

Action spectroscopy of H_3^+ and D_2H^+ using overtone excitation

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The H_3^+ ion and its deuterated isotopologues H_2D^+ , D_2H^+ and D_3^+ play an important role in astrophysical and laboratory plasmas. The main challenge for understanding these ions and their interaction at low temperatures are state-specific experiments. This requires manipulation and a simple but efficient *in situ* characterization of their low-lying rotational states. In this contribution we report measurements of near infrared (NIR) absorption spectra. Required high sensitivity is achieved by combining liquid nitrogen cooled plasma with the technique of NIR cavity ringdown absorption spectroscopy. The measured transition frequencies are then used for exciting cold ions stored in a low-temperature 22-pole radiofrequency ion trap. Absorption of a photon by the stored ion is detected by using the laser-induced reactions technique. As a monitor reaction, the endothermic proton (or deuteron) transfer to Ar is used in our studies. Since the formed ArH^+ (or ArD^+) ions are detected with near unit efficiency, the stored ions can be characterized very efficiently, even if there are just a few of them.

Keywords: spectroscopy; H_3^+ ; D_2H^+ ; cavity ringdown spectroscopy;
hydrogen plasma; action spectroscopy

1. Introduction

Triatomic hydrogen and deuterium containing ions H_3^+ , H_2D^+ , D_2H^+ and D_3^+ have been the subject of a number of studies over the years. The main reason is the fundamental interest in these ions owing to their simplicity. Another important reason is also their great astrophysical significance. It has long been expected that, particularly in cold interstellar regions, deuterated H_3^+ will be present (Geballe 2000; Millar *et al.* 2000; Roberts *et al.* 2003, 2004). Recently, millimetre and sub-millimetre spectroscopy of the dense interstellar medium has shown that, in cold dense regions, deuterated molecular species are highly abundant, in some cases reaching more than 10% of their non-deuterated analogues. Doubly and triply deuterated species were also observed (Roueff 2000; Vastel *et al.* 2003, 2004; Roueff *et al.* 2005). This seems very surprising if we

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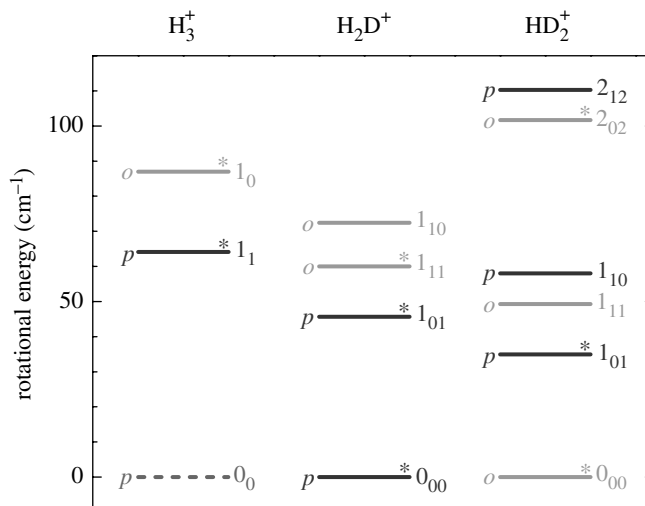


Figure 1. Lowest rotational energy levels of studied ions (Ramanlal *et al.* 2003; Ramanlal & Tennyson 2004; J. Tennyson 2005, personal communication). The letters *p* and *o* indicate para and ortho states, respectively. The stars indicate the states observed by CRDS in the microwave discharge cell.

realize that the general cosmic abundance of D is approximately 10^{-5} that of H. These recent astronomical observations, together with new experiments (Hirao & Amano 2003; Amano & Hirao 2005) and the recent theory of recombination, stimulated intensive studies of reactions of H_3^+ , H_2D^+ , D_2H^+ and D_3^+ ions with neutrals and electrons.

Owing to the large separation between the rotational energy levels (see figure 1) of these ions, particular interest is on the state-specific low-energy interactions relevant to the interstellar conditions.

