Spectroscopic measurement of Fulcher-α band of microwave discharge H_2/D_2 plasmas

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We examine Fulcher-α band spectrum of microwave discharge H_2/D_2 plasmas with their discharge pressure about 1 Torr, and determine rotational and vibrational populations of the upper state of the Fulcher-α band, d $^3\Pi_u$ state. It is found that the rotational temperature becomes lower with increasing vibrational quantum number, and that its dependence is stronger for H_2 plasma than for D_2 plasma. Rotational and vibrational temperatures are examined as functions of H_2/D_2 mixture ratio in the feed gas, which reveals that high partial pressure of D_2 increases the rotational temperatures for constant total discharge pressure, except for pure D_2 discharge.

1. Introduction

Hydrogen plasma plays important roles in various engineering fields, such as material processing for diamond thin film preparation. On the other hand, in the boundary area of magnetically confined thermonuclear fusion reactors like divertors, chemical kinetics of various atoms and molecules recombined are quite crucial for the energy transport of thermonuclear fusion processes as well as for the particle transport of hydrogen isotopes.

Intensive researches have been carried out for the boundary domain of thermonuclear fusion reactors, particularly, on spectroscopic observation of Balmer series and Fulcher-α band [1, 2]. For detailed estimation of energy-loss as well as particle loss, we must understand characteristics of the plasmas that are generally in the state of non-equilibrium. However, the molecular processes that may cause such non-equilibrium are not fully understood yet, particularly concerning molecular isotope effects. There will be D_2, DT, T_2 molecules in the divertor region as a result of recombination into molecules, and consequently, difference in the vibrational quanta as well as difference in the inertia moment can cause further ambiguity for the thermal load to the divertor plate of the reactor. In addition, the energy transport characteristics including translational, rotational and vibrational motions should be fully understood including non-equilibrium induced by isotopic differences.

Based on these backgrounds, it is considered as worthwhile to study spectroscopic characteristics of molecular levels of hydrogen isotopes even in the discharge plasmas of hydrogen isotopic mixtures with low-temperature and low-density, particularly on the vibrational and rotational populations, which is precisely the objective of the present study.

2. Experiments

2.1. Experimental apparatus

Figure 1 shows a schematic diagram of the experimental setup. We generate a H_2/D_2 gas mixture plasma by using a rectangular waveguide with a cavity and a quartz tube, one end of which is inserted into a vacuum chamber. The quartz tube (26 mm inner diameter) is aligned in the direction of the electric field of the waveguide with an adjustable short-circuited plunger. The chamber and quartz tube are evacuated by an oil-rotary pump, where the ultimate pressure is about 0.02 Torr, and the pressure is monitored by a membrane manometer. The microwave frequency is 2.45 GHz and its power is set at 350 W. The plasma is generated in the quartz tube, where the discharge pressure is set at 0.5 – 3.0 Torr. The total feeding rate is set at about

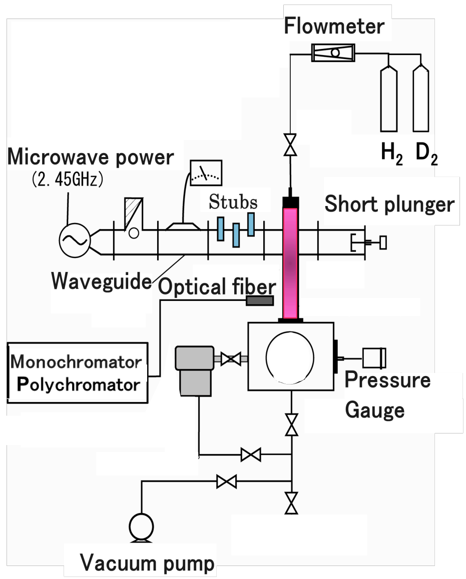

Fig. 1 Schematic diagram of experimental setup.

