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## 3100 A BAND SYSTEM OF WATER

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### INTRODUCTION

Although an exact calculation of the energy of the lowest triplet state of  $H_2O$  is lacking, previous theoretical approximations by Niira (1) and Laidler (2) predicted the lowest state of  $H_2O$  to lie below the first singlet state. A semiempirical estimate (3) of the singlet-triplet transition energy can be inferred from the work of La Paglia (4) to be  $\sim 3.8$  e.v. The importance of this triplet state in the radiation chemistry of water was discussed at the National Research Council's conference (5) on Basic Mechanisms in Radiobiology. Since that time at least three researchers in electron Physics, (Schulz (6), Raff (7), and Compton (3, 8)) have reported a broad inelastic loss process for electron in water vapour with an onset between 3.5 and 4.4 e.v. Larzul (9) and co-workers utilized a new differential absorption technique and detected a broad absorption in water between 2600 and 3000A. Henriksen (10) reported a few emission bands in the region 3090-3022A for a mixture of CO and Argon gas which proved to be elusive and did not appear following every filling of the discharge tube under identical conditions each time. It was suspected that these bands were due to an impurity of water vapour. Stickler and Arakawa (11) observed similar bands from Argon, at pressures of the order of 1 atm, excited by  $\alpha$  particles and associated them with the presence of water vapor. Brocklehurst (12) also found two band heads in an emission of Argon excited by X-rays at 3078 and 3088  $\pm 5A$  but he identified them as the Q-heads of the 3064 band (the O<sub>2</sub> band of  $2\epsilon^+ 2\pi^-$  transition) of OH molecule. We have observed (13) about fifteen bands in the region 3090-3020A from an excitation of a mixture of  $H_2O$ ,  $C_6F_6$  and Xenon. These bands, which were observed each time following every filling of the discharge tube, are analysed and the results are reported in this paper.

### EXPERIMENTAL METHOD AND RESULTS\*

Spectrograms of the 3100A system of the mixture of  $H_2O$ ,  $C_6F_6$  and Xenon were photographed on a Baush and Lomb Quartz spectrograph having a reciprocal dispersion of 4A/mm in the region 3000A. The mixture was excited in an ozonise type discharge tube using a four mega cycle exciter and the spectra were recorded on Kodak 103-0 plates using exposure times of three to four hours. Metal valves were used in the vacuum system which was baked at 400°C and evacuated to  $10^{-7}$  Torr. each time before filling the quartz ozoniser tube. Reagent grade xenon was obtained in break seal flasks from Air Reduction Company; the

\*Work done at the University of Georgia

hexafluorobenzene was quoted by Pierce Chemical Company to exceed 98% purity. High purity water was obtained from the Southeastern water Laboratory.

Excitation of the mixture of Xenon (at pressure of 50-75 cm of mercury) at  $C_6F_6$  (at pressures just to allow the discharge at room temperature) resulted in an appearance of a band system around 3400A, which has been assigned to XeF molecule by Krishnamachari, Narasimham and Singh (14), along with weak SiF and  $C_2$  Bands. When a very small amount of water vapor was added to the mixture of Xenon and hexafluorobenzene and the mixture was excited, a new band system around 3100A, along with 3043 A C-H band and above mentioned bands, appeared which could not be assigned to any known molecules like  $OH, C_2, CHO$  and  $H_2CO$ . The vibrational structure of this band system, which consists of Violet degraded bands extending from 3090-3020A, suggested that it should be assigned to  $H_2O$  molecule. On exciting the mixture of  $H_2O$  and xenon, the 3064 band of  $2\epsilon \times 2\pi$  transition of OH appeared suggesting that  $H_2O$  molecules were completely dissociated in H and OH radicals. The presence of  $C_6F_6$  vapour was found necessary to check the complete dissociation of  $H_2O$  molecules and to obtain this band system.

