Cavity ring-down spectroscopy of D_3^+-dominated low-temperature plasma

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Introduction

Reactions of deuterated analogues of H_3^+ ions with HD form a deuteration reaction-chain $H_3^+ \leftrightarrow H_2D^+ \leftrightarrow D_3^+$ suggested by Philips and Vastel [1] to justify the expectation of high $[D]/[H]$ ratio in prestellar cores. The right-to-left direction in the chain ("de-deuteration") is highly improbable in the conditions of the interstellar medium prior to star formation ($T < 10$ K) if the reactant H_2 are in para nuclear spin states and resulting deuterated ions are in their ground levels, because of the endothermicity $\Delta H \sim 100$ K. However the observed abundances of the ions may surprise those astrophysicist who do not take the state-specific dissociative recombination with electrons into account: different states of H_3^+, H_2D^+, D_2H^+ and D_3^+ may recombine with different rates. Therefore the reexamination of the assumption that the population of the nuclear spin states of the ions correspond to the thermodynamic equilibrium (TDE) becomes crucial.

Our group was the first and the last which showed that the recombination rate coefficient for para-H_3^+ ions is 10 times higher than for ortho-H_3^+ at the temperature 77 K by direct observation of the populations of the nuclear spin states [2]. Results of the measurements with other temperatures were published recently [3]. Moreover, we have observed that the population of para-states does not necessarily equal to the value corresponding to the thermodynamic equilibrium (TDE) probably because the nuclear spin conversion of H_3^+ by the collision with H_2 is restricted by non-trivial selection rules [4]. Similarly, the dissociative recombination of D_3^+ is nuclear-spin-state specific:

$$^{\mathrm{o,m,p}}D_3^+ + e \xrightarrow{^{\mathrm{o,m,p}}\alpha_{\mathrm{eff}}} \text{neutral products} \qquad (1)$$

(superscripts o, m, p stand for ortho, meta, para nuclear spin states, respectively). Studies of the reaction (1) with nuclear spin states not resolved are going to be published soon. Here we will show that ensemble of D_3^+ ions in our experiments at temperatures above 77 K is in TDE and therefore obtained α_{eff} values correspond to TDE values.

Experimental

We use a method of the cavity ring-down spectroscopy in a continuous wave modification (cw-CRDS) [5] as a diagnostics tool to measure number densities of D_3^+ ions. A schematic

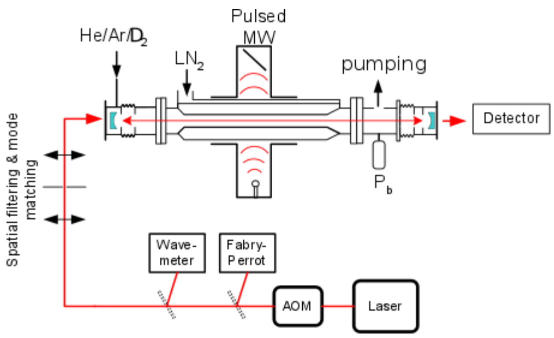

Figure 1: The discharge tube equipped with an optical resonator (not in scale). The discharge is ignited inside the optical resonator in He/Ar/D_2 gas mixture. Injection of the light to the optical resonator is synchronised with the discharge by the acoustooptic modulator (AOM) and measured by InGaAs photodiode.

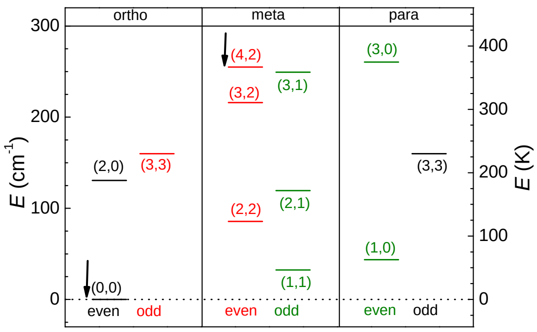

Figure 2: The lowest rotational levels of the ground vibrational state. Each rotational level is indicated by corresponding quantum numbers (J,G). The energy levels were taken from [6].

picture of the apparatus is shown in figure 1. A microwave discharge is periodically ignited in He/Ar/D_2 gas mixture (see the sequence of reactions in Hejduk et al. [4]) with typical concentrations 10^{17},10^{14},10^{14} cm^{-3}, respectively. The glass discharge tube is cooled by the liquid nitrogen or its vapours to a desired temperature.

The population of the low-lying rotational levels of the vibrational ground state corresponding to ortho and meta D_3^+ ($^{o}D_3^+$, $^{m}D_3^+$, see figure 2) is monitored in the discharge and in the afterglow. The line positions (5793.92 cm^{-1} for $^{o}D_3^+$-(0,0) and 5792.68 cm^{-1} for $^{m}D_3^+$-(4,2)) were calibrated with the spectra of water and the relative position between used wavelengths is monitored by the Fabry-Perrot spectrometer. The kinetic temperature of D_3^+ ions is evaluated from the Doppler broadening of the absorption lines.

