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Ion-molecule reactions in quadrupole ion trap mass spectrometry: implications for lightweight gas analysis

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Abstract

The novel application of a quadrupole ion trap mass spectrometer (QITMS) to permanent gas analysis was recently presented by our laboratory. The quantitative performance of the QITMS equaled or surpassed that of other mass analyzers evaluated; however, concern was raised as to the impact of ion-molecule reactions observed within the ion trap. Hydrogen, helium, oxygen, and argon, four permanent gases currently monitored during Space Shuttle launch preparations by the National Aeronautics and Space Administration, were examined in their reactions with common atmospheric and mass spectrometer background components. Rapid charge-exchange and protonation reactions occurred. Greater than 99.8% of hydrogen and 98% of helium ions trapped are lost during a scan cycle predominately through reactions with background nitrogen. The neutralization rate of argon ions varied with water concentration, while increased concentrations of all three gases inflated the oxygen ion signal intensity through charge-exchange. Although such dramatic effects challenge the analytical sensitivity and robustness of QITMS for permanent gas analysis, through proper understanding and control of relevant experimental conditions the QITMS can still function in monitoring applications.

Keywords: Ion trap; Ion-molecule reaction; Charge-exchange; Proton transfer; Permanent gas analysis

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1. Introduction

The National Aeronautics and Space Administration (NASA) has used mass spectrometers to detect cryogenic fuel leaks since the start of the Space Shuttle program in 1981 [1]. Mass spectrometers offer low detection limits, stable readings, with fast analyses, and were effective in detecting cryogenic fuel leaks on numerous occasions throughout the years (STS6 in 1985, STS35 and STS38 in 1989, and STS93 in 2000) [1,2]. However, due to fragility and bulkiness, NASA has historically been limited to using only two remotely located systems [3], which precludes real-time simultaneous monitoring of all Space Shuttle compartments and excludes leak detection during the last critical minute prior to launch. Recognizing these limitations, NASA sought a new compact, rugged, and less costly mass spectrometer so that multiple systems could be situated up-close to the Space Shuttle providing rapid monitoring of all internal compartments throughout pre-launch until lift-off. The advanced hazardous gas detection (AHGD) project was initiated to meet this directive. As part of this work, a compact quadrupole ion trap mass spectrometer (QITMS) was designed, fulfilling NASAs performance requirements for monitoring hydrogen, helium, oxygen, and argon in a nitrogen purged atmosphere [4,5].

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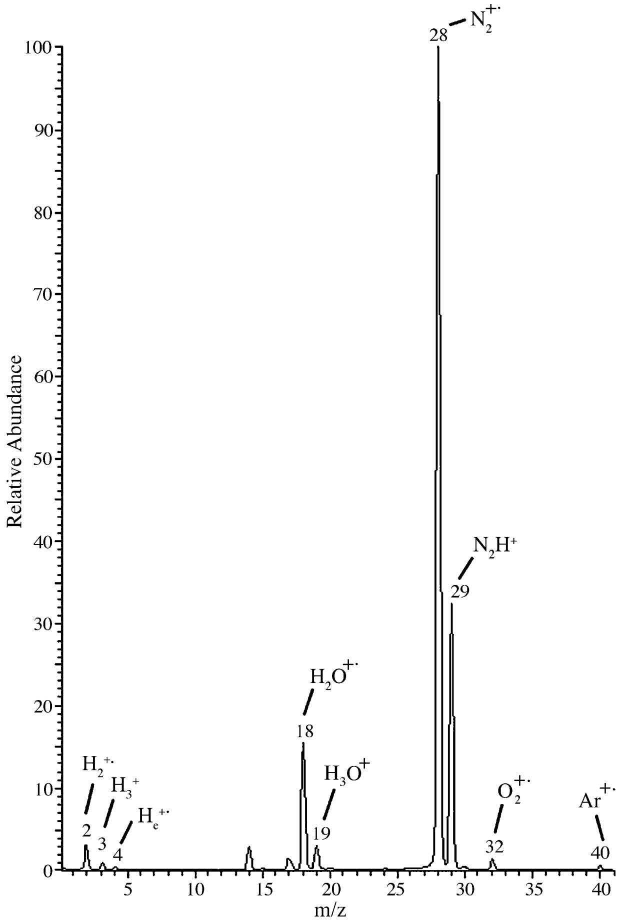

Fig. 1. Mass spectrum of lightweight gases analyzed by the QITMS gas analyzer developed at the University of Florida. Ion signals at *m/z* 3 (H_3^+), 19 (H_3O^+), and 29 (N_2H^+) show that ion-molecule reactions are occurring within the ion trap, affecting QITMS quantitative performance.

