Spectroscopic Examination of Fulcher-α Band of Microwave Discharge H_2-D_2 and H_2-He Plasmas

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My Laboratory

- Fundamentals of low-temperature plasmas
  - Diagnostics based on optical emission spectroscopy measurement
    - Collisional radiative modeling to determine T_e and N_e
    - Rotational temperature determination
    - Actinometry measurement
  - Arc-jet along magnetic field
    - Effect of magnetic nozzle
    - Lowering of space potential

1. Introduction

Hydrogen plasma

— Industrially & fundamentally interesting

- Microelectronics, surface processing of SiC substrate
- Preparation of Carbon Thin Films
- Boundary Region of Thermonuclear Fusion Reactors Confined Magnetically, **Particularly, Divertor Region**

One of Key Issues — Isotope Effect

- **Characteristics of non-equilibrium of H_2 plasma should be understood**
  - Vibrational Distribution Function (**VDF**)
  - Rotational temperature

- Particularly, **Non-Equilibrium molecular isotope effect**
  - Vibrational quanta
  - Inertia moment, thermal conductivity, .etc.
  - Even for H_2/D_2 discharge plasmas, not fully studied

For precise analysis of thermal load in divertor region,

Energy relaxation of neutral hydrogen molecular isotopes should be studied experimentally.

- Vibrational/rotational non-equilibrium

Fulcher-α band of H_2 and D_2 of pure H_2, D_2 and their 1:1-mixture plasmas [1].

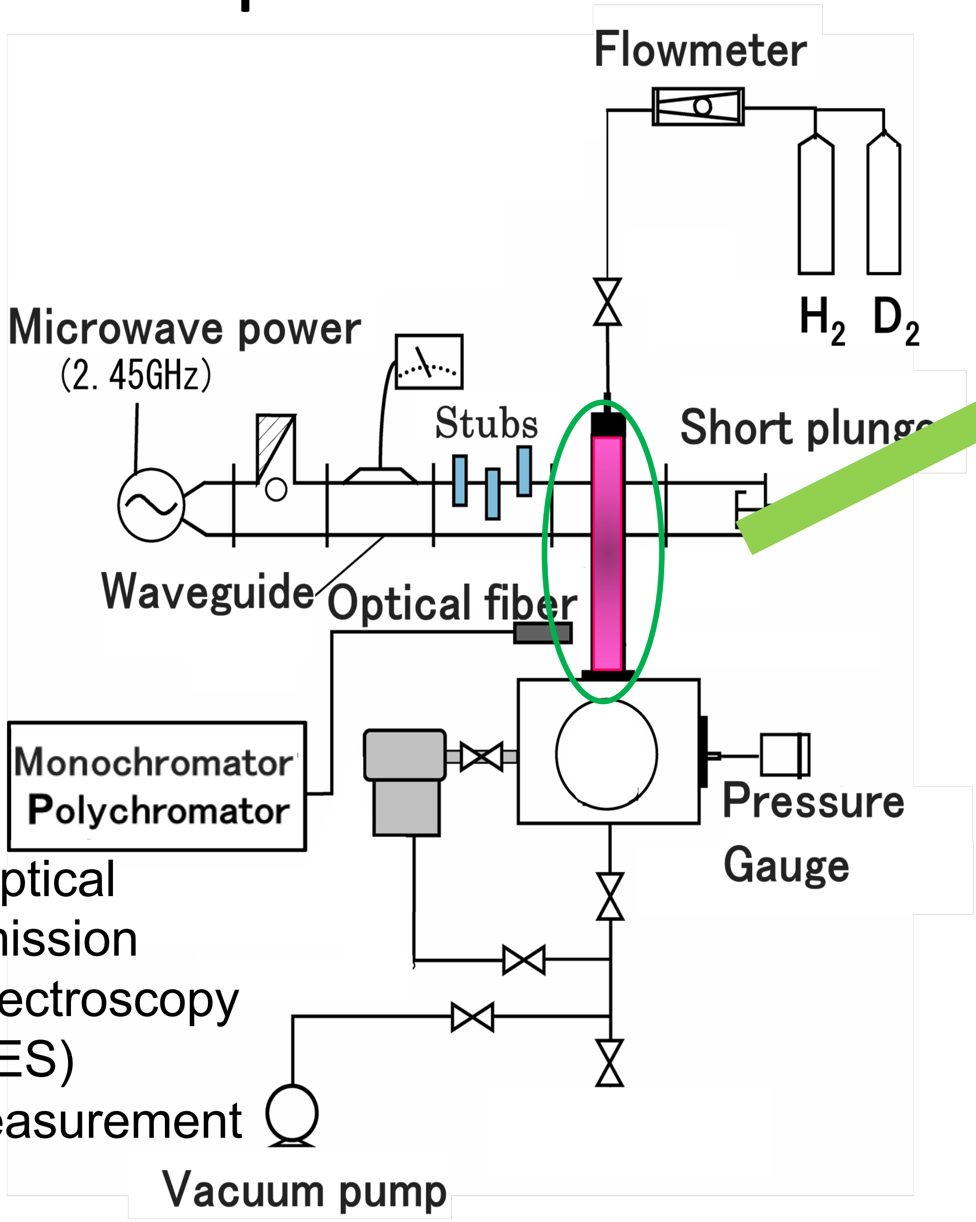
– In [1], however, only 1:1 mixtures, and no observation of other mixture ratio.

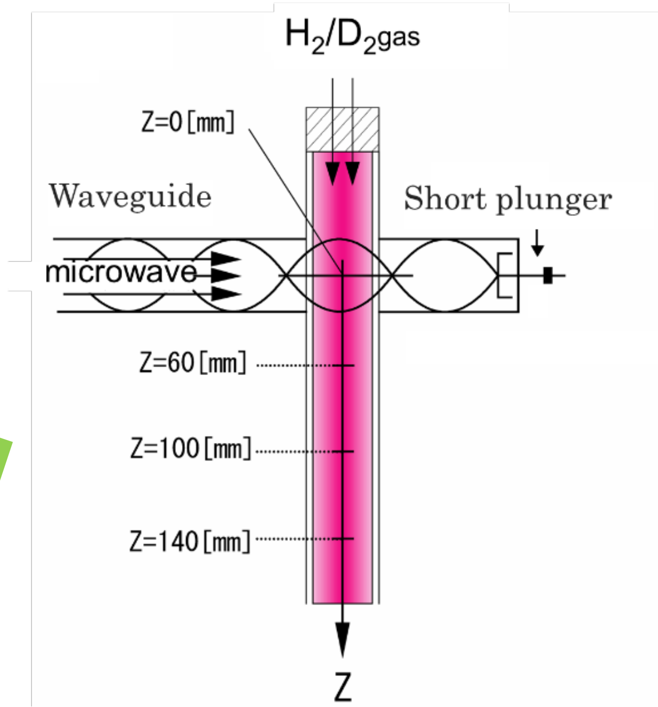
Objective of this study

- To examine T_{vib} and T_{rot} of microwave discharge H_2, D_2 mixture plasmas, and H_2-He mixtures of H_2/HD/D_2-Fulcher-α band (d $^3\Pi_u$ → a $^3\Sigma_g^+$)
  - and to find their differences, if any.

- To examine dependence of T_{vib} and T_{rot} of H_2/HD/D_2 on the H_2/D_2 mixture ratio.