Having in mind the available experimental techniques such as beams (Kreckel *et al.* 2005*b*), traps (Gerlich *et al.* 2002) and plasma experiments (Fárník *et al.* 2002; Plašil *et al.* 2002; Macko *et al.* 2004*a*), it is clear that an *in situ* characterization and/or manipulation of low-lying rotational states is imperative. We decided to use the near infrared (NIR) laser absorption spectroscopy for the *in situ* characterization of these ions. The decision was based on the availability of the highly accurate calculations of the transitions for these ions (Ramanlal *et al.* 2003; Ramanlal & Tennyson 2004; J. Tennyson 2005, personal communication). Nevertheless, for a real high-resolution study of these ions (e.g. in an ion trap), it is necessary to measure the actual transition frequencies in a well-defined and very sensitive experiment. The recently developed NIR cavity ringdown absorption spectroscopy (NIR-CRDS) is a very convenient method for such type of measurements. Using NIR-CRDS, we obtain several second overtone transition frequencies from lowest rotation states of H_3^+ , H_2D^+ and D_2H^+ (see figure 1). Having this information we were able to study these ions in a 22-pole ion trap by the laser-induced reaction (LIR) technique. The LIR technique allows characterization of studied ions even if there are just a few of them stored in the trap.

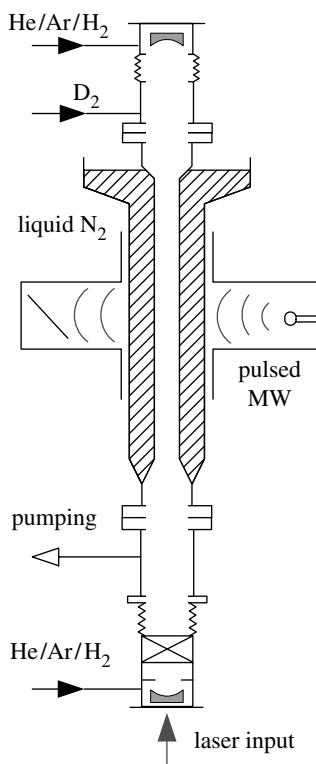


Figure 2. Microwave discharge cell. The optical cavity of the CRDS with the microwave cavity and the liquid nitrogen cooled discharge tube.

2. Experiments

The experiments were carried out in three laboratories. The absorption spectra were first measured in a plasma experiment—in a ‘microwave discharge cell’ (Macko *et al.* 2004a) equipped with a CRDS (Charles University in Prague). Actual LIR studies were carried out using two low-temperature radiofrequency (RF) ion traps (MPIK Heidelberg and TU Chemnitz).

(a) Near infrared cavity ringdown absorption spectroscopy studies using microwave discharge cell

In the present experiment, ions were produced in a pulsed microwave discharge in a He–Ar mixture with small admixture of H_2 and D_2 . The discharge was ignited by a 4 ms long microwave pulse in a liquid nitrogen cooled discharge cell. The discharge tube was made from silicate glass (inner diameter = 2.3 cm). The total pressure in the discharge was 6–8 mbar. The wave guide cavity is optimized for coupling energy to plasma. Figure 2 shows a schematic diagram of the microwave discharge cell. Positions of the mirrors of the optical cavity are also indicated. The gas handling system and the discharge cell are based on ultrahigh-vacuum technology in order to avoid reactive decay of plasma owing to reactions with ‘impurity molecules’. A large flow of ultra pure He was used to dilute possible

