Far-Infrared Spectrum of Sodium Hydride[1]

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Rotational spectra in the $v = 0, 1, 2,$ and 3 levels of the ground ($^1\Sigma$) state of sodium hydride have been observed using tunable far-infrared radiation generated from the difference frequency between two CO_2 lasers. The Dunham coefficients, which have been determined without the use of optical data or isotopic scaling relations, are $Y_{01} = 146\ 999.138(38)$ MHz, $Y_{02} = -10.29481(54)$ MHz, $Y_{03} = 6.243(49) \times 10^{-4}$ MHz, $Y_{11} = -4109.912(68)$ MHz, $Y_{12} = 0.14695(68)$ MHz, $Y_{21} = 33.341(34)$ MHz, $Y_{22} = -2.69(20) \times 10^{-3}$ MHz, and $Y_{31} = -1.0517(55)$ MHz. The constants are typically an order of magnitude more accurate than the best values previously available, and where comparison is possible, agreement is found to be excellent. © 1987 Academic Press, Inc.

INTRODUCTION

The gas phase alkali hydrides have been the subject of extensive theoretical study as well as a growing body of experimental work. As simple diatomic hydrides, they are particularly amenable to ab initio studies, and have served as prototypical systems for electronic structure and potential curve calculations (*1–7*). In addition, the lighter members of the series have been used to test theories concerning corrections to the Born–Oppenheimer approximation (*2b, 8, 9*). Despite their fundamental appeal, however, experimental difficulties have limited the quantity of available data for these systems and [with the exception of the infrared spectrum of LiH (*10*)] spectroscopic data have been largely limited to those derived from optical absorption and emission work (*1–7, 11, 12*). It is only relatively recently that advances in infrared and millimeter wave technology have permitted the observation of the low rotational transitions of LiH (*9*) and NaH (*8*) and their isotopic derivatives, as well as an infrared spectrum of KH (*13*).

One of the difficulties encountered in utilizing high-resolution rotational spectra of the lighter alkali hydrides to test theories concerning breakdown of the Born–Oppenheimer approximation has been that only the lowest transitions have been accessible using existing millimeter wave techniques (*8, 9*). The higher rotational transitions fall well into the far-infrared region but cannot be observed by laser magnetic resonance spectroscopy since the ground state of these systems is nonmagnetic. As a result, the most accurate spectroscopic constants have been derived by combining the rotational data at low *J* with available optical data, and by invoking isotopic scaling relations to

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estimate constants of the hydride from measured constants of the deuteride. The direct measurement of the higher rotational transitions of an alkali hydride, however, would enable the determination of a very accurate set of spectroscopic parameters without the use of optical data or isotopic scaling laws and would clearly provide a check for such procedures. Using the technique of tunable far-infrared generation recently developed in our laboratory (14), we have observed rotational spectra of the ground ($^1\Sigma$) state of NaH up to the $J = 7 \leftarrow 6$ transition in the $v = 0$ vibrational level, the $J = 8 \leftarrow 7$ transition in the $v = 1$ level, and the $J = 6 \leftarrow 5$ transition in both the $v = 2$ and $v = 3$ levels. The data have provided a revised and extended set of Dunham coefficients for this molecule and the larger data set has indeed eliminated the need to constrain parameters to optical or isotopically scaled values. The constants determined are typically an order of magnitude more accurate than the best values previously available and the agreement with earlier work is found to be excellent.

EXPERIMENTAL PROCEDURE

The tunable far-infrared spectrometer used in this work has been described elsewhere (14). Briefly, far-infrared radiation is generated from the difference frequency between two CO_2 lasers using a tungsten–nickel point-contact diode (15) as the nonlinear mixing device. One laser is stabilized using the saturated fluorescence technique, and is frequency modulated at 500 Hz. Radiation from a second (waveguide) CO_2 laser is mixed with that of the first laser on the point-contact diode to produce radiation at the far-infrared difference frequency. The waveguide laser is frequency offset locked to a third fluorescence-stabilized CO_2 laser and is tuned in order to sweep the difference frequency. Far-infrared radiation emitted from the diode is collimated with a parabolic mirror of 10-mm focal length and passed through a Pyrex absorption cell with polyethylene windows. Upon exiting the absorption cell, the signal is detected using a 1.5 K germanium bolometer and a lock-in amplifier. Proper choice of CO_2 isotopes and lasing lines allows the generation of nearly any far-infrared frequency between 300 and 6000 GHz. In several experiments, however, where generation of the desired frequency would have required flowing an expensive CO_2 isotope through the waveguide laser, the radiation was instead produced by mixing the far-infrared difference frequency from an alternative pair of CO_2 lasing lines with microwave radiation from an X-band klystron. This "third-order" mixing experiment (16) was accomplished by replacing the nickel base of the diode with cobalt and coupling the microwave radiation directly onto the tungsten whisker via coaxial transmission cable.

