

Measurement of Kinetic Temperature of H_3^+ Ions in 22-pole Ion Trap

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Abstract. H_3^+ ions are widespread in the interstellar medium and play an important role in cosmic chemistry. The reaction between H_3^+ and H_2 with ortho-para conversion of H_3^+ ions is going to be studied. The 22-pole ion trap was used in the present study. This trap may be cooled to 10 K by a closed-cycle helium cryocooler. In order to determine the population of rotational quantum states of H_3^+ ions, we used the Laser Induced Reaction (LIR) of H_3^+ with Ar. The kinetic temperature of H_3^+ ions was obtained from the Doppler broadening of absorption lines of H_3^+ ions at different conditions.

Introduction

Due to the widespread presence of H_3^+ ions in the interstellar medium (ISM) and the important role that it plays in cosmic chemistry [Smith *et al.*, 1993; Oka, 2006; Oka, 2012], reactions involving H_3^+ have been the subject of numerous studies in the past century, both theoretical and experimental [Oka, 2006, Larsson *et al.*, 2008, Albertsson *et al.*, 2014, Le Bourlot *et al.*, 2023].

H_2 molecule has two types of nuclear spin state configurations — ortho and para. H_2 with antiparallel proton spins (antisymmetric nuclear spin state wavefunction) is called para- H_2 with the total spin $I = 0$. An ortho- H_2 has $I = 1$, its proton spins are parallel (symmetric nuclear spin state wavefunction). H_3^+ ion possesses similar symmetry properties as the H_2 molecule with two nuclear spin state configurations — ortho ($I=3/2$) and para ($I=1/2$). A radiative transition between ortho/para configurations is forbidden due to the selection rule $\Delta I=0$ (conservation of spin) [Lindsay *et al.*, 2001]. For this reason, both spin configurations of H_3^+ can be considered as separate chemical species in the ISM and each one has its manifold of rotational states [Le Bourlot *et al.*, 2023].

Even though H_3^+ was discovered by Thomson [1911] at the beginning of the 20th century, its absorption spectrum was first observed only in 1980 by Oka [1980]. Later on, H_3^+ ions were detected in the diffuse ISM (the first observation was towards Cygnus OB2 No.12 [McCall *et al.*, 1998]). Also, it was observed in the ionospheres several planets such as Jupiter, Saturn, and Uranus [Geballe *et al.*, 1996; Trafton *et al.*, 1993]. The spectrum of H_3^+ was also detected towards the Galactic Center [Miller *et al.*, 2020].

H_3^+ ions react easily with many species of neutral molecules by ion-neutral reactions of the type $\text{H}_3^+ + \text{X} \rightarrow \text{XH}^+ + \text{H}_2$, where X is some neutral atom or molecule [Albertsson *et al.*, 2014; Le Bourlot *et al.*, 2023]. In different words, H_3^+ ions play an important role in cosmic chemistry as a universal proton donor [Oka, 2006].

As discussed in [Le Bourlot *et al.*, 2023], there exists some discrepancy between the temperature obtained from the two lowest rotational states of H_3^+ ions and the temperature inferred from the two lowest states of the H_2 molecule. Albertsson *et al.* [2014] in their time-dependent modeling of the para-fractions of H_2 and H_3^+ in the diffuse ISM summarise that the ortho/para ratio of H_3^+ is partially controlled by the destruction of the lowest rotational states of H_3^+ by dissociative recombination. The best agreement between their model and the astronomical observations was achieved when the values of the recombination rate coefficient for ortho and para H_3^+ ions were set to be the same. On the other hand, a recent study by Le Bourlot [2023] implies that the difference between observed rotational (or rather nuclear spin) temperatures of H_3^+ and H_2 is largely given by non-thermal populations of some metastable states of H_3^+ ion. In order to improve the models of interstellar chemistry, state selective studies focused on reactions of H_3^+ ions with H_2 molecules (nuclear spin state changing collisions) or electrons are needed.

