

Fulcher- α Band Spectra in Mixed Hydrogen Isotope Plasmas

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The Fulcher- α ro-vibronic band spectra in mixed hydrogen isotope plasmas were investigated. The spectra were measured in H₂ and D₂ mixed plasmas as well as calculated for D₂ and T₂ mixed plasmas. In both the measured and calculated spectra, several overlaps were observed. In order to avoid an error in the ro-vibrational temperature estimation, detailed assignment of the spectral line shapes are required. The coronal model combined with a fitting procedure which is not largely disturbed by the decrease in the number of available lines was adopted to evaluate the ro-vibrational temperatures. The estimated vibrational temperatures of H₂, D₂, and HD isotopes were not fully equilibrated, and may be explained by a combination of the electron-impact and Eley-Rideal surface recombination processes. The rotational temperatures, on the other hand, were basically in equilibrium, and suggest a correlation with the surface temperature.

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1. Introduction

In the edge region of fusion relevant devices, ro-vibrationally excited hydrogen molecules play significant roles in the molecular assisted recombination (MAR) process, and in the production of the so-called Franck-Condon atoms which determine the neutral penetration depth across the separatrix. The diagnosis of the ro-vibrational temperatures of hydrogen molecules can give helpful clues to understand detailed molecular and atomic processes related to such phenomena. In the analysis of the ro-vibrational population, the Fulcher- α band Q-branch spectra ($d^3\Pi_u^- \rightarrow a^3\Sigma_g^+$) have been used since their transition wavelengths are in the visible region and there are relatively few perturbations. Up to now, the Fulcher- α band have been measured mainly in plasmas containing single hydrogen isotopes like H₂ or D₂ [1–4]. From a practical point of view, however, it is important to investigate mixed hydrogen isotopes [5]. In the mixed condition, overlaps of the spectra can cause an error in the temperature estimation. This can be severer under strong magnetic fields because of the Zeeman split in the spectral line shapes [6]. Moreover, the difference in the ro-vibrational temperatures with respect to the molecular species is expected. Generally, the electron impact processes, surface recombinations, and relaxations by inter-molecular collisions determine the ro-vibrational temperatures. The thorough picture of these excitation mechanisms has not yet been fully re-

vealed. In the present paper, we have performed measurements of the Fulcher- α band spectra in H₂ and D₂ mixture plasmas and calculations of those in D₂ and T₂ mixture plasmas.

2. Methods

2.1 Calculation of the Fulcher- α ro-vibronic spectra

The Hamiltonian of the valence electron including the ro-vibronic and spin-orbit interaction energies gives sufficiently precise energy levels in the range of the present experimental resolution. With the aid of the Born-Oppenheimer (BO) approximation, the ro-vibronic Hamiltonian matrix is calculated numerically using a semi-empirical expansion [7]. The obtained ro-vibronic energies as a summation of the electronic, vibrational, and rotational energies are

$$E_{\text{ro-vibronic}} \simeq T_e + \omega_e \left(v + \frac{1}{2} \right) + B_e N(N+1) + \dots, \quad (1)$$

where T_e is the electronic energy, ω_e is a vibrational constant, B_e is a rotational constant, v and N are, respectively, vibrational and rotational quantum numbers. The spin-orbit interaction Hamiltonian can be evaluated based on the spherical tensor techniques [6,8]. These calculations were performed using the molecular constants compiled in a database [9]. For T₂ and DT, part of the constants does not exist, and the extrapolation using the relationship of the

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reduced mass [7] was used. The extrapolation based on the constants of H₂ gives the minimum error.

The Fulcher- α ro-vibronic transition intensity $I_{av''N''}^{dv'N'}$ between the upper ($d^3\Pi_u^-$) and lower ($a^3\Sigma_g^+$) states is expressed as

$$I_{av''N''}^{dv'N'} = h\nu_{av''N''}^{dv'N'} n_{dv'N'} A_{av''N''}^{dv'N'} \quad (2)$$

where $h\nu_{av''N''}^{dv'N'}$ is the photon energy, $n_{dv'N'}$ is the d -state population, and $A_{av''N''}^{dv'N'}$ is the spontaneous emission coefficient. The population $n_{dv'N'}$ can be deduced using the coronal model as described below. The spontaneous emission coefficient $A_{av''N''}^{dv'N'}$ is defined as