2. Experiments



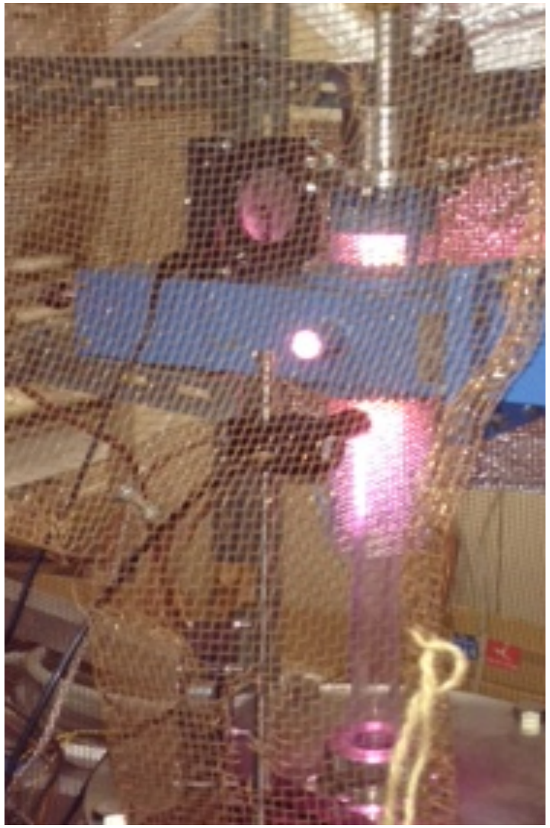


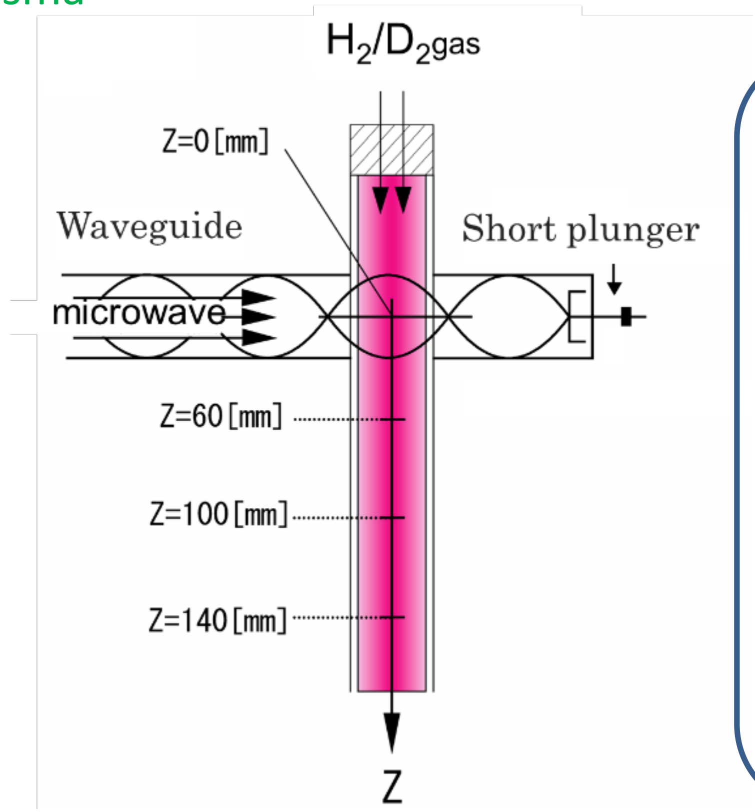
・Optical Emission Spectroscopy (OES) Measurement

- Ultimate pressure : 0.01 Torr
- Discharge gases: H_2, D_2, He (purity 99.5 %) and their mixture
- Discharge pressure: 0.5 – 3 Torr
- Microwave frequency: 2.45 GHz
- Microwave power: 350 W
- Inner diameter of cylindrical quartz tube: 26 mm

2. Experiments (1) H_2/D_2 mixture plasma

Microwave discharge H_2 plasma





H_2/D_2 mixture ratio

$H_2 : D_2 = 4:0$

$H_2 : D_2 = 3:1$

$H_2 : D_2 = 2:2$

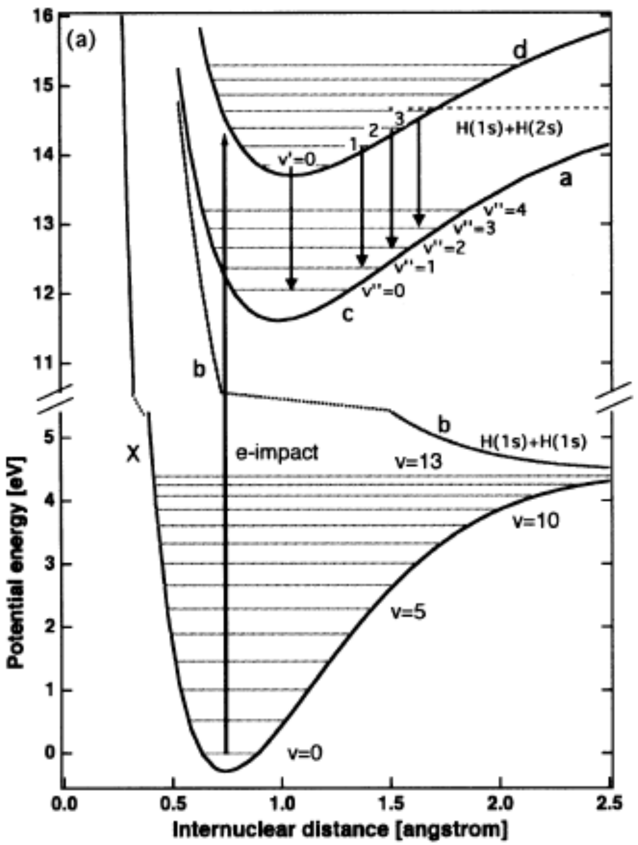
$H_2 : D_2 = 1:3$

$H_2 : D_2 = 0:4$

At each position specified above, we conduct OES measurement of Fulcher-α band spectrum.

3. Remarks for Data Analysis

— Fulcher-α band



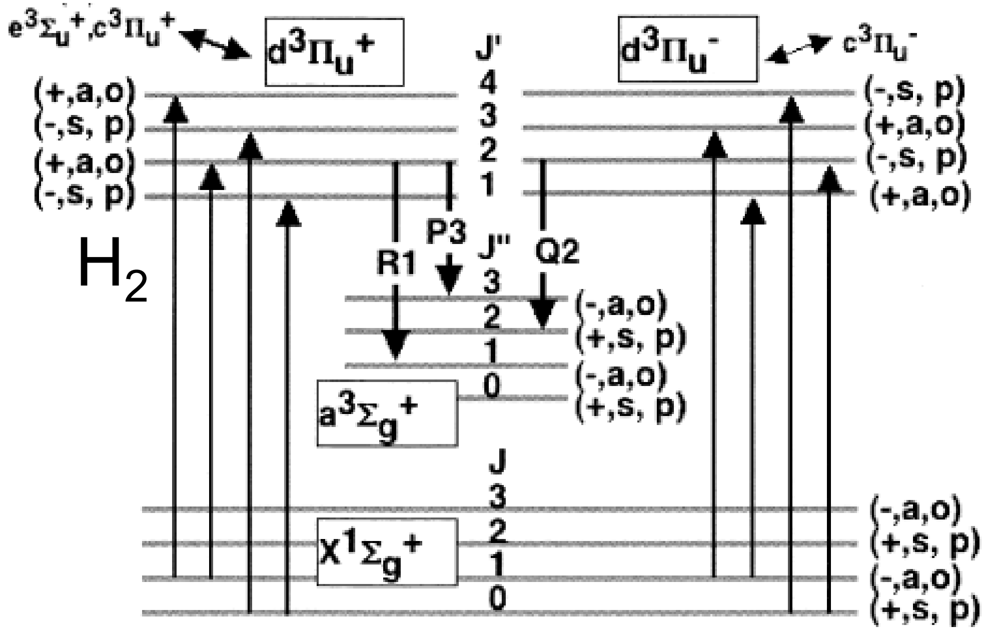
Potential curves of electronic levels of H_2 molecule related with Fulcher-α band

