



Mass spectrometric sampling from the atmospheric pressure ion source
by Douglas Robert Zook

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in
Chemistry

Montana State University

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Abstract:

Atmospheric Pressure Ionization Mass Spectrometry (APIMS) is an established method for ultra-trace chemical analysis. However it is infrequently applied to fundamental study of gas phase ion chemistry. This is attributable to sampling errors which preclude the accurate observation of relative ion abundances within the ion source. The objective of this thesis is characterization of sampling errors to permit application of APIMS to the fundamental study of several chemical systems. Three sampling errors are examined: 1) Perturbations encountered in sampling cluster ions, 2) mass and ion-type discrimination effects, and 3) aperture contact potentials. The former two errors are caused by dynamics occurring within a free jet expansion that accompanies non-effusive sampling of ion source contents into a mass spectrometer vacuum chamber. Both can grossly perturb relative ion currents. Contact potentials, when present, significantly diminish absolute mass spectral ion currents. The chemical systems of study include 1) two-channel dissociative electron capture reactions, 2) ion-molecule clustering reactions, and 3) cluster assisted decomposition reactions. It is demonstrated that following quantitative evaluation of APIMS sampling mass bias, observed mass spectral ion currents can be corrected to obtain accurate ion source relative ion abundances. This protocol has revealed the important influence pressure exhibits for influencing observed relative product ratios of two-channel dissociative electron capture reactions. From this study it is deduced that excited electron capture intermediates have lifetimes against dissociation which allow for internal energy modification through collisions with buffer gas, resulting in alteration of the favored channel of dissociation. Regardless of ion source sampling conditions, it is shown that useful ion molecule relative clustering propensities are available from APIMS from which qualitative fundamental information can be obtained. This is demonstrated for isomer dependent clustering between nitroaromatic molecular anions and dimethylsulfoxide. APIMS has allowed observation of previously unreported halide and dihalide hydrate cluster ions generated in the APIMS free jet expansion, for which preferred stabilities are noted. Investigations of new cluster assisted decomposition reactions for some perfluorinated molecular anions explain the occurrence of unexpected ions encountered during perfluorocarbon analysis by thermospray mass spectrometry.

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A thesis submitted in partial fulfillment
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Doctor of Philosophy

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Chemistry

MONTANA STATE UNIVERSITY
Bozeman, Montana

September 1990

D378
Z762

APPROVAL

of a thesis submitted by
Douglas Robert Zook

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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ACKNOWLEDGEMENT

Toward completion of this dissertation I thank my advisor, Prof. Eric P. Grimsrud for the interesting and varied research experiences. Also, I would like to express gratitude to group members that have greatly assisted in my progress. Drs. W. Berk Knighton, L. Joe Sears, and R. Steve Mock always provided welcomed advice and friendship. All of the group members have made my time at M. S. U. truly memorable.

Finally to family and friends alike, who inspire and support, go equal acknowledgement and gratitude.

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ABSTRACT

Atmospheric Pressure Ionization Mass Spectrometry (APIMS) is an established method for ultra-trace chemical analysis. However it is infrequently applied to fundamental study of gas phase ion chemistry. This is attributable to sampling errors which preclude the accurate observation of relative ion abundances within the ion source. The objective of this thesis is characterization of sampling errors to permit application of APIMS to the fundamental study of several chemical systems. Three sampling errors are examined: 1) Perturbations encountered in sampling cluster ions, 2) mass and ion-type discrimination effects, and 3) aperture contact potentials. The former two errors are caused by dynamics occurring within a free jet expansion that accompanies non-effusive sampling of ion source contents into a mass spectrometer vacuum chamber. Both can grossly perturb relative ion currents. Contact potentials, when present, significantly diminish absolute mass spectral ion currents. The chemical systems of study include 1) two-channel dissociative electron capture reactions, 2) ion-molecule clustering reactions, and 3) cluster assisted decomposition reactions. It is demonstrated that following quantitative evaluation of APIMS sampling mass bias, observed mass spectral ion currents can be corrected to obtain accurate ion source relative ion abundances. This protocol has revealed the important influence pressure exhibits for influencing observed relative product ratios of two-channel dissociative electron capture reactions. From this study it is deduced that excited electron capture intermediates have lifetimes against dissociation which allow for internal energy modification through collisions with buffer gas, resulting in alteration of the favored channel of dissociation. Regardless of ion source sampling conditions, it is shown that useful ion molecule relative clustering propensities are available from APIMS from which qualitative fundamental information can be obtained. This is demonstrated for isomer dependent clustering between nitroaromatic molecular anions and dimethylsulfoxide. APIMS has allowed observation of previously unreported halide and dihalide hydrate cluster ions generated in the APIMS free jet expansion, for which preferred stabilities are noted. Investigations of new cluster assisted decomposition reactions for some perfluorinated molecular anions explain the occurrence of unexpected ions encountered during perfluorocarbon analysis by thermospray mass spectrometry.

