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Near infrared second overtone cw-cavity ringdown spectroscopy of D_2H^+ ions

P. Hlavenka[a], R. Plašil[a], G. Bánó[b], I. Korolov[a], D. Gerlich[c], J. Ramanlal[d], J. Tennyson[d], J. Glosík[a,*]

[a] *Charles University in Prague, Faculty of Mathematics and Physics, V Holešovičkách 2, 180 00, Prague, Czech Republic*
[b] *Research Institute for Solid State Physics and Optics, HAS, Budapest, Hungary*
[c] *Institut für Physik, Technische Universität, 09107 Chemnitz, Germany*
[d] *Department of Physics and Astronomy, University College London, London WC1E 6BT,UK*

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Abstract

A study of D_2H^+ ions in their lowest rotational states is presented. The ions are generated in pulsed discharge in liquid N_2 cooled He/Ar/H_2/D_2 gas mixture. Near infrared (NIR) second overtone transitions in the 6534–6536 cm^{-1} (1.529–1.530 μm) region are used to identify the ions and determine their degree of rotational excitation. The data were obtained using NIR cavity ringdown absorption spectroscopy (NIR-CRDS). The sensitivity obtained was typically 5×10^{-9} cm^{-1}. The measured second overtone transition frequencies are in very good agreement (better than 0.02 cm^{-1}) with ab initio predictions. From the Doppler broadening the kinetic temperature of ions is estimated to be (220 ± 50) K. The absolute number density of D_2H^+ as a function of H_2/D_2 mixing ratio and time is measured.

Keywords: D_2H^+; Cavity ringdown spectroscopy; Second overtone; Hydrogen plasma; Deuterium plasma

1. Introduction

Since hydrogen is by far the most abundant element in the universe, with molecular hydrogen dominating in the cold regions, the formation and destruction of $H_3{}^+$ ions is of great astrophysical significance. The discovery of $H_3{}^+$ in diffuse interstellar molecular clouds [1,2] has confirmed the long expected presence of $H_3{}^+$ in space and has reopened interest in the problem of the interaction of this simplest polyatomic molecular ion with electrons and with molecules. The ions $H_3{}^+$ and its deuterated isotopologues (H_2D^+, D_2H^+ and $D_3{}^+$) play important roles in the kinetics of media of astrophysical interest [3,4], planetary atmospheres [4] and also in laboratory produced plasmas. The physics of $H_3{}^+$ gets more complicated when deuteration processes [4–6], which are driven by exothermicity of H/D exchange reactions, have to be considered in plasma environment. It has long been anticipated that enhanced isotopic fractionation effects should occur in cold interstellar regions driven by the fact that deuteration is energetically "down hill [7].

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 nondeuterated analogues. This is a very high number if we consider that the general cosmic abundance of D is about 10^{-5} that of H. Surprisingly, doubly and triply deuterated species can be observed [8–11]. These observations stimulated an intensive search for H_2D^+ and D_2H^+ ions [10]. The key work in the astronomical search for D_2H^+ is the laboratory measurement of the para ground-state transition by Hirao and Amano [12,13] and theoretical calculations by Ramanlal and Tennyson [14,15]. The search led to the detection of H_2D^+ and D_2H^+ in cold dense interstellar clouds [8,10]. These observations have heightened interest in further laboratory and theoretical studies of partially deuterated molecular ions.

The kinetics of the formation of $H_3{}^+$, H_2D^+, D_2H^+ and $D_3{}^+$ ions in H_2/D_2 containing plasmas is well understood – at least at room temperature. Relevant rate coefficients and products of ion molecule reactions were successfully studied using swarm (SIFT

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[*] Corresponding author. Tel.: +420 221 912 329; fax: +420 284 685 095.
E-mail address: juraj.glosik@mff.cuni.cz (J. Glosík).

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[16,17]), beam and RF ion trap experiments [18]. The kinetics gets particularly complicated at low temperatures, where ortho and para states and nuclear spin restrictions have to be considered [18–23]. The main challenge for future experiments is a state-to-state description of the underlying ion–molecule reactions. Equally important is to understand the recombination processes; again internal excitation of the ions has to be explicitly considered and hence determined [24]. Differences in rates and products branching ratios of dissociative recombination of H_3^+, H_2D^+, D_2H^+ and D_3^+ ions may also be partly responsible for the enhanced population of deuterium [5,25].

