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EQUILIBRIUM IN LOW TEMPARATURE H_3^+-DOMINATED PLASMA, APPLICATION OF CAVITY RING-DOWN

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We examine establishing of a thermal equilibrium in a H_3^+-dominated plasma (produced by a microwave discharge ignited in He-Ar-H_2 gas mixture) and in its afterglow at temperatures 77–220 K by Cavity Ring-Down Spectroscopy. With respect to the observed population of lowest rotational states of the ground vibrational state of H_3^+ ion, we conclude that the rotational temperature is well defined and stable. It is equal to the He buffer gas temperature and to the kinetic temperature of the ions. By using para-enriched H_2 gas, we achieve high population of para nuclear spin states of H_3^+ ions in the discharge. This population is not constant in time and evolves towards a steady state (asymptotic) value which is not equal to the thermodynamic equilibrium value for a given temperature. The fact that the value of the steady state para-H_3^+ fraction does not vary with the concentration of para-enriched H_2 indicates that degradation of para-enrichment of H_2 in the discharge is negligible.

1. Introduction

H_3^+ is the simplest polyatomic ion, which is present in interstellar space and planetary atmospheres [*Herbst*, 2000, *Geballe and Oka*, 1996, *McCall et al.*, 1998, *Trafton et al.*, 1989, *Miller et al.*, 2000]. From astrophysical point of view, dissociative recombination (DR) is one of the main destruction processes of H_3^+ ions. Understanding of a dependence of this process on nuclear spin states (called para and ortho) is crucial for explanation of its spectroscopically observed abundances [*Crabtree et al.*, 2011a].

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After long series of mutually inconsistent experiments [*Leu et al.*, 1973, *Adams et al.*, 1984, *Larsson and Orel*, 2008, *Oka*, 2000, *Johnsen*, 2005, *Smith and Španěl*, 1993, *Amano*, 1990, *Plašil et al.*, 2002, *Laubé et al.*, 1998], storage ring measurements [*Kreckel et al.*, 2005, *McCall et al.*, 2003, *Petrignani et al.*, 2009, *Tom et al.*, 2009b] and the latest theory (going beyond the Born-Oppenheimer approximation and accounting for Jahn-Teller coupling, *Kokoouline et al.* [2001]) started approaching each other. However, nuclear spin state selective dissociative recombination cross sections resulted from such experiments didn't correspond with the theoretical predictions quantitatively [*Kokoouline and Greene*, 2003, *dos Santos et al.*, 2007, *Pagani et al.*, 2009]. The main reason turned out to be a rotational temperature higher than the value claimed to be in previous experiments [*Petrignani et al.*, 2011]. The exact determination of internal temperatures of the studied H_3^+ ion ensembles seems to be one of the biggest problems in the H_3^+ recombination study at low (< 300 K) temperatures.

According to our group's recent research, recombination of H_3^+ with electron in He-Ar-H_2 plasma can not be explained purely by two-body process—there also exists the ternary He-assisted mechanism [*Glosík et al.*, 2008]. The overall effective rate coefficient for recombination of H_3^+ with electrons α_{eff} is given by

$$\alpha_{\mathrm{eff}}(T, [\mathrm{He}]) = \alpha_{\mathrm{bin}}(T) + K_{\mathrm{He}}(T)[\mathrm{He}]\,, \tag{1}$$

where α_{bin} is the binary recombination rate coefficient and K_{He} is the ternary recombination rate coefficient.

