## The millimeter wave spectra of NaH and NaD

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# The millimeter wave spectra of NaH and NaD

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Utilizing a glow discharge absorption cell, we have detected the  $v = 0, 1, 2, and 3, J = 0 \rightarrow 1$  transitions of NaH and the  $v = 0, 1, 2, and 3, J = 1 \rightarrow 2$  and  $v = 0, J = 2 \rightarrow 3$  transitions of NaD in the millimeter and submillimeter regions of the spectrum. The derived Dunham constants (MHz) are

	NaH	NaD
Y <sub>01</sub>	146 999. 10(30)	76 659, 59(20),
Y11	- 4 108, 99(80)	- 1 546.94(40),
Y <sub>21</sub>	32, 83(50)	8.76(20),
Y31	- 0, 96(7)	-0.16(4),
Y 02	- 10, 307(20)	-2.802(6).

A significant breakdown of the Born-Oppenheimer approximation has been observed.

## I. INTRODUCTION

As a class the light hydrides represent the most stringent test of diatomic molecule theory. They have inspired numerous theoretical treatises and a substantial body of experimental work. However, because their pure rotational spectra fall at short millimeter and submillimeter wavelengths, most of the information that exists on the rotational structure of these species has come from the analysis of the rotational fine structure of optical and infrared spectra.

We have previously reported an extensive millimeter and submillimeter microwave study of the chemically stable hydrogen halides.<sup>1</sup> In addition, the J=0-1transitions of both the ground and first excited vibrational states of <sup>6</sup>LiD and <sup>7</sup>LiD have been reported by Pearson and Gordy.<sup>2</sup> Until the present work, this had been the only microwave study of the alkali hydrides. This state of affairs exists both because of the high frequencies of their rotational transitions and because of their chemical instability at the temperatures required for vaporization. Since this instability increases with increasing molecular weight, lithium hydride, in its deuterated form to make the transition frequencies more accessible, was the most favorable for the hot cell experiment of Pearson and Gordy.<sup>2</sup>

The instability problem has resulted in substantially fewer studies of sodium hydride than lithium hydride in all spectral regions. Previous work has been limited to a relatively small number of optical experiments including the classical experiments of Hori, <sup>3, 4</sup> Olsson, <sup>5</sup> and Pankhurst<sup>6</sup> who recorded and analyzed extensive spectra in emission and absorption of both sodium hydride and deuteride. For the absorption spectra, NaH was produced in equilibrium abundance by reaction of sodium and hydrogen under a high pressure hydrogen atmosphere at elevated temperatures. These early studies revealed the anomalous behavior of the  $A^{1}\Sigma^{+}$ excited electronic state and provided the first few coefficients of the rotational-vibrational energy level expansions for the X and A states to optical accuracy.

Recently, Giroud and Nedelec<sup>7</sup> have utilized a laser fluorescence technique to observe fluorescence to a wide variety of vibrational states of the ground electronic state. These authors report rotational constants  $B_{v'}$ , to v'' = 15 for NaH and to v'' = 20 for NaD. Previous optical work had been carried out only up to v'' = 8 for NaH and v'' = 1 for NaD. Giroud and Nedelec<sup>7</sup> used a microwave discharge to produce the NaH vapor. Laser fluorescence has also been used to study the radiative lifetime for  $A^{1}\Sigma^{+}$  NaH.<sup>8,9</sup> In one of these studies,<sup>9</sup> NaH was produced in a supersonic nozzle expansion.

A variety of theoretical calculations have also been undertaken on NaH, including Hartree-Fock, <sup>10</sup> MCSCF, <sup>11</sup> and CI<sup>12</sup> studies and the results compared with existing optical data. In general, recent theoretical studies are in good agreement with these data.

In this paper, we report the first millimeter and submillimeter wave spectroscopic study of  $X^{1}\Sigma^{*}$  NaH and NaD. For NaH, we have measured the  $J=0 \rightarrow 1$  transition in the four lowest vibrational states, while for NaD we have measured the  $J=1\rightarrow 2$  transition in the four lowest vibrational states plus the  $J=2\rightarrow 3$  transition of the ground vibrational state. In addition to obtaining highly refined molecular constants, we have probed a significant breakdown in the Born-Oppenheimer approximation. The  $J=0\rightarrow 1$  NaH transition frequency should prove useful to interstellar astronomers searching for NaH in dense clouds.