However, despite enormous efforts, the results of experimental studies aimed at determining the rate of recombination of H_3^+ and D_3^+ ions with electrons have been found to yield values that vary by at least one order of magnitude from 1×10^{-8} to 3×10^{-7} cm^3 s^{-1} for H_3^+ [26–30] and 2×10^{-8} to 2×10^{-7} cm^3 s^{-1} for D_3^+ [24,31–35]. Poor characterisation of internal excitation of recombining ions in these experiments may well be at least partly responsible for these discrepancies. Very recent experiments with rotationally cold ions indicate that rotational excitation of H_3^+ can have a significant influence on the recombination rate coefficient of these ions [36–41]. These recent measurements largely agree with the recent and successful theoretical studies of dissociative recombination of H_3^+ and D_3^+ made by Kokoouline and Greene [24,42,43]. Despite the good agreement that has recently emerged between theory and the storage ring experiments, the case of recombination of H_3^+, H_2D^+, D_2H^+ and D_3^+ ions with electrons is far from closed.

The motivation of the present study of D_2H^+ using overtone spectroscopy in low temperature plasma is the search for a tool for simple in situ characterisation of the internal state of the reacting/recombining D_2H^+ ions. Results of the present experiments will be used in parallel studies of laser induced ion–molecule reactions (LIR) carried out in a low temperature RF trap. For such studies very accurate transition frequencies are required [44–48]. Our approach can be simply stated. We use high sensitivity and high resolution Near Infrared Cavity Ringdown Absorption Spectroscopy (NIR-CRDS) to obtain the second overtone absorption spectra of D_2H^+ ions in their lowest rotational states. These spectra are then used to monitor the concentration and rotational population of the ions.

2. Experimental

2.1. Test tube

To study recombination of different internal states of H_3^+-like ions we have recently built a test tube apparatus. In the present experiment D_2H^+ ions were produced in pulsed microwave discharge in He/Ar/H_2/D_2 mixture. The discharge was ignited by 4 ms long pulses of microwave (60–120 W) in a waveguide with repetition period 10 ms inside a silicate glass tube with internal diameter of 2.3 cm. After adjustment, the plasma column has effective length ~5 cm. Fig. 1 shows a schematic diagram of the apparatus and indicates position of mirrors of the optical cavity, which is described in detail in next section. The discharge tube actually has double walls and the space between the tubes is filled by liquid nitrogen to cool the buffer gas and plasma.

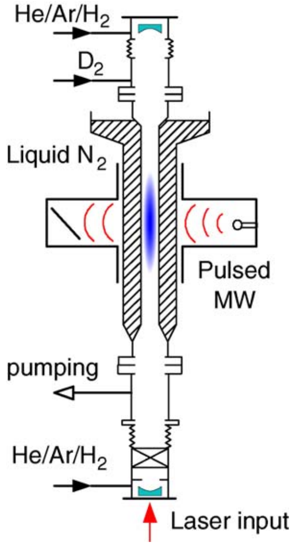

Fig. 1. Schematic diagram of the test tube. The pulsed microwave discharge takes place in a liquid nitrogen cooled tube. For CRDS two highly reflective mirrors are mounted on tilt stages inside the vacuum.

Since already impurities of a few ppm lead to a loss of the D_2H^+ ions within a millisecond, the apparatus is based on UHV technology and all reactant gases pass through liquid nitrogen traps. He ions and metastable atoms created during the microwave discharge are rapidly converted to H_3^+ (and deuterated analogues) by a sequence of ion–molecule reactions involving Ar^+ and ArH^+ as intermediate ions. The production scheme is well known and has been previously verified by kinetic modelling and mass spectrometric observations in FALP (Flowing Afterglow Langmuir Probe) and SA (Stationary Afterglow) [35]. In addition in the presence of hydrogen and deuterium the formation of H_3^+, H_2D^+, D_2H^+ and D_3^+ takes place. At 6–8 mbar the total gas flow Φ_{tot} was around 800 sccm (standard cubic centimetre per minute) with the $\Phi_{He}/\Phi_{Ar}/\Phi_{H_2}/\Phi_{D_2}$ ratio equal to 800/1.3/1/(0.05–1).