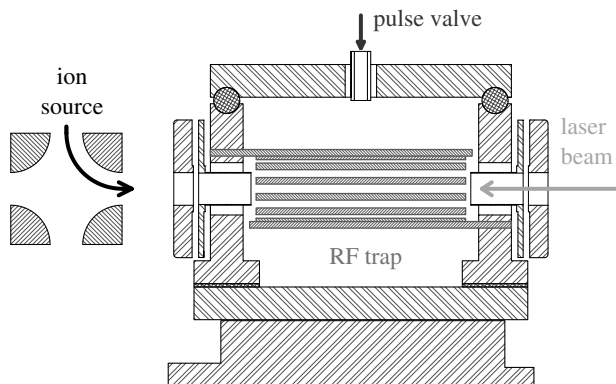


Figure 3. The 22-pole RF ion trap with the ‘off axis’ ion source and the pulsed monitor gas inlet. The version used at TU Chemnitz for D_2H^+ studies.

impurities owing to outgassing from the walls during the discharge. The kinetics of the formation of the studied ions is well established (Poterya *et al.* 2002; Glosík *et al.* 2003, 2005) and will be described only briefly here. The He^+ ions created during the microwave discharge are at high He pressure and low temperature (approx. 7 mbar and $T_{He} = 100$ K) rapidly converted to He_2^+ . These molecular ions together with metastable atoms (He^m) are rapidly converted in collisions with Ar to Ar^+ . In successive reactions with hydrogen or deuterium, H_3^+ , H_2D^+ , D_2H^+ and D_3^+ ions are formed. These ions relax in further collisions with neutral atoms and molecules to states corresponding to the buffer gas temperature (T_{He}). Actually, the kinetic temperature of the ions is slightly higher during the discharge but comes immediately down when the microwaves are switched off (Macko *et al.* 2004b). Discharge conditions and timing are adjusted to optimize the population of the studied ions and hence maximize the signal from CRDS. The physical principles of the continuous wave cavity ringdown spectroscopy have been described in numerous publications (Romanini *et al.* 1997; Morville *et al.* 2004). The actual set-up used in the present experiments is based on fibred distributed feedback laser diode.

Because the ions are generated by a pulsed discharge, a synchronous detection was applied to increase the sensitivity of detection (Hlavenka *et al.* 2006b). Absolute values of wavelengths were measured by a wavemeter based on a Michelson interferometer combined with a Fabry–Pérot etalon. In order to obtain the line positions with high accuracy, an *in situ* calibration of the wavemeter has been accomplished using absorption by traces of H_2O and DHO in He buffer gas. In some experiments, a reference absorption cell was used to calibrate the wavenumber scale.

(b) 22-pole radiofrequency trap

Two standard 22-pole RF low-temperature ion traps were used for the study of ion relaxation and LIRs. The main task was to characterize the kinetic and the internal energy of the stored ions. The ion trap at MPIK Heidelberg was originally built as the ion source for TSR (Test Storage Ring; Mikosch *et al.* 2004; Kreckel *et al.* 2005a). The ion trap in TU Chemnitz was recently built for studies

of ion–molecule reactions and collisional relaxation of low-temperature ions (down to 4 K). The configuration of the second ion trap is depicted in figure 3. The main body of the ion trap is made from copper and it is placed on the top of a cold head. The He buffer gas is precooled by flowing through the copper block of the ion trap base. The reactant gas can flow into the trap with the buffer gas or it can be injected to the trap as a pulsed beam from the side (see figure 3). The number densities of the gases in the trap are measured by a calibrated ionization gauge. The number densities of reactant gases can also be estimated by measuring the rates of known ion molecule reactions. Ions are produced by electron impact in a separated storage ion source and mass selected prior to injection to the trap.

In the ion trap, up to 10^6 particles can be stored, but in the conditions required for low-temperature LIRs experiments just a few hundred ions can be effectively stored and used. The main limitations are given by pressure limits (in the ion source and the trap) and amplitudes of RF and DC field. In the pulsed regime, where ions have to be detected in a short time, the limit is also given by time constants of the detector system. Owing to the low number of ions, data over thousands of cycles have to be accumulated to obtain good signal-to-noise ratio. This is very time consuming and requires a good stability of the system. The laser system and frequency measurement are identical with the one described earlier. In addition, an absorption cell with NH_3 was used for calibration.

