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A novel chemical reactor suited for studies of biophysical chemistry: Construction and evaluation of a selected ion flow tube utilizing an electrospray ion source and a triple quadrupole detection system

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Abstract

A novel electrospray ion source/selected ion flow tube/triple quadrupole detector mass spectrometer has been constructed for the study of the kinetics and product distributions of reactions of a diverse array of electrosprayed ions reacting with neutral molecules. The electrospray source provides a near-universal source for ions of biological and other interests. The operation of the instrument is demonstrated with a selection of reactivity and kinetic measurements and threshold collision-induced dissociation determinations. Reactions investigated include H/D exchange between protonated bradykinin and deuterated ammonia, the protonation of the oligo-nucleotide anion [AGTCTG – 5H⁺]^{5–} with HBr, the ozonolysis of Ca²⁺, the reaction of protonated phthalic anhydride with dimethyl disulfide, and the Argon collision-induced dissociation of Ba(C₆H₆)²⁺.
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Keywords: Selected ion flow tube; Ion-molecule reactions; Electrospray ionization; Mass spectrometers

1. Introduction

The selected ion flow tube (SIFT) has been a productive tool for the measurement of rate coefficients and branching ratios for a large number and variety of ion-molecule reactions [1,2]. A variety of techniques has been employed with SIFT instruments for the generation of ions including electron impact, microwave excitation, glow discharge and laser ablation, to name a few. The various techniques that have been applied to the SIFT for ion generation and detection have been reviewed elsewhere [1,2].

The selected ion flow tube (SIFT) instrument has been in use at York University for some time, and has been described elsewhere [3,4]. Recently, a versatile inductively coupled plasma (ICP) ion source [5] was employed as a source for atomic metal ions in conjunction with the SIFT and this combination has proven to provide a powerful tool for the studies of chemical reactions with atomic cations [6–10]. Here we report on the

addition of an electrospray ion source and several other modifications to our basic SIFT instrument and demonstrate that this combination is invaluable for studies of biophysical chemistry. The use of electrospray ion sources in conjunction with flow techniques was first introduced by Bob Squires almost 10 years ago [11] and shortly thereafter by Chava Lifshitz [12,13].

We have greatly expanded the capabilities of our flow tube technique by incorporating three significant new features. First, we have fitted an electrospray ion source prior to the up-stream ion selection quadrupole. Also, we have incorporated a radio-frequency ion guide reaction region immediately after the electrospray source. Finally, a triple quadrupole mass spectrometer (extended mass range) has been added after the flow tube. This new configuration symbolized as an ESI/qQ/SIFT/QqQ mass spectrometer provides a powerful and versatile means to investigate the kinetics and energetics of reactions of biological and other ions that can be generated in solution. Further, the flow tube serves as an excellent source of mono-energetic ions, critical in determining onset energies for collision-induced dissociation.

While mass spectra of electrosprayed species can be composed of few or sometimes a single peak, this behavior is not

