Laboratory Studies of Hydrogen Ion Chemistry

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Abstract

We have combined a simple time-of-flight (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 interval which is used to create the ions. At precisely determined times following electron impact, the stored ions are extracted from the trap into a 76-cm flight path terminated by an active-film 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, inter-planetary, and early universe plasmas. Measurements are being carried out to study collisions of H^+ and H_2, by monitoring the loss of protons from the trap, and to study the rapid reaction of H_2^+ with H_2 to produce H_3^+, by simultaneously monitoring the loss of H_2^+ and growth of H_3^+.

Motivation

Current models for the creation of structure in the early Universe indicate that during the epoch of first star formation, H_2 and HD were the dominant coolants for collapsing primordial gas clouds at temperatures between ~10^2 K and ~10^4 K. The importance of these molecules is supported by the recent Wilkinson Microwave Anisotropy Probe detection of reionization at high redshift. These results require star formation at these redshifts to produce the ionizing radiation, which implies that molecular hydrogen cooling is important for early star formation.

Considering the pivotal role that H_2 and HD play, [1, 2, 3, 4, 5, 6, 7] an accurate understanding for their creation and destruction in the early Universe is crucial for understanding the formation of hierarchical structure. Of particular importance is the charge exchange process $H_2 + H^+ \rightarrow H_2^+ + H$ which is predicted to be the dominant destruction mechanism of H_2 during the epoch of first star formation (until the collapsing gas clouds begin to emit ionizing radiation). However, significant uncertainties exist in the published atomic data for these two reactions. For example, the collision rate coefficient k differs among the published calculations by orders of magnitude. The uncertainties in this reaction translates into major inaccuracies in the predicted relative abundances of H_2 at this key epoch.

Here we present our initial efforts toward a measurement of the collision rate coefficient k for the reaction $H_2 + H^+ \rightarrow H_2^+ + H$ at a series of ion temperatures of order 10^4 K.

Experimental Procedure and Results

Our measurements use 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 H_2 gas pressure and the time t after the electron impact ionization interval ends. The trap can be tuned to store only H^+. However, for as long a ~200 ms following the Fill interval, some higher masses (H_2^+ and H_3^+) persisted inside the storage volume as shown in Fig. 2. The mass-filtering ability of the trap then excluded all other ions from any significant level of storage.

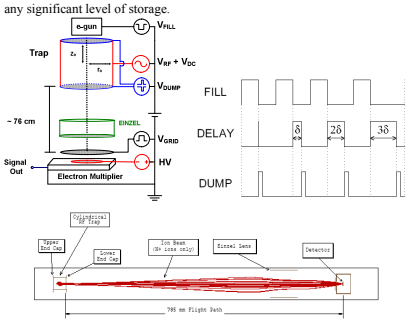

Figure 1. [not to scale] (Left) Schematic of experimental apparatus. **(Right)** A timing diagram for the data acquisition sequence that leads to time-resolved TOF spectra. **(Bottom)** For the data presented here the trap assembly was floated (~200V) above ground and an Einzel lens was installed about 15 cm above the electron multiplier assembly to improve the mass resolution and detection efficiency of the apparatus.

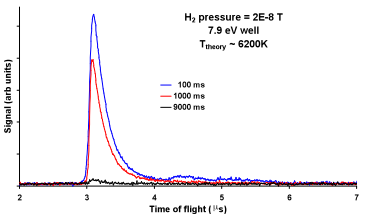

Figure 2. TOF signal for three different DELAYs/extraction times. Note, for the 100 ms extraction time evidence of H_2^+ remains in the TOF signal. Our relative proton count was determined by integrating the dominant proton signal from 2.7 to 4.1 μs following the ion extraction pulse.

Because H^+ has no excited states, the trapped ion population will be entirely in the same state. The resulting decay curve for the trapped ion population could then be described by a single-component exponential function

$$N(t) = N_o e^{-\gamma t}$$

where γ represents the ion loss rate, N_o the initial number of stored ions, and N the number stored at time t. The loss rate can be expressed as

$$\gamma = (k + k_e)n + (k' + k'_e)n' + \gamma_{rf}$$

where k is the rate coefficient for CX reaction between H^+ and H_2 at a density of n; k′ is the rate coefficient for CX reactions between the H^+ ions and the residual background gas of the vacuum system with a density of n′; $k_e(k'_e)$ are effective rate coefficients for elastic and quasi-elastic collisional losses, which could include ion-neutral rf-heating losses due to rf-driven elastic collisions between the ions and the neutral gas at a density of n(n′); and γ_{rf} is the field-coupled rf-heating loss rate for the trapped ions due, in part, to rf-driven collisions between the ions.

Given previously published work [8], we expected that these elastic and quasi-elastic losses would be at most a small systematic correction to our measurement of k. Similarly, the $(k' + k'_e)n' + \gamma_{rf}$ is small for the residual background gas (Fig. 4a), and furthermore is not a source of error for the reaction rate coefficients. Each rate coefficient in the expression for γ consists of the respective reaction cross section convolved with the ion-neutral spread in relative velocity. Because the neutral particles exist at room temperature in the vacuum system (T ≈ 300 K), the relative velocity is dominated by the ion velocity of the trapped ions (T ≈ 10^4 K). To obtain a record of the stored ion number as a function of time, we used the TOF-enhanced data acquisition technique, described above, which was initially developed to correct radiative decay curves for collisional ion losses[9]. 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 timing schematic of Fig. 1. It was necessary to average the TOF spectra for each Delay interval over several (typically 4) Dump pulses to account for the shot-to-shot variability in ion production by electron impact. The amplitude for a given mass peak in a TOF spectrum is proportional to the number of those ions in the trap at the time of extraction. To analyze the temporal evolution of the stored H^+ population, we integrated the proton peaks and converted those integrated signals to a proton count using our measured gain of the electron multiplier; which was typically operated at -1750V corresponding to a gain of $3 \times 10^5 \pm 7\%$. The resulting data sets (e.g. Fig. 3) provide a measurement of the H^+ depletion function $N(t) = N_o e^{-\gamma t}$ for a given gas pressure or sum of partial pressures for a gas mixture. From this, we extracted the value of γ using a non-least-squares fit to $N(t) = N_o e^{-\gamma t} + B$, where B is a constant background parameter and was routinely statistically consistent with zero.