30 – 400 mL/min by a flow rate controller. For the optical emission spectroscopic (OES) examination, the distance along the discharge tube from the intersection with the waveguide z is chosen to be 60, 100 and 140 mm. The discharge apparatus is basically the same as that described elsewhere [3].

2.2. Fundamentals of analysis of OES data

We measure rotational and vibrational number density distributions of H_2/HD/D_2 d $^3\Pi_u$ state by OES measurement of Fulcher-α band, which also lead to the rotational and vibrational temperatures, respectively. Fulcher-α band is originated from the radiative transition of d $^3\Pi_u$ to a $^3\Sigma_g$, where its emission band is observed over the wavelength range 590 – 640 nm. If we denote the line intensity for the transition from the upper state (d, v', J') to the lower state (a, v'', J'') as $I^{\mathrm{d}v'J'}_{\mathrm{a}v''J''}$, it can be related with the number density of its upper state $N_{\mathrm{d}v'J'}$ as follows:

$$I^{\mathrm{d}v'J'}_{\mathrm{a}v''J''} = \frac{hc}{\lambda^{\mathrm{d}v'J'}_{\mathrm{a}v''J''}} A^{\mathrm{d}v'J'}_{\mathrm{a}v''J''} N_{\mathrm{d}v'J'}, \qquad (1)$$

where h is the Planck constant, c is the velocity of light, $\lambda^{\mathrm{d}v'J'}_{\mathrm{a}v''J''}$ is the wavelength of the transition from the state (d, v', J') to (a, v'', J''), v and J are the vibrational and rotational quantum number, respectively, and $A^{\mathrm{d}v'J'}_{\mathrm{a}v''J''}$ is the corresponding transition probability. After that, we apply the following equation by making the Boltzmann plot for vibrational and rotational levels (v', J'). Then we can determine the vibrational temperature $T^{\mathrm{d}}_{\mathrm{vib}}$ and rotational temperatures of each vibrational level $T^{\mathrm{d}}_{\mathrm{rot}}(v'')$ by the following equation [4];

$$\frac{N_{\mathrm{d}v'J'}}{g^{J'}_{\mathrm{as}}} = N_{\mathrm{d}}\left(2J'+1\right)\exp\left[-\frac{F_{\mathrm{d}}\left(J',v'\right)}{kT^{\mathrm{d}v'}_{\mathrm{rot}}} - \frac{G_{\mathrm{d}}\left(v'\right)}{kT^{\mathrm{d}}_{\mathrm{vib}}}\right], \qquad (2)$$

where N_{d} is the number density of the d states summed over the vibrational and rotational quantum states, k is the Boltzmann constant, $F_{\mathrm{d}}(J', v')$ and $G_{\mathrm{d}}(v')$ are the energies of the rotational state (d, v', J'), and vibrational state (d, v') at rotational ground state, respectively, g_{as} is the statistical weight of the rotational state J' with regard to the symmetry of nuclear wave function, where s and a denote ortho- and para-states, respectively. In the present study, we measure the diagonal transition $\Delta v = 0$, since the Franck-Condon principle almost exactly holds for this transition. Also we analyze Q-branch $\Delta J = 0$, since P and R branches always accompany anomaly due to strong coupling with other electronically excited states [4].

3. Results and discussion

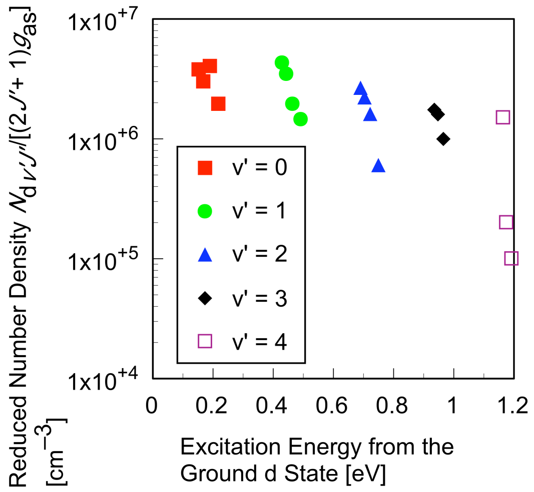

Fig. 2 A Boltzmann plot of d state of H_2 in the microwave discharge H_2 plasma. Discharge pressure $P = 1$ Torr, longitudinal position $z = 6$ cm.