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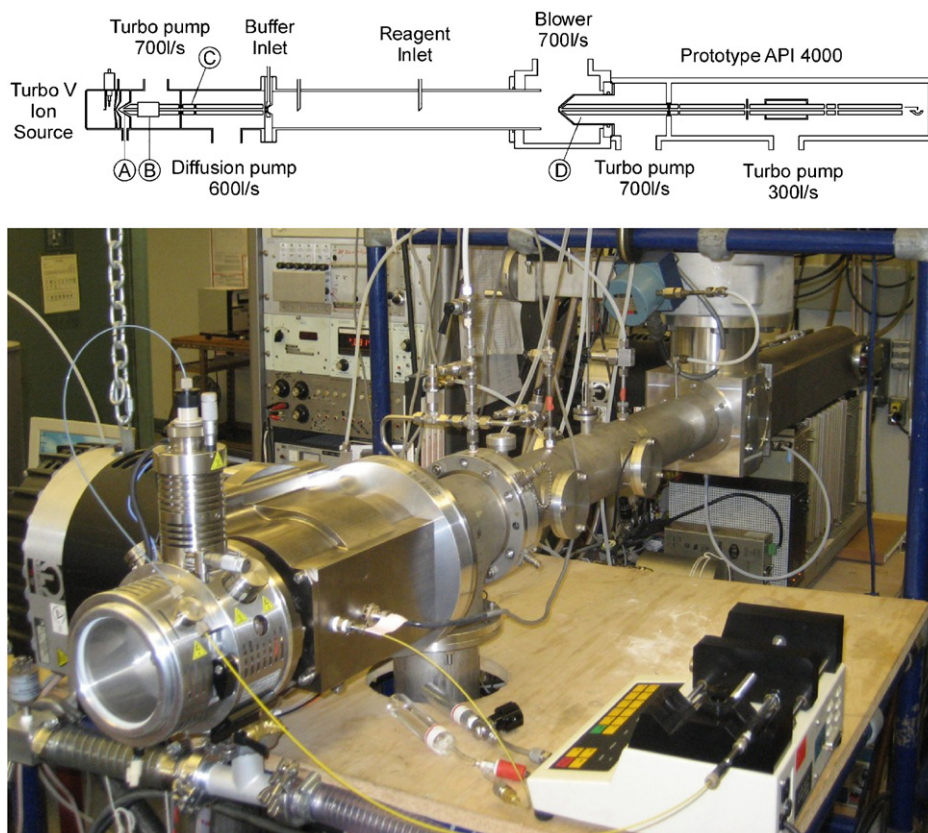


Fig. 1. (Top) Schematic of the details of the ESI/qQ/SIFT/QqQ instrument: (A) the modified floating skimmer; (B) the q0 reaction cell; (C) the extended stubbies; (D) the extended q0 rod set. (Bottom) Pictorial view.

universal. Mass selection, post ion spray, is often highly desirable. The earlier instruments [11–13] developed in this vein suffered from complications associated with a lack of pre-selection and the resulting lack of definition of charge state distributions, isotope distributions, and solvation. The ESI interface in our instrument permits desolvation of electrosprayed ions. Moreover, this desolvation region can be used to fragment weaker covalent bonds, further extending the diversity of reactant ions generated by the ESI source. Mass selection prior to entering the flow tube removes complications due to charge state distributions and can ameliorate complications due to isotope distributions.

We are aware of one recent report by Schwarz and co-workers [14] of an instrument in which mass selection is performed post-spray and prior to the flow tube reaction region in a newly constructed SIFT-guided ion beam instrument of quite complex geometry. The instrument reported here is similar in function but maintains a straight ion flight path along the length of the instrument. Also, a reaction region has been created in the Q0 region of the SIFT selection quadrupole in our instrument. The addition of this reaction cell permits the modification (by chemical reaction) of nascent electrosprayed ions prior to entering the reaction flow tube. Separation into two distinct reaction regions greatly simplifies the execution and interpretation of kinetics data in, for example, the analysis of a catalytic cycle. Here we report some of our first results that illustrate the power of our extended flow tube instrument.

2. Construction of the ESI/qQ/SIFT/QqQ

The selected ion flow tube (SIFT) instrument has been in use at York University for some time, and has been described elsewhere [1,2]. To create the new instrument (see schematic and pictorial view in Fig. 1), substantial modifications had to be carried out. In brief, a commercial electro-spray triple quadrupole mass spectrometer (a prototype SCIEX API 4000) was split at the source/analyzer interface with the source being fitted to the up-stream selection quadrupole and the analyzer being fitted after the sampling cone of the flow tube. More precisely, the up-stream quadrupole mass filter was supplemented with rf-only ‘stubbies’ and a high-pressure rf-only ion guide. The two quadrupoles are differentially pumped and ions are communicated through a 1 mm aperture. A SCIEX TurboVTM ion source and source interface were added prior to the rf-only quadrupole. Pumping is indicated in Fig. 1. This arrangement in essence duplicates the Source/q0/Q1 stage of a commercial SCIEX API 4000 mass spectrometer. The radio frequency for the stubby rod set and the q0 ion guide were parasitically tapped from the resolving quad using 22 and 100 pF capacitors, respectively.

