New absorption bands of the $A^1\Sigma^+ - X^1\Sigma^+$ system of NaH molecule

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Abstract : Absorption spectra of the $A^1\Sigma^+ - X^1\Sigma^+$ system of the NaH molecule have been photographed on a 3.4 meter Ebert spectrograph at a reciprocal dispersion of 2.6 A mm^{-1} New data on the absorption spectra of the $A^1\Sigma^+ - X^1\Sigma^+$ system are reported. Rotational and vibrational analysis of the new bands have been made and the Rydberg-Klein-Rees potential energy curve of the $A^1\Sigma$ state has been calculated upto $v' = 25$

1. Introduction

The first studies on both the absorption and emission spectrum of NaH were undertaken by Hori [1]. It was found that somehow the vibrational numbering to the bands was assigned incorrectly which were later corrected by Olsson [2]. Pankhurst [3] reported the spectrum of NaH in emission of 66 bands involving $v'' = 0 - 8$ and $v' = 1 - 20$. This work was extended by Orth *et al* [4] and their results included the $v' = 0$ state. Studies on the rotational spectra of NaH and NaD have been made by Sastry *et al* [5]. Maki and Olson [6] reported observations of vibrational transitions in the infrared region $(v'' = 1 \leftarrow 0,3 \leftarrow 2)$. Rafi *et al* [7] performed experiments on the absorption spectra of the $A^1\Sigma^+ - X^1\Sigma^+$ system of NaH using the second order of a 3.4 meter Ebert spectrograph at a reciprocal dispersion of 2.6 Å mm^{-1}. They reported the new rotational structure of the transitions from $X^1\Sigma^+$ $v'' = 0,1)$ to $A^1\Sigma^+ (v' = 20 - 22, 13 - 25)$ and evaluated the spectroscopic constants of the observed bands. All these observations show that in the A state, the vibrational energy level spacing increases to a maximum value at $v = 9$ and then

decreases monotonically. Similar behavior is shown by the rotational constants where B_v is maximum at $v = 6$. This is the reason that the vibrational spacing is anomalous and the anharmonicity constant $\omega_e x_e$ is negative.

Studies by laser induced spectroscopy were also undertaken by a number of workers. Giroud and Nedlec [8] reported seven different NaH fluorescent series with $v' = 6 - 14$ fluorescing to $v'' \leq 15$. They also reported six different fluorescent series of NaD with $v' = 10 - 15$ fluorescing to $v'' \leq 20$. Brieger *et al* [9] reported excitation spectra of the (15, 0) band. Leopold *et al* [10] used tunable far-infrared radiation generated from the difference frequency between two CO_2 lasers in their studies on the $X^1\Sigma^+$ state of NaH. Magg and Jones [11] observed 19 transitions in a vibration-rotation spectrum of NaH using diode laser spectroscopy. It is found that laser spectroscopy was helpful in extending the $X^1\Sigma^+$ state of NaH to $v'' \leq 15$ but an extension of the $A^1\Sigma^+$ state beyond $v' \geq 20$ could not be made. As mentioned earlier, Rafi *et al* [7] managed to extend the $A^1\Sigma^+$ state to $v = 25$.

The spectroscopic constants of the $A^1\Sigma^+$ state have been determined by a number of workers. The vibrational numbering made by Hori [1] is incorrect. Fitting errors in the rotational (but not vibrational) constants of Pankhurst [3] have been pointed out by Orth et al [4]. Pardo et al [12] reproduce their B'_v values but there is inconsistency between their reported vibrational constants and $G(v')$ values. The constants produced by Orth et al [4] are, however, regarded as reliable and are recommended by Stwalley et al [13] to $v' = 20$ Rafi et al [7] determined the constants of NaH $X^1\Sigma^+$ ($v = 0$, 1) to $A^1\Sigma^+$ for $v'= 13$ to 22 from $v''=0$ and $v' = 18$ to 25 from $v'' = 1$.

The molecular constants of the $A^1\Sigma^+$ and $X^1\Sigma^+$ states of NaH have been used to determine their Rydberg-Klein-Rees (RKR) [14-16] potential curves. We presented as comment the RKR potential energy curve of the $A^1\Sigma^+$ state [17]. However, we describe below the full account of the studies made by us in the spectra of the $A^1\Sigma^+ - X^1\Sigma^+$ system.