$$A_{av''N''}^{dv'N'} \equiv \frac{64\pi^4}{(4\pi\epsilon_0)^3} \nu_{av''N''}^{dv'N'}{}^3 \frac{|\langle\phi'|\mu_e|\phi''\rangle|^2}{2N'+1}, \quad (3)$$

where μ_e is the transition dipolar moment. The factor $|\langle\phi'|\mu_e|\phi''\rangle|^2$ is expressed with a wave function $|\phi\rangle$ and the BO approximation as

$$|\langle\phi'|\mu_e|\phi''\rangle|^2 = \langle R_e \rangle^2 q_{v'v''} S_{N'N''}, \quad (4)$$

where $\langle R_e \rangle^2$ is the electronic dipolar transition moment, $q_{v'v''}$ is the Franck-Condon (FC) factor, and $S_{N'N''}$ is the Hönl-London (HL) factor. The FC factor can be found in a database [10] and the HL factor can be calculated based on the spherical tensor techniques [6]. For the Q-branch spectra ($\Delta N = 0$) the HL factor is obtained as

$$S_{N'N''} = [2 - \delta_{0,\Lambda'+\Lambda''}](2S'+1) \left(N' + \frac{1}{2} \right) \quad (Q), \quad (5)$$

where δ is Kronecker's delta, Λ is the projection of the total angular momentum \mathbf{L} onto the inter-nuclear axis, and S is the total spin quantum number.

2.2 Coronal model

The population in the excited states was estimated using the coronal model [4, 6, 11]. In the coronal equilibrium, the d -state population $n_{dv'N'}$ can be written by a balance between the electron-impact excitation from the electronic ground state ($X^1\Sigma_g^+$) and the radiative de-excitation to the a -state as

$$n_{dv'N'} = \frac{n_e \sum_{v,N} [n_{XvN} R_{XvN}^{dv'N'}]}{\sum_{v''N''} A_{av''N''}^{dv'N'}}, \quad (6)$$

where n_e is the electron density, n_{XvN} is the population in the X -state, and $R_{XvN}^{dv'N'}$ is the electron-impact excitation rate coefficient. Assuming the thermal equilibrium, the population n_{XvN} is expressed as

$$n_{XvN} = n_{Xv=0} \exp \left[-\frac{\Delta G(v)}{kT_{\text{vib},X}} \right] \times \frac{g_{\text{as}}(2N+1) \exp \left[-\frac{\Delta F(N,v)}{kT_{\text{rot},X}} \right]}{\sum_N^{\infty} g_{\text{as}}(2N+1) \exp \left[-\frac{\Delta F(N,v)}{kT_{\text{rot},X}} \right]}, \quad (7)$$

where $n_{Xv=0}$ is the population in the vibrational ground state, g_{as} is the nuclear-spin statistical weight, $\Delta G(v)$ and

Table 1 Plasma parameters for H₂ and D₂ experiments : neutral gas pressure (p_0), electron temperature (T_e), and electron density (n_e).

fueling gas	H ₂	D ₂	H ₂ + D ₂
p_0 (Pa)	13	18	22
T_e (eV)	3.1	3.7	3.1
n_e (m ⁻³)	5.4×10^{16}	4.9×10^{16}	5.9×10^{16}

$\Delta F(N, v)$ are, respectively, the vibrational and rotational energies from their ground states, and $T_{\text{vib},X}$ and $T_{\text{rot},X}$ are, respectively, the vibrational and rotational temperatures of the X -state. $T_{\text{vib},X}$ and $T_{\text{rot},X}$ can be deduced from the experimentally observed $n_{dv'N'}$ using Eqs. (6) and (7).