After mass selection ions are transmitted to the flow tube through a venturi-type aspirator, entrained in a buffer gas (usually Helium) and flow down the flow tube, as has been described previously [3,4]. The skimmer cone, typically grounded in an API 4000 interface, was electrically isolated from ground and operated at a slight positive potential (ca. 8 V) with reference

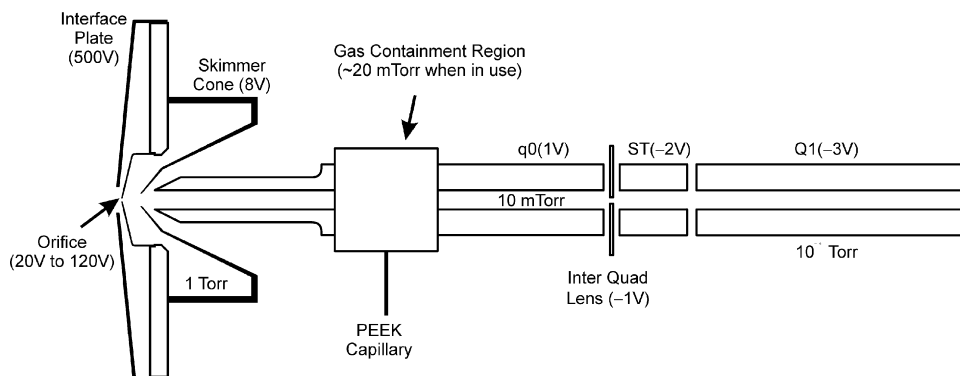


Fig. 2. Detail of the pre-flow tube ion selection region along with some operating conditions.

to ground. This ensured that the ions, possessing ca. 1 eV of translation energy in $q0$ were able to make it through the ground potential Venturi aspirator into the flow tube. The typical commercial implementation uses a grounded skimmer with $q0$ at a slight negative (ca. -10 V) potential. Ions having 1 eV translation energy in $q0$, fixed at -10 V w.r.t. ground, would then be 9 eV deficient in energy to enter the flow tube.

The single quadrupole detector of the SIFT was replaced with the triple quadrupole of the prototype API 4000. The rf-only $q0$ stage was extended 4 cm to position the rod tips near the downstream side of the sampling nose cone to increase ion gathering efficiency. Three turns were removed from the inductors of the quadrupole rf-power supply to balance the added capacitance of the extended $q0$ rod. The collision gas system on the commercial instrument was bypassed using a 1 l reservoir and a 15 turn, micro-metering needle valve (Parker Hannifin, part number 4F-H1A-V-SS-TC). In this way the selection of collision gas is not limited to nitrogen seconded from the interface region.

Temperature control hardware for the interface and nebulizer gas was not installed on the prototype instrument so heating of the interface region was accomplished with a 250 W infrared heat lamp placed 10 cm from the viewing window of the spray source and directed at the curtain gas plate. This arrangement provides sufficient heat in the orifice region to prevent condensation on the interface plate and to aid in solvent evaporation.

The rf-only ion guide after the electrospray ionization source was converted to a reaction cell by the addition of a polycarbonate sleeve 6 cm in length and with an inner diameter matching the outer diameter of the quadrupole rod set (see Fig. 2). The sleeve was centered 10 cm from the start of the $q0$ rod set. Reaction gas is admitted radially through a hole in the side of the sleeve via a PEEK capillary approximately 30 cm long and with an inner diameter of 0.178 mm. No attempt was made to close off either end of the cell. Flow to the cell is controlled by: capillary length, capillary inner diameter or reagent pressure. The addition of nitrous oxide to the cell at a flow rate of ca. 50 scc min^{-1} was sufficient to convert several selected atomic metal cations (typically an exothermic reaction [6]) to their respective oxides. The oxide signal was typically ca. 50% of the atomic signal. The range of declustering potentials (the electric potential difference between the orifice and the skimmer) available (0–200 V) is sufficient to generate atomic ions from acetates or chlorides of the

respective metals. Chen and co-workers [15,16] have extensively modeled fragmentation processes in orifice skimmer regions.

