Sayers and Smith [6] at Birmingham and reported at a Faraday Society meeting a few months earlier. Also in these cases the measured rate constants were approximately equal to the collision rate constant, which seemed unlikely to be a chance coincidence. From that point on, FA rate constants for ionospheric ion-molecule reactions emerged in a steady stream. The pre-FA rate constants of all categories numbered in the ~ 100 range [7], a number quickly surpassed in Boulder.

The hydrodynamic analysis was quickly improved, with the help of an NBS mathematician, Steve Jarvis, leading to uncertainties on the order of only about 5% for chemically simple reactions. We were working in the uncharted ionospheric chemistry field where there were order of magnitude questions to be answered (even yes/no questions as in the case of the $He^+ + N_2$ reaction, the $N_2^+ + O$ reaction, and others), and we were quite satisfied with this accuracy. By this time there had been a number of US and Soviet rocket-

borne mass spectrometer measurements of atmospheric ion composition, and there were fertile fields to plow with the first lab data.

The huge advantage of the FA arose from the separation of the ion production region from the neutral addition region, which in turn led to the still unsurpassed chemical versatility of the FA. With regard to ions, successive reactions prior to neutral addition could be used to produce a great variety of ions, indeed, all those ions of early ionospheric interest. For example, the reaction of He^+ with N_2 gave both N^+ and N_2^+ ions for further reaction (e.g., with O_2). Penning ionization by the abundant He metastables in the afterglow was also an efficient ionization source for any neutral, even such unlikely prospects as iron and magnesium, vaporized from small furnaces introduced into the FA for atmospheric meteor ion chemistry studies. Negative ions could be formed either by direct electron attachment or by sequences of ion-neutral reactions. Later, for lower ionosphere studies, it was necessary to study cluster ion chemistry, and modifications in the flow tube by David Fahey [8] allowed multiply hydrated (or otherwise solvated) ions to be produced for reaction studies.

Of course, the physical separation of the neutral reactant from the ionization source region eliminated the problems associated with neutral excitation by the ionization source. The early errors in SA measurements of the $O^+ + N_2$ reaction were later traced to vibrational excitation of the N_2 by the ionizing discharge pulse. The Birmingham and London SAs had produced quite different rate constants because the ionizing pulse lengths were different, leading to different extents of vibrational excitation of the N_2 and consequently quite different $O^+ + N_2 \rightarrow NO^+ + N$ reaction rate constants. The measurement in the FA of this rate constant as a function of N_2 vibrational quantum number remains a classic experiment of chemical kinetics [9]. I believe it is still the only ion-molecule reaction measured as a function of vibrational state of the *neutral* reactant, if one neglects the somewhat qualitative study of the reactions of He^+ and Ne^+ with $H_2(v)$ [10], carried out in Chuck DePuy's laboratory, which verified the huge rate constant enhancement for v > O, predicted by Preston et al. [11]. [A project undertaken because of my (unfounded) skepticism that a change of one vibrational quantum could give a one hundredfold change in rate constant.] It is a simple matter to vibrationally excite N_2 with a microwave cavity discharge in the N_2 reactant inlet line, achieving vibrational temperatures as high as ~ 6000 K. The real trick was in measuring the resulting T_v, which was done spectroscopically utilizing our discovery that the Penning ionization of N_2 to the radiating $N_2^+(B)$ state is approximately vertical, i.e, Franck-Condon. Thus, to a good approximation the population of $N_2^+(B, v)$, as deduced from the measured $N_2^+(B, v) \rightarrow N_2^+(X, v)$ intensity (B → X being again an almost vertical transition), reflected the pop-

ulation of neutral $N_2(X, v)$ attained in the microwave discharge. The efficiency of N_2 vibrational excitation is due to the existence of the short-lived N_2^- resonance near ~ 2 eV. This procedure does not work for O_2, of course, where the potential curves are extremely nonvertical and therefore no measurements exist of ion reactions with O_2 as a function of the vibrational state of the O_2.

With regard to neutrals, it was possible to introduce into the FA unstable neutrals, such as O, N, H atoms and OH radicals using "titration" techniques developed for neutral atmospheric kinetic studies. Harold Schiff, from York University in Toronto, collaborated with us on these studies. For example, the major loss process of N_2^+ ions in the ionosphere is the reaction

$$N_2^+ + O \rightarrow NO^+ + N \qquad (1)$$
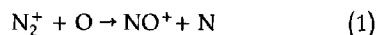
which had been predicted on theoretical grounds to be slow, but which from atmospheric ion profiles appeared to be very fast. We resolved this conflict with a measurement showing the rate constant to be about one-half the Langevin collision rate constant [12].