Because of many configurations, H_2 and H_3^+ reactions between its species can be separated into 16 reactions. Two of these reactions are forbidden by nuclear spins [Hugo *et al.*, 2009] and they are not taken into account. And some of them take place without ortho–para conversion of H_3^+ ions. As a result, only the following reactions were considered for the study of nuclear spin state changing reaction rate

coefficients [Hernández Alvarez *et al.*, 2022]:



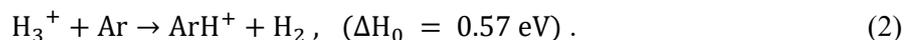
where superscript o/p means ortho or para H_3^+ ions and ortho or para molecules of H_2 .

Experiment

The 22-pole radiofrequency ion trap was used for this study. A detailed description of the experimental setup can be found e.g. in [Gerlich, 1992, 1993; Zymak *et al.*, 2013] and only a short overview will be given here. The apparatus can be divided into the following parts: a storage ion source, two mass filters, 22-pole trap and an MCP detector. Moreover, the optical system and para hydrogen generator play an important role specifically in the present experiment.

In storage ion source (SIS) H_3^+ ions are produced by electron bombardment of pure H_2 precursor gas. The electrons in SIS are produced by emission from a rhenium filament. Created ions are then mass selected during the passage through the first mass filter. Several additional electrodes including a quadrupole bender guide the ions into the 22-pole ion trap. All reactions, that we study, are happening directly in that place. All reactants and buffer gas are injected to 22-pole trap and pumped down by the turbomolecular pumps backed by a scroll pump. The trap can be cooled down to 10 K by Cold Head. The temperature of 22-pole trap is measured by a silicon diode, that is attached directly to a copper body of 22-pole trap. After the set time, the trap is opened and the products of the reactions are mass separated by a second mass filter and detected by a microchannel plate (MCP) detector.

The Laser Induced Reaction technique (LIR) [Schlemmer *et al.*, 1999, Mikosh *et al.*, 2004] was used to probe the number of ions in specific rotational (and nuclear spin) states of H_3^+ ions in the trap, utilizing endothermic reaction



The additional energy can be obtained from the vibrational excitation of H_3^+ ions. Therefore, we used an infrared laser (IR) to stimulate the second overtone transitions of ortho or para H_3^+ ions.

A special optical system was prepared for the present experiments (see Figure 1). It consists of two lasers, an optical isolator, a shutter (SH05 from Thorlabs) and a system of static and movable mirrors. The shutter is a rotary, electro-mechanical actuator to provide shutter operation. The optical isolator was used for the infrared laser to prevent back reflections to the laser. After going through a system of mirrors the IR light can get into the trap via a remotely controlled shutter. In this way, we are able to control the time interval when the lasers radiation passes through the 22-pole trap with a time resolution on the order of tens of ms. The alignment of the IR laser into the trap is assisted by a red laser on the same optical path with a movable mirror used to switch between the lasers. A camera with a large focal length was used to monitor the correct alignment of the red laser and thus of the IR one.

By using the combination of the optical system and the LIR technique we are able to measure the number of ArH^+ ions produced in reaction (2) from H_3^+ ions excited to the higher vibrational level. The number of detected ArH^+ ions is thus proportional to the number density of H_3^+ ions pertaining to the lower state of the used transition.

Results and Discussion

Two transitions were used during the LIR experiment. The transition $3v_2^1(2,1) \leftarrow 0v_2^0(1,1)$ at 7237.298 cm^{-1} originating in the lowest para state of H_3^+ and the transition $3v_2^1(2,0) \leftarrow 0v_2^0(1,0)$ at 7241.262 cm^{-1} from the lowest H_3^+ state with ortho nuclear spin symmetry. The first number in the parentheses in the transition notation is the rotational quantum number J , while the second number denotes $G = |K - l|$, where K is the projection quantum number and l is the quantum number for vibrational angular momentum (the superscript in the notation of the corresponding vibrational mode is equal to the value of l). More information about the notation can be found in Crabtree *et al.* [2013] and Lindsay *et al.* [2001]. An example of the measured absorption line of ortho H_3^+ is presented in Figure 2.