The up-stream mass selection quadrupole is adjusted manually while the down-stream triple quadrupole is controlled by the AnalystTM software package supplied with the instrument. This software package is used to collect ion intensity data acquired in a kinetic run or a CID profile. Pressure and flow information related to the flow tube and the neutral reagent are collected on a second computer. For kinetic studies the Analyst data and flow data are later merged via proprietary software and analyzed to yield rate coefficients.

Low-mass ions as light as sodium have been generated by the ES source in sufficient intensity for observation in our SIFT. This complements our previously used plasma ion source [5], which has limited sensitivity below 40 Da and produces (with few exceptions) only positive atomic ions.

3. Experimental results and discussion

We present here a range of selected results that illustrate the performance and flexibility, as well as limitations, of our new ESI/ qQ /SIFT/ QqQ mass spectrometer.

3.1. Bradykinin H/D exchange

To test the newly constructed instrument, the previously examined [12] proton exchange reactions between [Bradykinin + 2H]²⁺ and methanol and between [Bradykinin + 2H]²⁺ and ammonia were studied. High intensity and high resolution were obtained in the down-stream mass analyser. See inset of Fig. 3 for a sample mass spectrum of [Bradykinin + 2H]²⁺ showing half-mass resolution at ca. 500 Da. To derive accurate proton exchange kinetics it is necessary to de-convolute the isotope overlap. The isotope de-convolved profile for proton exchange with ND₃ is shown in Fig. 3. The curvature in the semilogarithmic decay could be attributed to the accumulation of error associated with the isotope de-convolution procedure.

Apparent rate coefficients for the individual sequential transfer steps determined from kinetic fits to the data are 7.5×10^{-10} , 2.9×10^{-10} and $3.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with an estimated uncertainty of $\pm 30\%$, for the first three proton exchange steps. This is in reasonable agreement with the apparent rate

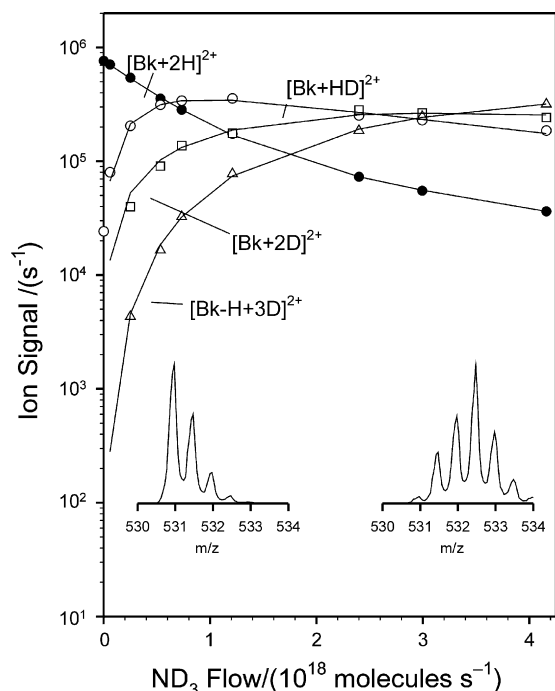


Fig. 3. Reaction kinetics for protonated bradykinin H/D exchange. $[\text{Bk} + 2\text{H}]^{2+}$ reacting with ND_3 at $295 \pm 2 \text{ K}$ in helium buffer-gas at a pressure of $0.35 \pm 0.01 \text{ Torr}$.

coefficients derived by Lifshitz and co-workers [12]. Lifshitz, however, goes on to further analyse the apparent rate coefficients in terms of a site specific mechanism [12] that permits the sequential proton exchange to occur at sites in any order, not specifically from most labile to least labile. This extension is not reiterated here.