#### **II. EXPERIMENTAL**

Although the alkali hydrides exist as stable solids, at temperatures high enough to obtain a significant gas phase component it is found that their equilibrium vapor consists primarily of molecular hydrogen rather than the hydride. The equilibrium is governed by reactions such as

MH(c.	l = MH(g)	. ()	L)
		,	-,

$$2MH(g) = 2M(l) + H_2(g) , \qquad (2)$$

$$\mathbf{M}(l) = \mathbf{M}(\mathbf{g}) , \qquad (3)$$

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FIG. 1. A schematic view of the glow discharge absorption cell.

where M is an alkali metal. At the low pressures [(0.01-1.0) Torr] required for high resolution millimeter and submillimeter spectroscopy, it is difficult to produce sufficient equilibrium hydride vapor for spectroscopic detection. Heretofore, the only alkali hydride that had been successfully studied in this spectral region was LiD, for which the thermodynamics is relatively favorable.<sup>2</sup> Calculations indicate that heating a sample of LiH to 900-1000 K should produce a vapor with a hydride mole fraction of ~10<sup>-3</sup>-10<sup>-4</sup>. For NaH, on the other hand, whether one heats solid NaH or solid Na and H<sub>2</sub> gas, it is difficult to produce a vapor at the necessary low pressure that has a hydride mole fraction exceeding 10<sup>-5</sup>-10<sup>-6</sup> and absolute gas density exceeding  $10^{10}-10^{11}$  cm<sup>-3</sup>.

This problem has been overcome by preparing NaH via reaction of sodium vapor and hydrogen in a nonequilibrium glow discharge. Although discharges produce substantial index of refraction noise at lower microwave frequencies and emit significant interfering radiation at shorter wavelengths, arguments can be made that the region around 1 mm is ideal for absorption spectroscopy.<sup>13</sup>

The possible formation mechanisms for NaH in a discharge include  $^7$ 

 $Na^* + H_2 \rightarrow NaH + H$ , (4)

$$Na_2 + H - NaH + Na$$
, (5)

$$Na + H_2(v)^{\dagger} \rightarrow NaH + H .$$
 (6)

Based on analogous studies of CsH formation in a cell containing Cs and  $H_2$  vapors plus laser radiation,<sup>14</sup> it is likely that mechanism (4) is dominant with Na<sup>\*</sup> possibly in a *Rydberg* state. In support of this conjecture, we note that intense Na optical emission from highly excited electronic states can be observed when strong signals of NaH are seen.

Figure 1 shows the reaction cell. This cell consists of a 10 cm diameter, 2 m long Pyrex pipe, pumped by a 10 cm diffusion pump. Inside the vacuum jacket were inserted cylindrical discharge electrodes separated by a 1 m long, 2.5 cm diameter Pyrex tube, flared to 9 cm at each end. This inner tube was seeded with approximately 1 g of sodium metal in small pellets and hydrogen gas was flowed through the cell at approximately 0.2 Torr. The discharge current (~1 A) was confined inside the small diameter tube and after about 5 min the bright yellow glow characteristic of the sodium D lines appeared along with the microwave spectrum. We have previously discussed our millimeter and submillimeter spectroscopic techniques in some detail.<sup>15, 16</sup> For this experiment, klystrons in the 50 GHz region were used to drive a crystal harmonic generator, whose output was focused through the cell by quasioptical techniques and detected by a 1.5 K InSb detector. We observed that the v=0, J=0+1 transition of NaH absorbed about 1% of the microwave power in an effective path length of 1 m. From this percentage absorption, we can estimate the number density of NaH from the relation<sup>17</sup>

$$\alpha_{\rm max}(\rm cm^{-1}) = \frac{(4.94 \times 10^{-3}) \ \mu^2 \nu_0^3 P_{\rm NeH}}{\Delta \nu T^3 / 300} \quad , \tag{7}$$