S. Kado: "Molecular Spectroscopy in Fusion Plasmas~Spectra of Hydrogen Molecules in Visible Region~", Plasma Phys. Control. Fusion, Vol. 80, No. 9, pp. 749 – 755. (2004)

- $d\ ^3\Pi_u \rightarrow a\ ^3\Sigma_g^+$
- Observed over 590 – 640 nm
- Kado *et al.* confirmed validity of Franck-Condon principle for diagonal transition for Fulcher-α transition [3 – 4].
- Selection rules
  - $\Delta J = 0, \pm 1$ (except $0 \rightarrow 0$)
  - $(-) \leftrightarrow (+)$ ▪ $g \leftrightarrow u$
  - $s \leftrightarrow s$, $a \leftrightarrow a$, $s \nleftrightarrow a$
  - $\Sigma^+ \nleftrightarrow \Sigma^-$ as Hund (a, b)

Rotational structure in the transition

- We must consider
  parity (+, –),
  symmetry of nuclei (s, a),
  nuclear spin (o, p).



The upper state of Fulcher-α, d $^3\Pi_u$, is doubly degenerated.

- d $^3\Pi_u^-$ — For even J', H_2(–, s, p), D_2(–, s, o)
  For odd J', H_2(+, a, o), D_2(+, a, p)
- d $^3\Pi_u^+$ — For even J', H_2(+, a, o), D_2(+, a, p)
  For odd J', H_2(–, s, p), D_2(–, s, o)

Q-branch should be measured!

- Due to selection rule s $\nleftrightarrow$ a,

  ΔJ = 0 corresponds to d $^3\Pi_u^-$ (Q-branch),

  $\Delta J = \pm$ 1 to d $^3\Pi_u^+$ (R and P branches).

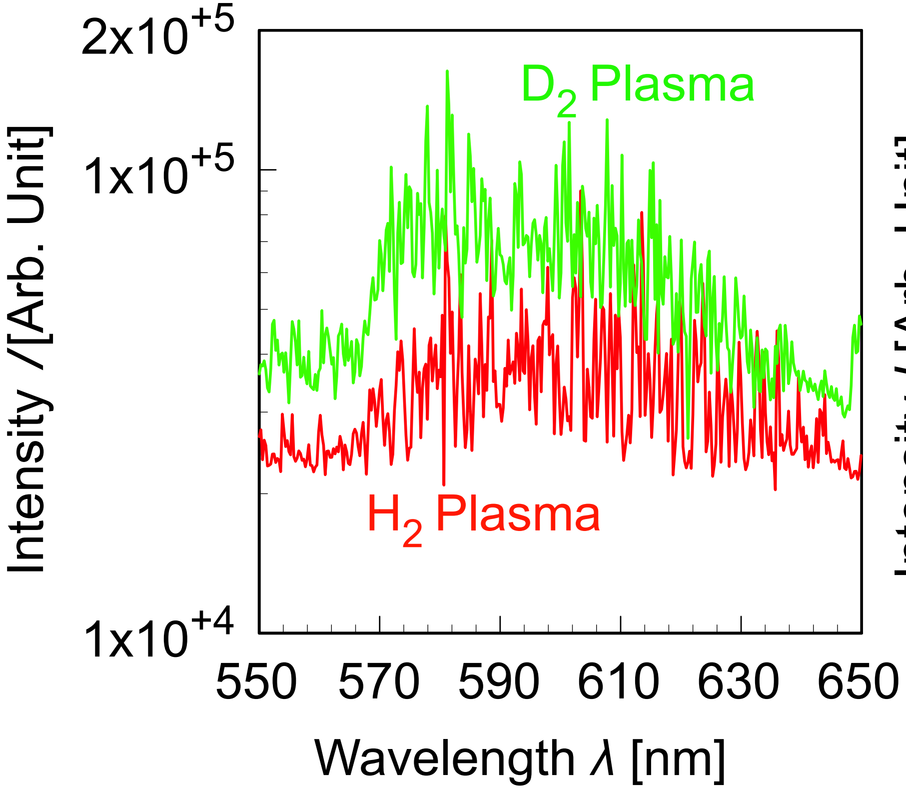
  - d $^3\Pi_u^+$ state must not be chosen, since its coupling with level e $^3\Sigma_g^+$ is too strong, in addition to the respect that d $^3\Pi_u^+$ state can predissociate.

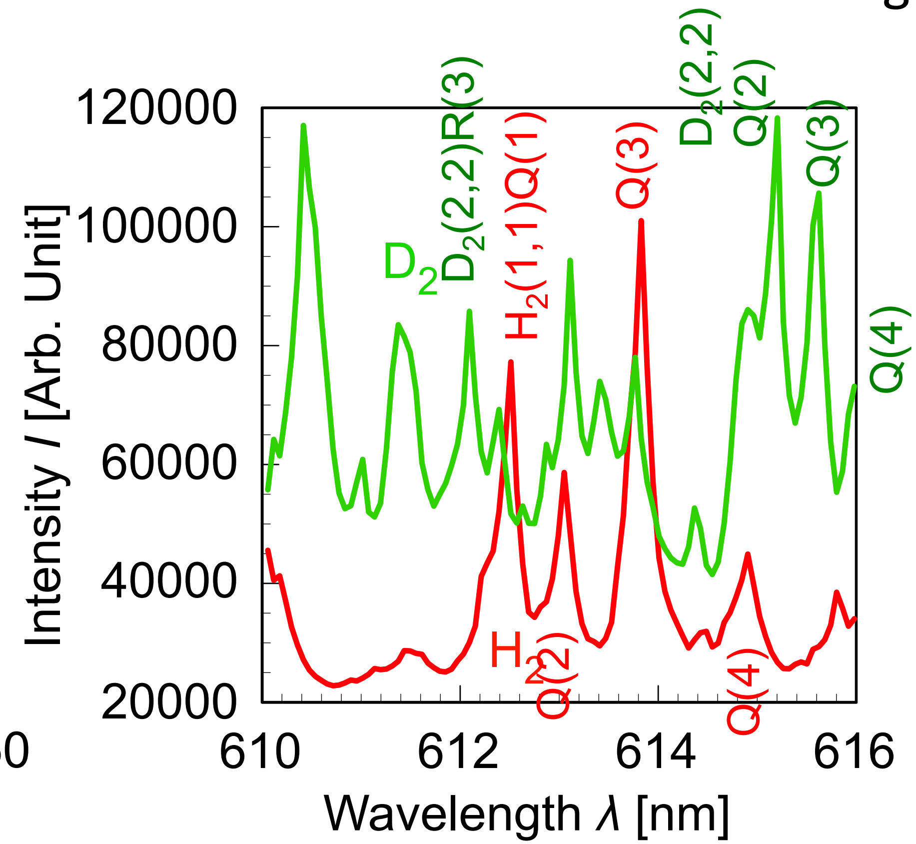
- P and R branches are also known to show anomaly with respect to Hönl-London factor.