Equation (1) applies both to para and ortho-H_3^+, yet the values of the coefficients are different for each nuclear spin state. These differences between nuclear spin manifolds were studied at the gas temperature of 77 K first [*Varju et al.*, 2011]. The nuclear spin state specific effective coefficients ${}^{\mathrm{p}}\alpha_{\mathrm{eff}}$ and ${}^{\mathrm{o}}\alpha_{\mathrm{eff}}$ ("p" in leading superscript stands for para, "o" for ortho) were obtained by comparing the decay of He-Ar-H_2 plasma with two different fractions of para (ortho) states ${}^{\mathrm{p}}f_3 = [\text{para-H}_3^+]/[\mathrm{H}_3^+]$ (${}^{\mathrm{o}}f_3 = [\text{ortho-H}_3^+]/[\mathrm{H}_3^+]$) — note ${}^{\mathrm{p}}f_3 + {}^{\mathrm{o}}f_3 = 1$. If H_3^+ is a dominant ion in the plasma, then a concentration of electrons $n_e = [\mathrm{H}_3^+] = [\text{para-H}_3^+] + [\text{ortho-H}_3^+]$ and the rate equation for the electron density in the afterglow plasma is

$$\frac{\mathrm{d}n_e}{\mathrm{d}t} = -({}^{\mathrm{p}}\alpha_{\mathrm{eff}}\,{}^{\mathrm{p}}f_3 + {}^{\mathrm{o}}\alpha_{\mathrm{eff}}\,{}^{\mathrm{o}}f_3)n_e^2 - \frac{n_e}{\tau_{\mathrm{D}}} = -\alpha_{\mathrm{eff}}\,n_e^2 - \frac{n_e}{\tau_{\mathrm{D}}}\,, \tag{2}$$

where the coefficient τ_{D} is a characteristic diffusion time. If we measure two decay curves described by this equation for two different values of ${}^{\mathrm{p}}f_3$ (but with all other parameters kept same), we have two equations with two variables ${}^{\mathrm{p}}\alpha_{\mathrm{eff}}$ and ${}^{\mathrm{o}}\alpha_{\mathrm{eff}}$. The determination of the values of ${}^{\mathrm{p}}\alpha_{\mathrm{eff}}$ and ${}^{\mathrm{o}}\alpha_{\mathrm{eff}}$ is then straightforward. Moreover, ${}^{\mathrm{p,o}}\alpha_{\mathrm{bin}}$ and ${}^{\mathrm{p,o}}K_{\mathrm{He}}$ can be extracted from the dependence of effective coefficients on He concentration according to equation (1).

Our main aim is to study temperature dependence of nuclear spin state specific recombination rate coefficients. In order to achieve this goal, we have to form thermal equilibrium in H_3^+-dominated plasma, where the temperature of He buffer gas T_{He}, the

TABLE 1. Used transitions and their wavenumbers. In the text we refer to each spectral line by the name given in this table (e.g. "line (1,1)").

transition	name of spectral line	wavenumber (cm^{-1})	nuclear spin state
$0\nu_2^0(1,1) \rightarrow 3\nu_2^1(2,1)$	(1,1)	7237.285	para
$0\nu_2^0(1,0) \rightarrow 3\nu_2^1(2,0)$	(1,0)	7241.245	ortho
$0\nu_2^0(3,3) \rightarrow 3\nu_2^1(4,3)$	(3,3)	7234.957	ortho

kinetic temperature of the ions T_{Kin} and rotational temperature of the ions $T_{\mathrm{Rot\text{-}ortho}}$ (meaning of the subscript explained later) are same, i.e. $T_{\mathrm{He}} = T_{\mathrm{Kin}} = T_{\mathrm{Rot\text{-}ortho}}$. Ensemble of H_3^+ ions can be described further by the "nuclear spin temperature" T_{spin} given by the value of ${}^{\mathrm{p}}f_3$. This article deals with definition and determination of aforementioned temperatures.

2. Experimental method

The state selective recombination of H_3^+ ions with electrons was studied by tracking the evolution of concentrations of para and ortho-H_3^+ in stationary afterglow plasma by Cavity Ring-Down Spectroscopy (CRDS, a principle is described in *Romanini et al.* [1997]). The actual arrangement of the apparatus is described in [*Hlavenka et al.*, 2006, *Macko et al.*, 2004]. We monitor the population of three of the lowest rotational states (that belong to the ground vibrational state) in time—the state $(J, G) = (1, 1)$ corresponds to para nuclear spin state and states $(1, 0)$ and $(3, 3)$ to the ortho state—see table 1 for used transitions.

