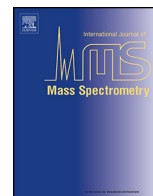




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Incorporating time-of-flight detection on a selected ion flow tube apparatus

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ABSTRACT

A new ion detection scheme incorporating both time-of-flight and quadrupole instrumentation has been implemented on a variable temperature selected ion flow tube and is described here. The new detection region retains typical quadrupole detection for the study of most systems, and adds time-of-flight capability to study systems over a wide mass range while minimizing the effects of mass discrimination. Experiments verify the accuracy of the kinetics obtained with time-of-flight detection. We find excellent agreement with previously published rate constants and product branching for the reactions of Ar⁺ with SF₆ and C₂H₄. Additionally, new results are presented for the reaction of Ar⁺ with WF₆, observing a rate constant of $1.23 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, with product branching of 0.9 and 0.1 to WF₅⁺ and WF₆⁺ respectively.

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1. Introduction

This section of the special issue starts with an excellent history of flowing afterglows and their variations (see Bierbaum, in this issue). It is clear from reading that contribution that innovation plays a primary role in new discoveries. The National Oceanic and Atmospheric Administration (NOAA) group in Boulder, CO that first applied flow tubes to plasma chemistry started that trend. Having been taught by that pioneering group, we have strived to continue to devise new twists on this technique in order to explore new areas of plasma chemistry. This is particularly important because the Air Force has interest in extreme conditions and species, and therefore, we have explored regimes and species other groups have not been motivated to study. Here we detail the addition of an orthogonal-acceleration time-of-flight mass spectrometer (TOF) at the detection end of a selected ion flow tube (SIFT) while retaining the capability of using the standard quadrupole mass selector. In keeping with the “History of mass spectrometry” nature of this special issue, we first highlight several of the main advances in flow tube technology which have been developed in our laboratory.

The NOAA group made initial temperature [1] and kinetic energy [2] dependency measurements using a drift tube. Our laboratory's first major innovation was to do both using the same instrument. While a few previous studies were done elsewhere [3] with a temperature variable drift tube, interpretation of that data missed the dynamical interpretation and we were the first to show that such an instrument could be used to study reactivity not only as a function of energy and temperature, but also internal energy [4,5]. While the technique could not be used to study reactions in as much detail as molecular beam experiments [6,7], it allowed for large amounts of data to be taken quickly so that trends could be derived. Using this technique, it was found that rotational energy had a minimal effect on most ion-molecule reactions, i.e. rotations simply acted as energy, except for several systems with exceptionally large rotational constants. For larger polyatomic systems vibrational energy also acted simply as energy. Expansion of the temperature range of a flowing afterglow to 1800 K [8,9] made clear that in atomic ion plus diatomic reactions, vibrational effects could be exceedingly large and common [10].

Once extreme temperatures could be studied, it was important for our interest in combustion and reentry chemistry to explore higher-pressure regimes. For that purpose we developed the turbulent ion flow tube (TIFT) [11], which was modeled on the work of the Molina group for neutral chemistry [12]. With it we extended the pressure range of plasma flow tubes from ~1 Torr to 760 Torr. Combining the data from this instrument with statistical theory,

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energy transfer parameters important to unimolecular reactions were derived [13].

Most new techniques involve new hardware. However, the final advance we mention involves neither electronics nor stainless steel chambers but a novel data acquisition approach for a flowing afterglow – Langmuir probe (FALP) apparatus [14]. Before this technique, kinetics data in ionic flow tubes were exclusively taken by varying either the neutral concentration or the reaction time (i.e. distance). In our variable electron and neutral density attachment mass spectrometry (VENDAMS) technique, the initial plasma density at a neutral inlet is varied and the resultant ion branching fractions are determined and then modeled [14]. That has opened numerous novel areas of plasma kinetics. For instance, the only complete product distributions for ion-ion mutual neutralization have been measured using this technique [15–17]. Measurement of electron attachment to radicals is now routine, and this work has been used to develop a relatively easy method for extrapolating and predicting attachment rate constants for the first time [15,16,18–22]. Mutual neutralization rate constants are now also routinely measured [23]. VENDAMS has been used to provide evidence that electrons catalyze mutual neutralization [24,25]. Often a variety of processes are measured at the same time.

With respect to the innovative use of flow tubes for continued growth of our understanding of fundamental chemical processes, the work presented here details our efforts to add time-of-flight detection to our variable temperature selected ion flow tube (VT-SIFT). The temperature dependence of rate constants and product branching, when properly interpreted using statistical modeling, lends a unique insight into exothermic ion-molecule reactions [13,26]. Application of this methodology to potential photocatalysts and energy dense materials is of great interest to the Air Force, and the study of these systems will be greatly enhanced by the resolution, sensitivity, and lack of mass discrimination available from a TOF detection scheme.