3.2. Proton transfer reactions

The electrospray ion source readily produces both cation and anion species. We have readily generated intense anion signals of multiply deprotonated oligonucleotide six-mers and studied the reprotonation kinetics using HBr as the source of protons. The oligonucleotide AGTCTG (purchased from Invitrogen, Carlsbad, CA, USA) was sprayed in water/methanol (80/20) and yielded intense peaks corresponding to the series $[\text{AGTCTG} - n\text{H}]^{n-}$, where $n = 2, 3, 4, 5$. Hydrogen bromide (Matheson, USA) was metered into the flow tube as a 3% solution in Helium. Proton transfer from HBr to the anionic oligonucleotide $[\text{AGTCTG} - 5\text{H}]^{5-}$ was observed to proceed essentially at the collision rate in three steps to form the $[\text{AGTCTG} - 2\text{H}]^{2-}$ anion. The reaction profile for the rapid sequential proton transfer is illustrated in Fig. 4. Extensive HBr clustering to the oligonucleotide also was observed but is omitted from this figure for clarity and gives rise to the curvature in the observed decay of $[\text{AGTCTG} - 5\text{H}]^{5-}$. Also not shown are the profiles recorded for the observed appearance of the product ions Br^- and $\text{Br}^- \text{HBr}$. It should be noted that the singly charged species could not be produced via proton transfer from a higher anion. A more complete examination of the observed proton transfer chemistry will be the subject of a future report.

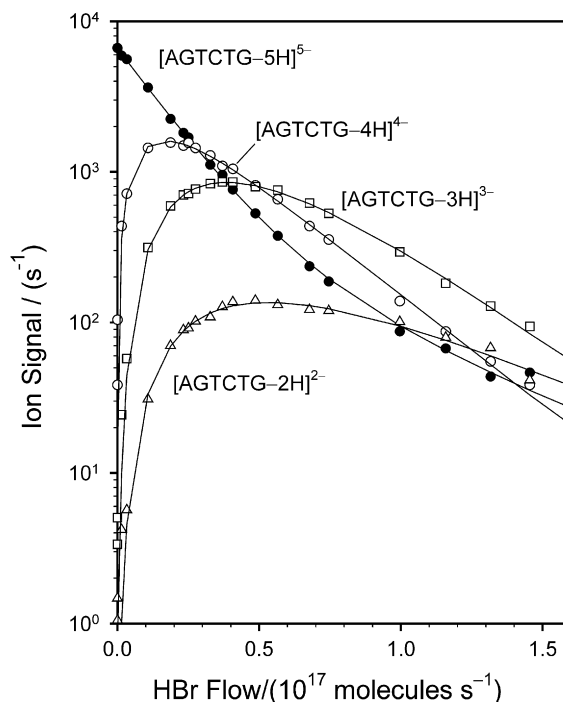
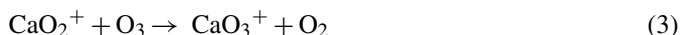
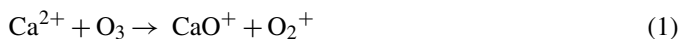


Fig. 4. Reaction kinetics for HBr reacting with the oligo-nucleotide $[\text{AGTCTG} - 5\text{H}]^{5-}$ showing consecutive proton transfer from HBr at $295 \pm 2 \text{ K}$ in helium buffer-gas at a pressure of $0.35 \pm 0.01 \text{ Torr}$. Clusters of $\text{AGTCTG}/\text{HBr}_n$ ($n = 1-7$) are omitted for clarity.