The H_3^+-dominated plasma is produced by a pulsed microwave discharge ignited in He-Ar-H_2 mixture (with typical concentrations 10^{17}, 10^{13}, 10^{14} cm^{-3}) in a discharge tube that forms an optical cavity together with two highly reflective mirrors. The enhanced population of para-H_3^+ (i.e. ${}^{\mathrm{p}}f_3 > 0.5$) is achieved by using para-enriched H_2 (> 87% of para-H_2 in H_2) that is produced outside the apparatus by conversion of normal H_2 gas (25% of para-H_2 in H_2) in presence of Fe_2O_3 catalyst at 10–18 K (in the way same as in *Tam and Fajardo* [1999], *Tom et al.* [2009a]). The discharge is switched on for a specified time (discussed below) to produce H_3^+ in a steady state ortho:para ratio (discussed later) and then switched off to let the plasma decay. Recombination rate coefficients are obtained from the evolution of para/ortho-H_3^+ density during the decay period as described in the Introduction.

A temperature of the He buffer gas T_{He} is set by liquid nitrogen surrounding the discharge tube (in case of 77 K) or the flow of the cold nitrogen vapor on the walls of the tube.

3. Results and discussion

Here we will discuss a definition and a determination of the temperatures T_{Kin}, $T_{\mathrm{Rot\text{-}ortho}}$ and T_{spin} in H_3^+-dominated plasma and their stability. We evaluate the temperatures mainly from the spectrum (consisting of three lines from table 1) in the active discharge period since the signal is stronger there because of high concentration of H_3^+ ($[H_3^+] \sim 10^{11}\,\mathrm{cm}^{-3}$). Even though the electrons have temperature $T_e \sim 1$ eV in the discharge, they do not affect discussed temperatures according to our measurements. This is caused by intensive cooling of degrees of freedom of H_3^+ ions by He buffer gas (note $[\mathrm{He}]/[H_3^+] > 10^5$). Electrons in the afterglow are rapidly cooled down by collisions with neutral He atoms.

T_{Kin} is evaluated from Doppler broadening of the spectral line. Rotational temperature is evaluated from the ratio between populations of states (1,0) and (3,3) (both corresponding to ortho nuclear spin state), therefore we mark it as $T_{\mathrm{Rot\text{-}ortho}}$.

3.1 Analysis of stability of temperatures

The evolution of the kinetic temperature T_{Kin} of the ions in discharge and during the early afterglow for temperatures of the discharge tube 170 K and 132 K is plotted in Figure 1. Closed symbols are T_{Kin} obtained from Doppler broadening of line (1,1) (see table 1) in the discharge with para-enriched H_2, open symbols are T_{Kin} evaluated from line (1,0) in the discharge with normal H_2. The figure shows that $T_{\mathrm{Kin}} = T_{\mathrm{He}}$ in the discharge and during the early afterglow. The kinetic temperature is maintained at a stable value. Later afterglow values are burdened by big error because of the rapid decrease of the signal due to the decrease of the ion density.

Figure 2 shows the comparison of T_{Kin} with $T_{\mathrm{Rot\text{-}ortho}}$ (profiles of the lines (1,0) and (3,3) at $T_{\mathrm{Kin}} = (140 \pm 10)$ K are shown in the inset of the figure). Data originate from measurements with para-enriched and normal H_2. We can see that $T_{\mathrm{Kin}} = T_{\mathrm{Rot\text{-}ortho}}$ satisfactorily.