Ion depletion curves, such as those shown in Fig. 3, were collected at a series of H_2 pressures and also at a set H_2 pressure and a varying He or Ne partial pressure. Proton loss rates γ were determined from the ion depletion curves at each pressure or partial pressure combination and plotted versus neutral particle density.

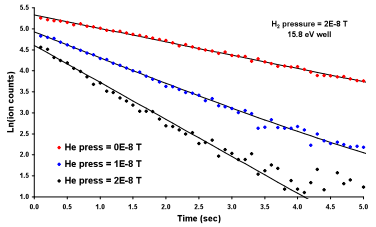

Figure 3. Proton depletion curves for a H_2 partial pressure of 2×10^{-8} T and the He partial pressures shown. (The pressures measured shown on this diagram have not been gauge corrected for H_2 or He.)

The respective particle densities were determined using published ionization gauge correction factors for the relevant gases and the ionization gauge controller readout. We used a matched ionization gauge/controller combination from Helix Technologies with a NIST-traceable calibration quoted to within 4% for the pressure measurements. We also verified that calibration independently.

Examples of the proton-loss rate versus particle density plots are shown in Figures 4a and 4b. For each pressure or mixture of partial pressures, the data are fit to a straight line whose slope corresponds to the sum of the CX and elastic collision rate coefficients and the intercept, as shown in the previous panel, is related to the respective background gas density and ion-ion rf heating.

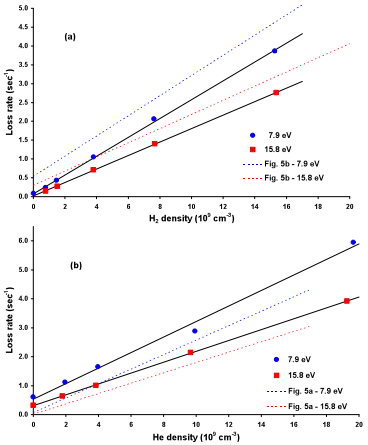

Figure 4. The data points (● = 7.9 eV well, ■ = 15.8 eV well) are the measured proton loss rates and the black solid lines are the straight-line fits to the loss rates as a function of **(a)** H_2 density and **(b)** He density with a fixed H_2 density. In **(a)** the dashed red and blue lines are the fit results from (b) and in **(b)** the dashed colored lines are the fit results from (a). In each, case the slope corresponds to the sum of the collision rate coefficients for the desired H^+/H_2 CX reaction and elastic collisional processes (which can include collisionally-induced rf heating) with the either H_2 or He. The measured intercepts are small as expected, however the slopes indicate the desired H^+/H_2 CX collisional rate coefficient is dominated by elastic processes.

The combined CX and elastic collisional loss rate coefficients ($k + k_e$) are shown in Table 1. The results are statistically indistinguishable versus H2 and He density. The combined rate coefficients are nominally smaller at the deeper trap well.

Discussion and Summary

	H_2	He	Ne
7.9 eV well	2.6×10^{-10}	2.6×10^{-10}	9×10^{-10}
15.8 eV well	1.8×10^{-10}	1.8×10^{-10}	6×10^{-10}

Table 1. Combined CX and elastic collision rate coefficients (cm^3/sec) versus trap well depth for different neutral targets (H_2, He, or Ne). The statistical errors 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 H_2 density extrapolation and ±20% for the He and Ne 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 shown experimental work.

Our current results indicate that elastic collisional losses dominate the H^+/H_2 CX 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 rates are important not only in this experiment but also in the coupling of protons and H_2 flow in sunspots [10] and starspots [11]. As the data indicate, the primary systematic problem corresponds to elastic collisional losses of protons from the 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 reaction product H_3^+, but this is complicated by the fact that H_2^+ reacts rapidly with H_2 to produce H_3^+, as seen in Figure 5, when the trap is tuned to store ions heavier than protons.

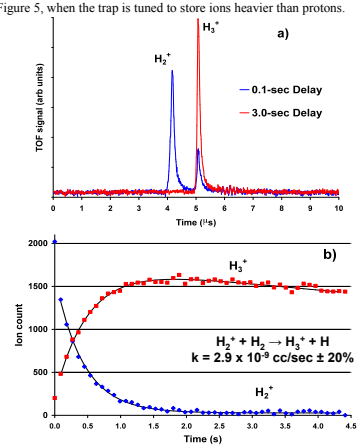

Figure 5. a) TOF spectra with the trap tuned to store H_2^+. **b)** The integrated mass peaks of the TOF spectra as a function of DELAY time to ion extraction. An exponential decay was fit to H_2^+ data, yielding a loss rate of 2.17 ± 0.06 sec^{-1}, while a double exponential was fit to the H_3^+ data, yielding a loss rate of 0.05 ± 0.01 sec^{-1} and a growth rate of 2.01 ± 0.11 sec^{-1}, at a H_2 density of 7×10^8 cm^{-3}. The measured rate coefficient is consistent with the literature [e.g. 12].

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