INTRODUCTION

Background

Atmospheric Pressure Ionization Mass Spectrometry (APIMS) originated from studies concerning the ion chemistry occurring within flames, electric discharges, and the electron capture detector (ECD) (1-4). APIMS has evolved over the past two decades to become an established and valuable method for ultra-trace chemical analysis. APIMS is well suited for direct real time whole air monitoring since no vacuum interlocks are needed to introduce samples to the ionization chamber (5-7). Because of high collision frequencies characteristic of ambient pressure conditions, reactant and product ions are formed with nearly thermal energies making APIMS a soft ionization technique with little mass spectral fragmentation. The chemical analytical potential of APIMS has been well characterized and detection limits at the femtogram (10^{-15} g) level have been demonstrated for analytes of environmental and biomedical interest (8-10). Several review articles have appeared over the past decade which summarize the chronological development of APIMS and detail important chemical analytical aspects which have provided the motivation for study and continual innovation (11-15).

Despite the impressive applied chemical analytical

utility of APIMS, the method has not found wide application for fundamental study of gas phase ion chemistry. Because of sampling errors, the observed APIMS mass spectral ion currents cannot be assumed to be proportional to the concentration of ions present within the API reaction chamber. This has widely been understood to be due to the non-effusive flow characteristics associated with the transfer of ions and neutral buffer gas molecules under ambient pressure conditions of the ion source through a tiny orifice into the vacuum chamber of a mass spectrometer. The gross pressure difference between the source and the expansion chamber is nearly seven orders of magnitude. These conditions violate the normally accepted criteria for perturbation-free ion sampling because the mean free path is much shorter than the dimensions of the sampling orifice (16). Such non-effusive flow dynamics result in an adiabatic free jet expansion. Cooling which accompanies the expansion may promote aggregation and net clustering between ions and polar molecules entrained within the jet. An opposing force to aggregation is collisionally induced dissociation, which may occur as ions pass through shock waves that occur at the periphery of the expansion boundaries (12). Equilibrium relative ion abundances which are known to exist within the API ion source are therefore very difficult to observe due to these sampling difficulties (16).

Gas phase conditions provide the necessary means for probing intrinsic chemical properties and reactivities of

ionic species in an isolated system free of bulk solvent effects (17,18). Broad interest in the fundamental aspects of gas phase ion chemistry has propelled much of the mass spectrometric research activity in the past quarter century or longer. The established methods for fundamental studies, such as the Pulsed e-beam High Pressure Mass Spectrometer of Kebarle (19), are all confined to pressures very low in comparison to APIMS. These relatively low pressure ionization methods presumably do not have associated significant sampling errors. However, because of the pressure limitations of the established fundamental techniques, relatively little is known of the interesting ionization conditions involving higher reagent concentrations and higher collision frequencies which occur with use of total pressures of one atmosphere.

Statement of Problem

To extend the utility and understanding of APIMS a number of significant sampling problems will be investigated. Following the characterization of sampling errors, the APIMS will be utilized for several fundamental studies. The sampling errors to be characterized fall into three broad categories :

- 1) Cluster ion sampling perturbations,
- 2) Mass and Ion type discrimination effects, and
- 3) Occurrences of sampling aperture contact potentials

All of these APIMS sampling errors complicate mass spectral

ion current interpretation. The former two are of particular importance because their existence precludes from direct observation the relative ion abundances which are present within the API ion source. The third category of sampling error, contact potentials, may totally inhibit ion transit through the sampling orifice.

The chemical systems to be studied for fundamental information fit into two broad categories. The first concerns two-channel dissociative electron capture reactions for which the importance of pressure will be investigated in determining the observed relative product ratios from the available dissociation channels. In order to approach this fundamental problem, the characterization of mass bias errors will be of central importance. The second category of fundamental study will involve ion-molecule clustering reactions. A range of molecular anion structural isomers that can be made to cluster with dimethylsulfoxide will be investigated to determine if qualitative clustering propensities are retained despite sampling perturbations. Then the cooling dynamics of the free jet expansion will be employed for generation of halide and dihalide hydrate cluster ions which have not been previously observed. Finally a new cluster assisted decomposition reaction recently studied by PHPMS methods will be examined by APIMS.

