OBSERVATION OF ORTHO-PARA $H_3{}^+$ SELECTION RULES IN PLASMA CHEMISTRY. A TIME DEPENDENT STUDY IN A HOLLOW CATHODE DISCHARGE.

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During the past two Columbus meetings, we reported our observation of a nonthermal ortho-to-para distribution of $H_3{}^+$ in hydrogen plasmas, where we found selection rules on nuclear spin modifications to hold in a chain of plasma chemical reactions. The solution of rate equations incorporating nuclear spin branching ratios gave an ortho-to-para ratio of $H_3{}^+$ in good agreement with experiments. However, our observations were limited to steady-state plasma conditions, and no direct information relative to the kinetics of the plasma could be derived.

For this reason, a new time dependent experiment has been carried out in a hydrogen plasma. Our study consisted of monitoring the evolution of ortho- and para-$H_3^+$ absorptions during and after a short pulse discharging normal $H_2$ or para-$H_2$ confined in a hollow cathode. Deviations from thermal conditions were found stronger than those observed in the steady-state work, and the study of the $H_3^+$ absorption signals allowed a more detailed analysis of the chemical processes occurring during the thermalization of the o-$H_3^+$ and p-$H_3^+$ in the cell. An experimental value for the ratio of rate constants of the proton hop ($\widetilde{H_2} + H_3^+ \rightarrow \widetilde{H_2}H^+ + H_2$) and the hydrogen exchange ($\widetilde{H_2} + H_3^+ \rightarrow H_2\widetilde{H}^+ + H\widetilde{H}$) reactions has been obtained to explain the ortho-to-para $H_3^+$ ratios observed in the pulsed plasma.