Influence of Internal States on Ion-Molecule Reactions in a Temperature Variable 22-Pole Ion Trap

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Spectroscopy and Reaction Kinetics

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Abstract

Chemical reactions between ions and neutral gas are very important in the interstellar medium. This is due to the fact, that they usually have much lower barriers than neutral-neutral reactions. Thus, they are more likely to take place at low temperatures.

In this work, the endothermic reactions of CH_2D^+, H_2D^+, and N^+ with H_2 have been investigated. At low temperatures, they depend very sensitively on the translational and internal energies of the reaction partners. This sensitivity can be applied to gain information on the energy levels or the population of the internal states.

The investigations were performed in a temperature variable (10 to 300 K) 22-pole ion trap. Inside the trap, the pressure is low enough, to investigate chemical processes under typical astrophysical conditions. The setup of the ion trap apparatus and three different types of measurements that can be performed in it (mass spectroscopy, reaction kinetics, spectroscopy of ions) are presented in Chapter 4. This chapter also includes the brief description of the assembly of new Daly detectors for the two new ion trap experiments in Cologne.

For the investigation of all endothermic reactions of ions with molecular hydrogen at low temperatures, it is important to know the fractions of each of the two symmetries of nuclear spin configuration *ortho* and *para* in H_2.

Investigations on the ortho-to-para ratio and improvements on the Cologne para hydrogen generator performed in this work are described in Chapter 5. Two different methods can be applied in Cologne to test this ratio, Raman spectroscopy and the influence of the different internal energies of ortho and para hydrogen on chemical equilibria at low temperatures ($H_2D^+ + H_2$, $N^+ + H_2$). The results of Raman spectroscopy and of the equilibrium of the reaction of H_2D^+ with H_2 are also presented in Chapter 5. The results from the reaction of N^+ with H_2 are presented in Chapter 6 as this reaction system was investigated

in more detail.

The reaction of N^+ with H_2 is the first step in the formation of interstellar ammonia. It has been investigated with various methods by several groups over the last three decades, but still many open questions remain. For example, it is not known whether the reaction is really endothermic or just hindered by a barrier, and to what extend the energy of the fine-structure states of N^+ is available to support the reaction. Measurements on this reaction system are presented in Chapter 6.

The recent tentative astronomical detection of CH_2D^+ called for more precise predictions of the ion's pure rotational lines. Thus, the spectroscopy of CH_2D^+ was revived in several groups. Measurements on the rovibrational transitions of two vibrational bands were performed in the ion trap, as high resolution spectra can be obtained by the method of laser induced reactions (LIR). These measurements and the resulting predictions for pure rotational transitions are presented in Chapter 7.

Many lines observed with LIR show deviations from the Gaussian line profile. These deviations do not hinder the precise frequency determination, as their mathematical description is known qualitatively. As the correlation between the experimental parameters and those of the function for the saturated LIR lines is unknown, it is not possible to derive other information such as translational and rotational temperatures of the ions from the observed non-Gaussian lines. Investigations towards a quantitative description of the involved processes are presented in Chapter 8.

In this work, the already mentioned sensitivity of endothermic reactions on internal excitations of the reaction partners was applied for two different types of investigations. It enables high resolution spectroscopy of CH_2D^+ and thereby improved predictions for pure rotational transitions of this ion. First steps were made towards a detailed understanding of the processes in laser induced reactions. Additionally, the explained sensitivity allowed to determine the purity of para hydrogen samples and yielded insight into the reaction kinetics of the system $N^+ + H_2$.