2. Experimental method

The NaH molecule was formed in a 1.5 meter long steel pipe with a 2.5 cm inner diameter by placing 100 grams of spectroscopically pure sodium metal in an atmosphere of hydrogen. The steel tube was heated directly by a 10 kVA transformer giving 800 amperes at 10 volts. It was found that a temperature of 950°C gave the optimum results. The windows were cooled.

Table 1. Wave numbers (cm^{-1}) of the P and R branches of $A^1\Sigma^+ - X^1\Sigma^+$ system of NaH.

J	(18 – 1) R(J)	P(J)	(19 – 1) R(J)	P(J)	(20 – 1) R(J)	P(J)
0.	......	......	......			
1.	27424.50	......	27754.57	......	.. ...	28068.70
2.	27415.71	......	27745.84	......	28069.06	......
3.	......	27377.37	27730.72	27707.64	......	28031.45
4.	27380.57	27350.46	......	27678.19	28032.25	28003.61
5.	......	27317.28	27682.51	27646.20	28004.88	27969.76
6.	27321.25	27277.76	......	27606.70	27971.19	......
7.	27282.60	27232.53	27609.90	27560.50	27931.55	27883.47
8.	27238.23	27181.34	27564.44	27509.16	27885.50	27831.39
9.	27187.58	27124.41	27513.01	27451.51	27833.70	27773.34
10.	27131.18	27061.80	27456.07	27388.31	27775.75	......
11.	27069.08	26993.66	27393.24	27318.65	......	27639.64
12.	27001.33	26919.34	27324.00	27244.12	27642.47	27563.90
13.	26927.78	26839.59	27249.68	27163.66	......	27482.11
14.	26848.70	26754.30	27169.25	27077.17	27485.52	27394.85

15.	26763.94	26663.53	27083.37	26985.53	27398.21	27302 1:
16.	26673.67	26567.06	26992.12	26887.91	27306.09	27204 2'
17.	26577.97	26465.75	26894.77	26785.29	27208.22	271007
18.	26476.81	26358.60	26792.18	26677.05	27104.59	269919
19.	26370.18		26684.36	26563.89	26995.98	268776
20.			26571.38	......	26881.97	...
21.			26453.44	26322.38		
22.			26329.84	26193.74		
23.			26201.18	26060.57		
24.			26068.37	25922.81		
25.			25930.42	......		

J	(21 – 1) R(J)	P(J)	(22 – 1) R(J)	P(J)	(23 – 1) R(J)	P(J)
0.	......	......	28717.10	......	......	
1.	28379.56	28388.22*	28713.80	28704.35*	......	
2.	28388.22*	28372.34*	28704.35*	28688.69	.....	
3.	28372.34*	......	28688.38	28666.56*	.....	.. .
4.	......	28323.15*	28666.56*	28638.25	......	289511
5.	28323.15*	28288.82	280637.83	28603.97	28949.23	289163
6.	28289.14	28248.53	28602.54	28563.15	28913.64	288748(
7.	28248.89	28202.02	28561.30	28516.12	28871.72	.....
8	28202.41	28149.13	28514.45	..... .	28823.72	287736
9	28149.44	28090.62*	28461.14	28403.71	28769.55	287136
10.	28090.62*	28025.81	28401.39	. . . .	28708.98	28647 5'
11.	. .....	27955.15*	28335.96	... ..	28642.46	28575 5.
12.	27955.15*	27878.96*	.....	28189.45	28569 92	28496 9:
13.	27878.96*	27796.34	28186.39	......	28490.94	284126?
14.	27796.57	27708.35	28103.16	......	28406.47	28322 9:
15.	27708.65	27614.88			28315.80	28226 69
16.	27615.24	27515.54*			28218.99	.. ...
17.	27515.54*	27410.76			28116.33	28017 51
18.	27410.00	27300.60*			28008.69	2790472
19.	27300.60*	27185.25*			27895.58	27785.9:
20.	27185.25*	27064.53*			27776.29	276619:
21.	27064.53*	26938.29*			......	27533 10
22.	26938.29*	......			27522.25	27398 44
23.	......	26671.92			27387.74	27259 14
24.	26671.51	26530.87			27247.38	271152?
25.	26530.41	26385.66			27102.59	269667?
26.	26385.00	26236.22			26953.11	268126'
27.	26235.34	26082.00			26798.66	266546;
28.	26080.57	25923.62			26640.09	264919:
29.					26476.91	263254,
30.	—	—			26309.64	......