The time constants for ion-molecule reactions are some tens (~20) of microseconds at the gas partial pressures used. The partial population of individual ions and the degree of deuteration depends on the temperature and on the partial pressures of hydrogen and deuterium. As the primary aim of this paper is the experimental determination of transition frequencies in the NIR region, we focused on achieving high concentration of D_2H^+ in the lowest rotational states rather than on kinetics studies of processes in plasma discharge. Once the transition frequencies are known, the D_2H^+ ions can be studied at even lower number densities.

2.2. CRDS – absorption spectroscopy

Transition frequencies and intensities for the H_3^+, H_2D^+, D_2H^+ and D_3^+ ions have been calculated with high precision [15,49] and some transitions were observed in the microwave (see e.g., [50]) and Mid-IR [22]. However, there is no exper-

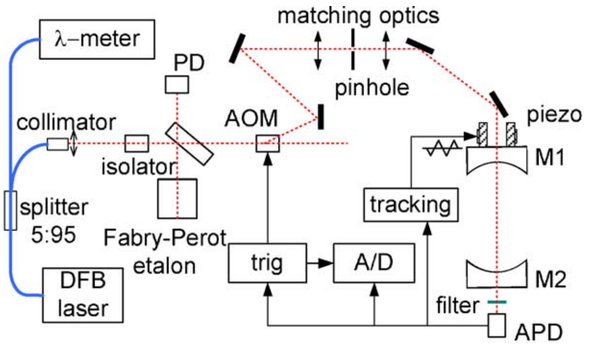

Fig. 2. Set-up of the cw-CRDS experiment: The laser beam from fibre-coupled telecom DFB laser diode is collimated to a free beam, passing though an optical isolator, acousto-optic modulator (AOM), that acts as a fast optical switch and matched by a spatial filter to mode TEM_{00} of optical cavity ($l = 0.75$ m) composed of two concave mirrors M1 and M2 ($r = 1$ m) with reflectivity 99.990%. The entrance mirror is mounted on a piezo transducer. The signal behind second mirror is detected by InGaAs avalanche photodiode (APD) and recorded by a computer. A cut-off filter suppresses the light emission of plasma. A wavemeter and a Fabry–Pérot etalon are used for wavelength calibration.

imental data on the second overtone region for the deuterated species.

The high sensitivity of continuous wave cavity ringdown spectroscopy (cw-CRDS) makes the technique suitable for investigating the spectra of ions and radicals in plasma [51]. The physical principles of cw-CRDS have been described in numerous publications (see, for instance [52,53] and references cited therein). The present NIR-CRDS set-up is a modification of the version used in our previous work on H_3^+ recombination studies [44,54,55] where a detailed description of our NIR-CRD spectrometer can be found. The actual set-up used in the present experiments (see Fig. 2) is based on a fibered DFB laser diode.

In CRDS experiments, the exponential decay of the intensity of the laser light coupled into a high finesse optical cavity is measured. The characteristic decay time depends on losses in the resonator and on absorption by the medium that is enclosed in the cavity. Each intensity decay (ringdown) is fitted by an exponential function. Without absorbing media a typical decay time τ_0 was ~31 μs. The value τ_0 is a property of the resonator and varies little with the frequency change. The actual absorption coefficient α of the absorbing medium can be directly calculated from the measured decay time τ (ringdown time)

$$\alpha = \left(\frac{1}{\tau_0} - \frac{1}{\tau}\right)\frac{d}{l \times c},$$

where c is the speed of light, d the length of cavity, and l is the length of the plasma. Theoretically, $1/\tau_0$ should appear as a smooth baseline of $1/\tau$, and it should be straightforward to obtain the required $(1/\tau_0 - 1/\tau)$. This subtraction can be complicated by disturbance of the baseline, such as an etaloning effect caused by a back-reflection (on any optical component) of the light leaking from the resonator. This can be suppressed by positioning all elements at a slight tilt from the axis. In our setup the liquid nitrogen cooling of the discharge tube affected the thermal, thus mechanical, stability of the rigid cavity construction and resulted in non-deterministic modulation of the baseline in time. This made the subtraction of baseline unreliable and a synchronous detection with a direct τ_0 measurement had to be developed.

2.3. Synchronous detection

An advanced time resolved CRDS data acquisition system has been developed for our previous studies of H_3^+ recombination [54]. For the data evaluation the time (delay from the synchronisation pulse) at which each ringdown started was recorded. Using this additional information and by applying an iterative algorithm we are able to monitor the fast decay of the ion number density caused by recombination. This technique proved able to monitor absorption variations with time constant below 50 μs. For a more detailed description see [54,56].