3. Results and discussion

(a) D_2H^+

The high-resolution second overtone absorption spectra (vibrational transition, $\nu_1 + 2\nu_3 \leftarrow 0$) of D_2H^+ containing three low-lying energy levels were measured with the CRDS in the microwave discharge cell in the pulsed He–Ar– H_2 – D_2 discharge. Description of the technical details, experimental conditions and some additional results are given in a separate publication (Hlavenka *et al.* 2006*a*). All measured absorption frequencies were in a very good agreement ($\pm 0.015 \text{ cm}^{-1}$) with calculated values (Ramanlal *et al.* 2003; Ramanlal & Tennyson 2004; J. Tennyson 2005, personal communication). The prediction of the transition frequencies was better for D_2H^+ (Hlavenka *et al.* 2006*a*) than for H_2D^+ (Hlavenka *et al.* 2006*b*; S. Schlemmer 2006, private communication) and H_3^+ ions (Mikosch *et al.* 2004). With the knowledge of the accurate values of transition frequencies we started the experiments with the RF ion trap.

To characterize the ions stored in the ion trap, with just a few hundreds of them in one filling cycle of the trap, we used the resonant absorption of NIR photons by the stored ions—LIR method (Schlemmer *et al.* 2002; Mikosch *et al.* 2004; Kreckel *et al.* 2005*a*). The principle of LIR is very simple. In the presence of a suitable reactant, the internal energy of an excited ion (by the absorption of the NIR photon, approx. 0.9 eV) is opening an otherwise endothermic reaction channel and a formed product ion is detected by a mass spectrometer. In this way, even absorption of one single photon can be detected. The absorption probability and hence the signal is proportional to the laser beam intensity. The probability of the product ion formation is, in addition, proportional to the reactant number density (Ar in the present experiment) and to the lifetime of

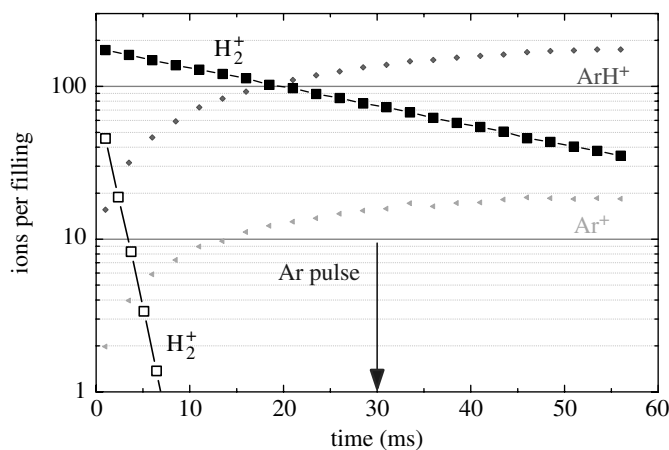


Figure 4. The test of the pulsed Ar beam at 14 K. The slow decay ($\tau=35$ ms) of H_2^+ (closed symbols) and the corresponding slow formation of the product ions are measured with low constant concentration of Ar (less than $5 \times 10^{10} \text{ cm}^{-3}$). The fast decay ($\tau=1.5$ ms) of H_2^+ (open squares) is observed when the pulsed Ar beam is used. Indicated is the position (time delay) of the Ar pulse.

the excited ions (which in general is not known). The Ar number density has to be high enough to monitor the excited ions and as low as possible in order to minimize condensation on the electrodes of the trap. Owing to the problems with the condensation of Ar at low temperatures (approx. 10 K in experiment with D_2H^+), we decided to use a pulsed Ar beam. The pulse valve was opened 30 ms after the injection of the ions and the pulse duration was 0.3 ms. The ions were detected (the trap was opened) 60 ms after the injection of the ions. From previous measurements with the pulsed valves in the present geometrical configuration, we know that during the pulse, the Ar number density is over two orders of magnitude higher than 30 ms after the pulse.