3.1. Distributions of vibrational and rotational excited states of H_2 molecule

Figure 2 shows a measured Boltzmann plot of rot-vibrational number density distribution $N_{\mathrm{d}v'J'}$ of the H_2 plasma. These plots give the rotational temperature $T_{\mathrm{rot}}^{\mathrm{d}v'}$ for each vibrational level v' of d-state and the vibrational temperature $T_{\mathrm{vib}}^{\mathrm{d}}$ for each discharge condition. It is found that $0.39 \leq T_{\mathrm{vib}}^{\mathrm{d}}$ [eV] ≤ 0.41, which is almost independent of the longitude position z. Here, the vibrational temperature is determined as a lope of the Boltzmann plot over the vibrational range $0 \leq v' \leq 3$. The vibrational population density of the state $v' = 4$ is found to be much lower than the extrapolated value from $0 \leq v' \leq 3$. It is considered that this is due to the existence of the predissociation level to H(1s) + H(2s) states between $v' = 3$ and 4 levels of the d state.

Meanwhile, the rotational temperature, which is shown in Fig. 3, is found to become higher as the plasma flows to the downstream direction within the observed range, $6 \leq z$ [cm] ≤ 14. It is considered that this is because energy relaxing process from electron and vibration motions to rotating motions occurs over the time-scale for several-centimeter flowing. The microwave, the only energy supplier in the present experiment, first heats electrons. After that, the electron energy will be transferred to vibrational motion of molecules, and finally, rotational and translational motion of H_2 molecules.

Next finding to be remarked is the dependence of the rotational temperature $T_{\mathrm{rot}}^{\mathrm{d}v'}$ on the vibrational quantum number v'. Obviously, the higher vibrational states have lower rotational temperature. As a qualitative discussion, we can summarize the reason for the monotonic decrease in the rotational temperature as follows. Namely, this is because the higher vibrational levels of H_2 molecule have the

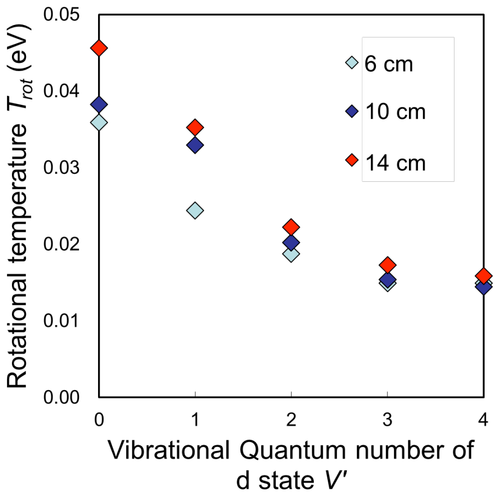

Fig. 3 Rotational temperature of d state of H_2 in the microwave discharge H_2 plasma. Discharge conditions are the same as in Fig. 2.

larger intermolecular distance, and consequently, larger inertia moment I. Near corona equilibrium holds for the present hydrogen plasma. Therefore, the H_2 d state must have the same angular momentum $I\omega$ with the original ground state, since the mass of electron is negligibly small. That is, the higher vibrational level of d state must have smaller ω. Then, the consequential rotational energy $I\omega^2/2$ becomes smaller for the higher vibrational level. Then, the rotational temperature as indication of rotational energy distribution shows monotonic decrease as the increasing vibrational quantum number [5].