3.3. Ion-molecule reactions

The electrospray source is also suited to the production of selected singly or multiply charged atomic cations. For example, Ca^{2+} dications are produced at high declustering potentials (220 V) from a $100 \mu\text{M}$ solution of calcium acetate, $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$, in water and acetone (40:60 vol.%). The addition of ozone into the flow tube provided the data shown in Fig. 5. Ozone was chosen because of our interests in the chemistry of the earth's ionosphere and is produced here in the manner described previously by Williams et al. [17]. The atomic dication reacts with ozone by O-atom transfer accompanied by electron transfer, the charge separation reaction (1), and further oxidation of the singly charged calcium oxide proceeds by sequential O-atom transfer as indicated in reactions (2) and (3):



The kinetic fits to the individual ion profiles provides rate coefficients of $15, 6.5$ and $7.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reactions (1)–(3), respectively, with an estimated uncertainty of $\pm 30\%$.

Interest in our laboratory in chemical noise reduction in mass spectrometry using ion-molecule reactions with dimethyldisulphide (DMDS) has prompted an investigation of the kinetics of ion-molecule reactions with this molecule [18]. For example,

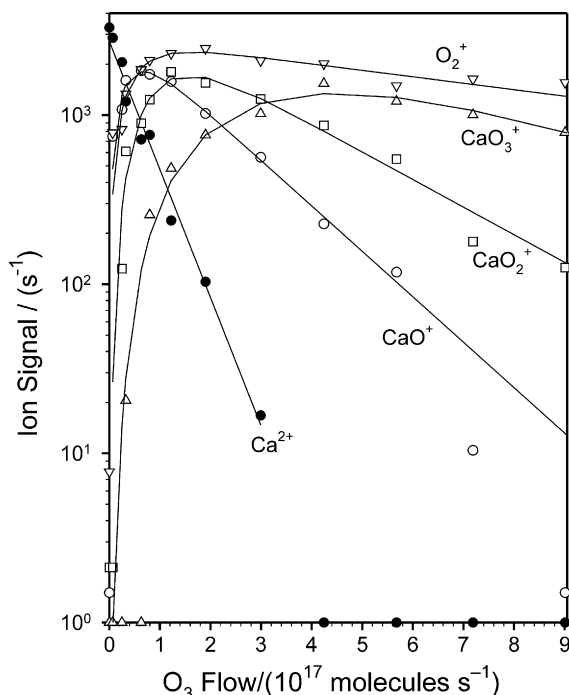


Fig. 5. Measured ion profiles for the reaction of Ca^{2+} with ozone at 295 ± 2 K in helium buffer-gas at a pressure of 0.35 ± 0.01 Torr. The solid lines represent kinetic fits to the experimental data. See text for the details of the chemistry.

Fig. 6 shows results obtained for the reaction of DMDS with protonated phthalic anhydride (PHANH^+), a common background ion in mass spectrometry, which was sprayed from a $50 \mu\text{M}$ phthalic acid solution in (70:30:1 vol.%) $\text{H}_2\text{O}/\text{CH}_3\text{OH}/\text{formic}$

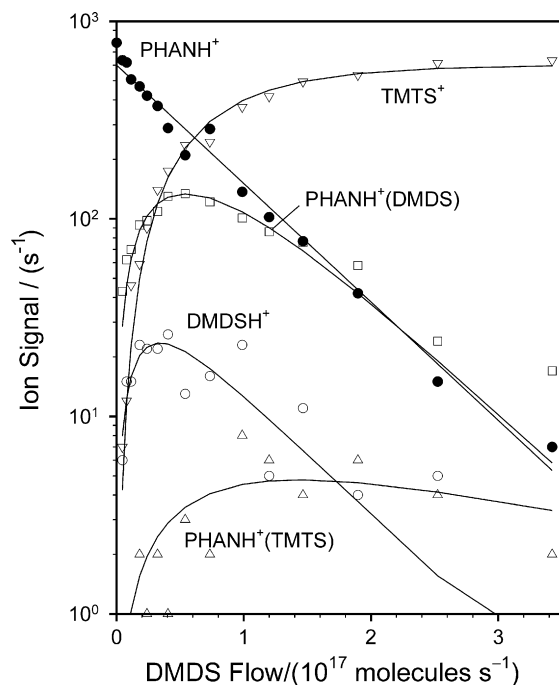
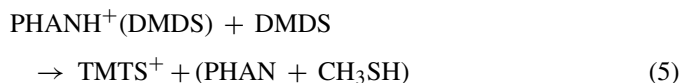