The system was tested by a fast reaction of H_2^+ with Ar. We measured that 30 ms after the Ar pulse (i.e. at the end of the cycle and at the start of the following cycle) the reaction time is less than 1.5 ms. From this, it follows that the reaction time during the Ar pulse is of the order of 10–100 μs . We assume that the lifetime of the excited ions is longer or comparable with this measured reaction time. The timing, the decay of primary ions (H_2^+) and the formation of the product ions (ArH^+ and Ar^+) are shown in figure 4. The test is very important because a reliable calculation of the ‘proper’ Ar number density in the 22-pole at approximately 14 K will be very difficult.

After the adjustment of the duration and intensity of the Ar beam, the LIRs of D_2H^+ ions were studied. The ion composition was measured 60 ms after the injection. We observed ArH^+ and ArD^+ ions formed in reactions of D_2H^+ ions with Ar in the first few collisions after the ion injection, prior to the relaxation in collisions with He. The formation of these ions cannot be avoided in the present experiment. The observed production of ArH^+ was by a factor of two higher than the production of ArD^+ . This can indicate very strong isotope effect in the reaction of excited D_2H^+ with Ar. When the trap is irradiated by IR laser, the additional D_2H^+ ions are excited and in reaction with Ar new ArH^+ and ArD^+ ions are formed. With a few milliwatt laser diode, this process is very slow. To obtain

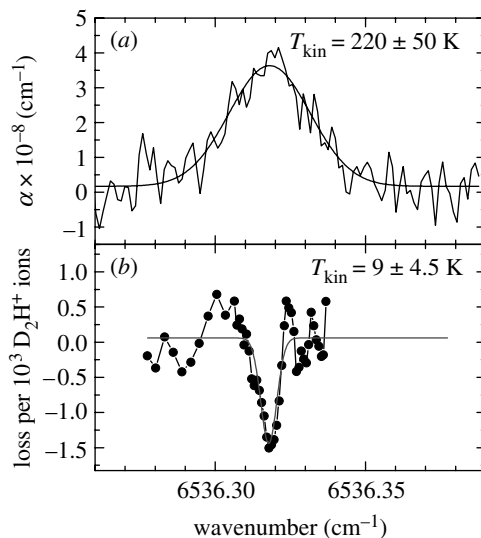


Figure 5. Absorption spectra of the ground state HD_2^+ ions corresponding to $(v_1 + 2v_3 \leftarrow 0) 0_{00} \leftarrow 1_{11}$ transition. (a) CRDS measurements in the plasma at 100 K, the measured kinetic temperature of the ions $T_{\text{kin}} = 220$ K. The measured transition frequency is $6536.319(2) \text{ cm}^{-1}$. (b) LIR measurements at 10 K. The measured transition frequency is $6536.317(8) \text{ cm}^{-1}$, $T_{\text{kin}} = (9 \pm 4.5) \text{ K}$. In this experiment removal of HD_2^+ ions is monitored.

variation of D_2H^+ signal owing to LIR, the laser wavelength was modulated and the synchronous detection was used to increase sensitivity. By scanning the frequency of the laser, the absorption spectra corresponding to the ground state ions were obtained (see figure 5). From the Doppler broadening of the absorption line, the kinetic temperature of the absorbing ions was obtained. Note that the kinetic energy of the absorbing ions, not the temperature of the monitoring gas (Ar), determines the line broadening. The temperature of the trap was measured by a silicon diode placed on the copper block, but the reading can be slightly higher than the actual temperature of the He buffer, partly owing to distortions by the trap RF field. Having transition frequencies, we have made several attempts to measure absorption by the lowest *para* state (see figure 1), but we were not successful; this can indicate a low population of ions in this state in the trap.