3. Experiments

The experiments were performed using a hollow-cathode discharge chamber [12] without a magnetic field. Plasma parameters and molecular emission were measured using, respectively, a double probe and optical emission spectroscopy. DC-glow discharge was sustained in the cathode region which had a diameter of 19 mm with three different fueling gases of H₂ (13 Pa), D₂ (18 Pa), and their equal mixture (22 Pa). The discharge current was fixed to 70 mA, and the discharge voltages were 295 V for H₂, 314 V for D₂, and 331 V for the mixed case. These discharge parameters resulted in the electron temperatures and densities of 3.1 eV and 5.4×10^{16} m⁻³ for H₂, 3.7 eV and 4.9×10^{16} m⁻³ for D₂, and 3.1 eV and 5.9×10^{16} m⁻³ for the mixed case evaluated using the double-probe which consisted of a glass insulator 8 mm in diameter and tungsten electrodes 0.5 mm in diameter and 7 mm in length separated by 3 mm. Note that in the mixed condition, the electron density was evaluated under an assumption that each ion species reaches its own sound velocity at the sheath edge [13]. The measured plasma parameters are listed in Table 1. Emission from the cathode region was collected using a objective lens and dispersed by a Czerny-Turner mounted spectrometer with a focal length of 1 m equipped with a 2400 Grooves/mm holographic grating. The dispersed spectrum was detected using a photo-multiplier tube detector (PMT : Hamamatsu R928). The measurements were performed using a slit width of 80 μm which gives a wavelength resolution of $\Delta\lambda_{\text{fwhm}} \approx 0.023$ nm.

4. Observation of the Fulcher- α Spectra in H₂ and D₂ Mixture Plasmas

The Fulcher- α band spectra were measured in the three different fueling gas conditions. In Fig. 1, the spectra observed in the H₂ and D₂ mixed case are shown in a wavelength range of 610 to 616 nm. Compared to the pure H₂ or D₂ case, several overlaps of the spectra are observed. The available (\circ) and overlapped (name of isotopes) Q-branch spectra are listed in Table 2. In the pure case, the

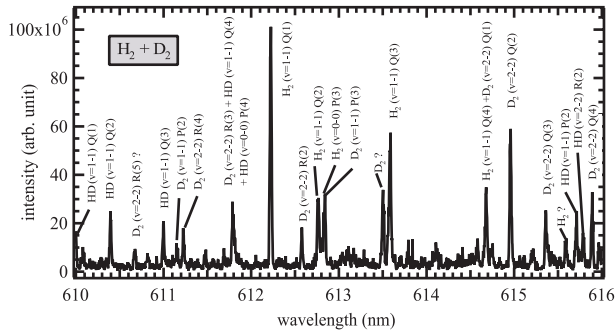


Fig. 1 Observed Fulcher- α band spectra in the H_2 and D_2 mixed gas condition.

Table 2 Available and overlapped Q-branch spectra for H_2 ($v \leq 3$), D_2 ($v \leq 4$), and HD ($v \leq 3$).

	H_2	D_2	HD
Q1 ($v = 0-0$)	○	○	○
Q2	○	○	○
Q3	○	○	○
Q4	D_2	○	
Q5	HD	○	
Q1 ($v = 1-1$)	○	○	○
Q2	H_2	○	○
Q3	○	○	○
Q4	D_2, HD	○	D_2, HD
Q5	H_2	○	
Q1 ($v = 2-2$)	H_2	H_2	○
Q2	○	○	D_2
Q3	D_2	○	H_2, D_2
Q4	D_2	HD	D_2
Q5	○	○	
Q1 ($v = 3-3$)	○	○	○
Q2	○	○	○
Q3	○	○	H_2
Q4	○	H_2	
Q5	○	H_2	
Q1 ($v = 4-4$)		○	
Q2		○	
Q3		○	
Q4		H_2, D_2	
Q5		H_2	

number of spectra without the overlap was 17 for H_2 ($v \leq 3$) and 24 for D_2 ($v \leq 4$). In the mixture case, on the other hand, the number of spectra without the overlap was 12 for H_2 , 19 for D_2 , and 9 for HD ($v \leq 3$). The number of available lines was decreased to 70 % for H_2 and 80 % for D_2 due to the overlap. Reduction of the available lines can cause an error in the ro-vibrational temperature analysis. For instance, it may be difficult to evaluate the vibrational temperature using the summation of bright rotational lines like Q(1) and Q(3) as representatives for H_2 , and Q(2) and Q(4) for D_2 [1]. Although this procedure can provide al-

