Reexamination of the hydrogen-molecular spectral constants relevant to the Fulcher-α band observed in H_2 discharge plasma

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The history of spectroscopic measurement of hydrogen molecules can be traced back to before 1930, and many studies have been done so far. In particular, the Fulcher-α band (d $^3\Pi_u$ – a $^3\Sigma_g^+$) is in the visible wavelength region and is convenient to observe spectroscopically. In general, when measuring the rotational temperature of a Fulcher-α band, the theoretical calculation of the emission spectrum of this band is applied, and the temperature is determined as a kind of best-fitting parameters. The purpose of this research is to re-examine of the spectroscopic constants, especially the rotational constants, of the hydrogen molecule used in that calculation.

Figure 1 shows the experimental setup used in this research. Hydrogen gas with its gas pressure of 1 Torr was irradiated with microwaves of 600 W and 2.45 GHz, and surface wave hydrogen plasma was generated in a quartz glass tube with an inner diameter of 26 mm, and optical emission spectrometry was performed. As a result of previous actinometric measurement experiments, it has already been found that the degree of dissociation is approximately 4% [1].

Table 1 shows the spectroscopic constants of the upper and lower levels of the Fulcher-α band, d $^3\Pi_u$ and a $^3\Sigma_g^+$ levels, respectively, published by Dieke and Blue *et al.* [2], together with those proposed to correct by the results of the present study based on the best-fitting method for the spectrum observed experimentally with theoretical calculation of the Fulcher-α of the hydrogen molecule. The molecular rotational constants in this study are calculated by the least-squares method, using the lower-level spectral constant as a variable from the position of the peak of the spectrum obtained from the theoretical formula and the experiment. In the course of fitting procedure, the systematic discrepancy was found

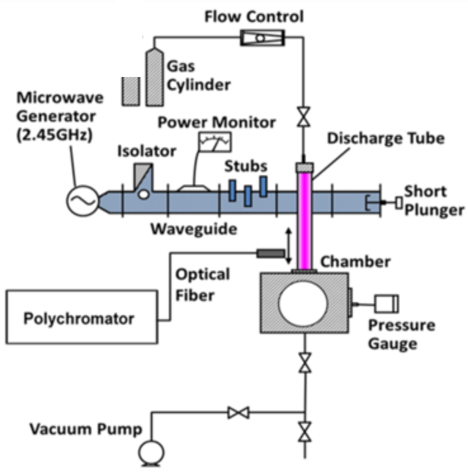

Figure 1. Experimental apparatus to generate microwave discharge H_2 plasma [1].

Table 1. Rotational constants in cm^{-1}of H_2 d $^3\Pi_u$ and a $^3\Sigma_g^+$ levels by (a) Dieke and Blue [2], and (b) the present study based on the best fitting of the spectrum observed experimentally with theoretical calculation.

(a)			(b)		
State	d $^3\Pi_u$	a $^3\Sigma_g^+$	State	d $^3\Pi_u$	a $^3\Sigma_g^+$
B_e	30.364	34.261	B_e	30.364	33.399
α_e	1.545	1.671	α_e	1.545	1.515
–	–	–	γ_e	–	0.049
D_e	0.0191	0.0216	D_e	0.0191	0.0216

between the observed one and the calculated one, which was found to be attributed to the rotational constant B_v of the lower level a $^3\Sigma_g^+$. Regarding the theoretical formula of the rotational energy for the upper-level d $^3\Pi_u$, the one proposed by Kado *et al* [3] was adopted. Meanwhile, for the better agreement of the wavelength of the spectral-lines, it was found that the systematic modification of the constant B_v is necessary from conventional linear function of v to quadratic one introducing another parameter γ_e as follows:

$$B_v = B_e - \alpha_e\left(v+\frac{1}{2}\right) + \gamma_e\left(v+\frac{1}{2}\right)^2.$$

Figure 2 shows an example of fitting. This is the case when the vibrational quantum numbers of the upper and the lower levels are both 0. Using the molecular constants proposed in this study, it was found that the mean-square error for the wavelength was improved from 0.124 to 0.028. Even now, the spectroscopic constants of H_2 molecule adopted so far need to be reexamined.

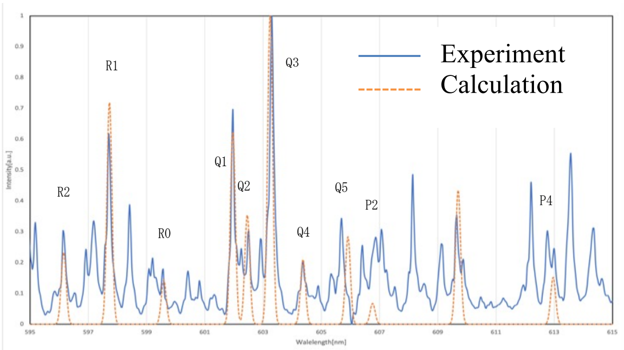

Figure 2. Example of spectrum fitting of the Fulcher-α band with $(v', v'') = (0,0)$.

References

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