As the aim of the present experiment was to determine transition frequencies, we have used slower modulation of the microwave power to reduce the noise in the electronics circuits. Monitoring of the ion number density with CRDS remains as fast as in the previous experiments. Fig. 3 shows the time evolution of the H_3^+ and D_2H^+ ion number density during the active discharge and during the post discharge period. Approximately, ~3 ms after switching off the microwave the absorption signal drops to zero. For transition frequency measurements we selected two sets of ringdowns; those in the time range 1.5–4 ms are treated as signal and those in the range 7.5–10 ms, where the absorption can be neglected, give the baseline at a particular wavelength.

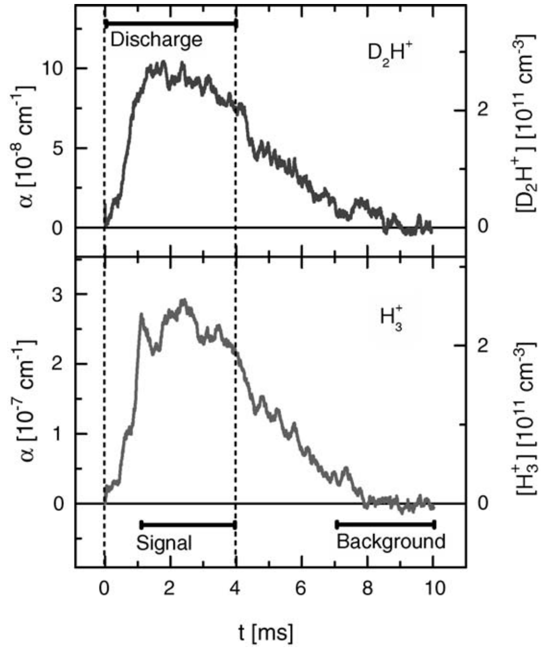

Fig. 3. Time evolution of number densities during the measurement period, measured on the centre of absorption peak. Upper panel: $D_2H^+(v = 0)$ number density according to the $2_{02} \leftarrow 3_{13}$ transition. The ratio $D_2/(D_2 + H_2)$ was 0.4. Lower panel: $H_3^+(v = 0)$ number density, measured on the centre of $v_2 = 3 \leftarrow 0$ (P_{22}) H_3^+ transition at 6877.546 cm^{-1}. Marked are the time intervals corresponding to "Signal" and to "Background" (baseline), used by synchronous detection for determination of τ and τ_0 respectively. The assumptions used in the density calculations are discussed in text.

To test the synchronous detection and to characterise the properties of the discharge a known [57] $\nu_2 = 3 \leftarrow 0$ (P_{22}) H_3^+ line was measured. From the measured absorption of ions in one single state one can derive the overall ion number density, if one assumes rotational equilibrium and hence a rotational temperature. At $T = T_{\mathrm{KinIon}} = T_{\mathrm{Rot}} = 180$ K, derived from Doppler broadening, the absorption coefficient in the line centre is, according to [58], $1.13 \times 10^{-18}\ \mathrm{cm}^{-1}$ per molecule cm^{-3}. Using this value gives an H_3^+ number density during the discharge of $[H_3^+] \sim 2.5 \times 10^{11}\ \mathrm{cm}^{-3}$. This value is in good agreement with our previous H_3^+ measurements in similar conditions [17,54].

2.4. Wavenumber retrieval

The DFB laser diode was scanned with constant laser current by a computer controlled temperature scan. A Fabry–Pérot etalon was used to linearise the wavenumber scale. During all D_2H^+ scans the absolute wavenumber position at each wavelength was obtained from a wavemeter based on a Michelson interferometer with a temperature stabilised He-Ne laser reference. The wavemeter was constructed recently in our laboratory as a modification of the design described in [59]. In order to obtain the line positions with high accuracy, an in situ calibration of the wavemeter has been accomplished. For this calibration we used CRD spectra of traces of HDO and H_2O at room temperature desorbed from the liquid nitrogen trap of the D_2 inlet. We compared them with the recently published data on NIR spectra of H_2O and HDO [60]. The calibration procedure was repeated several times during the experiment confirming the high stability and accuracy of the system. We estimate the accuracy of the wavenumber calibration to be better than $\pm 0.002\ \mathrm{cm}^{-1}$.