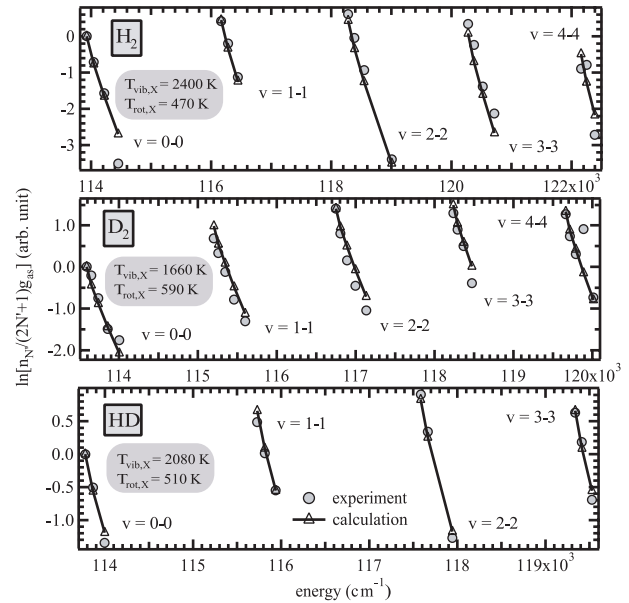


Fig. 2 Boltzmann plots of the measured d -state populations and the fitting results using the coronal model.

most correct temperatures for the pure case, the error becomes larger for the mixed case. We adopted a fitting procedure including all the available transitions so as to make the χ^2 minimum [4, 11]. This procedure is not largely disturbed by the decrease in the number of lines.

Figure 2 shows semi-logarithm plots, the so-called Boltzmann plots, of the measured d -state populations for H_2 , D_2 , and HD in the mixed gas condition. In the figure, the circles represent the experiments and triangles and lines represent the fitting results based on the coronal model calculation. The populations were divided by the nuclear-spin and rotational statistical weights. The evaluated ro-vibrational temperatures are shown in Table 3. The difference in $T_{\text{vib},X}$ is observed to be several hundreds K, while $T_{\text{rot},X}$ gives a similar value of around 500 K. In addition, $T_{\text{vib},X}$ and $T_{\text{rot},X}$ were normalized to the vibrational (ω_e) and rotational (B_e) molecular constants, respectively, as shown in the table. These ratios are the relative values to the pure H_2 case. The almost equal ratio of $T_{\text{vib},X}/\omega_e$ indicates that the difference in $T_{\text{vib},X}$ can be attributed to the difference of the molecular mass which determines the molecular constants. In contrast, $T_{\text{rot},X}/B_e$ depends on the isotopes.

In the present experimental configuration, there can be two major mechanisms of ro-vibrational excitations: electron-impact processes in plasma and surface recombinations. In the former processes, the dissociative attachment and the collisional radiative redistribution via $B^1\Sigma_u^+$ and $C^1\Pi_u^+$ states as well as the electron-impact pure ro-vibrational excitation give the excited populations. In the latter processes, the Eley-Rideal (ER) reaction, where the molecules are formed by the recombination of adsorbed and gas atoms: $A(\text{ads}) + B(\text{gas}) \rightarrow AB(\text{gas})$, gives ex-

Table 3 Estimated ro-vibrational temperatures.

molecule	H ₂	D ₂	H ₂ + D ₂		
			H ₂	D ₂	HD
$T_{\text{vib},X}$ (K)	2400 ± 100	1810 ± 140	2400 ± 120	1660 ± 150	2080 ± 80
$T_{\text{vib},X}/\omega_e$	1.0 (normalized)	1.1	1.0	0.98	1.0
$T_{\text{rot},X}$ (K)	410 ± 120	660 ± 60	470 ± 130	590 ± 60	510 ± 30
$T_{\text{rot},X}/B_e$	1.0 (normalized)	3.2	1.1	2.9	1.7

