Reactions of NH^+ with H at low temperatures

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Ion–molecular reactions are one kind of significant reactions in astrochemistry. Studying them is essential to understand a chemical evolution in interstellar clouds. Using the apparatus of the radiofrequency 22–pole ion trap we are able to study reactions of ions with neutrals at low temperatures (10 – 300 K) and at low pressures. The presented research of the reaction $NH^+ + H \rightarrow N^+ + H_2$ follows the previous research of the reaction $N^+ + H_2 \rightarrow NH^+ + H$, which has been also studied by using 22–pole trap apparatus.

1. Introduction

The nitrogen is after H, He, C, O, and probably Ne, one of the most abundant element in a solar neighborhood. Ion N^+ is formed by reaction of He^+ with N_2 or N. By subsequent reactions and dissociative recombination NH_3 has been formed in dark and dense gas clouds [1].

$$He^+ + N_2 \rightarrow N^+ + N + He, \quad (1)$$

$$N^+(^3P_{ja}) + H_2(j) \rightarrow NH^+(^2\Pi_\Omega) + H, \quad (2)$$

$$\cdots$$

$$NH_3^+ + H_2 \rightarrow NH_4^+ + H, \quad (3)$$

$$NH_4^+ + e^- \rightarrow NH_3 + H \quad (4)$$

The rate coefficient of reaction (2) depends on fine–structure states ($j_a = 0, 1, 2$) of N^+ and on rotation states ($j = 0, 1, 2,\ldots$) of H_2. This reaction has been studied theoretically and experimentally and it seems to be endothermic with ΔH_1 around 220 K [2]. There is a question whether the reaction is really endothermic or there is a barrier on the reaction path.

The study of the reverse reaction

$$NH^+ + H \xrightarrow{k} N^+ + H_2 \quad (5)$$

can give us a different view of the problem.

The knowledge of the bonding energy of NH^+ would bring the solution, but bonding energy (precisely dissociation energy of NH^+) is not known with good accuracy. Some experimental and computed values of dissociation energy of NH^+ can be seen in [3]. For example dissociation energies computed according to the experimental results of [4] is 213.5 K and by [5] it is 132.2 K. The reason why the bonding energy of NH^+ is elusive is the interesting fact about NH^+ that the difference of the lowest rotational states of the basic electronic state $X^2\Pi$ and of the first electronically excited state $a^4\Sigma^-$ is only a few hundred kelvin [6].

2. Experimental method

2.1. The apparatus

The apparatus of radiofrequency 22–pole ion trap allows us to achieve the conditions similar to the interstellar place. The trap allows us measuring at temperatures around 10 K, which are typical in interstellar medium. A number density of reactants in the trap may be as low as 10^6 cm^{-3}.

Primary ions NH^+ are produced in a storage ion source via electron bombardment of NH_3. The ions are precooled in the storage ion source, extracted, selected by a quadrupole mass spectrometer, bent by electrostatic quadrupole and injected into the 22–pole ion trap.

The 22–pole ion trap consists of two sets of 11 rods, which create an inhomogeneous radiofrequency field, which confines the ions in radial direction. The ions are confined in the axial direction by the voltages, which are applied on the entrance and the exit electrodes of the trap. The trap is surrounded by a copper box, which is mounted onto the cold head of the He refrigerator with a closed–cycle (Leybold RGD 210), which can cool the trap down to 10 K.

H atoms are produced from H_2 in H atom source by the rf discharge. From the discharge they are flowing to the accommodator (Figure 1) and they are cooled there. The speed of atoms of the H atom beam fits to Maxwell speed distribution well (it has been proved by using time–of–flight measurement). We can say that temperature of H atoms corresponds to, or is more close to, temperature of the accommodator [7]. The accommodator is connected to the cold head. Temperature may be changed from 7 K to 300 K. There is a mechanical shutter, which can stop the H atom beam.

In the trap the primary ions are stored, cooled in the collisions with helium buffer gas and they react with neutral reactants. After well defined time, they are extracted and detected by an MCP detector.