THEORY

Non-Effusive Flow Aperture Sampling

The accepted criteria for perturbation free cluster ion sampling, as stated in the introduction, usually dictate that the flow conditions associated with the sampling aperture be effusive. This means that the dimensions of the sampling aperture must be very small in relation to the mean free path of ions and neutrals to be sampled. The Knudson number is an established flow dynamics index for determining whether the mass transport of a gas is effusive (20), meaning that no collisions occur between the gas molecules during the transit through an orifice, and is given by equation 1,

$$K = \lambda / D \quad (1)$$

where λ is the mean free path of a molecule or ion in the gas to be sampled, and D is the diameter of the sampling orifice. A Knudson number of less than 0.01 indicates viscous flow through the aperture. A value greater than 1.0 is indicative of effusive flow. Mean free path is a function of the gas collision rate, $v_{\text{collision}}$, number density, n , and average thermal velocity, v_{ave} , and may be estimated by equation 2,

$$\lambda = (v_{\text{collision}} n)^{-1} v_{\text{ave}} \quad (2)$$

At atmospheric pressure, assuming $v_{\text{collision}}$ of $1 \times 10^{-9} \text{ cm}^3$ molecule $^{-1} \text{ sec}^{-1}$, n of 2×10^{19} molecule cm^{-3} , and v_{ave} of $2 \times 10^4 \text{ cm sec}^{-1}$, one may predict an ion or neutral collision free trajectory of approximately $10^{-2} \mu\text{m}$. This is far below the dimensions of the typical APIMS ion sampling aperture of 20 to 50 μm . The Knudson number for sampling an atmospheric pressure gas through a 20 μm diameter orifice from equations 1 and 2 is 5×10^{-4} , a value four orders of magnitude below the effusive flow limit. The high collision frequency which accompanies non-effusive ion and neutral buffer gas sampling into a vacuum chamber results in an adiabatic free jet expansion.

Free Jet Expansion

The study of free jet expansions, pioneered by J.B. Fenn and others, have been the subject of many studies involving their unique physical characteristics and applications for simplification of complex molecular spectroscopy problems (21), and investigation of nucleation phenomena (22).

A free jet expansion embodies the conversion of the random motion of gas molecules in a high pressure reservoir into a directed mass flow of gas molecules expanding through a small aperture into a vacuum chamber (23). Disregarding the possibility for heat conduction in the expansion chamber, the energy required for this process is provided by the internal energy of gas molecules, thereby resulting in a self cooling effect. Molecular vibrations and rotations can be cooled to

temperatures far below the freezing point of the entrained gas molecules, and are known to decrease into the low Kelvin range (21). Aggregation processes may accordingly follow. Cooling, which is proportional to the pre-expansion pressure and orifice diameter, is the result of two body collisions which occur very early in a region called the silent zone, in which gas velocities are uniform, and with similar trajectories. The number density and local temperatures decrease with increased distance from the sampling aperture. The highest velocities are attained on axis of the direction of flow, and estimated at approximately 10^5 cm sec⁻¹. Surrounding the silent zone, are regions of shock waves, which are the boundaries between the directed flow of the jet and the random motion of the background gas in the expansion chamber. The barrel shock wave is longitudinally symmetrical, and the mach disk as a shock wave encountered normal to the direction of flow. The sampling orifice-to-mach disk separation, X_M , is estimated by the following empirical equation 3 (24),

$$X_M = 0.67 D_o (P_o / P_i)^{1/2} \quad (3)$$

where D_o is the sampling orifice outside diameter, P_o is the pre-expansion pressure, and P_i is the expansion chamber pressure. These shock waves are regions of extensive scatter and collision. Figure 1 illustrates the approximate free jet expansion dimensions as predicted by equation 3 for sampling

from the atmospheric pressure ion source that is the subject of this thesis. The passage of ions and neutrals from the silent zone through a shock wave serves to raise the internal energy of the species, and may potentially result in collisionally activated dissociation.

The factors governing aggregation and nucleation phenomena in a free jet expansion are :

- (1) the molecular weight of the expansion gas,
- (2) the relative percentage of the aggregatable species to expansion gas,
- (3) the initial upstream (pre-expansion) pressure,
- (4) the initial upstream temperature, and
- (5) the design of the sampling aperture.