3.2 Stability of para:ortho ratio

We have observed the time evolution of ${}^{\mathrm{p}}f_3$ in the discharge with para-enriched H_2. It seems that H_3^+ are formed in the reaction of ${H_2}^+$ with H_2 with a high population of para-H_3^+ (so called "initial" value). Then the ${}^{\mathrm{p}}f_3$ decreases as H_3^+ ions undergo collisions with H_2 (as was described in *Cordonnier et al.* [2000]). This slow decrease of ${}^{\mathrm{p}}f_3$ towards a "final" asymptotic value is shown in the upper panel of the inset of Figure 3. The bottom panel of the inset shows the evolution of the concentration of the para- and ortho-H_3^+ ions. The gradual increase of ortho-H_3^+ concentration is obvious. This effect is probably caused by spin conversion reaction

$$\text{para/ortho-}H_3^+ + \text{para/ortho-}H_2 \rightarrow \text{para/ortho-}H_3^+ + \text{para/ortho-}H_2\,. \qquad (3)$$

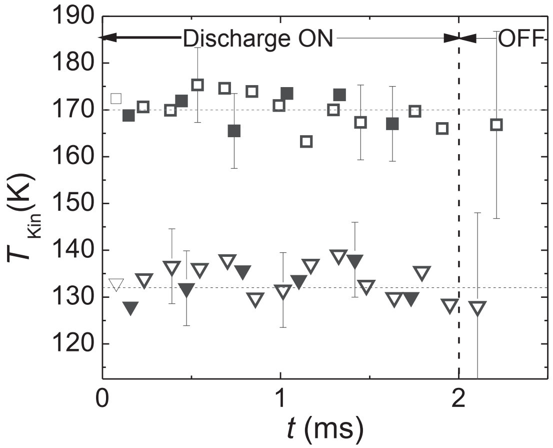

FIGURE 1. Evolutions of T_{Kin} of the ions for two temperatures of the discharge tube (170 K and 132 K). Closed symbols are evaluated from the Doppler broadening of the line (1,1) (see table 1) in the discharge with para-enriched H_2. Open symbols are calculated from the profile of line (1,0) in the discharge with normal H_2. Because of the fast decay of the plasma, values in afterglow have big errors.

Nuclear spin selection rules of this reaction have strong dependence on the temperature [*Crabtree et al.*, 2011b,c]. As we didn't observe any striking fluctuation of ${}^{p}f_3$ in the afterglow [*Varju et al.*, 2011], we assume that the rate of reaction (3) is higher than the rate of recombination because of sufficiently high concentration of H_2. This assumption was verified by *Hejduk et al.* [2010] by a numerical model.

The main frame of Figure 3 shows that there is no significant dependence of ${}^{p}f_3$ on para-enriched hydrogen concentration, which would indicate the degradation of para-enrichment of source H_2 gas. The minor negative slopes of the lines fitted to "initial" and "final" values can rather be caused by the aforementioned temperature dependence of nuclear spin selection rules of reaction (3).

As we know this spin conversion process exists, we choose the duration of discharge long enough to let the para:ortho ratio converge to a steady state (i.e. to let ${}^{p}f_3$ reach the "final" value). There is no such evolution in discharge with normal H_2, because in such case the resulting ${}^{p}f_3$ equals to the thermodynamic equilibrium value for temperatures above 77 K at which we operate, i.e. $T_{spin} \approx T_{Kin}$ in such case. Of course, this does not hold for the discharge with para-enriched H_2, where ${}^{p}f_3$ is higher then thermodynamic equilibrium value, i.e. $T_{spin} < T_{He}$.