Nitrogen gas, diluted in He carrier gas, was introduced in the reactant port side tube and subjected to a microwave discharge that dissociated a few percent of the N_2. The stream of N atoms so produced could then be used for reaction studies as, e.g., the reaction

$$O_2^+ + N \rightarrow NO^+ + O \qquad (2)$$
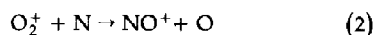
also an important ionospheric reaction. To produce O atoms, NO, in measured flows, was added to the discharged nitrogen and the fast reaction

$$N + NO \rightarrow N_2 + O \qquad (3)$$
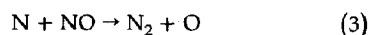
quantitatively exchanged N for O. The titration endpoint, i.e., the measured NO flow at which all of the N atoms are converted to O atoms, determines the absolute concentration of [O] for reactions like 1, or [N] for reactions like 2. The endpoint is indicated dramatically in the detected ion signals (and by visual inspection of the titration reaction in a darkened room!).

Of course, the N_2/N (and N_2/O) ratios were very large and one could only measure reactions of ions that did not react with N_2 as, e.g., N_2^+ or O_2^+. At least for N, this is not a limitation in the atmosphere because the N_2/N ratio is also large there, and only the N atom reactions of ions that do not react with N_2 are of practical interest.

Only relative values of ion concentrations are required to obtain FA rate constants, but absolute concentrations of the neutrals are required, working in the pseudo first order regime that usually prevailed, [Neutral reactant] $\gg$ [Ion reactant], so that the neutral

which has a rate constant $\sim 1/3\ k_L$, establishes that at least one third of the 24 O_2^- potential curves arising from $O^-(^2P) + O(^3S)$ must be attractive into the autodetaching region, a fraction far in excess of the theoretically expected value at the time, which has subsequently been supported, however, by detailed quantum calculations by Harvey Michels. Reaction 25 is very fast, $k \sim k_L$, establishing that the single HF^- potential curve must be attractive, resolving a dispute between theoretical calculations then existing, two yielding attractive curves and two yielding repulsive curves!

The ion chemistry of the ionosphere, the D-, E-, and F-regions above ~ 60 km, was fairly clear by the early 1970s. Efforts continued to refine this chemistry, improve rate constant accuracy, extend energy dependences, etc.; but the emphasis was on the study of the lower atmosphere chemistry, the subionospheric stratosphere and troposphere. This involved both positive-ion and negative-ion reactions and both binary and three-body reactions. It also involved measurement of the reactions of negative ions with HNO_3 and H_2SO_4, which are critical in the stratosphere.

The only measurements of gas-phase sulfuric acid (by Frank Arnold, Heidelberg) utilize the laboratory reaction studies [28] in conjunction with his balloon-borne measurements of HSO_4^- ions.

Detailed studies of sodium ion chemistry [29] allowed the later deduction [30] that there were no gas-phase sodium compounds below 60 km; any gas-phase sodium compounds present would react with the ambient proton hydrates to yield protonated NaOH clusters (or equivalently hydrated Na^+ clusters).

A novel and interesting experiment was carried out at JILA and CU in Boulder by Veronica Bierbaum, Barney Ellison, Jean Futrell, and Steve Leone [31] in which they made the first ion-molecule infrared chemiluminescence measurements using an FA with sensitive detection of infrared emission from the reaction products. Specifically, they observed 4.3 μ emission of the antisymmetric stretch of CO_2 produced in reaction 19. It follows from the generally very fast process of exothermic autodetachment that associative-detachment neutral product molecules will usually be highly vibrationally excited. The electron departs the negative-ion product initially produced in the collision very promptly, following the negative ion-neutral curve crossing so that a large fraction of the reaction exothermicity is left in product vibrational modes. Subsequently, results from this program included a measurement of the vibrational population of $NO^+(X^1\Sigma^+, v)$ from $v = 1$–14, produced in the reaction of N^+ with O_2 [32]. This important ionospheric reaction showed a marked bimodal product vibrational distribution. Studies involving FA-visible chemiluminescence in Leone's lab allowed measurement of the $O(^3P)$, $O(^1D)$, and $O(^1S)$ product branching ratio for the $N^+ + O_2 \rightarrow O + NO$ reaction [33],

again an important atmospheric process. It is clear that such experimental extensions and sophistications of the FA technique will contribute greatly to both practical and mechanistic understanding of ion-molecule reactions.

From time to time we made astrophysically relevant ion-molecule reaction rate measurements, usually prompted by a phone call from Alex Dalgarno. One of the earliest was reaction 21 discussed above. Another was the reaction

$$O^+ + H \rightarrow H^+ + O \qquad (26)$$

of great importance both geophysically and astrophysically [34].

The intense interest generated in interstellar molecule formation by the rapidly increasing discovery of their existence by radio astronomers led to a strong motivation for laboratory ion-molecule reaction rates because it was quickly recognized that ion-molecule chemistry must be a dominant contributor to molecule formation in the low-temperature, low-pressure environment.

Astrophysics was not in our mission, however, and the overwhelming contribution to this field was made by Nigel Adams and David Smith in Birmingham. This has been a source of satisfaction to us because Nigel was one of our earliest Post-Docs, and certainly one of our most productive; and David has been a friend from the earliest days of our program and subsequently a frequent collaborator of mine. David and Nigel introduced the powerful SIFT (selected ion flow tube) technique in 1976, in which single ions from a low pressure ion source could be injected into the flow tube by means of an aspirator [35]. This vastly increased the versatility of the FA and has been a standard feature for some time.