Because of the very high ratio of neutral expansion gas (atomics or polyatomics) to entrained ions, virtually all collisions experienced by ions will be with the expansion gas. Therefore removal of ion internal energy is dependent upon collision with the expansion gas. The extent of cooling of an entrained species is dependent upon the relative velocity of the entrained ions and neutrals and the expansion gas, since similar velocities will result in higher collision frequencies (point 1). The average molecular speed of a molecule is dependent upon its mass and collisional cross section. The varying relative velocities of expansion gas and species entrained in the expansion gas forms the basis of the velocity slip effect, which accounts for the relative inefficiency of

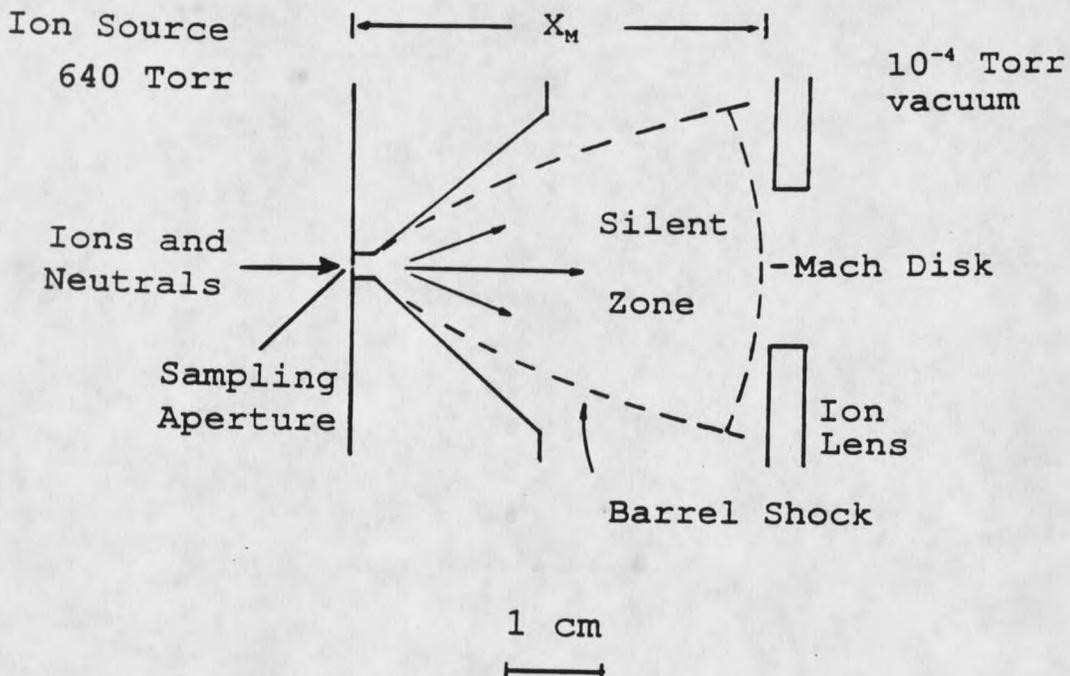


Figure 1.

Illustration of the free jet expansion associated with sampling from API ion source for study apparatus shown in Figure 2 based upon equation (3), $X_M = 0.67 D (P_o / P_1)^{1/2}$, with $D = 50 \mu\text{m}$, $P_o = 640 \text{ Torr}$, and $P_1 = 5 \times 10^{-4} \text{ Torr}$. Cooling and condensation events may occur in region of Silent zone. Collisions may occur upon transit through Mach disk prior to focussing and mass analysis. Adopted from Bruins, reference 12.

lighter mass expansion gases, such as helium, to vibrationally cool entrained species (25). The lighter the mass of the expansion gas, the higher its velocity relative to the entrained species. Maximal cooling occurs with a heavier expansion gas which may more efficiently serve to increase residence times of entrained species within the Silent zone, thereby allowing for more internal energy lowering collisions and subsequent cooling. The cooling results in enhancement of aggregation and condensation events.

The extent of aggregation is also determined by the probability of an encounter between entrained species. If the number densities are very low in the expansion, few van der Waals complexes may form (point 2).