Fig. 6. Measured ion profiles for the reaction of dimethyldisulfide (DMDS) with protonated phthalic anhydride (PHANH^+) at 295 ± 2 K in helium buffer-gas at a pressure of 0.35 ± 0.01 Torr. The solid lines represent kinetic fits to the experimental data. See text for the details of the chemistry.

acid. The sequence of ion-molecule reactions that was observed is given by reactions (4)–(6):



A rate coefficient of $(7.5 \pm 2.3) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was determined for reaction from the decay of the primary ion shown in Fig. 6. Secondary reactions (5) and (6) both form the trimethyl trisulfide cation, $(\text{CH}_3)_3\text{S}_3^+$ (TMTS^+) [19].

3.4. q0 reactions

The up-stream quadrupole pre-filter q0 has been modified to optionally act as a reaction cell. Atomic oxidation chemistry and benzene clustering chemistry have been successfully carried out in this reaction cell (see Fig. 2).

For example, to create the series of $\text{Ba}^{2+}(\text{C}_6\text{H}_6)_{1,2,3}$ ions, a $100 \mu\text{M}$ solution of BaCl_2 in H_2O and CH_3OH (70:30 vol.%) was sprayed, declustered at 200 V, and reacted with benzene. Benzene vapor, in equilibrium with liquid (v.p. $100^\circ\text{C} = 98$ Torr), was drawn from a 100 mL glass bulb through the PEEK inlet capillary. A spectrum showing ions generated by spraying BaCl_2 at high declustering potential is shown in Fig. 7(a). Notably Ba^{2+} is the dominant ion at high declustering potential. A spectrum of the generation of this series of cluster ions is shown in Fig. 7(b). These cluster ions were subsequently exposed to approximately 10^5 collisions with helium and then studied under multi-collision conditions in q2 of the down-stream quadrupole.

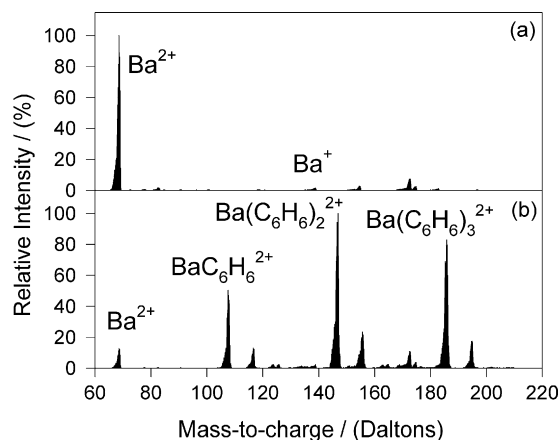


Fig. 7. Mass spectra of: (a) Ba^+ and Ba^{2+} produced from spraying barium chloride in water/methanol (50/50) and with a declustering potential of 200 V, and (b) under above stated conditions, but with the addition of benzene vapour to the q0 reaction cell.

3.5. Collision-induced dissociation (CID)

On the previous version of our SIFT instrument (single quadrupole down-stream detector) multi-collision-induced dissociation (mCID) was performed by varying the potential on the collection nose-cone. Ions were continuously accelerated though the helium buffer gas resulting in a slow deposition of internal energy. In this case it is appropriate to interpret data in terms of sequential bond breaking events.