Measurements are made using iron arc emission lines as wavelength standards. The measured wavelengths and frequencies of the bands with visually estimated intensities are given in Table 1. The band at 3022.7 A and the vibrational bands associated with it are called the  $\alpha$  system ( ${}^3B_1 \rightarrow {}^1A_1$  transition) while the band at 3086.3 A and other bands associated with it are reported as  $\beta$  system ( ${}^3A_1 \rightarrow {}^1A_1$  transition).

## DISCUSSION

The lowest electron configuration of water molecule is reported (15) to be  $(1a_1)^2 (2a_1)^2 (1b_2)^2 (3a_1)^2 (1b_1)^2$ , and the ground state of the molecule belongs to  ${}^1A_1$  symmetry.  ${}^1B_1, {}^3B_1$  energy levels arise when an electron is excited from the  $b_1$  orbital to the Rydberg orbitals ( $3sa_1$ ) or ( $3pa_1$ ). The excitation of an electron from  $3a_1$  orbital to Rydberg orbital  $3sa_1$  and from  $1b_1$  orbital to Rydberg orbital  $3pb_1$  give rise to  ${}^3A_1, {}^1A_1$  states. The singlet - singlet transitions of  $H_2O$  molecules have been reported by Watson (16) and Wilkinson and Johnston (17) and Bell (18) respectively. These singlet - singlet (S→S) transitions are both spin and symmetry allowed transitions. The triplet→singlet (T→S) transitions,  ${}^3B_1 \rightarrow {}^1A_1$  and  ${}^3A_1 \rightarrow {}^1A_1$ , are symmetry allowed but spin forbidden. They should also appear as weak transitions due to spin orbit coupling  $\lambda^3 B_1$  and  ${}^3A_1$  states with  ${}^1A_1$  and  ${}^1B_1$  states respectively (19). In these transitions, the 0,0 band should be present and the totally symmetric vibrations would be directly superposed over the 0,0 transition.

The band spectra lying between 3090A - 3020A, which is attributed to T→S transitions, is weak. It is according to the expectations because the energy gap between singlet states  ${}^1A_1$  and  ${}^1B_1$  and triplet states  ${}^3B_1$  and  ${}^3A_1$  is great enough ( $\sim 5$  eV) which will allow a weak interaction only. The band at 3022.7A and the vibrational bands associated with it ( $\alpha$  system)

form a sequence  $\Delta v = 0$  with  $1595 \text{ cm}^{-1}$  as ground state ( $v''$ ) and  $1405 \text{ cm}^{-1}$  as excited state ( $v'$ ) fundamental. The bands at  $3086.3$ ,  $3081.5$ ,  $3076.5$ ,  $3072.3$  and  $3068.3\text{A}$  are mentioned as  $\beta$  system. These are (0,0), (1,1), (2,2), (3,3) and (4,4) transitions of a fundamental which has the value of  $1595 \text{ cm}^{-1}$  in the ground state and  $1647 \text{ cm}^{-1}$  in the excited state. Bell (18) has reported  $1407 \text{ cm}^{-1}$  as the value of ( $v_2$ ) totally symmetric bending vibration of  $\text{H}_2\text{O}$  molecule in  ${}^1\text{B}_1$  and  ${}^1\text{A}_1$  states respectively while the ground state value for this fundamental is  $1595 \text{ cm}^{-1}$ . The values of the ground and excited state bending vibration in the  $\alpha$ - and  $\beta$ - system reported here are nearly the same as given by Bell (18) in the singlet-singlet ( ${}^1\text{A}_1 \rightarrow {}^1\text{A}_1$  and  ${}^1\text{A}_1 \rightarrow {}^1\text{B}_1$ ) transitions (Table II).