where  $\alpha_{max}$  is the peak absorption coefficient,  $\mu$  is the dipole moment in D,  $\nu_0$  is the transition frequency in GHz,  $\Delta\nu$  is the linewidth in MHz,  $P_{NaH}$  is the sodium hydride partial pressure in Torr, and T is the rotational temperature. Setting T = 600 K,  $^7 \mu = 6.7$  D,  $^{11}$  and  $\Delta\nu = 4$  MHz, we obtain an NaH number density of ~ 10<sup>12</sup> cm<sup>-3</sup> and a J = 0 number density of ~ 10<sup>10</sup> cm<sup>-3</sup>. These number densities are at least an order of magnitude in excess of what can be achieved in thermal equilibrium at our operating pressures.

We have observed for NaH that the J=0-1 absorption signal decreased by a factor of approximately 3 for each higher vibrational state, corresponding to an effective vibrational temperature of 1500-1600 K. In previous diagnostic studies of molecules in glow discharges, <sup>13, 18</sup> we have found that low-lying rotational states are in equilibrium with the translational temperature and that vibrational temperatures can vary widely. Our rotational temperature estimate for Eq. (7) is based on the measurement of Ref. 8 for a microwave discharge and our earlier glow discharge measurements.

Time resolved experiments have also been carried out. In these experiments the discharge current was pulsed synchronously with the klystron sweep rate (60 Hz) and a duty cycle of  $\sim 2/1$  on/off established. It was found that the NaH signal decayed to an unobservable level in a time equal to or small compared with the decay time of the index of refraction ( $\sim 1/2$  ms). Since we observed the J=0-1 transition of v=0 NaH, and since the rotational and vibrational cooling that occurs out of the current pulse should *increase* the signal strength of this transition, we conclude that the lifetime of the species in the gas phase is  $\leq 0.5$  ms. A simple model for destruction in which the sodium hydride random walks to the wall and condenses predicts a lifetime of  $\sim 0.5$  ms. It must be noted, however, that this random walk would involve  $\sim 1000$  collisions and that NaH could be destroyed chemically on a much shorter time scale by reaction with, for example, atomic hydrogen.

## **III. THEORETICAL BACKGROUND**

Diatomic molecules in well-behaved  ${}^{1}\Sigma$  electronic states are ordinarily analyzed in terms of the Dunham<sup>19</sup> expansion

$$\frac{E(v, J)}{h} = \sum_{l,m} Y_{l,m} (v+1/2)^l J^m (J+1)^m .$$
(8)

For most molecules, this expansion converges rapidly and five to seven terms characterize to microwave accuracy (~0.1 MHz) the rotational-vibrational spectra over wide ranges of states. For example, the constants  $Y_{01}(\sim B_e), Y_{11}(-\alpha_e), Y_{21}(\gamma_e), Y_{31}, Y_{02}(-D_e), Y_{12}(-\beta_e), and$  $Y_{03}$  characterize the AlI spectra to an accuracy of < 0.05 MHz through v = 14 and J = 39. However, inspection of the relations between the  $Y_{11}$ 's and the Dunham potential constants, the  $a_i$ 's, shows that  $Y_{l+1,1}/Y_{l1} \propto B_e/\omega_e \propto 1/\sqrt{\mu}$ , where  $\mu$  is reduced mass. Thus, the convergence of the rotational-vibrational expansion is expected to be worst for the lightest species. For these molecules, the basis of Dunham's theory, the Born-Oppenheimer approximation, begins to break down<sup>1</sup> and the effects of higher order corrections must be considered, especially in the reduction of the  $Y_{l,m}$  to mechanical parameters (e.g.,  $B_{e}$ ) and in the use of the Dunham isotope relation<sup>19</sup>

$$Y'_{1,m}/Y_{1,m} = (\mu/\mu')^{1/2+m} .$$
<sup>(9)</sup>

These higher order effects were first discussed by Van Vleck<sup>21</sup> and extensively treated by Rosenblum, Nethercot, and Townes.<sup>22</sup> They include several corrections to  $Y_{01}$ . The nonspherical distribution of valence electrons about their respective nuclei gives rise to both the molecular g factor  $g_{J}$  and a correction  $\Delta B$  to  $Y_{01}$ :