... not observed   * blended lines

Table 1. *(Cont'd.).*

J	(24 – 1) R(J)	(24 – 1) P(J)	(25 – 1) R(J)	(25 – 1) P(J)
0	......	......	......	
1	29336.28	29327.06	... ..	......
2	29326.16	29311.72	......	......
3	29309.55	29289.34	......	......
4	29286.45	29260.51	......	29569.91
5	29256.89	29225.23	29564.70	29534.33
6.	29220.88	29183.54	29528.01	29492.15
7	29178.47	29135.48	29485.10	......
8	29129.68	29081.08	29435.33	......
9	29074.55	29020.39	29379.32	29326.92
10	29013.13	28953.45	29315.64	29258.80
11	28945.46	28880.33	29247.91	29184.50
12	28871 61	28801.09	29172.31	29104.69
13	28791 63	28715.78	29091.49	..... .
14	28705.59	28624.48	......	28925.68
15	28613.55	28527.28	28910.50	......
16	28515 61	28424.48	28810.57	......
17	28411.83	28315.47	.....	28612.01
18	28302 31	28201.04	28594.07	28496.50
19	28187.13	28081 06	28477.29	28374.56
20	28066.39	27955.62	28354.58	28247.49
21	27940.21	27824.85	... .	28114.91
22	27808.68	27688.85	28092.91	27977 03
23			27954.38	27833.98
24			27810.08	27685.88
25			27661.14	27532.76
26			27507.23	......

A xenon high pressure lamp of 450 W was used as a continuum source. This light was incident on the slit of the spectrograph after passing through the furnace. Absorption spectra were taken in the second order of a 3.4 meter Ebert spectrograph at a reciprocal dispersion of 2.6 Å/mm. The photographs were obtained on Q-2 plates with an exposure time of about 20–30 minutes. The Abbe comparator was used to make the measurements of the lines to an accuracy of ±0.01 Å for unblended lines. An iron arc was used to get iron standards. The iron wavelengths were taken from MIT tables [18]. The vacuum wavenumbers were obtained from the data of Coleman *et al* [19].

3. Structure and analysis

We have taken the spectrograms of the absorption bands of the $A^1\Sigma^+ - X^1\Sigma^+$ system of NaH molecule. The observed spectrum consists of the rotational structure of the vibrational bands (13, 0) to (22, 0) and (18, 1) to (25, 1). All these bands consist of R and P branches usually extending to $J = 20$ for most of the cases. The assignment of J-values to the R and P branches is made by using the following relation :

$$\Delta_2 F''(J) = R(J-1) - P(J+1). \tag{1}$$

The lower state combination differences are known from the studies made in previous work [6]. We, were therefore, in a position to build the upper state combination differences and find the B'_v and D'_v values from the following relation :

$$\Delta_2 F'(J) = R(J) - P(J)$$
$$= 4B_V(J+1/2) - 8D_v(J+1/2)^3. \tag{2}$$

The band origins are also worked out from the relation :

$$R(J-1) + P(J) = 2v_0 + 2\left(B'_v - B''_v\right)J^2 + \cdots. \tag{3}$$

Table 2 contains the molecular constants and the band origins of the newly observed bands (18, 1) to (25, 1).

Table 2. Molecular constants (in cm^{-1}) of the vibrational levels of the $A^1\Sigma^+ - X^1\Sigma^+$ transition of NaH.

Bands	Band origin	B'_v	$D'_v \times 10^{-4}$
(18–1)	27424.0 ± 3.1	1.685 ± 0.006	1.51 ± 0.06
(19–1)	27753.3 ± 1.9	1.654 ± 0.006	1.65 ± 0.05
(20–1)	28077.9 ± 0.3	1.611 ± 0.006	1.37 ± 0.06
(21–1)	28396.7 ± 2.6	1.573 ± 0.008	1 19 ± 0.06
(22–1)	28713.9 ± 0.21	1.531 ± 0.005	1.20 ± 0.04
(23–1)	29026.4 ± 2.6	1.501 ± 0.004	1.39 ± 0.03
(24–1)	29336.5 ± 1.6	1.446 ± 0.003	1.13 ± 0.04
(25–1)	29644.7 ± 5.2	1.400 ± 0.005	1.01 ± 0.06

The spectroscopic constants used in constructing the RKR curve of the $A^1\Sigma^+$ state of NaH are found from the Dunham-like expressions given by :

$$E_{v,J} = \sum Y_{il}(v+1/2)^i J^l(J+1)^l, \tag{4}$$

where the Y_{il}'s are called Dunham spectroscopic constants. We have used the $B(v)$ values fitted to a polynomial in $(v + 1/2)$ in the following equation :

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