- Therefore, we must examine **Q-branch**.

4. Results 1.

- Observed Fulcher-α band spectra d $^3\Pi_u \rightarrow$ a $^3\Sigma_g^+$





- Imaging Monochromator Spectrograph MS3504i, SOL Instruments Ltd.,
- Line density 1800 mm^{-1}, blaze 400 nm (resolution 0.04 nm)
- Cooled CCD Detector DU420A-OE, Andor Technology Ltd.

5. Data Analysis for Population Density

- Line intensity for the transition from the upper state (d, v', J') to the lower state (a, v'', J'') as $I_{\mathrm{a}v''J''}^{\mathrm{d}v'J'}$, is given by

$$I_{\mathrm{a}v''J''}^{\mathrm{d}v'J'} = \frac{hc}{\lambda_{\mathrm{a}v''J''}^{\mathrm{d}v'J'}} A_{\mathrm{a}v''J''}^{\mathrm{d}v'J'} N_{\mathrm{d}v'J'}$$

where

- h — the Planck constant
- c — velocity of light
- $\lambda_{\mathrm{a}v''J''}^{\mathrm{d}v'J'}$ — wavelength of the transition
- $A_{\mathrm{a}v''J''}^{\mathrm{d}v'J'}$ — corresponding transition probability
- $N_{dv'J'}$ — number density of the level (d, v', J')

The transition probability

- The transition probability is given by

$$A_{\mathrm{a}v''J''}^{\mathrm{d}v'J'} = \frac{16\pi^3}{3h\varepsilon_0\left(\lambda_{\mathrm{a}v''J''}^{\mathrm{d}v'J'}\right)^3}\left(\overline{R}_{\mathrm{e}}\right)^2 q_{v'v''}\frac{S_{J'J''}}{2J'+1}$$

  – where
    - ε_0 — vacuum permittivity
    - $\left(\overline{R}_{\mathrm{e}}\right)^2$ — the transition moment
    - $q_{v'v''}$ — the Franck-Condon factor
    - $S_{J'J''}$ — the Hönl-London factor,
    - $S_{J'J''}{}^{Q} = J' + 1/2$

Determination of the rotational temperature of the upper state (d, *v'*):

- Then, we have following equation to determine the rotational temperature of the upper state (d, *v'*):

$$N_{\mathrm{d}v'J'} = \frac{N_{\mathrm{d}v'}(2J'+1)g_{as}^{J'}\exp\left[-\frac{F_{\mathrm{d}}(J',v')}{kT_{\mathrm{rot}}^{\mathrm{d}v'}}\right]}{\sum_{J'}\left\{(2J'+1)g_{as}^{J'}\exp\left[-\frac{F_{\mathrm{d}}(J',v')}{kT_{\mathrm{rot}}^{\mathrm{d}v'}}\right]\right\}}$$

  - $F_{\mathrm{d}}(J', v')$: Energy level of state (d, *v'*, *J'*)

Statistical Weight

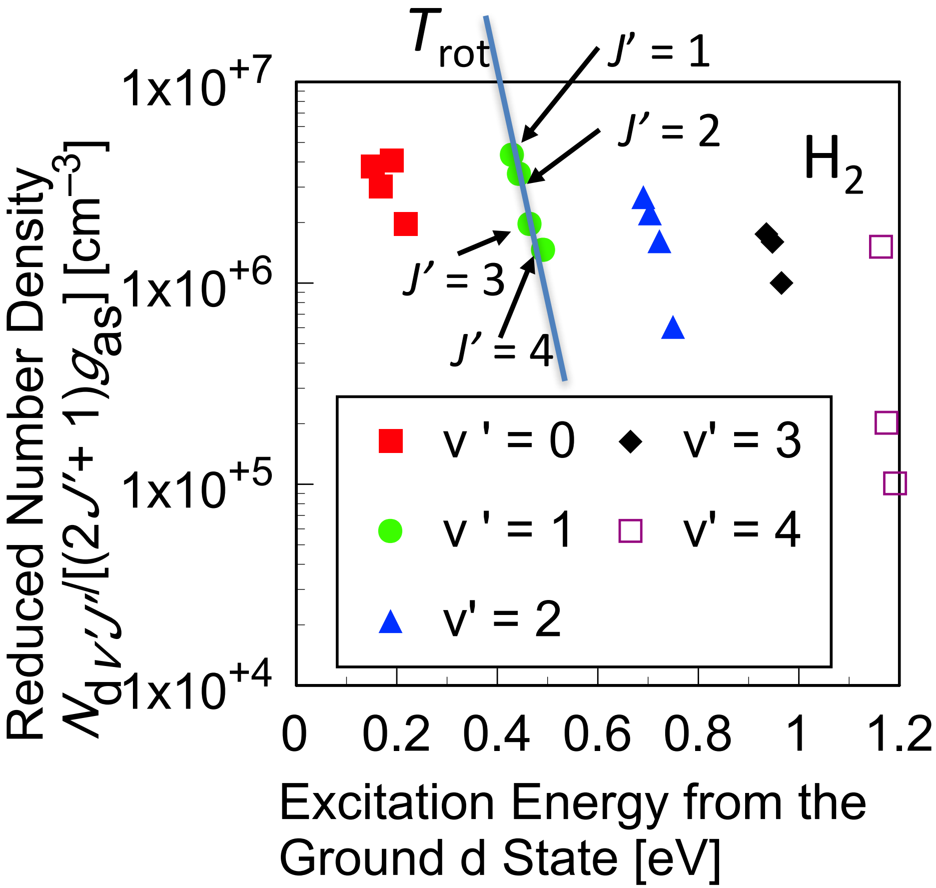
- For H_2,
  - For J = 2, 4, ..., of d $^3\Pi_u^-$ (= para), $g^H{}_a = 1$
  - For J = 1, 3, ..., of d $^3\Pi_u^-$ (= ortho), $g^H{}_s = 3$