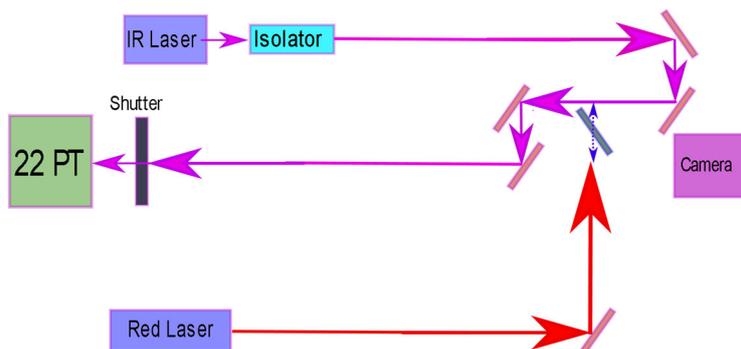


Figure 1. The optical system for the LIR experiment. It consists of two lasers — a red one and an infrared one. The optical isolator was used to prevent back reflection towards the laser. The shutter was used to send the laser radiation into the trap within a specified time. Dotted arrows denote a movable mirror that is used to select which of the two laser beams (sharing the same optical path) passes through the trap by changing its position. A Camera with an adjustable focal length is used for the alignment of the laser beam to the centre of the trap

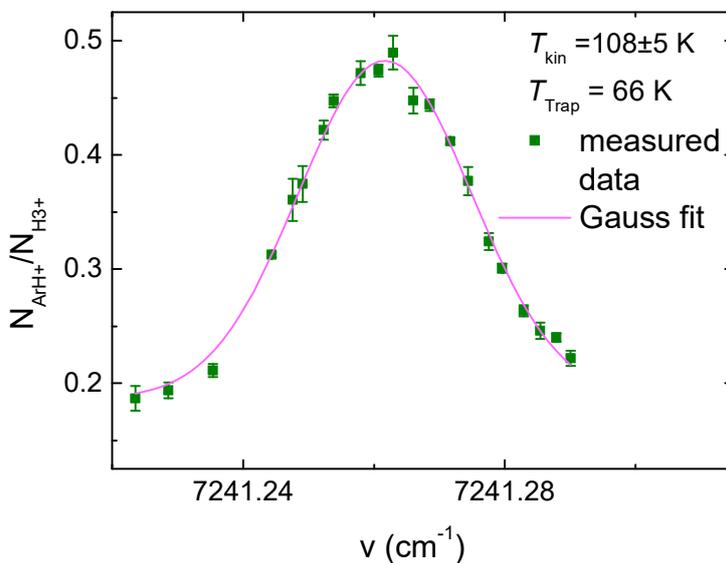


Figure 2. An example of the measured absorption line of ortho H_3^+ ions. The kinetic temperature of the H_3^+ ions $T_{\text{kin}} = 108 \pm 5$ K was obtained from the Doppler broadening of the absorption line. The trap temperature $T_{\text{trap}} = 66$ K was measured by a silicon diode positioned on the 22 pole trap. The number densities of reactants are $[\text{H}_2] = 1.34 \times 10^9 \text{ cm}^{-3}$, $[\text{Ar}] = 2.11 \times 10^{11} \text{ cm}^{-3}$, $[\text{He}] = 6.52 \times 10^{12} \text{ cm}^{-3}$. The amplitude of the RF voltage in the trap was 65 V.

As can be seen from Figure 2, the kinetic temperature of the H_3^+ ions, obtained from the Doppler broadening of the absorption line, is substantially higher than the temperature that was measured by the silicon diode on the 22 pole trap. We have identified several sources of additional heating of the H_3^+ ions. First and the most helpful step was significantly decreasing the amplitude of the radiofrequency field in the trap from 65 V to 40 V. Also, the voltages on the entrance and exit electrodes of the trap were decreased. Ions are moving in the axial direction under the action of the voltage between these electrodes. The voltage on an entrance electrode was decreased from 3.0 V to 1.4 V. The voltage on an exit electrode was decreased from 5.8 V to 1.5 V. The trap potential was 1.1 V. The previous conditions were used to study heavier OH^- ions. The temperature T_{trap} was measured by a silicon diode positioned on the copper box containing the 22-pole trap and also obtained from the Doppler broadening of the measured absorption lines (T_{kin}). Previous studies have indicated that $T_{\text{kin}} = T_{\text{trap}} + (5 \pm 5)$ K [Plašil *et al.*, 2023]. An example of the measured absorption line of ortho H_3^+ after changing the amplitude of the