(b) H_3^+

In a continuous microwave discharge, pulsed microwave discharge and during an afterglow the second overtone NIR absorption spectra of $H_3^+(v=0)$ were measured using the CRDS (Macko *et al.* 2004*a,b*; Plašil *et al.* 2005; Hlavenka *et al.* 2006*b*). The measurements were carried out at several pressures and at several temperatures of the buffer gas. Altogether, we measured 10 transitions, mostly corresponding to the absorption by the ions in the lowest rotational states. The measured transition frequencies were in good agreement with the theoretical predictions by Neale *et al.* (1996) and earlier experiments (Ventrudo *et al.* 1994). These CRDS measurements were part of our studies of recombination of $H_3^+(v=0)$ ions with electrons (Glosik *et al.* 2005). Very precise values of the transition frequencies corresponding to the absorptions of ions in

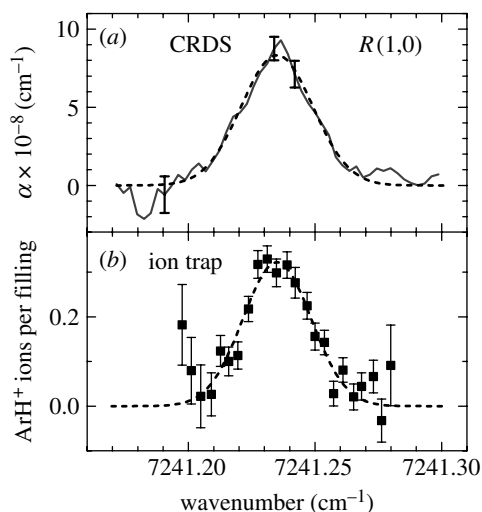


Figure 6. The absorption spectra of the ground state H_3^+ , corresponding to $(3v_2 \leftarrow 0)$ R(1,0) transition. The measured transition frequency is $7241.235(17) \text{ cm}^{-1}$. (a) CRDS measurements in the plasma at 130 K. (b) LIR measurements at approximately 120 K. In this experiment production of ArH^+ ions is monitored.

three lowest rotational states were used in LIR measurements of excited H_3^+ with Ar (Mikosch *et al.* 2004; Kreckel *et al.* 2005a). The ion trap, which was optimized as an ion source for TSR, had the gas inlets passing through the copper base of the trap; therefore, the measurements were possible only for temperatures in which Ar was not frozen completely. Actually, the temperature was stabilized at 55 ± 5 K. Again the laser was modulated and synchronous detection was applied. In this experiment, the ArH^+ product ions were monitored. Examples of the absorption line obtained in both CRDS and LIR experiments are shown in figure 6.

The results and conclusions from this study were used in the characterization of the H_3^+ ions injected to the TSR for recombination studies (Kreckel *et al.* 2005b).

4. Conclusion

The second overtone absorption spectra of hydrogen and deuterium containing ions H_3^+ , H_2D^+ and D_2H^+ were measured (see compilation in figure 1) using NIR-CRDS of the plasma in the microwave discharge and during the afterglow. The obtained transition frequencies were then used for LIR studies of H_3^+ , H_2D^+ (in progress) and D_2H^+ in an RF ion trap with Ar (pulsed and diffused) as a monitor gas. The kinetic temperature of the trapped ions was obtained from the Doppler broadening of the measured absorption lines. When using the beam of Ar, we were able to characterize the trapped ions at temperatures down to 9 K.

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Discussion

The four following questions are connected with experimental studies of recombination of H_3^+ with electrons in afterglow plasma. The new results of these studies indicating the dependence of the effective recombination rate on He pressure were mentioned in the introductory part of the lecture.

C. H. GREENE (*University of Colorado, Boulder, USA*). Do your newest afterglow experiments determine an approximate value for the gas phase two-body dissociative recombination rate for $e^- - \text{H}_3^+$?

D. ZAJFMAN (*Weizmann Institute of Science, Israel; Max-Planck Institute, Heidelberg, Germany*). Can you measure the dissociative recombination in your apparatus as a function of He gas density?

E. HERBST (*Ohio State University, Columbus, USA*). Can you extrapolate the effective two-body rate for $H_3^+ + e^-$ to determine real two-body coefficient?