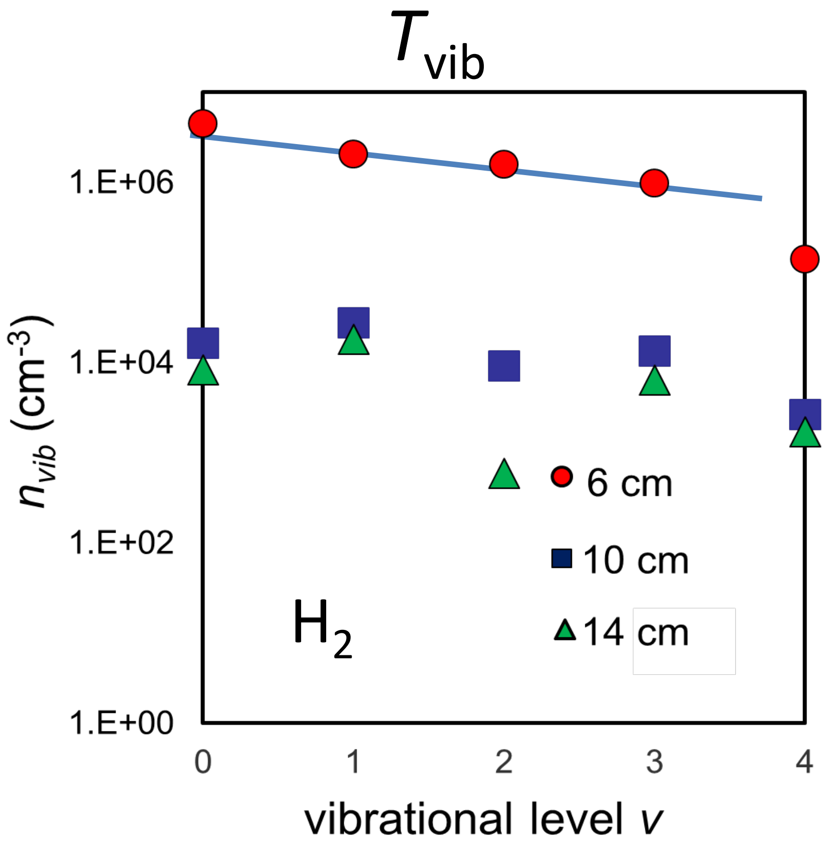
- For D_2,
  - For J = 2, 4, ..., of d $^3\Pi_u^-$ (= ortho), $g^D{}_s = 6$
  - For J = 1, 3, ..., of d $^3\Pi_u^-$ (= para), $g^D{}_a = 3$

6. Results and discussion

6.1 Boltzmann plots and rot-vibrational distributions of d state

(A) H_2 plasma

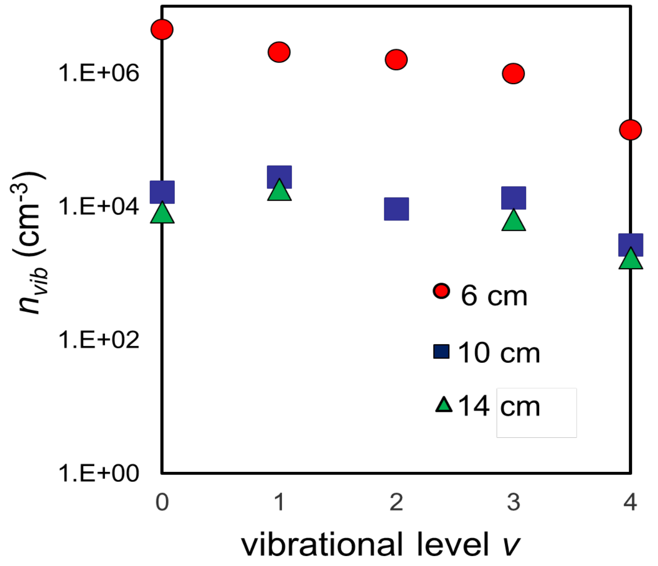




- T_{vib} ~ 0.39 – 0.41 eV over $0 \leq v' \leq 3$, almost independent of z.

6. Results and discussion

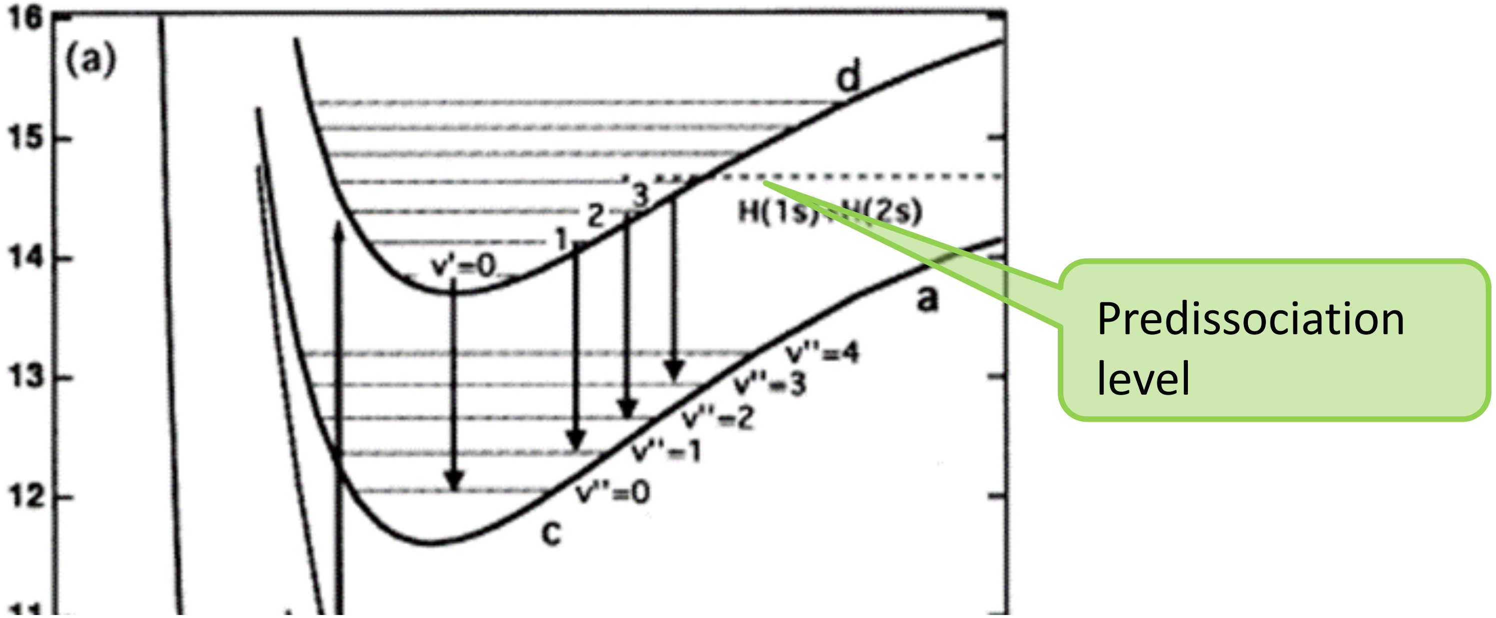
6.1 Boltzmann plots and vibrational distributions of d state (Contd.)



Levels v' = 0 – 3 Characterized by T_{vib}.