citation. Rettner has reported [14] that the ER reaction distributes binding energy of desorbed atoms to the rotational, vibrational, and translational energies in the order of several thousands K. Following a quantum mechanical calculation of the energy transfer by the intermolecular collisions [15], the vibration-translation, and rotation-translation relaxation time of H₂ can be estimated to be $\tau_{\text{vt}} \approx 0.4$ s and $\tau_{\text{rt}} \approx 1.4 \times 10^{-5}$ s, respectively. The relaxation time between the translational and surface temperature is much shorter. Considering the average residence time of molecules in the chamber, roughly estimated to be $\tau_{\text{res.}} \approx 1.6 \times 10^{-2}$ s using the 3-dimensional random-walk model with a system size of 0.1 m in the gaseous phase, one can say that the vibrational temperature is not fully equilibrated with the translational temperature ($\tau_{\text{vt}} \gg \tau_{\text{res.}}$). The observed $T_{\text{vib},X}$, therefore, may reflect the excitation results determined by a combination of the electron-impact and ER processes. Meanwhile, the rotational temperature can be basically regarded to be in equilibrium ($\tau_{\text{rt}} \ll \tau_{\text{res.}}$). So far, this relaxation process has been used for the deduction of the translational gas temperature [3] and extended to the measurement of the surface temperature [16]. The obtained almost constant value of $T_{\text{rot},X}$, thus, may suggest a correlation between the surface temperature. It should be pointed out, however, that the measured $T_{\text{rot},X}$ seems slightly higher than the expected surface temperature with the discharge input power of only 21 W. Further verifications involving the information of the surface temperature are needed.

5. Calculation of the Zeeman-Split Fulcher- α Spectra in D₂ and T₂ Mixture Plasmas

In order to apply the Fulcher- α band diagnostics to future fusion reactors, it is necessary to investigate D₂ and T₂ mixture plasmas under a strong magnetic field. As a preliminary analysis, we have calculated the expected spectral shapes with the Zeeman effect. Similar to the procedure described in the preceding section, the transition energy and intensity were evaluated from the Hamiltonian involving the energies of the ro-vibronic, spin-orbit interaction, and Zeeman effect [6]. For simplicity, equal d -state populations for all the molecular species and Boltzmann distributions of $T_{\text{vib},d} = 3000$ K and $T_{\text{rot},d} = 500$ K were assumed. Figure 3 shows the calculated Fulcher- α band spectra from the D₂, T₂, and DT molecules with no magnetic field and

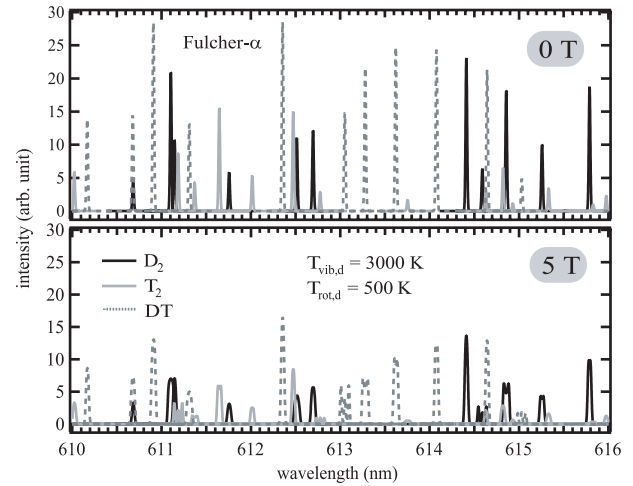


Fig. 3 Calculated Fulcher- α spectra for the D₂ and T₂ mixture plasmas.

5 T. As was observed in the H₂ and D₂ mixed case, several lines were overlapped even in the case of no magnetic field. With a magnetic field strength up to 5 T, corresponding to the ITER divertor, each rotational spectrum was split by the Zeeman effect and this further increases the number of overlaps. We can say from these results that a detailed analysis of the Zeeman-split spectral line shapes as well as the assignment of the overlapped spectra are significant for fusion applications.

6. Summary and Conclusion

The Fulcher- α band spectra were measured in H₂ and D₂ mixture plasmas, and were calculated for D₂ and T₂ mixture plasmas with a magnetic field strength of 5 T. In these mixed gas conditions, decreases in the number of available lines for analysis occurred by the overlaps of the rotational lines. Moreover, the Zeeman split of the spectra caused by the strong magnetic field can further increase the number of overlaps. In order to improve the accuracy of the ro-vibrational temperature measurement, a fitting procedure taking all the usable lines into consideration so as to give the minimum χ^2 was adopted. The experimentally estimated vibrational temperatures in the H₂ and D₂ mixed plasma were not fully equilibrated among the translational and rotational temperatures, and may be explained by a combination of the electron-impact and ER surface recombination processes. The rotational temperatures, on

the other hand, were basically equilibrated, suggesting a correlation with the surface temperature. However, to confirm these results, further investigations on the detailed processes will be conducted in a future work.

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