3.2. Distributions of vibrational and rotational excited states of D_2 molecule

Next, we discuss experimental results of pure D_2 discharge. Figures 4 – 5 show the same plots for D_2 discharge plasma as were shown for H_2 plasmas in Figs. 2 – 3. Qualitatively, the same tendency as H_2 plasma can be observed for D_2 plasma, i.e., the rotational temperature becomes higher as the plasma flows to the downstream direction. This is considered to be for the same reason. We can also found the monotonic decrease of the rotational temperature with respect to the vibrational quantum number, although the absolute value of the decrease is smaller than that of H_2 plasma. That is, $T_{rot}^{dv'}(H_2) > T_{rot}^{dv'}(D_2)$ for $v' = 0$, 1, and $T_{rot}^{dv'}(H_2) < T_{rot}^{dv'}(D_2)$ for $v' = 2 – 4$. To this experimental result, we must notice that the vibrational quanta, or the energy gaps between the vibrational levels are larger for lighter isotopic molecules. That is, the larger energy gap will cause larger scale of non-equilibrium. The rotational temperature difference will be more emphasized for H_2 molecule than for D_2 molecule. Of course, the difference in the thermal conductivity

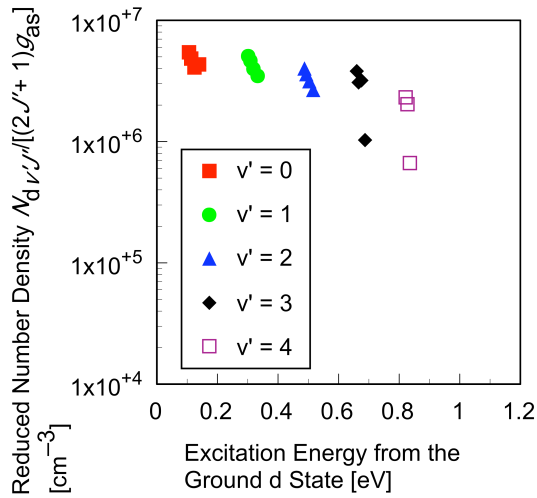

Fig. 4 A Boltzmann plot of d state of D_2 in the microwave discharge D_2 plasma. Discharge pressure $P = 1$ Torr, longitudinal position $z = 6$ cm.

between isotopes should be also considered due to their mass difference, which should be further discussed in the future.

Concerning vibrational temperature, again we found that the dependence on the longitudinal position is weak also for D_2 plasma. However, one different feature was also found, i.e., the number density of vibrational level of $v' = 4$ is also described by the common vibrational temperature with $v' = 0 – 3$, which was not the case for H_2 plasma. This is because the predissociation limit level exists between the vibrational levels $v' = 4$ and 5 due to the smaller vibrational quanta of D_2 than that of H_2.

3.3. Comparison of rotational temperatures of H_2/HD/D_2 molecules in H_2-D_2 mixture plasma

It is already found that the Fulcher-α band with its vibrational quantum number $v' = 2$ cannot be

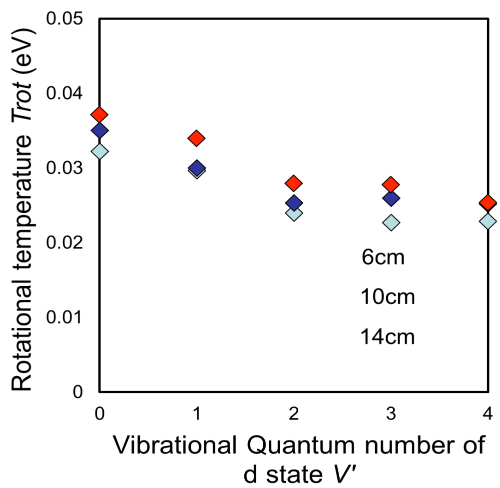

Fig. 5 Rotational temperature of d state of D_2 in the microwave discharge D_2 plasma. Conditions are the same as in Fig. 4.

applied for OES analysis due to spectral overlapping with one another for H_2/D_2 mixture discharge plasma [6]. Consequently, we observe Fulcher-α band with $v' = 0, 1, 3$. Figure 6 shows rotational temperature of H_2, HD and D_2 molecules for $v' = 0$, plotted against H_2 partial pressure ratio. For vibrational levels $v' = 1$ and 3, we found similar dependence of the rotational temperature on the partial pressure ratio.

