Abstract
We have combined a simple time-offlight (TOF) mass spectrometer in tandem with a cylindrical RF ion-trap to monitor the temporal evolution of an ion population as it reacts with a neutral gas buffer following an electron impact ionization process that is used to create the ions. At precisely determined times following electron impact, the ionized species are extracted from the trap into a 15-20 ns flight path traversed by an active Faraday detector. An analysis of the TOF spectra as a function of the extraction time and neutral gas pressure can yield relevant collision-rate coefficients for modeling of solar, stellar, planetary, interstellar, and early universe plasma.

Measurements are being carried out to study collisions of H and HD, by determining the radiative and elastic loss rates of H2, HD, and H2O at pressures up to 300 Torr. The measurements are intended to provide a direct measure of the rate coefficients for the simple one-component exponential functions that describe the ion population as it reacts with a neutral gas buffer following an electron impact ionization process. The TOF apparatus installed in our laboratory is capable of detecting the ion population through a single-component exponential function
\[ N(t) = N_0 e^{-kt} \]
where \( N \) represents the ion loss rate, \( N_0 \) the initial number of ions, and \( k \) the rate constant. The TOF spectrometer can be used to determine the rate constant by measuring the ion loss rate at various pressures or partial pressures of the neutral gas.

Motivation
Current models for the creation of structure in the early universe indicate that during the epoch of star formation, H and HD were the dominant elements in the universe. The ion population as it reacts with a neutral gas buffer following an electron impact ionization process can yield relevant collision-rate coefficients for modeling of solar, stellar, planetary, interstellar, and early universe plasma. The measurements are being carried out to study collisions of H and HD, by determining the radiative and elastic loss rates of H2, HD, and H2O at pressures up to 300 Torr. The measurements are intended to provide a direct measure of the rate coefficients for the simple one-component exponential functions that describe the ion population as it reacts with a neutral gas buffer following an electron impact ionization process.

Experimental Procedure and Results
Our measurements used a tandem ion trap/TOF apparatus represented in Figure 1 in order to monitor the relative number of ions remaining in the trap as a function of the H2 gas pressure and the time after the electron impact ionization event. The trap can be tuned to store only H2. However, for a long ~200 ms following the Fill interval, some higher masses \( \text{H}_2 \text{O}^+ \) and \( \text{H}^+ \) persisted inside the storage volume as shown in Figure 2. The mass filtering ability of the trap then excluded all other ions from any significant detection.

Figure 2. TOF signal for three different DELAY extraction times. Note, for the 100 ms extraction delay, the derivative of \( \text{H}_2^+ \) remains in the TOF signal. Our relative proton count was determined by integrating the dominant proton signal from 2.7 to 4.1 \( \text{amu} \) following the ion extraction pulse. Because \( \text{H}_2^+ \) has no excited states, the trapped ion population will be entirely in the same state. The resulting decay curve for the trapped ion population should then be described by a single-component exponential function
\[ N(t) = N_0 e^{-kt} \]
where \( k \) represents the ion loss rate, \( N_0 \) the initial number of ions, and \( N \) the number at time \( t \). The loss rate \( k \) can be expressed as
\[ k = \frac{\gamma}{\sqrt{1 + \beta}} \]
where \( \gamma \) is the rate coefficient for CX reaction between \( \text{H}_2^+ \) and \( \text{H} \), \( \beta \) is a rate coefficient for CX reactions between the \( \text{H}_2^+ \) ions and the residual background gas. The assumed expression is the rate coefficient for elastic and quasi-elastic collisions, which could include neutral losses due to rf-driven elastic collisions between the ions and the neutral gas at a density of \( n \), and \( \beta \) is the cold-elastic inelastic rate for the trapped ions due to rf-driven collisions between the ions.

Given previously published work [8], we expected that these elastic and quasi-elastic losses would be at a small magnitude and we are confident in our measurement of \( k \). Similarly, the \( \beta \) term is small for the \( \text{H}_2 \) density extrapolated in the vacuum system (\( 10^9 \text{ Torr} \)), the relative velocity is dominated by the ion velocity of the trapped ions (\( 10^9 \text{ Torr} \)). To obtain a good measurement of the neutral density as a function of time, we used the TOF enhanced data acquisition technique, described above, which was initially developed to correct for the density of ions within a cylindrical RF ion trap. At a given target gas pressure, we collected a series of TOF spectra for ions extracted from the trap following a set of precisely-determined and increasing DELAY intervals, as shown in the schematic timing of Figure 1. The TOF apparatus was designed to average the TOF spectra for each DELAY interval over several ions and to average the TOF spectra for each DELAY interval over several pressures or partial pressures of the neutral gas. We fitted our measured proton loss rates and the black solid lines are the straight-line fits to the loss rates at each pressure or partial pressure combination and plotted versus neutral density.

Discussion and Summary
Table 1. Combined CX and elastic collision rate coefficients (cm³/sec) versus trap well depth for different neutral targets (H, H2, or H2O). Measurements are associated with the straight-line fit to the loss rates versus respective target density were quite small. However, we estimate the uncertainty in the measured rate coefficients at 10%. For the H2 target, the density extrapolation and 20°C, for the H2 and H2O density extrapolations. We have initiated a computational study of the elastic and inelastic proton collision processes in a cylindrical RF ion trap, for which preliminary results agree with our measured results.

Our measurements indicate that elastic collisional losses dominate the H2, H, and HD collision process in the ion trap. As a consequence, we are unable to report a CX collision rate coefficient at this time. However, we note that these elastic collision rate coefficients are important not only in this experiment but also in the coupling of protons and H, HD, and HD collision processes in the ion trap. For which preliminary results agree with our measured results.

Our current results indicate that elastic collisional losses dominate the H2, HD, and H2O collision process in the ion trap. However, we plan to continue to study this problem computationally and perhaps with a more elaborate (i.e., difficult) data acquisition scheme, we will be able to resolve the CX collision rate coefficient in the future. In particular, we are considering a time-resolved measurement of the recombination product \( \text{H}_2 \), but this is complicated by the fact that \( \text{H}_2 \) reacts rapidly with \( \text{H}_2 \), to produce \( \text{H}_2^+ \), as seen in Figure 5, when the trap is tuned to store ions heavier than protons.

Figure 5. a) TOF spectra with the trap tuned to store \( \text{H}_2 \). b) The integrated mass peaks of the TOF spectra as a function of DELAY time to ion extraction. An exponential decay time \( \tau \) was fit to \( \text{H}_2 \), yielding a loss rate of 2.17 ± 0.07 sec⁻¹, while a double exponential was fit to \( \text{H}_2^+ \), yielding a loss rate of 0.05 ± 0.01 sec⁻¹ and a growth rate of 2.01 ± 0.15 sec⁻¹ at a density of 10⁶ cm⁻³. The measured rate coefficient is consistent with the literature [e.g. 12].

References

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