Level v' = 4

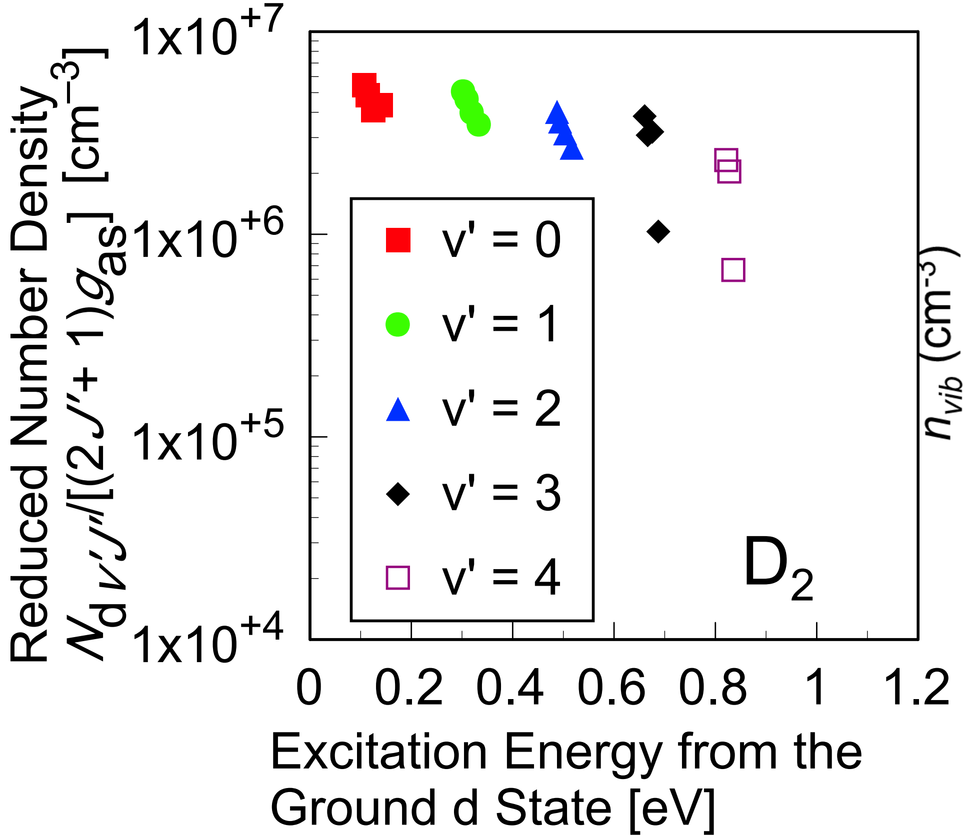
$n(v'$ = 4) is found to be much less populated than the extrapolated value from 0 ≤ v' ≤ 3, due to predissociation level to H(1s) + H(2s) states between v' = 3 and 4 of d state.