The appearance of  $\Delta v = 0$  sequence only in both  $\alpha$  and  $\beta$  system suggests that the potential functions in ground and excited states are nearly alike. Similar to the spectra (20, 21) of  $\text{CF}_2$  and  $\text{SiF}_2$ , no evidence for an excitation of the symmetrical stretching vibration of triplet states of water molecule is found. This absence further suggests that the  $v_1'' = v_1'$  and that the bond-lengths are closely similar in the ground and excited states of both T $\rightarrow$ S transitions. These observations are in conformity with John's analysis (22) of the 0,0 band of the first member of np  $a_1$   ${}^1\text{B}_1$  series of  $\text{H}_2\text{O}$  and the conclusion (15) derived from the observation of simple Rydberg series with little vibrational structure that in the Rydberg states the X-H distance and H-X-H angle are not very different from the values in the ground states, and that the symmetry is the same, i.e.,  $\text{C}_{2v}$ . This type of intensity distribution is found (15) in many Rydberg transitions of polyatomic molecules, e.g.  $\text{CH}_2$ ,  $\text{CH}_3$  .... indicating that the ion has a potential function that is very similar to that of a neutral molecule. Taking all these facts into consideration, the  $\alpha$  system ( $3079.0\text{A} - 3022.7\text{A}$ ) and  $\beta$  system ( $3088.6\text{A} - 3068.3\text{A}$ ) are assigned to  ${}^3\text{B}_1 \rightarrow {}^1\text{A}_1$  and  ${}^3\text{A}_1 \rightarrow {}^1\text{A}_1$  transitions of  $\text{H}_2\text{O}$  molecule respectively.

Every band of  $\alpha$  and  $\beta$  system is accompanied with a band head towards longer wavelength at a separation of about  $25 \text{ cm}^{-1}$ . Bell (18) has also observed two strong peaks in the bands of  $\alpha$  systems of S $\rightarrow$ S transitions, which are separated by 19 and  $13 \text{ cm}^{-1}$  in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  respectively. The appearance of these band heads seems to be due to the rotational structure. These bands appear so weak that every attempt to resolve their rotational structure with an Ebert spectrograph (Plate factor -  $0.49\text{A}/\text{mm}$  in third order of grating) has failed so far.

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**TABLE I**  
**Assignments of H<sub>2</sub>O Band**

Band Head Designation	Wave-Length (Angstrom)	Wave-Number		<sup>(3</sup> B <sub>1</sub> - <sup>1</sup> A <sub>1</sub> )	
		Wave-Number (cm <sup>-1</sup> )	& System*	B System*	Assignment* (v' <sub>2</sub> ,v'' <sub>2</sub> )
A	3088.6	32368			
B	3086.3	32392		β <sub>1</sub>	(0,0)
C	3083.8	32418			
D	3081.5	32442		β <sub>2</sub>	(1,1)
E	3079.0	32469			
F	3076.5	32495	α <sub>4</sub>	(3,3)	β <sub>3</sub> (2,2)
G	3075.3	32518			
H	3072.3	32539		β <sub>4</sub>	(3,3)
I	3070.3	32561			
J	3068.3	32582		β <sub>5</sub>	(4,4)
K	3060.8	32661			
L	3058.2	32689	α <sub>3</sub>	(2,2)	β <sub>5</sub> (4,4)
M	3042.7	32857			
N	3040.2	32883	α <sub>2</sub>	(1,1)	
O	3022.7	33073	α <sub>1</sub>	(0,0)	

\* The excited state and ground state vibrational quantum numbers of v<sub>2</sub> fundamental of H<sub>2</sub>O are given.

**TABLE II**  
**Fundamental Frequencies of H<sub>2</sub>O**

	Ground State (a) <sup>1</sup> A <sub>1</sub>	Excited State			
		1240 A Band System (b) <sup>1</sup> B <sub>1</sub> <sup>1</sup> A <sub>1</sub>		3088 A Band System <sup>3</sup> B <sub>1</sub> <sup>3</sup> A <sub>1</sub>	
v <sub>1</sub> Cm <sup>-1</sup>	3657	3179	3268	-----	-----
v <sub>2</sub> Cm <sup>-1</sup>	1595	1407	1636	1405	1647
v <sub>3</sub> Cm <sup>-1</sup>	3756	-----	-----	-----	-----

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