$$\Delta B = -\left(m_e / m_p\right) g_J B_e , \qquad (10)$$

that must be included in the calculation of  $B_e$  from  $Y_{01}$ . A second correction arises from the wobble-stretch (ws) effect. Cross terms between the rotation of the molecule and electronic motions give rise to a stretching force which in diatomic molecules is along the internuclear axis. While one does not ordinarily have enough information about the electronic motion to calculate the contribution of this effect, it can be deduced from its inverse reduced mass squared dependence if

TABLE I. Observed rotational transitions of sodium hydride (MHz).<sup>a</sup>

NaH		NaD		
Transition	Observed	Transition	Observed	
$J = 0 \rightarrow 1$		J=1-+2		
v = 0	289 864.34	v = 0	303 463, 80	
<i>v</i> = 1	281 771, 81	v = 1	297 344, 69	
v = 2	273 793, 32	v = 2	291 290, 08	
v = 3	265 917.34	<i>v</i> = 3	285 296, 25	
		$J = 2 \rightarrow 3$		
		v = 0	455 028, 14	

<sup>a</sup>Estimated uncertainty  $\pm 0.2$  MHz.

TABLE II. Spectral constants of sodium hydride.

Constant	NaH		NaD		NaD <sup>a</sup>
Y <sub>01</sub> (MHz)	146 999. 10	(30) <sup>b</sup>	76 659, 59	(20)	76 640.43
Y <sub>11</sub> (MHz)	- 4 108, 99	(80)	- 1 546.94	(40)	-1546.86
$Y_{21}$ (MHz)	32,83	(50)	8.76	(20)	8, 92
$Y_{31}$ (MHz)	- 0, 96	(7)	-0.16	(4)	-0.19
Y <sub>02</sub> (MHz)	- 10. 307	°(20)	-2.802	(6)	• • •
B <sub>e</sub> (MHz)	147 076	(10)	76 680	(2)	
r <sub>e</sub> (Å)		1.8	86 54(10)		

<sup>a</sup>Calculated from the  $Y_{l,m}$  of NaH and Eq. (9).

<sup>b</sup>The spectral constants are tabulated to 1-10 kHz in order to allow accurate computation of spectral frequencies. The uncertainties shown propagate from the uncertainties in the measured lines.

<sup>c</sup>Calculated from  $Y_{02}$  of NaD and Eq. (9).

sufficient isotopic information is available.

In addition, Dunham<sup>19</sup> has shown in the context of his theory that

$$Y_{01} = B_{e} \left[ 1 + (B_{e}^{2} / \omega_{e}^{2}) \beta_{01} \right] = B_{e} + \delta , \qquad (11a)$$

where

$$\beta_{01} = Y_{10}^2 Y_{21} / 4Y_{01}^3 + 16a_1 (Y_{20} / 3Y_{01}) - 8a_1 - 6a_1^2 + 4a_1^3$$
(11b)

and

$$a_1 = Y_{11} Y_{10} / 6Y_{01}^2 - 1 . (11c)$$

Thus, we have finally that

$$B_e = Y_{01} - \delta + \Delta B + ws \quad . \tag{12}$$

Higher order corrections to the other  $Y_{l,m}$ 's can also be calculated, but because of their smaller size they do not make observable contributions.

#### IV. ANALYSIS AND RESULTS

The measured transition frequencies are shown in Table I. The analysis of these data to maximum advantage presents a rather different problem from the reduction of the optical data for sodium hydride. In the microwave problem, the number of data points is comparable to the number of parameters to be calculated but the accuracy of these data is very high. Thus, we must guard against apparently highly accurate results that are mere numerology.