Concerning the isotopic dependence of rotational temperature, it is generally found that heavier isotopic molecules have higher temperature, although the difference itself is not so remarkable and a couple of exceptions can also be found. It is also confirmed that the higher vibrational state has the lower rotational temperature, which is also common to pure H_2/D_2 discharge plasma.

Another important finding is that the higher concentration of D_2 results in the higher rotational temperature, except for pure D_2 discharge. This is particularly evident for vibrational level $v' = 0$, as shown in Fig. 8. For any vibrational levels, the rotational temperature becomes maximum with its partial pressure ratio of discharge gas $H_2:D_2 = 1:3$. It is considered that there are several reasons for this result. First, the heavier isotopic molecular gas has smaller thermal conductivity. Therefore, the discharge plasma with its main species H_2 should have lower gas temperature for the discharge with the same microwave power input. This could explain the lowering of rotation temperature of larger fraction of H_2 gas inlet, since the rotational temperature is basically equilibrated with gas translational temperature. The next difference between these isotopic species lies in the value of energy gap between the vibrational levels. The smaller the energy gap becomes, the more frequent becomes the collisional relaxation between

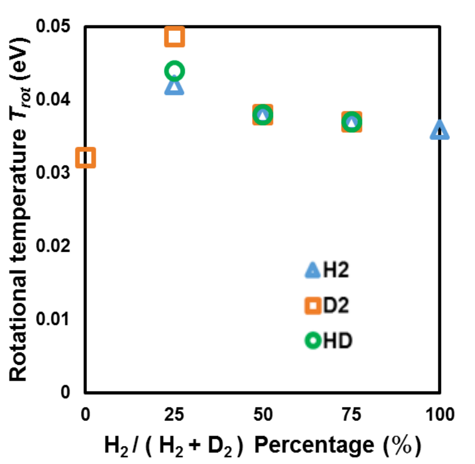

Fig. 6 Rotational temperature of d state of H_2, HD and D_2 molecules in the microwave discharge H_2/D_2 gas mixture plasma.

molecular vibration and rotational/translational motion, which results in the increase in the rotational temperature of high D_2 concentration in the discharge plasma.

On the other hand, it is still unclear why pure D_2 discharge has lower rotational temperature than the discharge plasma with $H_2:D_2 = 1:3$ mixture. One of the possible reasons is that the light mass itself of the H_2 molecule, which results in the higher rate of energy transfer from electron movement to vibrational or any kind of motion of molecules. Further study is necessary for the detailed analysis of energy relaxation processes between electron and H_2/D_2 molecules.

4. Summary

We examined Fulcher-α band of microwave discharge H_2/D_2 plasma by OES measurement. We found increase in the rotational temperature as the plasma flowed to the downstream direction, which is considered to be due to relaxation process from electron motion to molecular translational/rotational motion. We also found that the rotational temperature became lower for higher vibrational levels, which is considered to be due to the increase in the inertia moment of high vibrational levels. On the other hand, the observed vibrational temperature is almost constant over the longitude area observed, about 0.4 eV. Concerning isotopic effects for the rotational temperature, we found the difference in the dependence of the rotational temperature on the vibrational quantum number. The rotational temperature of highly vibrational levels of D_2 molecule did not decrease with vibrational quantum number so remarkable as that of H_2 molecule, i.e., $T_{rot}^{dv'}(H_2) > T_{rot}^{dv'}(D_2)$ for $v' = 0, 1$, and $T_{rot}^{dv'}(H_2) < T_{rot}^{dv'}(D_2)$ for $v' = 2 - 4$. For H_2/D_2 gas mixture discharge plasma, it was generally found that heavier isotopic molecules have higher temperature, It was also found that the higher concentration of D_2 results in the higher rotational temperature, except for pure D_2 discharge.

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