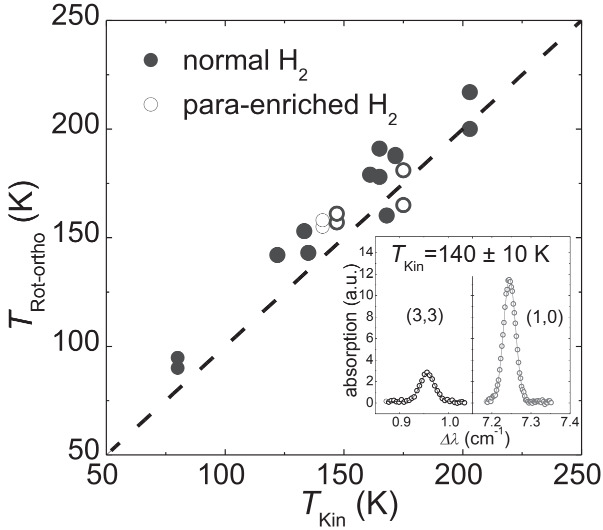

FIGURE 2. Comparison of rotational temperatures with kinetic temperatures. Values from measurements in para-enriched and normal H_2 are plotted. Dashed line: $T_{\text{Rot-ortho}} = T_{\text{Kin}}$ plot. Inset: Spectral lines (1,0) and (3,3) (see table 1) from which $T_{\text{Rot-ortho}}$ is evaluated (this example is taken from measurements at $T_{\text{Kin}} = (140 \pm 10)$ K). $\Delta\lambda$ (cm^{-1}) is a distance from the wavenumber 7234 cm^{-1}.

4. Conclusion

The kinetic temperature of the ions is stable throughout the discharge period and is maintained at the same value even in afterglow plasma (see Figure 1).

The stable population of rotational states within ortho nuclear spin manifold allows us to define a rotational temperature which was shown to be same as the kinetic temperature of the ions (Figure 2).

In the discharge with para-enriched H_2, the steady state population of para-H_3^+ is reached at the beginning of the afterglow and it does not significantly vary with the concentration of para-enriched H_2 (Figure 3).

Further studies about the spin conversion of H_3^+ ions in the discharge are in progress. Preliminary results of the study of the dissociative recombination at 200 K are described in *Dohnal et al.* [2011].

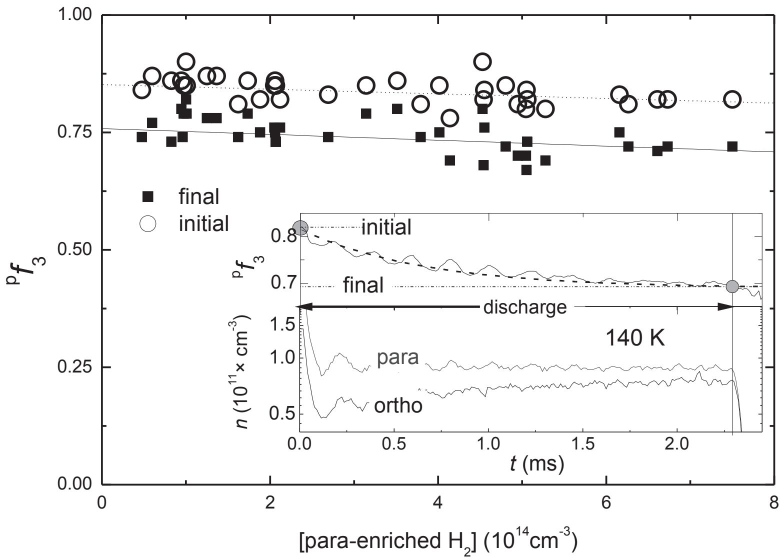

FIGURE 3. Population of para-H_3^+ vs para-enriched H_2 concentration in the range of temperatures 130–220 K. Two sets of values originating from the beginning and the end of the discharge period (initial and final values) are plotted. The lines serve for orientation. Inset: upper panel—initial and final values of ${}^{\mathrm{p}}f_3$ are explained; bottom panel—evolution of concentrations of para and ortho-H_3^+. For a discussion, see the text. Experimental conditions: [Ar] $= 1 - 20 \times 10^{13}$ cm^{-3}, [He] $= 1 - 15 \times 10^{17}$ cm^{-3}.

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