We choose to reduce our data initially for each isotope by the calculation of the Dunham  $Y_{l,m}$ 's from the relation

$$E_{R}(v, J)/h = Y_{01}J(J+1) + Y_{11}(v+1/2)J(J+1) + Y_{21}(v+1/2)^{2}J(J+1) + Y_{31}(v+1/2)^{3}J(J+1) + Y_{02}J^{2}(J+1)^{2} + Y_{12}(v+1/2)J^{2}(J+1)^{2} + \cdots,$$
(13)

where  $E_R$  is the rotational energy. First the data for NaD are fit to Eq. (13) with  $Y_{12}$  fixed at its optical value. This value is derived from NaH work<sup>3</sup> ( $Y_{12} = 0.09$  MHz) and relation (9) to be  $Y_{12} = 0.02$  MHz. The calculation, which has no redundancy, yields the  $Y_{01}$ ,  $Y_{11}$ ,  $Y_{21}$ ,  $Y_{31}$ , and  $Y_{02}$  shown in Table II. (The assumption that  $Y_{12} = 0$ 

	Experimental determinations				Theoretical determinations	
Constant	This work	Huber and Herzberg <sup>a</sup>	Pankhurst <sup>b</sup>	Giroud and Nedelec <sup>c</sup>	Sachs et al. <sup>d</sup>	Meyer and Rosmus <sup>e</sup>
		NaH				
$Y_{10} \text{ (cm}^{-1}\text{)}$	1171.2 <sup>f</sup>	1172.2	1172.2	1 <b>1</b> 76, 1	1183,2	1172.3
Y <sub>01</sub> (GHz)	146,99910	146.93	146.5	146.6	142.3	146.
Y <sub>11</sub> (GHz)	-4.10899	-4.056	-3.87	- 3, 93	-3.78	-3.96
Y <sub>02</sub> (MHz)	- 10, 307	- 9.95	-9.44	- 9, 98	- 9.23	
r <sub>e</sub> (Å)	1,88654	1.8874	1,885	1.889	1.918	1.88
		NaD				
Y <sub>10</sub> (cm <sup>-1</sup> )	845.9	826.1		847.7	826.60	
Y <sub>01</sub> (GHz)	76.65959	76.672		76.45	74.23	
Y <sub>11</sub> (GHz)	- 1.546 94	- 1.56		-1.5	-1.43	
Y <sub>02</sub> (MHz)	-2.802	-2.74		-2.7	-2.6	
r <sub>e</sub> (Å)	1.88654	1.8866		1.889	1.918	

	TABLE I	I. Com	parison	with	other	worl
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<sup>a</sup>Data from Olsson, Ref. 5.

<sup>b</sup>Reference 6.

<sup>c</sup>Reference 7.

<sup>d</sup>Reference 11. <sup>e</sup>Reference 12.

4)

<sup>f</sup>Calculated via Eq. (14).

yields virtually the same results because our low J data are not sensitive to this parameter.) The  $Y_{02}$  can be checked by comparison with the value calculated from<sup>19</sup>

$$Y_{02} \cong -4Y_{01}^3 / Y_{10}^2 , \qquad (1$$

if  $Y_{10}$ , the vibrational frequency, is known. Alternatively, relation (14) can be used to determine  $Y_{10}$  (Table III). Since  $Y_{02}$  contributes only about 40 MHz to the  $J=0 \rightarrow 1$  transition of NaH,  $Y_{02}$ (NaH) can be calculated from  $Y_{02}$ (NaD) via Eq. (9) without concern for contamination from higher order effects. The NaH data can then be used to calculate  $Y_{01}$ ,  $Y_{11}$ ,  $Y_{21}$ , and  $Y_{31}$ , again with no redundancy if  $Y_{12}$  is fixed at the optical value. These results are shown in Table II. The uncertainties listed are those that propagate from 0.2 MHz standard deviations in the experimental lines. Table II also includes the  $Y_{l,m}$ (NaD) calculated from the  $Y_{l,m}$ (NaH) via isotope relations [Eq. (9)]. Inspection of this table shows that the agreement between the  $Y_{l,m}$  (NaD) from our fit and from the isotope relations is good for all constants except  $Y_{01}$ , for which higher order effects are expected to be important. Nevertheless, small amounts of model error probably exist because of the lack of a  $Y_{41}$  term in the expansion of Eq. (13).