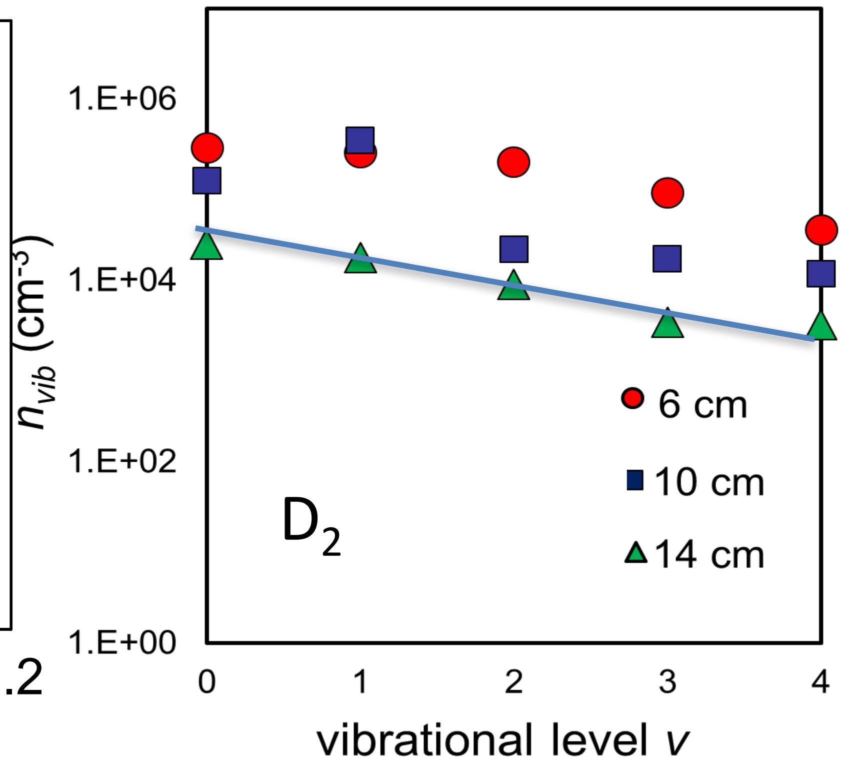


6. Results and discussion

6.1 Boltzmann plots and rot-vibrational distributions of d state

(B) D_2 plasma

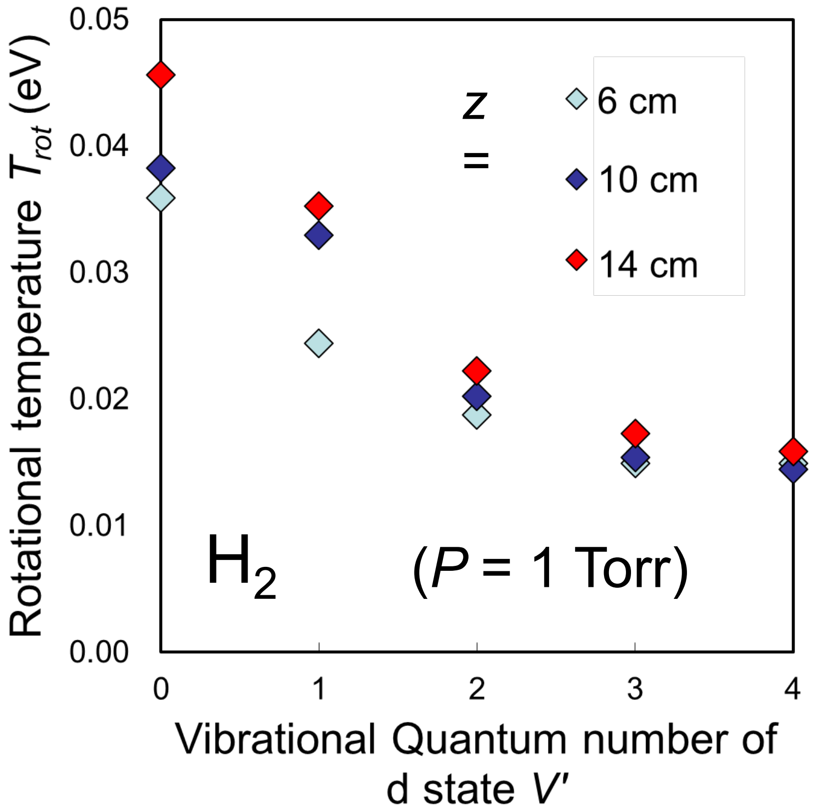


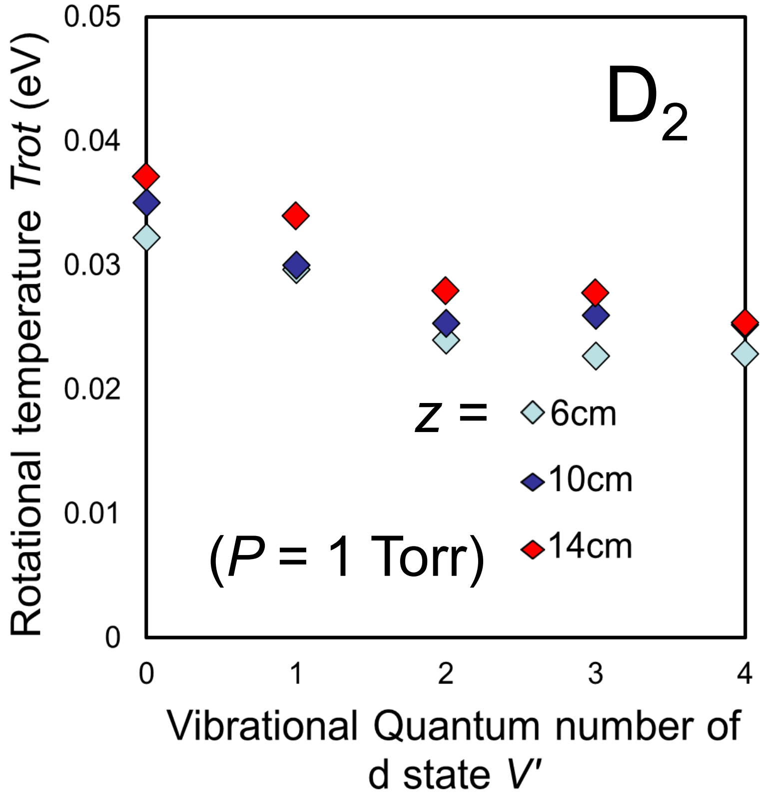


- T_{vib} ~ 0.39 – 0.41 eV, almost the same value with that of H_2.
- $n(v' = 4)$ is also described with the same T_{vib} with $0 \leq v' \leq 3$, due to predissociation level at $v' \geq 4$.

6. Results and discussion

6.2 T_{rot} of each vibrational level of d state





- **Essential finding**

$T_{rot}^{dv'}(H_2) > T_{rot}^{dv'}(D_2)$ for $v' = 0, 1$.

$T_{rot}^{dv'}(H_2) < T_{rot}^{dv'}(D_2)$ for $v' = 2 – 4$.

Both for H_2 and D_2

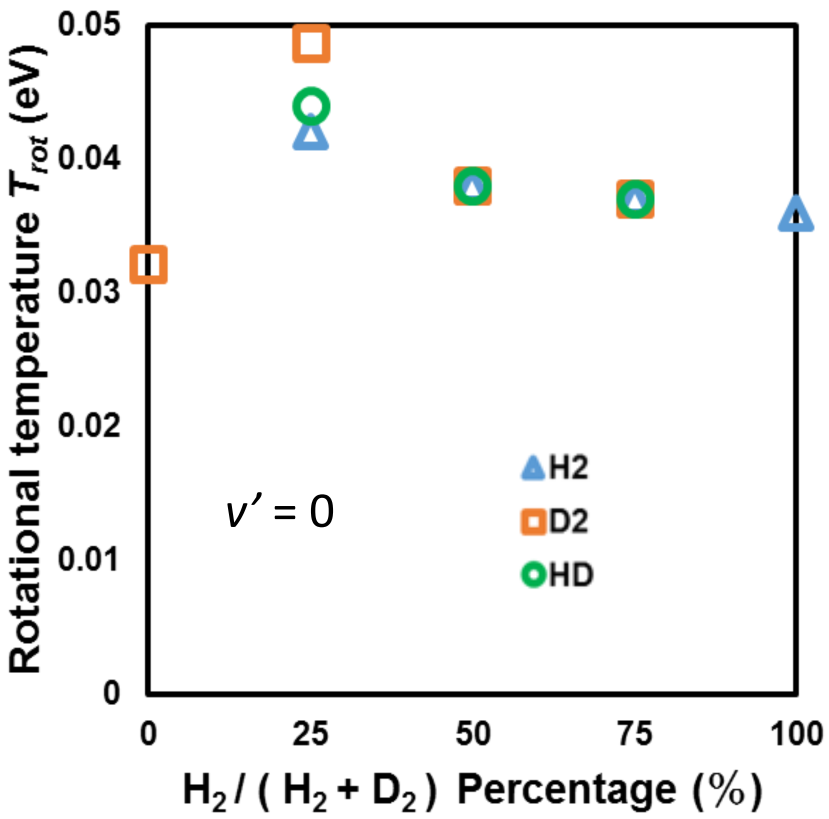
- T_{rot} becomes higher as flowing to the downstream, because of energy relaxation from electron and vibration to rotation.
  - Energy deposition process
    - Microwave → electron translation → (collisional excitation) → H_2 vibrations → (Relaxations) → H_2 rotations and translations
- The higher vibrational states have lower T_{rot}.
  - Angular momentum of H_2 molecule should be conserved in $H_2(X) + e^- \rightarrow H_2(d : v', J') + e^-$.
  - The higher the v' level, the larger the moment of inertia.
    - $I_X\omega_X = I_{dv1}\omega_{dv1} = I_{dv2}\omega_{dv2}$
    - If $I_{dv2} > I_{dv1}$, then $\frac{1}{2}I_{dv2}\omega_{dv2}^2 < \frac{1}{2}I_{dv1}\omega_{dv1}^2$ Hence, $T_{rot}^{v2} < T_{rot}^{v1}$

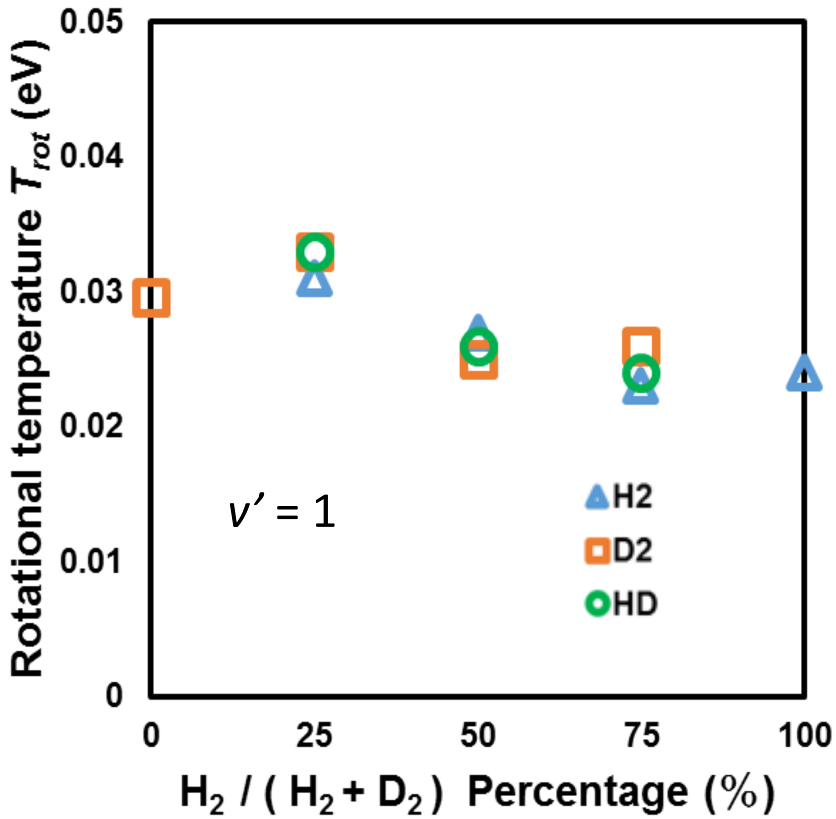
Difference between H_2 and D_2

- The vibrational quanta are larger for lighter isotopic molecules.
- The difference in T_{rot} will be more emphasized for H_2 than for D_2.
- The difference in the thermal conductivity should be also considered.