2. Experimental and theoretical methods

All experiments took place using the Air Force Research Laboratory's variable temperature selected ion flow tube. While the bulk of the apparatus has been described in detail elsewhere [4], the downstream end of the instrument has been upgraded to allow for either quadrupole or time-of-flight detection of ions (Fig. 1),

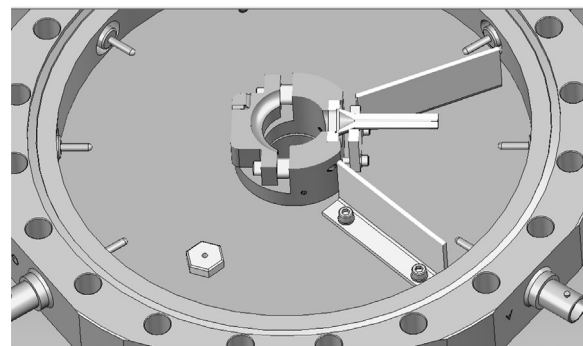


Fig. 2. Schematic of the in-line radial detector assembly from Ardar Technologies L.P.

with conversion time on the order of minutes with minor tuning. The upstream end of the apparatus is comprised of a number of versatile ion sources; however, in the experiments here, only Ar^+ ions are produced. Ar^+ cations are created in an electron impact ion source, selected by a quadrupole mass filter, focused by an einzel lens, and fed into a laminar flow tube via a Venturi inlet. Neutral reactant gases are added 59 cm from the end of the flow tube, allowing for reaction times on the order of 3 ms, depending on helium flow. The ions are extracted from the flow tube through the 2 mm diameter aperture of a truncated nose cone. The ions then pass through an einzel lens before entering a quadrupole with rod diameters of 0.625 in., which operates in either resolving mode for quadrupole detection or as a high pass filter for time-of-flight detection. Upon exiting the quadrupole the ions pass through an in-line radial detector assembly from Ardar Technologies L.P., shown in Fig. 2. Depending on applied voltages, the radial detector alternates as either a long focal length einzel lens, transporting ions to the TOF entrance optics, or as an in-line detector, consisting of a high voltage conversion dynode coupled with a continuous dynode electron multiplier capable of ion counting. When the conversion dynode, multiplier and center lens element have the same potential, those three elements function as the center tube lens element of an einzel lens. Powered separately, ions can be tuned to strike the specially shaped conversion dynode, with resulting secondary electrons focused by the dynode field to a continuous dynode electron multiplier, which is located 180° from the dynode, resulting in high efficiency ion counting. This radial detector is mounted onto an eight-inch double-sided conflat flange, which has electrical feedthroughs located radially, in between the bolt holes, allowing secure, noise-free connection of the high voltage and signal cables. All of the ion optics after the nose cone, up to and including the radial detector, are housed within a custom vacuum chamber that is pumped by two turbomolecular pumps (700 L/s and 550 L/s). The base pressure within the detector region, while the flow tube is maintained at 0.4 Torr, is about 2×10^{-5} Torr.

Ions are then further focused and collimated before introduction into an orthogonal acceleration time-of-flight mass spectrometer (Jordan TOF Products, Inc.) with a quoted resolution of 1500. The extraction region is housed in a six-way cross chamber, which is differentially pumped through the collimator orifice (a slit measuring about $1/25''$ by $3/8''$) by a 550 L/s turbomolecular pump that keeps the pressure at about 8×10^{-8} Torr, while the flight tube is pumped by a 300 L/s turbomolecular pump that maintains the pressure below 1×10^{-8} Torr. Ions are accelerated into the flight tube by a high voltage pulse (1–5 kV) produced by a high voltage switch (Belke Electronics) operated at 1 kHz, resulting in typical flight times of 1–100 μs . The detector may operate either as a linear TOF-MS, with a 25 mm diameter chevron microchannel plate at the end of the flight tube, or, as is the case here, as a reflectron TOF-MS. The

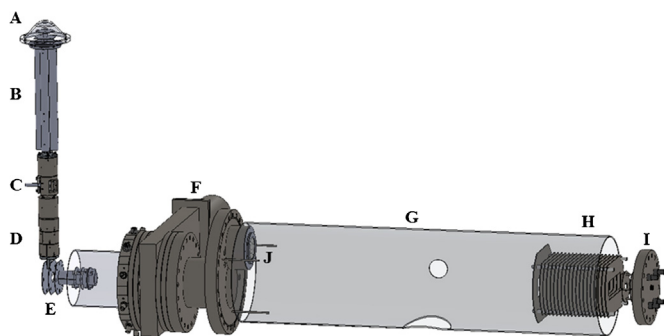


Fig. 1. Schematic of the new quadrupole and time-of-flight additions to the flow tube. After exiting the flow tube, the ions are sampled by the nose cone (A), travel through a quadrupole (B), an einzel lens with a specialized central element (C, see Fig. 2), an einzel lens and collimator (D), and enter the time-of-flight extraction region (E). Ions sampled by the extraction grids pass through a series of deflectors and lenses (right side of E), before entering the reflectron time of flight tube (G), which is separated from the upstream section of the time-of-flight by a gate valve (F). The reflectron (H) consists of twenty resistively coupled lenses, which either pass the ions to an 18 mm chevron configuration micro-channel plate detector (I) or reflect the ions to a 40 mm chevron configuration micro-channel plate detector (J).

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