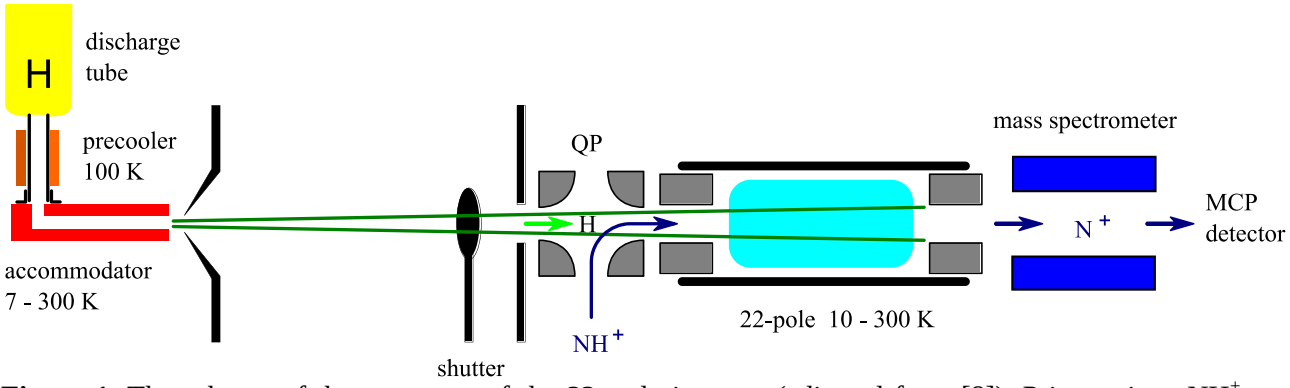

Figure 1. The scheme of the apparatus of the 22–pole ion trap (adjusted from [8]). Primary ions NH^+ are produced in the ion source, selected by mass spectrometer and then they are stored and cooled in the 22–pole trap, where they react with neutral H atoms, which come to the trap from the H–atom source.

The primary result of experiment is the number of ions $N_i(t)$ at different times. An example is in Figure 3.

2.2. Number density of atomic hydrogen

Number density of hydrogen atom [H] in reaction area has been calibrated by known reactions

$$CO_2^+ + H \xrightarrow{k_1} HCO^+ + O, \quad (6)$$

$$CO_2^+ + H_2 \xrightarrow{k_2} HCO_2^+ + H. \quad (7)$$

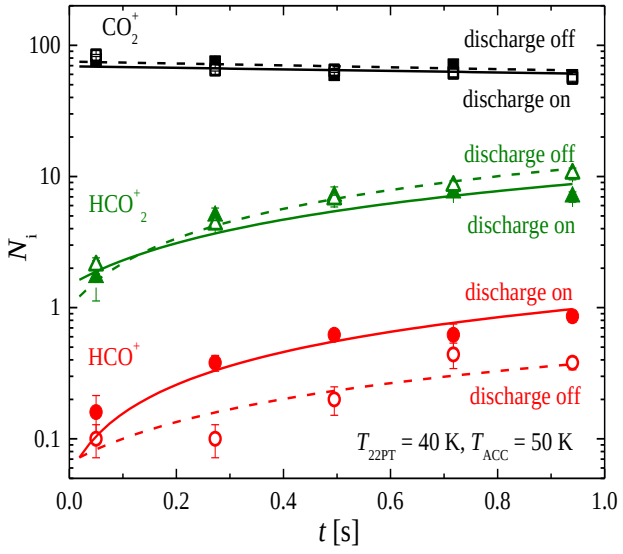

Figure 2. Calibration of a number density of hydrogen atoms. There is the time evolution of ions CO_2^+, HCO^+ and HCO_2^+ during turn on/off discharge for temperatures T_{22PT} = 40 K, T_{ACC} = 50 K. From this kind of data the number density of hydrogen atom [H] for corresponding temperatures has been calculated.

Number density of hydrogen atom [H] has been determined from evolution of numbers of ions (i.e. rate of decrease of ion CO_2^+ and rate of increase of ion HCO^+) and due to known rate constants $k_1 = 4{,}5\cdot10^{-10}$ cm^3·s^{-1} and $k_2 = 9.5\cdot(T/300\text{K})^{-0.15}\cdot10^{-10}$ cm^3·s^{-1} [7].

This [H] has been determine as
[H] = (30±3)·10^6 cm^{-3} for T_{ACC} > 40 K,
10 K < T_{22} < 21 K,
[H] = (7±1)·10^6 cm^{-3} for T_H < 10 K, T_{22} = 11 K.
T_{ACC} is temperature of the atomic hydrogen in the beam, T_{22} is temperature of the 22–pole trap. These values have been used for calculation of the rate coefficients.