Tropospheric ion chemistry has been held back by the horrendous technical problem of sampling and mass analyzing $\sim 10^3$ ions/cc in a background of $\sim 10^{19}$ neutrals/cc. Only recently has success been achieved in this endeavor by Fred Eisele and his colleagues at Georgia Tech [36, 37]. The neutral molecules involved (caprolactam, methyl sulfonic acid, methylquinoline, isoxazole, sarcosine) are such as to support the wisdom of a simple physicist in having abandoned the field of atmospheric ion chemistry at the stratospheric level.

In the later years of ion chemistry in NOAA, we utilized the FA technique to make the first systematic measurements of diatomic ion vibrational quenching [38, 39], work subsequently continued in Werner Lindinger's lab in Innsbruck [40–43], in Norman Twiddy's lab in Aberystwyth [44], and in John Paulsons's lab at AFGL in Boston [45]. The only experiment involving quenching by an electronically excited neutral ($NO^+(v) + O_2(^1\Delta g)$) was carried out in Chuck DePuy's lab at CU [46]. The critical factor for these studies was the use of a "monitor ion" to

determine the vibrational state of the ions. This involved addition of a neutral reactant into the flow tube just ahead of the mass spectrometer sampling whose reactivity depended on the ion vibrational state, as a consequence of the reaction energetics. Ar reacts only with vibrationally excited N_2^+, N_2 only with vibrationally excited HCl^+, SO_2 only with vibrationally excited O_2^+, etc. This was the technique used much earlier to measure reactions with electronically excited ions such as $O_2^+(a^4\pi u)$ [47].

One of the most satisfying research results from the later years was a comprehensive study of the reaction

$$O_2^+ + CH_4 \rightarrow H_2COOH^+ + H \qquad (27)$$

carried out in the Aeronomy Lab [48], Meudon and Birmingham [49], and Colorado University [50, 51], culminating in perhaps the most detailed understanding of the reaction mechanism for any ion-molecule reaction of such complexity, e.g., more than ~ 5 atoms.

The Boulder Aeronomy Lab Flowing Afterglow story terminated in 1984 with the ion vibrational relaxation studies and the $O_2^+ + CH_4$ studies carried out by our last visitors, Marie Durup-Ferguson from Orsay and Hans Böhringer from Heidelberg. The Aeronomy Lab scientists, Art Schmeltekopf, Fred Fehsenfeld, Dan Albritton, and David Fahey, were by then all busily (and productively) engaged in the challenging (and relevant) problems of neutral atmospheric chemistry.

The ion chemistry laboratory had been undergoing a transition for several years to a chemical kinetics laboratory for the study of neutral atmospheric reactions under the able direction of Carl Howard. This laboratory has continued a record of outstanding productivity and was subsequently bolstered even further by the addition of Akkihebbal Ravishankara. The old FA tubes are on occasion being used as "chemical ionization detectors" for free radicals to measure important neutral reaction rate constants and reaction products.

The Boulder Flowing Afterglow story has continued full-tilt, however, in the laboratory of Chuck DePuy and Veronica Bierbaum in the Chemistry Department of CU. We assisted the introduction of the FA technology into Professor DePuy's lab in 1973 and the outstanding success of that new direction in organic chemistry has been a continuing source of satisfaction to me for many years.

My own FA ion chemistry research did not end with the termination of the Aeronomy Lab program. Being less versatile and less adaptable (and older!) than my colleagues, I was not successful in adapting to a new field as they were and instead maintained research in ion-molecule chemistry. For this I relied on the friendship and generosity of many friends and former colleagues, particularly Aeronomy Lab alumni

Werner Lindinger at Innsbruck, Nigel Adams (and David Smith) at Birmingham, and Al Viggiano (and John Paulson) at AFGL; also colleagues and long-time friends, Norman Twiddy at Aberystwyth, Will Castleman at Penn State, and, most recently, Murray McEwan at Christchurch. Castleman and his group have built upon the FA technology, especially the modifications of David Fahey et al. [8], and have successfully implemented the poor-man SIFT technique to the production of quite large cluster ions. Their prolific studies are serving to bridge the gap between the gaseous and condensed state in terms of understanding solvation effects on reactivity.

Many of these friends and colleagues honored me with a Festschrift issue of the *International Journal of Mass Spectrometery and Ion Processes* [52], which gave an eloquent testimony to the continuing vigor of the field. It has truly been an exciting period for me, and ion chemistry continues to be an exciting and productive field for many old friends and young scientists that I have not had the good fortune to interact with.

The pleasure of working and associating with outstanding students, Post-Docs, and colleagues, as well as with the broader ion-molecule community, over these many years has equaled the satisfaction and excitement of the scientific results and leaves me with a deep reservoir of fond memories.

During the year 1983–1984 and between the years 1986–1990, I was privileged to work in the Laboratoire de Physico-Chimie des Rayonnements, Université Paris-Sud, during which time I enjoyed a stimulating and profitable interaction with Rose Marx and Gerard Mauclaire of that lab and also with Bertrand Rowe (an Aeronomy Lab alumnus) at nearby Meudon.

Acknowledgment

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