In the present case ions are accelerated to full collision energy prior to encountering the collision target gas. At all selected collision energies an intact reactant ion (made either in the q0 reaction region or the flow tube) can react via all energetically available channels at the first collision. Subsequent collisions can potentially access higher energy channels, assuming internal energy is deposited in the first collision. Alternately, ion fragments (made in prior collision events) can collide and react on subsequent collisions. The resulting profile is a complex convolution of absolute reaction cross sections statistically permuted with a Poisson distribution of multiple collision probabilities. Further complication results from the unknown disposition of translation energy into internal energy during the collision events. Drahos and Vekey have derived a master equation model for this physical process [20]. Still, the multi-collision-induced dissociation experiment can be used to establish crude estimates of binding energy and of ion structure. In comparative cases where a single fragmentation type is being examined across a series of similar compounds, relative binding energies should be reasonably accurate.

The mCID profile obtained for the fragmentation of $\text{Ba}(\text{C}_6\text{H}_6)_2^{2+}$ is shown in Fig. 8. The target gas was argon at an approximate pressure of 0.75 mTorr. Notably, the profile suggests that the ions have at least 6 eV of translation energy at the exit of the second q0 region as determined from the intercept of the $\text{Ba}(\text{C}_6\text{H}_6)_2^{2+}$ signal extrapolated to a normalized intensity of 1.0. In the commercial implementation of the triple quadrupole, ions are assumed to have near-zero translation energy in q0 and

the collision energy CE is taken to be the potential difference between q0 and q2.

The $\text{Ba}(\text{C}_6\text{H}_6)_2^{2+}$ profile is characterized by: a narrow low energy process involving loss of one benzene ligand, a narrow higher energy process that leads to Ba^{2+} (70%) and $\text{BaC}_6\text{H}_6^{2+}$ (30%), and a broad very high energy process that leads to Ba^+ . Importantly the higher energy channels can be the result of consecutive processes or the result of a multi-collision activation process.

4. Conclusion

The experimental results reported here indicate that the new ESI/qQ/SIFT/QqQ mass spectrometer constructed in our laboratory is well suited for measurements of a variety of ions, both positive or negative, singly or multiply charged, and atomic or biological, reacting with neutral molecules or dissociating upon collisions with argon collision gas. The electrospray, in combination with the q0 reaction cell, provides an extremely versatile source of ions that can be manipulated by dissociation or chemistry before being injected into the flow tube for further chemistry and/or dissociation. The CID function down-stream needs to be explored further and we plan to assess its suitability for quantitative bond energy determinations and to compare the performance of the new mode of CID to our earlier mCID mode of operation.

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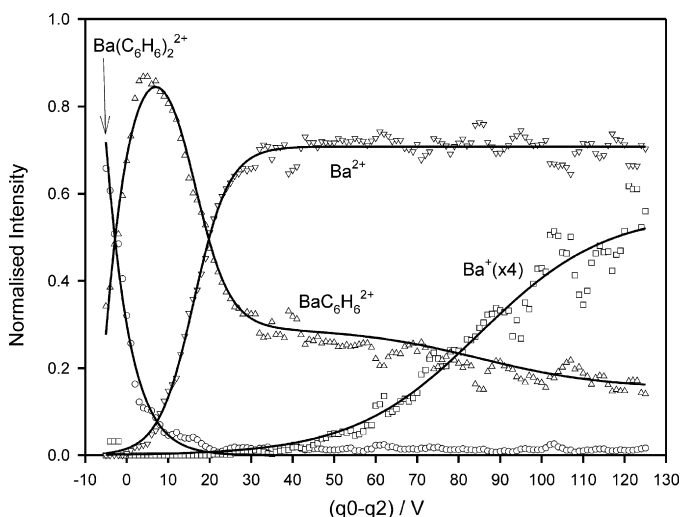


Fig. 8. Multi-collision-induced dissociation profile of the mixed $\text{Ba}(\text{C}_6\text{H}_6)_2^{2+}$ cluster species.

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