Results

The kinetic temperature T_{Kin} of D_3^+ ions is collisionally stabilised to the temperature of the He buffer gas T_{He}, which is given by the temperature of the discharge tube T_{Wall}:

$$T_{Kin} = T_{He} = T_{Wall}. \quad (2)$$

This was checked by comparing the T_{Kin} evaluated from the Doppler broadening of the lines (see figure 3 for illustration) and the temperature of the discharge tube measured by the thermocouple. T_{Kin} in the discharge and in the afterglow do not differ.

In the previous work with H_3^+ ions [4], we showed that if $\alpha_{\mathrm{eff}} \lesssim 10^{-7}\,\mathrm{cm}^3\,\mathrm{s}^{-1}$ and $[H_2] \sim 10^{14}\,\mathrm{cm}^{-3}$, the interconversion between the nuclear-spin states of H_3^+ in collision with H_2 molecules is fast enough to keep the population of the rotational states constant during the discharge and the afterglow. Also, at such $[H_2]$, a formation of H_5^+ is very slow – this fact allows us to study the recombination processes in the plasma where H_3^+ ions exist predominantly. Because of similarities with H_3^+, our experiments with D_3^+ are carried at same settings.

In the experiment with H_2 gas, we had the advantage of being able to monitor two states in the ortho manifold and hence to evaluate the rotational temperature T_{Rot}. The population of para and ortho states measured at that time corresponded to this T_{Rot}, which was equal to the kinetic temperature T_{Kin}. This held for the conditions both in the discharge and in the afterglow and allowed us to state that the H_3^+ ions ensemble is in TDE.

With D_3^+ions and our experimental apparatus, we are technically not able to observe plural number of lines within one nuclear spin manifold. Therefore we have to rely on the aforementioned experience with H_3^+ and define the “internal” temperature T_{Int} evaluated from the relative population of ${}^{\mathrm{o}}D_3^+$-(0,0) and ${}^{\mathrm{m}}D_3^+$-(4,2) as if the relaxation between these states towards the TDE populations was fast (even though they belong to different nuclear spin state manifolds). Figure 4 shows the comparison between T_{Kin} and T_{Int}. We can see that

$$T_{\mathrm{Int}} = T_{\mathrm{Kin}}\,. \tag{3}$$

This signs that nuclear spin states are populated in the amount corresponding to TDE at temperatures above 77 K (liquid nitrogen temperature).

Conclusion

We have shown that the kinetic and the internal temperatures of the ensemble of D_3^+ ions are equal in the conditions of the presented experiment at temperatures above 77 K. This allows us to interpret measurements (of D_3^+-electron recombination rate coefficients) carried out in the plasma described here as the measurements in the ensemble of D_3^+ ions with the TDE population of the states. Moreover, the results of the presented study indicate that D_3^+ recombination rate coefficients obtained with our flowing afterglow apparatus [7] also correspond to TDE conditions.

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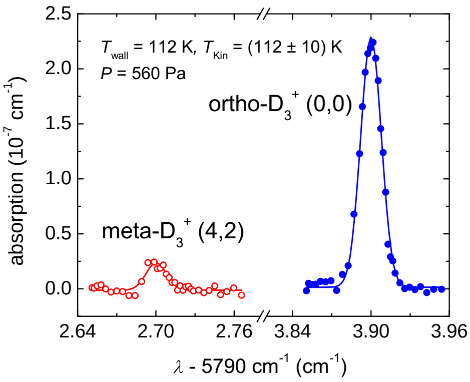

Figure 3: Absorption lines corresponding to two monitored states of D_3^+ ions for T_{Wall} = 112 K. The kinetic temperatures T_{Kin} of the ions in both states evaluated from the Doppler broadening are same.

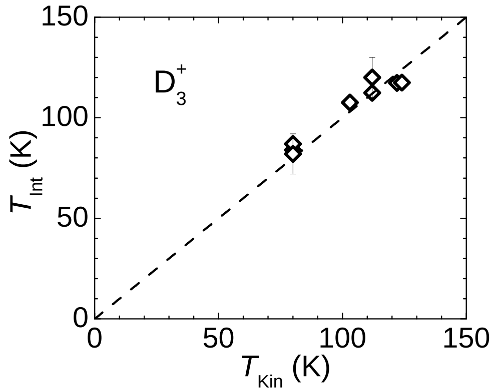

Figure 4: The comparison of T_{Int} and T_{Kin}. Data from the discharge and from the early afterglow are plotted together.

References

[1] T. G. Philips and C. Vastel, Future millimeter/submillimeter instrumentation and science opportunities: the example of deuterated molecules. In C L Curry and M Fich, editors, *Chemistry as a diagnostic of star formation, 21–23 August 2002*, Canada, University of Waterloo, NRC Press (2003)

[2] J. Varju, M. Hejduk, P. Dohnal, et al., Phys. Rev. Lett., **106**, 20:203201 (2011)

[3] P. Dohnal, M. Hejduk, J. Varju, et al., J. Chem. Phys., **136**, 24:244304 (2012)

[4] M. Hejduk, P. Dohnal, J. Varju, et al., Plasma Sources Sci. Techn., **21**, 2 (2012)

[5] D. Romanini, A. A. Kachanov, and F. Stoeckel, Chem. Phys. Lett., **270**, 5-6:538–545 (1997)

[6] J. Tennyson. private communication.

[7] T. Kotrík, P. Dohnal, I. Korolov, et al., J. Chem. Phys., **133**, 3:034305 (2010)