radiofrequency field and decreasing the voltage on an entrance and exit electrodes is presented in Figure 3. As can be seen from Figure 3., the difference between the kinetic and detected temperatures is smaller. Then, we decided to use the mechanical shutter in our optical system in order to send into the apparatus the laser light only in time, when ions have already been cooled by collisions with buffer gas. The shutter was opened 23 ms after injection of ions to the 22-pole trap. The absorption line of ortho H_3^+ that was measured after all changes is presented in the Figure 4. In that case the kinetic temperature is closer to the trap temperature, but still a little higher than the trap temperature.

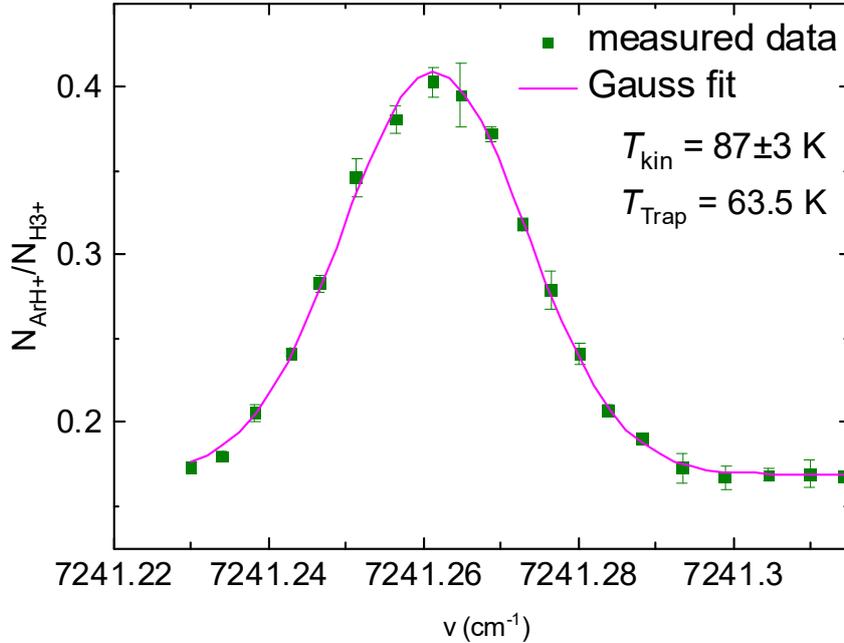


Figure 3. An example of the measured absorption line of ortho H_3^+ ions. The kinetic temperature of the H_3^+ ions $T_{\text{kin}} = 87 \pm 3$ K was obtained from the Doppler broadening of the absorption line. The trap temperature $T_{\text{trap}} = 63.5$ K was measured by a silicon diode positioned on the 22 pole trap. The number densities of reactants are $[\text{H}_2] = 1.34 \times 10^9 \text{ cm}^{-3}$, $[\text{Ar}] = 2.15 \times 10^{11} \text{ cm}^{-3}$, $[\text{He}] = 6.52 \times 10^{12} \text{ cm}^{-3}$. The amplitude of the RF voltage in the trap was 40 V.

