

**SPECIAL FEATURE:  
HISTORICAL****Atmospheric Chemistry and the Flowing  
Afterglow Technique****Robert R. Squires\***

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Eldon Ferguson and his co-workers Fred Fehsenfeld, Art Schmeltekopf, Harold Schiff and Paul Goldan developed the flowing afterglow instrument in the 1960s<sup>1</sup> in order to perform laboratory measurements of the kinetics of ionic reactions believed to be important in upper-atmosphere chemistry. In its simplest form, the instrumentation<sup>2,3</sup> consists of an ion source immersed in a flow of helium or other inert buffer gas which carries the ions through a meter-long reactor at pressures around 0.5 Torr (1 Torr = 133.3 Pa). The ions are thermalized by tens of thousands of collisions with the buffer gas. Ion–molecule reactions are initiated by addition of neutral reagent gases at different points along the flow reactor such that temporal and spatial resolution of the processes is achieved. Either positive or negative ions are sampled from the flow tube through a small orifice into a quadrupole mass analyzer. This configuration provides the ability to measure ion–molecule reaction rates with reaction efficiencies from as low as 0.0001. Because it is a flow reactor, one can examine the reactions of highly reactive species such as atoms and radicals that are externally generated by a microwave discharge.<sup>4</sup> Also, the temperature of the flow reactor can be varied over a wide range, thereby permitting extrapolation of measured reaction rates to temperatures that directly apply to atmospheric and interstellar conditions.<sup>5</sup>

The modularity of the flowing afterglow instrument has lent itself to developments that have extended its applications into a broad spectrum of physical and chemical problems.<sup>3</sup> Mass-selected primary ions are injected into the flow reactor in the powerful SIFT (selected ion flow tube) technique.<sup>6</sup> Ion drift tubes are used for studies of ion mobilities and ion–molecule reactions from thermal to elevated ion kinetic energies.<sup>7</sup>

Product ion characterization by tandem mass spectrometry has been achieved by incorporating a triple quadrupole analyzer.<sup>3,8</sup> A modern version of the fully developed instrument has a flowing afterglow ion source for a SIFT-type ion injector, a flow tube with an ion drift capability followed by a triple quadrupole analyzer.<sup>9</sup> The flowing afterglow is a chemically versatile ion source that has found applications in a wide variety of areas. These include negative-ion photoelectron spectroscopy,<sup>10</sup> guided ion beam studies of ion thermochemistry,<sup>11</sup> studies of the reactivity of organic,<sup>12</sup> main-group organometallic<sup>13</sup> and transition metal ions,<sup>14</sup> characterization of atomic metal ion reactions,<sup>15</sup> ion spectroscopy including laser-induced fluorescence and chemiluminescence<sup>16</sup> and even studies of biological ions through the interfacing with an electrospray ion source.<sup>17</sup>

Eldon Ferguson selected for this historical feature the paper 'Positive Ion–Neutral Reactions in the Ionosphere,' which was published in 1965 with F. C. Fehsenfeld, P. D. Goldan and A. L. Schmeltkopf in *The Journal of Geophysical Research*, and attached the following summary comments:

'Following the development of the flowing afterglow technique for the study of thermal energy ion–molecule reactions in the Boulder NBS labs in 1963, it became possible for the first time to measure the kinetics of ion–molecule reactions that control the ion composition of the Earth's ionosphere. Such measurements are reported in this paper. The kinetics were shown to be consistent with then current altitude profile measurements of ion and neutral compositions and solar ionizing flux, all obtained by means of rocket-borne probes. Of the dozen or so reactions reported, the most interesting was the reaction  $\text{N}_2^+ + \text{O} \rightarrow \text{NO}^+ + \text{N}$ , which is the major ionospheric loss process for  $\text{N}_2^+$ , as well as the major source of  $\text{NO}^+$  above 140 km. The ability to measure the kinetics for this reaction reflected the unique

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capability of the flowing afterglow to handle reactions of ions with chemically reactive species such as O atoms. This reaction was also of interest from a fundamental point of view because quantum theorists argued at that time that this reaction could not occur because it involves an electronic transition, i.e. is non-adiabatic and violates the adiabatic principle, which was believed at that time to preclude such processes at thermal energies. The reaction had been omitted

from all theoretical models of the ionosphere prior to the flowing afterglow measurements of the reaction rate constants. The large quantity of kinetic and thermochemical data that followed from the flowing afterglow studies led to a detailed understanding of the positive and negative ion chemistry in the upper and lower atmosphere and, in addition, contributed substantially to the present understanding of ion-molecule reaction mechanisms.

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