The initial pressure (point 3) will dictate the collision frequency attainable within the silent zone of the expansion. The initial internal energy of the expansion gas and entrained species are influenced by the bath gas temperature prior to the expansion (point 4). Finally, the design of the sampling aperture may strongly influence the physical characteristics of the jet, with corresponding impact on the dimensions of the effective Silent zone and location of shock waves (point 5). Reflections, or scattering from surfaces, may also influence the characteristics of the expansion.

Attainment of Gas Phase Ionic Equilibrium

A simplified rate controlled picture is presented to

illustrate that ion-molecule clustering reactions that can be made to occur within the API ion source will reach a state of chemical equilibrium. The API ion source is an ionization reaction chamber maintained at ambient pressure. To ascertain that chemical equilibrium conditions are attained within the API ion source, an examination of the steady state ionization events and rate processes for ion formation and destruction is necessary. The criteria for attainment of gas phase ionic chemical equilibrium, as put forth by Kebarle (17) follow :

- 1) the reactants and products must be in thermal equilibrium with their surroundings (carrier gas and reaction vessel walls),
- 2) The path(s) that reactively couple the ions engaged in the equilibrium must be appreciably faster than all other processes effecting the concentration of ions, and
- 3) sufficient time allowed for chemical reactions of interest to reach steady state equilibrium.

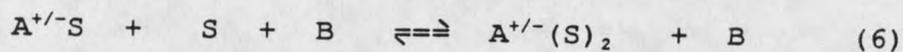
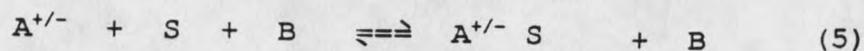
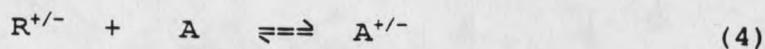
Thermalization is known to occur under conditions of sufficiently high pressures, and are considered to be attained within ion sources maintained in the low Torr range. Accordingly, thermalization is certainly attained in an ambient pressure gas by comparison. These latter two criteria require a clear understanding of the ion formation and destruction mechanisms, which will be considered below.

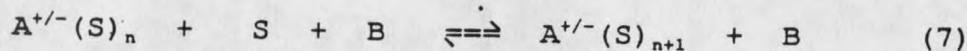
API Rate-Controlled Picture

The API ion source that is the focus of this study has a

^{63}Ni β^- activity of 15 mCi for 5.6×10^8 β^- ejections per second. The average nickel-63 β^- particle energy of 19 keV is sufficient to produce approximately 650 thermal energy electron-positive ion pairs for a steady state ion density of nearly 2×10^8 ions cm^{-3} . The primary ionization and electron thermalization period is estimated to occur in approximately one nanosecond (15). Following these primary ionization events, a multitude of ion formation and destruction processes rapidly occur as the ion chemistry evolves in time. The predominant destruction mechanisms include positive ion-electron recombination, ion diffusion to the source walls, and bulk ventilation of the ionized gas out from the source interior. Ion-molecule reactions continue to proceed until the ions are destroyed by one of the above three loss mechanisms. The ionization ultimately resides with the chemical entity, or entities, which possess the greatest propensity to retain the charge. It is this terminal ion population which is sampled by bulk ventilation into the mass spectrometer. Kebarle has estimated the time required to reach gas phase ionic equilibrium within the Pulsed e-beam High Pressure Mass Spectrometer (PHPMS) ion source to be on the order of 100 microseconds (26). Because of the much higher pressures and higher reagent concentrations possible within the API ion source, an even shorter period of time would be expected for attainment of equilibrium within the APIMS.

Cluster Ion Formation. Reactions 4 through 7 represent a generalized ion-molecule clustering system in which initially an ion of either polarity, $A^{+/-}$, formed by interaction with a reagent ion $R^{+/-}$ (reaction 4), is clustered with a solvating agent, S , (reaction 5) in the presence of a third body for the collisional stabilization of the clustering reaction product,



$$\vdots$$


after which many fast successive clustering steps are possible (reaction 6), proceeding rapidly to a state of dynamic chemical equilibrium for the particular conditions of ion source temperature and solvating agent source partial pressure. $R^{+/-}$ may be, for example, a stronger gas phase acid or base, or a thermalized electron, which ionizes A . S is any suitable solvating agent such as a molecule of water or dimethylsulfoxide. Reaction 7 constitutes the general forward clustering reaction in which an existing cluster ion successfully associates with a neutral solvating agent to form the next largest cluster ion. Therefore reaction 7 is the only clustering reaction necessary for the steady state model.