3. Results and discussion

3.1. Measurements of absorption spectra; transition frequencies of $D_2H^+(v=0)$ ions

The NIR second overtone absorption spectrum of $D_2H^+(v=0)$ was obtained by scanning over the region 6534 $-6537\ \mathrm{cm}^{-1}$ (corresponding to ~1.529–1.530 μm). Examples of measured absorption lines are plotted in Fig. 4. The transition frequencies obtained are listed in Table 1. Note that the measured transitions form a clear series. The in situ calibration enables us to measure frequencies with accuracy $\pm 0.002\ \mathrm{cm}^{-1}$.

The experiment was guided by the use of transition frequencies predicted using the ultra-high accuracy ab initio model of Polyansky and Tennyson (PT) [49], as applied by Ramanlal and Tennyson [15]. Assignments were made by analysing the calculated energy levels of D_2H^+. As can be seen from Table 1, there is excellent agreement between the measured and calculated transition frequencies. Indeed, this agreement is better than the still good agreement obtained in the $H_3^+(\nu_2 = 3 \leftarrow 0)$ studies, see studies in [54], the laser induced reaction study in [45] or the first overtone studies of H_2D^+ and D_2H^+ by Farnik et al. [22]. While this excellent agreement must in part be due to a fortuitous cancellation of errors, there are two reasons why the PT's model might be expected to work better for the transitions observed here than for the other overtone transitions cited. Firstly, the PT's model is particularly good at predicting the frequency of pure stretching transitions (see [49,61]) and the present overtone transitions involve one quantum of the ν_1 and two quanta of the ν_3 stretching mode, and secondly deuteration reduces the effects of the failure of the Born-Oppenheimer approximation which, although allowed for extensively in PT's model, is still probably the largest remaining cause of residual error in the calculations.

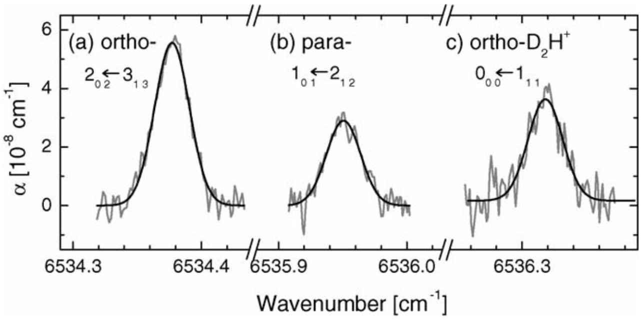

Fig. 4. Second overtone absorption spectra ($\nu_1 + 2\nu_3 \leftarrow 0$) of D_2H^+ measured by NIR-CRDS in modulated microwave discharge. Full lines indicate the best fits by Gaussian function. From the Doppler broadening of absorption lines the kinetic temperature $T_{\mathrm{KinIon}} = (220 \pm 50)$ K of ions in the microwave discharge was calculated. The rotational temperature $T_{\mathrm{Rot}} = (210 \pm 50)$ K was estimated by comparing the peak areas corresponding to 2_{02} and 0_{00} rotational ortho states.

3.2. Measurements of kinetic and rotational ion temperature

From the Doppler broadening of the measured absorption lines, the kinetic temperature of the $D_2H^+(v=0)$ ions in the microwave discharge was calculated to be $T_{\mathrm{KinIon}} = (220 \pm 50)$ K. These results are consistent with data obtained from the H_3^+ dominated discharge. The agreement is very good if we consider small differences between discharges in both mixtures He/Ar/H_2 and He/Ar/H_2/D_2. The observed ion

Table 1
Second overtone transitions ($\nu_1 + 2\nu_3 \leftarrow 0$) of D_2H^+ measured by NIR-CRDS

Ortho/para	$J'_{Ka'Kc'} \leftarrow J''_{Ka''Kc''}$	E'[K]	Wavenumber [cm^{-1}]		$\nu_{\mathrm{Exp}} - \nu_{\mathrm{Theor}}$	Intensity [cm^{-1}/cm^{-2}]
			ν_{Exp}	ν_{Theor}		
Ortho	$2_{02} \leftarrow 3_{13}$	146.3	6534.377(1)	6534.374	−0.003	1.89×10^{-9}
Para	$1_{01} \leftarrow 2_{12}$	50.2	6535.950(1)	6535.943	−0.007	9.68×10^{-10}
Ortho	$0_{00} \leftarrow 1_{11}$	0	6536.319(2)	6536.301	−0.018	1.09×10^{-9}