QITMS mass spectra, as in the case of Fig. 1, showed unexpected ion signals at *m/z* 3, 19, and 29 which were not readily observed on other non-trapping mass analyzers evaluated for the AHGD project. These peaks represented $(M + \mathrm{H})^+$ ions of hydrogen, water, and nitrogen, respectively. The proton transfer reactions leading to these ions have been characterized by mass spectrometry since 1916 when the H_3^+ ion at *m/z* 3 was first isolated [6]. In the 1950s, improved mass spectrometry technology and the advent of chemical ionization (CI) prompted further study of ion-molecule reactions. Three instrument configurations were commonly used: (1) tandem-in-space mass spectrometry (e.g., sector and triple quadrupole); (2) drift tube methods with either spectroscopic or mass spectrometric detection; and (3) tandem-in-time mass spectrometers (e.g., Fourier-transform ion cyclotron resonance and QITMS) [7]. Using tandem-in-space mass spectrometry, reactions were controlled by adjusting the gas pressure in the collision cell, while drift tube methods (e.g., selected ion flow tube, SIFT) monitored reaction in time. Tandem-in-time instruments were advantageous in that reactions could be controlled with respect to time and pressure [8,9].

Table 1
Energy values associated with ion-molecule reactions for ions and neutrals of interest

Ions/neutrals of interest		RE[a] (eV)	IE[b] (eV)	PA[c] (eV)
$H_2^{\bullet +}$	H_2	16.4–17.4	15.4	4.377
H_3^+		9.2		
$He^{\bullet +}$	He	24.6	24.6	1.843
$H_2O^{\bullet +}$	H_2O	12.4	12.6	7.16
H_3O^+		6.4		
$N_2^{\bullet +}$	N_2	15.3	15.6	5.118
N_2H^+		8.5		
$O_2^{\bullet +}$	O_2	11.2–11.3	12.1	4.36
$Ar^{\bullet +}$	Ar	15.8	15.8	3.827

[a] Recombination energy (RE) [6,15,16].
[b] Ionization energy (IE) of neutral [17].
[c] Proton affinity (PA) of neutral [18].

The concept of the quadrupole ion store or QUISTOR, first proposed by Lawson and Todd [10,11], was used explicitly for reaction studies, leading to the development of the low pressure CI source, where time (not pressure) was used to provide a sufficient number of collisions. Unwanted reactions in this process would affect quantitative performance by changing analyte ion signals and adding chemical noise such that even before its commercialization, QITMS was known to be affected by gas phase reactions.

1.1. *Ion-molecule reactions*

The average velocity of an ion inside the ion trap with $q_z = 0.25$ is 7 m/ms (see equation in [12]), and at an ambient ion trap pressure of 7×10^{-6} Torr the mean free path is 7 m. These parameters result in a collision every ms, allowing for numerous reactions within a 10–20 ms analysis time. There are three possible ion-molecule reaction pathways: charge-exchange, proton transfer, and hydrogen-atom transfer. Charge-exchange involves transfer of an electron from the ambient neutral to the analyte ion radical [6,13–16]. The reaction is exothermic when the recombination energy (RE) of the ion radical is greater than the ionization energy (IE) of the neutral (RE and IE values of interest are listed in Table 1). Brønsted acid ions, such as H_3^+, are formed by proton transfer when the conjugate neutral base has a higher proton affinity (PA) [6,18] (see Table 1 for PA converted to eV from Table 1 of [18]). Self-protonation also occurs since the PA value of a neutral gas phase acid is greater than that of its conjugate ion. The third less understood reaction involves the transfer of a hydrogen atom from a molecule to an ion radical [6,19–24], the energetics of which are similar to proton transfer, but the exact mechanism is still in dispute.

1.2. *Kinetics of ion-molecule reactions*

Ions will react within a QITMS given exothermic conditions and time. Studying reactions between analytes and resident neutrals is required to determine QITMS effec-