B. J. MCCALL (*University of Illinois at Urbana-Champaign, USA*). Do you view your dissociative recombination measurements as being in conflict with the storage ring measurements?

J. GLOSIK. We are studying recombination of H_3^+ with electrons in afterglow plasma at 100–300 K. Three different experiments were used in these studies—stationary afterglow (AISA; Glosík *et al.* 2000, 2001; Plašil *et al.* 2002; Poterya *et al.* 2002), flowing afterglow (FALP; Glosík *et al.* 2003, 2005) and microwave discharge cell with near infrared cavity ringdown absorption spectroscopy (NIR-CRDS; Macko *et al.* 2004a; Plašil *et al.* 2005). The pressure in these plasmas is 100–1500 Pa. In such conditions, ion collides with He every few ns. Electron collides with He several times in a ns. At hydrogen partial density approximately 10^{12} cm^{-3} , ion collides with H_2 every approximately 1 ms. At electron and ion densities $n_e \sim n_i \sim 10^9 \text{ cm}^{-3}$ ion collides with electron typically within 10 ms. Because of all these collisions, ions and electrons will be thermalized prior to their mutual collision.

If in a process of recombination a long-lived highly excited intermediate $H_3^{*'}$ is formed it can in principle happen that H_3^* will collide with He or H_2 before it will ionize or unimolecularly irreversibly dissociate (in the sense of dissociative recombination). In this collision, H_3^* can be ionized, quenched, dissociate or collision will be elastic. The rate of overall electron density decay will depend on the lifetime of H_3^* and on frequency of collisions with He and/or H_2 . If H_3^* is highly excited Rydberg state then the rate coefficient for interactions with neutral He or H_2 can be approximately $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ or even more for large principal quantum number. At a pressure of approximately 1000 Pa, this gives less than or equal to 3 ns between collisions. This 3 ns is comparable with lifetimes of highly excited Rydberg H_3^* molecules. In our very recent FALP experiment, we observed dependence of the overall recombination process on H_2 pressure and in addition to AISA experiments we observed also dependence on He pressure. These results are prepared for publication. These observations are not in conflict with recent storage ring results because if the lifetime of H_3^* is less than or equal to 3 ns it will dissociate within the recombination region; so mass 3 will not be observed between products. We expect that from the observed pressure dependencies we will be able to obtain (as a limit) real two-body coefficient. Further experiments to support our concept are in progress.

J. M. BOWMAN (*Emory University, Atlanta, GA, USA*). Can you determine information on the mode-specific reaction cross-sections from specific vibrational states of H_3^+ ? Also, do you have any information on mode-specific vibrational relaxation?

J. GLOSIK. The time-scales of our experiments are 500 and 60 ms for H_3^+ and D_2H^+ , respectively. Highly vibrationally excited ions react with Ar immediately after injection. The ions with low vibrational excitation are probably quenched in collisions with He or radiate. We expect the ions are vibrationally relaxed within a few ms (rovibrational relaxation was studied theoretically and experimentally by Kreckel *et al.* (2004)). At the low temperatures used, the ions can be excited

only rotationally and we can monitor the population of these states. The aim of the presented experiments is *in situ* characterization of ions in the trap, so state-specific reactions can be studied, but it means reactions of rotationally excited ions.

H. HELM (*Physikalisches Institut der Universität Freiburg, Freiburg, Germany*). Is there an explanation for the strong isotope effect in ArD^+ and ArH^+ ?

J. GLOSIK. In LIR study of D_2H^+ ions with Ar as a monitor gas, we observed ArH^+ (62%) and ArD^+ (38%) ions. The majority of these ions was produced immediately after the injection of D_2H^+ ions from the source, prior to cooling of these ions in collisions with He buffer. We cannot comment on internal excitation of injected ions and also we do not have an explanation for the strong isotope effect. In the experiments, we were measuring the decrease of D_2H^+ ion number density due to the laser excitation and consequent reaction with Ar (see [figure 5](#)). The synchronous detection was applied to obtain the corresponding signal.