Because of the higher order corrections to  $Y_{01}$ , the comparison in Table II shows significant deviation. We must calculate these corrections to arrive at  $B_e$  and  $r_e$ . [See Eq. (12).] Unfortunately, the chemical instability of sodium hydride has not allowed a measurement of  $g_J$ and its contribution to  $B_e$  must be deduced from its isotopic mass dependence. If we neglect a contribution due to the change of the center of mass under isotopic substitution, <sup>23</sup> this  $g_J$  correction is proportional to  $1/\mu^2$  as are the wobble-stretch and Dunham corrections. (Using a point-dipole model for NaH,<sup>23</sup> we estimate the deviation of the  $g_J$  correction term from  $1/\mu^2$  dependence to be ~4%.) Thus, the total correction to  $Y_{01}$  has an approximate inverse reduced mass squared dependence and the  $Y_{01}$  of NaH and NaD can be combined to calculate this total correction and the values of  $B_e$  and  $r_e$  shown in Table II.<sup>1</sup> The uncertainties listed for these equilibrium constants are estimates. The sizes of the combined Dunham-Born-Oppenheimer-breakdown contributions to  $B_e$ are approximately one part in 2000 (77 MHz) for NaH and one part in 4000 (21 MHz) for NaD. Based on <sup>6</sup>LiD and <sup>7</sup>LiD studies,<sup>2</sup> we estimate the three correction terms [Eq. (12)] to be of approximately equal magnitude.

### V. DISCUSSION

Table III shows a comparison of our results with the results of earlier optical experiments as well as with theoretical predictions. We have chosen to make the comparisons in terms of the Dunham  $Y_{1,m}$  constants rather than the  $B_e$ ,  $\alpha_e$ , etc. more commonly used by optical spectroscopists. To the number of significant figures obtained from optical studies, there is no distinction between the two sets of constants. Although the older optical work of Olsson<sup>5</sup> appears to be closer to our microwave results for  $Y_{01}(\neg B_e)$  and  $Y_{11}(-\alpha_e)$  than more recent studies,  ${}^{6,7}$  the laser fluorescence results<sup>7</sup> probe higher vibrational levels of the  $X^1\Sigma^*$  state and permit a check of the validity of our "fit" of four data points to four Dunham constants. In particular, we can compare our effective  $B_v$  values, defined by the relation

$$B_{v} = Y_{01} + Y_{11}(v + 1/2) + Y_{21}(v + 1/2)^{2} + Y_{31}(v + 1/2)^{3} ,$$
(15)

with the laser fluorescence data<sup>7</sup> for vibrational states higher than our observed states of v = 0-3. Such a comparison shows no discrepancy in excess of the optical scatter under approximately 9000 cm<sup>-1</sup> of excitation v = 9 for NaH and v = 12 for NaD. Above this excitation energy, discrepancies begin to appear.

For NaH, we can compare our results with both the MCSCF calculations of Sachs, Hinze, and Sabelli<sup>11</sup> and the PNO-CI and CEPA results of Meyer and Rosmus.<sup>12</sup> In general, the spectroscopic constants derived by Meyer and Rosmus<sup>12</sup> are in better agreement with our results and approach the accuracy of several of the experimental optical studies.

The experimental technique utilized to obtain the millimeter wave spectra of NaH and NaD appears to be applicable with some modification to a variety of alkali and alkaline earth hydrides. Studies of some of these species are planned in the near future.

Note added in proof. F. B. Orth, W. C. Stwalley, S. C. Yang, and Y. K. Hsieh [J. Mol. Spectrosc. 79, 314 (1980)] have recently published an optical study of NaH and obtained the constants  $Y_{10}$  (cm<sup>-1</sup>) = 1171.4,  $Y_{01}$  (GHz) = 146.96,  $Y_{11}$  (GHz) = -4.155,  $Y_{21}$  (MHz) = 56.81, and  $Y_{31}$  (MHz) = -3.48 for the  $X^{1}\Sigma$  state.

### VI. ACKNOWLEDGMENTS

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