Experimentally obtained transition frequencies, ν_{Exp}, with error estimates, are compared to theoretically predicted frequencies, ν_{Theor} [15].

kinetic temperature is also in good agreement with our previous studies carried out at very similar conditions (using the test tube). In these experiments we have obtained an enhancement of the ion kinetic temperature during the microwave discharge by 70–100 K [54,56]. In these experiments, the microwaves were switched off by a fast switch and during the early afterglow the relaxation of T_{KinIon} from 370 to 300 K (buffer gas temperature) was observed within 50 μs.

The comparison of the intensities corresponding to the two ortho states, 0_{00} and 2_{02} of D_2H^+ ($v = 0$), gives a rotational temperature $T_{\mathrm{Rot}} = (210 \pm 50)$ K (under the assumption of thermal equilibrium). The intensity corresponding to para state 1_{01} is smaller by a factor two than would be expected from thermodynamic equilibrium with the two observed ortho states. There are two possible explanations for this: the two groups of ions – ortho and para states – are not in thermodynamic equilibrium; or the calculated values of absorption coefficient are not accurate enough. It should be noted that there were also some unexplained discrepancies between the measured and calculated intensities in the overtone study of Farnik et al. [22]. More detailed calculations [62] completely failed to find any problems with the ab initio procedure used in the calculations and hence the source of this discrepancy (which actually only affected a single transition). In general, we are confident that intensities calculated using the PT's model are reliable. Indeed, the discrepancy with Farnik et al. remains the only one we are aware of, however, it is difficult to be certain which of the two explanations given account for the weaker than predicted para transition intensity.

When discussing these observations it is important to realise that the plasma in the microwave discharge used in present experiment is close to steady state, but it is not in thermodynamic equilibrium. Usually such plasma can be described as an assembly of "electron gas", "ion gas" and "buffer gas" consisting of electrons, ions, and neutral atoms and molecules, respectively. Electrons are hot, so they can excite ions [63,64] or recombine with them. For the ions and buffer gas the situation is similar to drift tube experiments, where ions are under the influence of the electric field cumulating kinetic energy, but buffer gas atoms (He in our case) are cold. In our previous experiment with similar conditions in a microwave discharge, we verified that the buffer gas is at the wall temperature by measuring absorption of H_2O during a discharge and an afterglow [54–56]. The ions have kinetic energy E_{KinIon} and corresponding T_{KinIon}, this temperature is coupled to Doppler broadening. The energy of ion–He collision E_{ColIon} (and corresponding T_{ColIon}) is lower than E_{KinIon} because the He atoms are cold. This E_{ColIon} determines the internal (rotational in our case) excitation of the ions. This is only a qualitative picture but one which points at a difference between E_{KinIon} and E_{ColIon} (for further reading see papers on drift tube experiments where many aspects of this problem are discussed including the reasons for introducing T_{KinIon} and T_{ColIon} [65–68]). To understand the actual role of certain type of collisions on the measured data we have to estimate the collision frequencies under the conditions of our experiment. At the partial pressures used in this experiment the frequency of collisions of D_2H^+ ions can roughly be estimated as 2×10^8 s^{-1} and 5×10^5 s^{-1} for collisions with He and H_2 (or D_2), respectively. The lifetime of D_2H^+ ions in a discharge is given by recombination (diffusion can be neglected here) and this is (at electron density $n_e \sim 2 \times 10^{11}$ cm^{-3} and the recombination rate coefficient $\sim 10^{-7}$ cm^3 s^{-1}) equal to ∼50 μs. From these estimates it follows that D_2H^+ ions, before recombining, will have few collisions with H_2/D_2 and thousands with He. Few collisions with H_2/D_2 are enough to quench the vibrational excitation but are probably not sufficient to equilibrate ortho and para states. There are probably enough collisions with He to establish equilibrium within the distinct ortho and para groups at a temperature corresponding to collisional energy of collisions with He, E_{ColIon} (characterised by T_{ColIon}). Further studies dealing with relaxation, spin conservation and state-to-state reactions in hydrogen/deuterium plasma are required (see e.g., discussion in [18–23,40,44,46,47]); the present study is just a step toward understanding these processes.