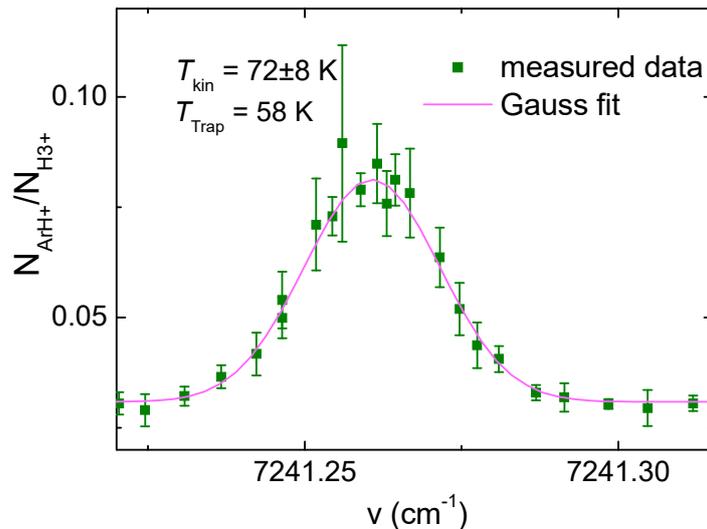


Figure 4. An example of the absorption line of ortho H_3^+ ions. The kinetic temperature of the H_3^+ ions was obtained from the Doppler broadening of the absorption line. The trap temperature was detected by silicon diodes within the 22 pole trap. The number densities of reactants are $[\text{H}_2] = 1.13 \times 10^9 \text{ cm}^{-3}$, $[\text{Ar}] = 2.25 \times 10^{11} \text{ cm}^{-3}$, $[\text{He}] = 1.38 \times 10^{13} \text{ cm}^{-3}$. The amplitude of the RF voltage in the trap is 40 V. The shutter was used in order to do time resolved measurement.

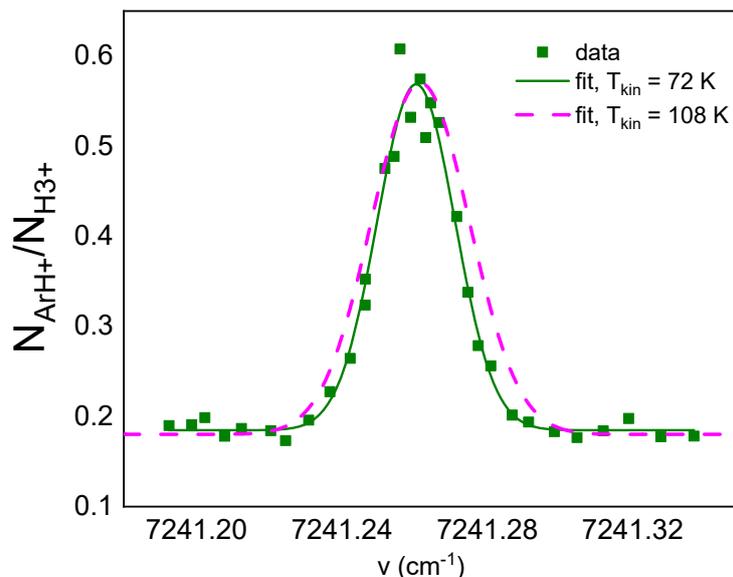


Figure 5. The comparison of two absorption lines originating in the lowest H_3^+ state with ortho symmetry obtained at different conditions. The absorption line measured at $T_{\text{kin}} = 108$ K (the same as in Figure 2) is marked in dashed purple. The absorption line obtained at $T_{\text{kin}} = 72$ K (the same as in Figure 4) in green.

We are aware that due to low number of ions in trap, the actual relative population of the upper states of used transitions could be non-negligible leading to deviation from Doppler profile. We will address it in our future publication.

Measurement with the shutter is presented in Figure 4. The storage time was 922 ms. The shutter was opened for 880 ms. Prior to this measurement we had done a few tests to determine the delay between the opening/closing of the shutter and the control TTL signal. Both delays were below 20 ms, so it is sufficient for time resolved measurements on the time scale of hundreds of ms or more.

The comparison of absorption lines measured at different conditions is shown in Figure 5. Depending on the decrease in temperature, the width of the absorption line decreases.

Conclusion

We have prepared the optical system for the measurement of the nuclear spin state specific reaction rate coefficients for the reaction of H_3^+ with H_2 using the LIR technique in the 22-pole RF ion trap. We are able to perform the time resolved absorption spectroscopy with just a few thousand ions in the trap. We have measured the kinetic temperature of H_3^+ ions in the trap and minimized sources of excessive heating of the ions. Further experiments focused on the actual determination of nuclear spin state change reaction rate coefficients for the $\text{H}_3^+ + \text{H}_2$ system are ongoing.

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