Spectroscopic Examination of Fulcher-α Band of Microwave Discharge H₂-D₂ and H₂-He Plasmas

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• 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 H₂ 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 H₂/D₂ 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 $T_{\text{vib}}$ and $T_{\text{rot}}$ of microwave discharge $\text{H}_2$, $\text{D}_2$ mixture plasmas, and $\text{H}_2$-$\text{He}$ mixtures of $\text{H}_2$/HD/D$_2$-Fulcher-α band ($d\,^3\Pi_u \rightarrow a\,^3\Sigma_g^+$) – and to find their differences, if any.

• To examine dependence of $T_{\text{vib}}$ and $T_{\text{rot}}$ of $\text{H}_2$/HD/D$_2$ on the $\text{H}_2$/D$_2$ mixture ratio.
2. Experiments

- Optical Emission Spectroscopy (OES) Measurement

- Ultimate pressure: 0.01 Torr
- Discharge gases: H₂, D₂, 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
At each position specified above, we conduct OES measurement of Fulcher-α band spectrum.
3. Remarks for Data Analysis

— Fulcher-α band

- $d \, ^3\Pi_u \rightarrow a \, ^3\Sigma^+_g$
- 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 $0 \rightarrow 0$)
  - $(-) \leftrightarrow (+)$ $\cdot$ $g \leftrightarrow u$
  - $s \leftrightarrow s$, $a \leftrightarrow a$, $s \leftrightarrow a$
  - $\Sigma^+ \leftrightarrow \Sigma^-$ as Hund (a, b)

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

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 \( J' \), \( H_2(-, s, p) \), \( D_2(-, s, o) \)
Due to selection rules, $\Delta J = 0$ 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 \( \text{d } ^3\Pi_u \rightarrow \text{a } ^3\Sigma_g^+ \)

- 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 \((d, \nu', J')\) to the lower state \((a, \nu'', J'')\) as \(I_{av''J''}^{dv'J'}\), is given by

\[
I_{av''J''}^{dv'J'} = \frac{hc}{\lambda_{av''J''}} A_{av''J''}^{dv'J'} N_{dv'J'}
\]

where

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

• The transition probability is given by

\[ A_{av''J''}^{dv'J'} = \frac{16\pi^3}{3h\varepsilon_0 \left( \lambda_{av''J''}^{dv'J'} \right)^3 \left( R_e \right)^2} q_{v'v''} \frac{S_{J'J''}}{2J' + 1} \]

— where

• \( \varepsilon_0 \) — vacuum permittivity

• \( \left( R_e \right)^2 \) — 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'):

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

\[- F_d(J', v') : \text{Energy level of state (d, v', J')} \]
Statistical Weight

• For $H_2$,
  – For $J = 2, 4, \ldots$, of $d^3\Pi_u^-$ (= para), $g^H_a = 1$
  – For $J = 1, 3, \ldots$, of $d^3\Pi_u^-$ (= ortho), $g^H_s = 3$

• For $D_2$,
  – For $J = 2, 4, \ldots$, of $d^3\Pi_u^-$ (= ortho), $g^D_s = 6$
  – For $J = 1, 3, \ldots$, 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\textsubscript{2} plasma

- \( T_{\text{vib}} \sim 0.39 - 0.41 \text{ eV over } 0 \leq v' \leq 3, \text{ almost independent of } z.\)
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 $0 \leq v' \leq 3$, 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

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

6.2 $T_{\text{rot}}$ of each vibrational level of d state

**Essential finding**

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

$T_{\text{rot}}^{d v'}(H_2) < T_{\text{rot}}^{d v'}(D_2)$ for $v' = 2 - 4$. 
Both for $H_2$ and $D_2$

- $T_{\text{rot}}$ becomes higher as flowing to the downstream, because of energy relaxation from electron and vibration to rotation.
  
  – Energy deposition process

  - Microwave $\rightarrow$ electron translation $\rightarrow$ (collisional excitation) $\rightarrow$ $H_2$ vibrations $\rightarrow$ (Relaxations) $\rightarrow$ $H_2$ rotations and translations

- The higher vibrational states have lower $T_{\text{rot}}$.
  
  – Angular momentum of $H_2$ molecule should be conserved in $H_2(X) + e^- \rightarrow H_2(d : \nu', J') + e^-$. 
  
  – The higher the $\nu'$ level, the larger the moment of inertia.

  - $I_X \omega_X = I_{d\nu_1} \omega_{d\nu_1} = I_{d\nu_2} \omega_{d\nu_2}$
  
  - If $I_{d\nu_2} > I_{d\nu_1}$, then $\frac{1}{2} I_{d\nu_2} \omega_{d\nu_2}^2 < \frac{1}{2} I_{d\nu_1} \omega_{d\nu_1}^2$ Hence, $T_{\text{rot}}^{\nu_2} < T_{\text{rot}}^{\nu_1}$
• The vibrational quanta are larger for lighter isotopic molecules.
• The difference in $T_{\text{rot}}$ will be more emphasized for $\text{H}_2$ than for $\text{D}_2$.
• The difference in the thermal conductivity should be also considered.
6. Results and discussion

6.3 Comparison of $T_{\text{rot}}$ 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 $T_{\text{rot}}$ of H$_2$/HD/D$_2$ in H$_2$-D$_2$ plasma (Contd.)

- Generally, heavier isotopic molecules have higher $T_{\text{rot}}$, although the difference is not so remarkable and with exceptions.
- The higher concentration of D$_2$ makes $T_{\text{rot}}$ 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 $T_{\text{rot}}$ 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 $T_{\text{rot}}$ higher.
7. Summary

• We examined Fulcher-α band of microwave discharge H₂/D₂ plasma by OES measurement.
  • $T_{\text{rot}}$ increased as the plasma flowed to the downstream direction.
  • $T_{\text{rot}}$ monotonically became lower for higher $\nu'$ levels, while $T_{\text{vib}}$ was almost constant $\sim 0.4$ eV.
  • $T_{\text{rot}}^{d\nu'}(H_2) > T_{\text{rot}}^{d\nu'}(D_2)$ for $\nu' = 0, 1$, while $T_{\text{rot}}^{d\nu'}(H_2) < T_{\text{rot}}^{d\nu'}(D_2)$ for $\nu' = 2 - 4$.
  • The higher concentration of D₂ resulted in increase in $T_{\text{rot}}$, except for pure D₂ discharge.
  • He admixture made $T_{\text{rot}}$ higher.