3.3. Measurements of ion number densities

Once transition frequencies for $D_2H^+(v = 0)$ ions were established, we used the strongest transition at 6534.377 cm^{-1} to study the plasma. The measured variation of the absolute number density of $D_2H^+(v = 0)$ ions is plotted in Fig. 3. The calculation of absolute number density was made under the assumption of thermal equilibrium $T = T_{\mathrm{KinIon}} = T_{\mathrm{RotIon}} = 220$ K. The microwaves were modulated, but nevertheless there was a time interval (∼1.5–4 ms), where microwave power was constant and the ion number density was nearly constant. This number density is the one we consider as the ion number density in the discharge.

Considering quasineutrality and the dominance of the $H_3{}^+$ ion, one can assume that the electron number density is equal to the measured $H_3{}^+$ ion density in $H_3{}^+$ test measurements. As we tried to keep the conditions used for $H_3{}^+$ and D_2H^+ measurements close to each other, we can assume that the electron density derived from the $H_3{}^+$ measurements is relevant to the D_2H^+ measurements, where the ratio between different isotopologues is unknown. From the plots in Fig. 3 we can see that number density of $H_3{}^+$ and D_2H^+ are almost the same. This is surprising if we realise that D_2H^+ ions represent only a fraction of ions in deuterium containing discharge. The observations indicate that an overall ion number density in deuterium containing gas at otherwise identical conditions is higher. This can be partially explained by a significantly different behaviour of the discharge with and without the D_2 admixture. The lower recombination rate coefficients of deuterated ions in comparison with recombination rate coefficient of $H_3{}^+$ could be the main reason for higher charge particles densities. The error in rotational temperature estimation could introduce a significant error to number density too. An alternative explanation requires a significant overestimation of the integral absorption coefficient of the D_2H^+ ortho state transitions. We regard an error of this magnitude in the theory as unlikely.

The measurements of D_2H^+ ion number densities were repeated for different ratios of partial pressures of D_2 and H_2. In Fig. 5 the $D_2H^+(v = 0)$ ion number density in the plasma is plotted as a function of relative number density of D_2 in respect to the overall number density of D_2 and H_2, indicated as $D_2/(D_2 + H_2)$.

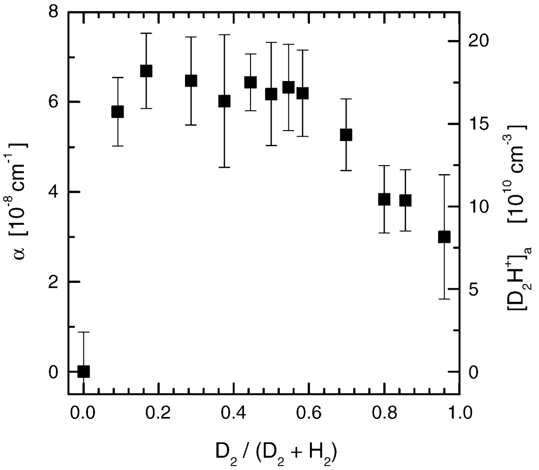

Fig. 5. Average population of $D_2H^+(v=0)$ as a function of D_2 to (D_2+H_2) relative number densities in He-Ar-H_2-D_2 plasma at 7 mbar and 110 W microwave pulse. The measurement in pure D_2 was not achievable because of an approximately 2% H_2 content in the D_2 gas bottle.

The relative population of D_2H^+ is in good agreement with the model and the experimental data introduced by Farnik et al. [22].

4. Conclusions

The measurement of the transition frequencies was guided by ab initio theoretical predictions, which proved to be extremely accurate. Interpretation of the results also relies on the accuracy of the theoretical intensity calculations. Given that there is much less intensity data to compare with, and a residual discrepancy with the intensity of one measured D_2H^+ transition [22], it may be necessary to seek further experimental confirmation of the calculated absolute intensities before they can be completely relied on for interpretation of the experiments.

From a plasma point of view this measurement presents a simple but very powerful plasma diagnostics tool applicable in hydrogen/deuterium containing plasmas, e.g., in ion sources. The obtained data can be used to characterise the excitation and kinetic temperature of ions in a RF ion trap, using laser induced ion molecular reactions (LIR) with cheap and compact DFB laser.

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