2.3. The rate coefficient

The rate coefficient of a reaction is usually calculated from a decrease of the primary ions and number density of neutral reactants but in this situation is the decrease of number of NH^+ not measurable. To determine the rate coefficient k of the reaction (5) an evolution of number of ions N^+ has been watched. Ions N^+ react with NH_3, which is coming to the 22–pole trap from the ion source, and more complex molecular ions are produced. These reactions are characterized by loss rate coefficient k_{loss}.

$$N^+ + NH_3 \xrightarrow{k_{loss}} \ldots \quad (8)$$

The rate coefficient k of reaction (5) is calculated from system of differential equations

$$\frac{dN^+}{dt} = k\cdot NH^+\cdot[H] - k_{loss}\cdot N^+\cdot[NH_3] \quad (9)$$

$$\frac{dNH^+}{dt} = -k\cdot NH^+\cdot[H] \quad (10)$$

Temperature of the H atom beam, controlled by the accommodator, can be different from temperature of ions stored in the 22–pole trap. For calculations of rate coefficient is used the weighted mean

$$T_{coll} = \frac{T_{Acc}\cdot m_{NH^+} + T_{22PT}\cdot m_H}{m_{NH^+} + m_H} \quad (11)$$

The rate coefficient is obtained as

$$k = k_{on} - k_{off}, \qquad (12)$$

on/off means that measuring took place with on/off discharge.

3. The results

As we can see in Figure 3 the experimentally determined rate coefficient at temperatures $T_{22} = 11$ K and $T_{ACC} = 150$ K is $k = (7 \pm 27)\cdot 10^{-11}$ cm^{3}s^{-1}. Very similar results have been given for other low temperatures (10 – 170 K). Due to low values of the rate constant we can assume that there is the reaction barrier on the reaction path. In contrast to reaction (2) the decrease of the primary ions NH^+ is not significant due to low number density of neutral reactant atomic hydrogen.

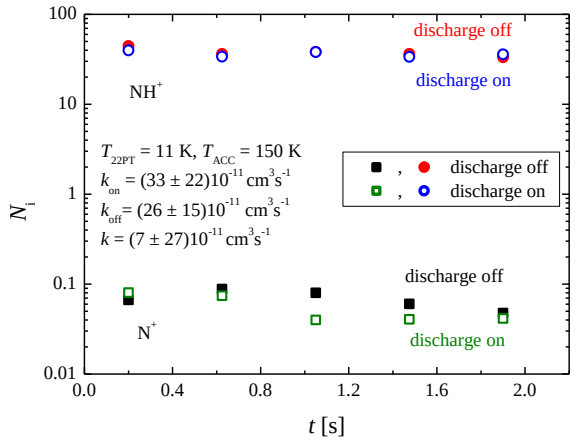

Figure 3. An example of measured data. In the picture there are numbers of the ions N^+ and NH^+ as a function of storage time. The rate constant of reaction $NH^+ + H \rightarrow N^+ + H_2$ has not been determined from decrease of primary ion as is typical due to weak decrease of ion NH^+ but was determined by fitting evolution of ion N^+. It is indicated in the formula (9).

Due to small values of rate coefficients, and due to the low [H], the errors are higher than corresponding values of rate coefficients The height of the right side of barrier is hard to determine, therefore the difference of ΔH_1 of reaction (2) and ΔH_0 of reaction (5) is not known precisely.

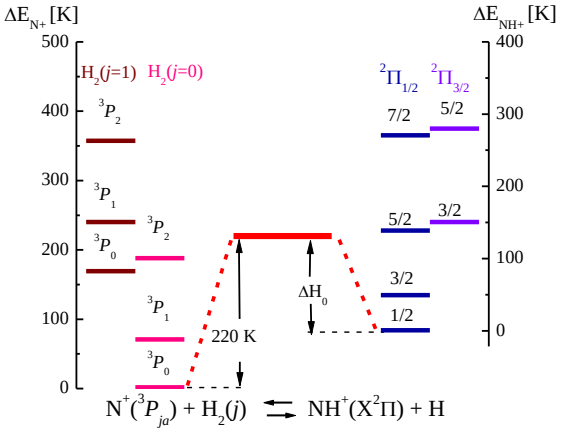

Figure 4. The lowest energetic states of system $N^+(^3P_{ja}) + H_2(j)$. The value of the left side of the barrier has been determined experimentally as 220 K [2]. The value of the left side of the barrier ΔH_0 is hard to be determined. From measured data it has been estimated that this value is higher than 150 K.

To fully understand this problem further measurements and evaluations of the reaction (5) are underway.

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