6. Results and discussion

6.3 Comparison of T_{rot} of H_2/HD/D_2 in H_2-D_2 plasma

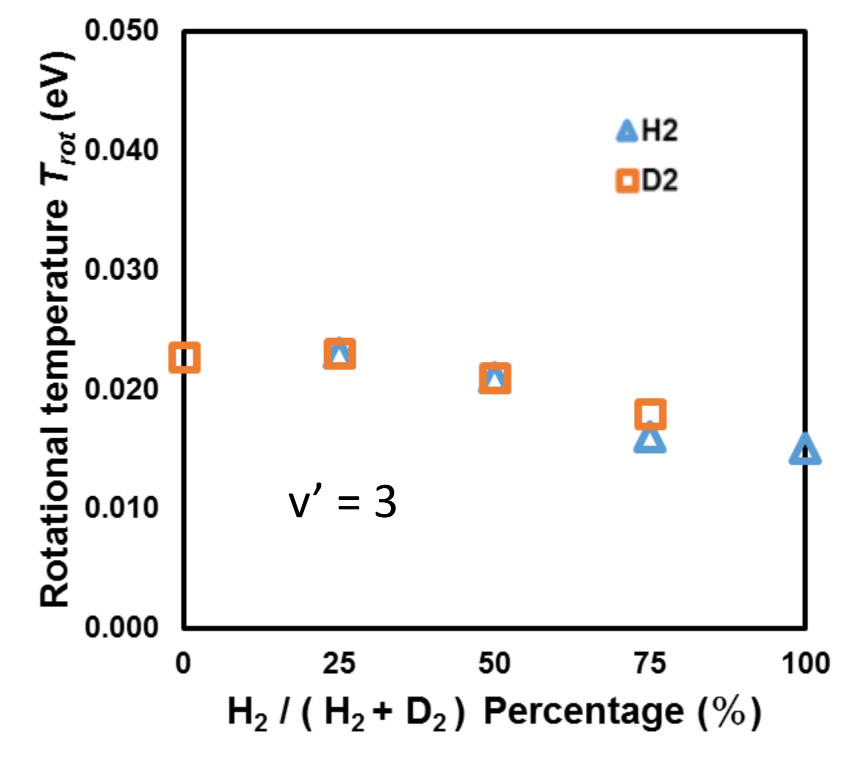




Levels with $v' = 2$ cannot be analyzed due to spectral overlapping.

6. Results and discussion

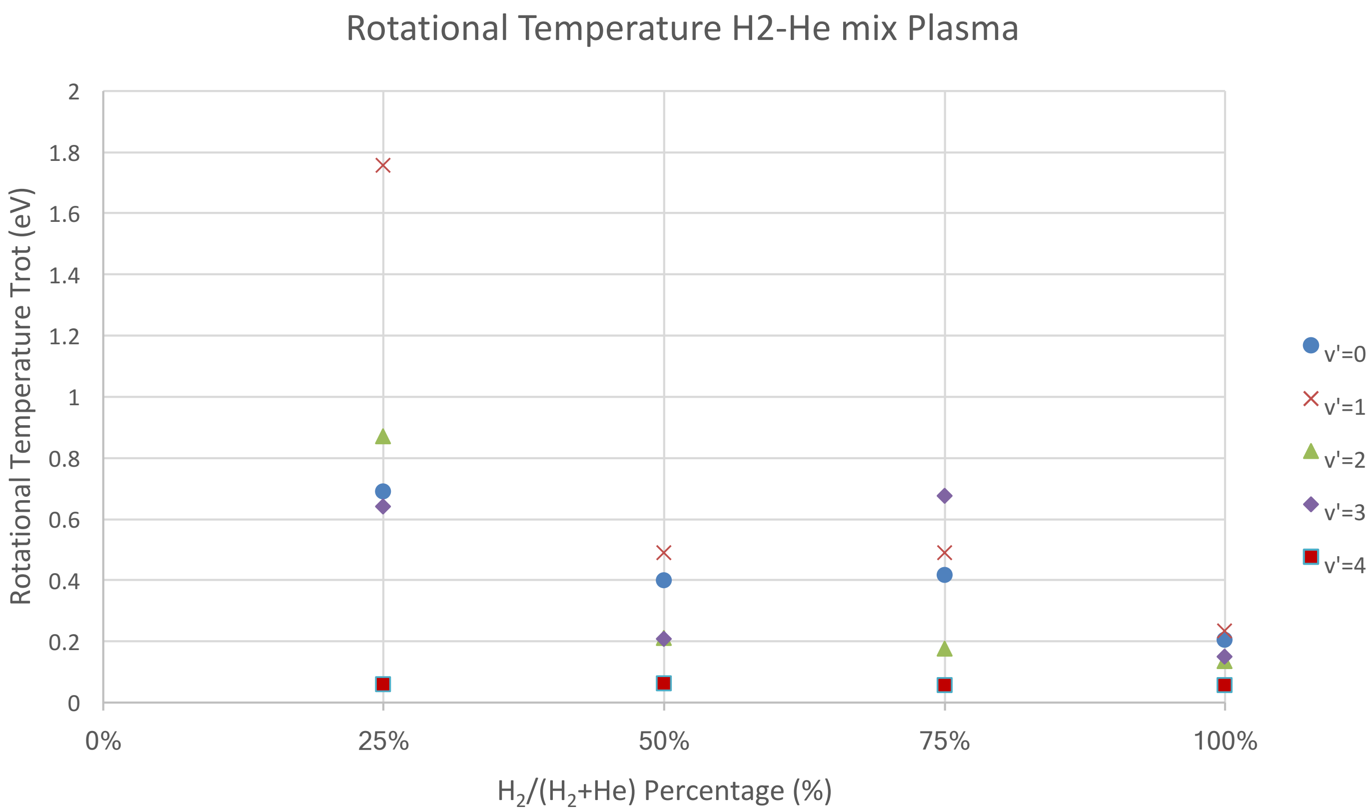
6.3 Comparison of T_{rot} of H_2/HD/D_2 in H_2-D_2 plasma (Contd.)



- Generally, heavier isotopic molecules have higher T_{rot}, although the difference is not so remarkable and with exceptions
- The higher concentration of D_2 makes T_{rot} higher, except for pure D_2 discharge.
- The heavier, the smaller thermal conductivity.
- The smaller the vibrational quanta, the more frequent the collisional relaxation becomes.
- It is unclear why pure D_2 discharge has lower T_{rot} than the that with H_2:D_2 = 1:3 mixture

For H_2 – He mixture plasma

- This time, microwave power is much larger than H_2-D_2 experiments, so the direct comparison is not appropriate.
  - But, in general, it is found that He admixture makes T_{rot} higher.



7. Summary

- We examined Fulcher-α band of microwave discharge H_2/D_2 plasma by OES measurement.
  - T_{rot} increased as the plasma flowed to the downstream direction.
  - T_{rot} monotonically became lower for higher v' levels, while T_{vib} was almost constant ~ 0.4 eV.
- $T_{rot}^{dv'}(H_2) > T_{rot}^{dv'}(D_2)$ for $v' = 0, 1$, while $T_{rot}^{dv'}(H_2) < T_{rot}^{dv'}(D_2)$ for $v' = 2 – 4$.
- The higher concentration of D_2 resulted in increase in T_{rot}, except for pure D_2 discharge.
- He admixture made T_{rot} higher.