Sodium hydride was produced by the method described previously for alkali hydrides ($8, 13$). A DC discharge through 20–25 Pa (150–200 mTorr) of flowing H_2 (pumped by a 0.5 m^3/min rotary mechanical pump) was operated at 0.25 to 0.50 A in a Pyrex cell, 1 m long and 19 mm in diameter. Six reservoirs of metallic sodium were placed at 0.15-m intervals throughout the tube and provided the metallic vapor upon heating by the discharge. Signal-to-noise ratios were typically between 5 and 100; the $J = 5 \leftarrow 4$ and the $J = 6 \leftarrow 5$ were the strongest in each vibrational state and the $J = 2 \leftarrow 1$ were the weakest. No features due to sodium nuclear quadrupole coupling were observed.

LEOPOLD ET AL.

RESULTS AND DISCUSSION

Table I gives the observed transitions for NaH and their assignments. Figure 1 shows the $v = 0$, $J = 6 \leftarrow 5$ transition and is the result of a single sweep using an instrumental time constant of 125 ms. From the observed peak percentage absorption for this transition, we estimate a sodium hydride number density in the vicinity of $10^{12}/cm^3$, in agreement with the estimate of Sastry et al. (8). The uncertainties in the frequencies reported are the standard deviations of the results of three increasing fre-

TABLE I

Rotational Transitions of Sodium Hydride

v	J″	J′	Frequency (a)	CO₂ Laser Lines(b)		(obs-calc)(a)
0	0	1	289864.34(20) (c)	–		0.45
0	1	2	579482.55(17)	IIP(24) – IIP(28) (d)		-0.02
0	2	3	868611.42(44)	IR(18) – IP(18) (f)		0.14
0	3	4	1157006.22(16)	IR(14) – IP(32) (f)		0.05
0	4	5	1444424.66(18)	IIP(24) – IIP(26) (e)		-0.06
0	5	6	1730626.20(9)	IIP(30) – IR(26)		-0.01
0	5	6	1730626.21(9) (g)	IP(10) – IP(22) (e)		0.00
0	6	7	2015372.33(36)	IIR(12) – IIP(14) (e)		0.14
1	0	1	281771.81(20) (c)	–		0.65
1	1	2	563300.65(28)	IR(4) – IP(18)		0.15
1	2	3	844346.63(16)	IR(12) – IP(22)		-0.05
1	4	5	1404028.99(17)	IR(32) – IP(28) (f)		-0.02
1	5	6	1682188.78(11)	IP(14) – IP(24) (e)		0.03
1	6	7	1958913.32(21)	IIP(26) – IR(20)		-0.03
1	7	8	2233970.43(30)	IIP(16) – IR(20)		-0.02
2	0	1	273793.32(20) (c)	–		0.48
2	4	5	1364202.77(20)	IP(14) – IIP(26) (e)		-0.02
2	5	6	1634433.26(20)	IP(22) – IIP(24) (e)		0.02
3	0	1	265917.34(20) (c)	–		1.03
3	4	5	1324882.95(20)	IR(38) – IP(22)		0.01
3	5	6	1587283.95(20)	IR(18) – IR(10) (e)		-0.01

(a) All values in MHz. (b) Laser lines refer to the common isotope, $^{12}C^{16}O_2$, unless otherwise specified. (c) Reference 8, not used in fit. See text for discussion. (d) $^{12}C^{18}O_2$. (e) $^{13}C^{16}O_2$. (f) Mixed with microwave radiation from an X-band klystron. (g) Additional measurement, not used in fit.
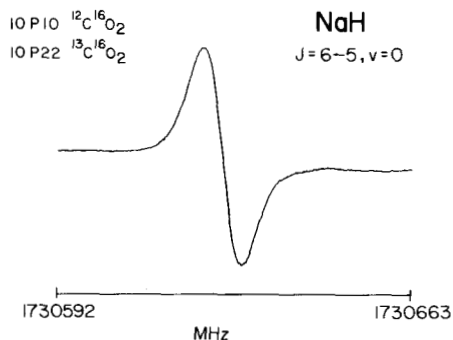
FIG. 1. The $v = 0$, $J = 6 \leftarrow 5$ transition of NaH ($X^1\Sigma$).

quency scans and three decreasing frequency scans and arise primarily from our ability to locate the center of the absorption line.

The data were analyzed according to Dunham's expression for the vibration–rotation energies, viz.,

$$E(v, J) = \sum_{l,m} Y_{lm}(v + \tfrac{1}{2})^l J^m (J + 1)^m$$

$$= \{ Y_{01} + Y_{11}(v + \tfrac{1}{2}) + Y_{21}(v + \tfrac{1}{2})^2 + Y_{31}(v + \tfrac{1}{2})^3 + \cdots \} J(J + 1)$$

$$+ \{ Y_{02} + Y_{12}(v + \tfrac{1}{2}) + Y_{22}(v + \tfrac{1}{2})^2 + \cdots \} J^2 (J + 1)^2 + \{ Y_{03} + \cdots \} J^3 (J + 1)^3.$$

TABLE II

Spectroscopic Constants for NaH ($X^1\Sigma$)[a]

	This Work[b]	Reference [8]
Y_{01}	146999.138(38)	146999.10(30)
Y_{02}	-10.29481(54)	-10.307(20) [c]
Y_{03}	6.243(49) x 10^{-4}	-
Y_{11}	-4109.912(68)	-4108.99(80)
Y_{12}	0.14695(68)	0.09 [d]
Y_{21}	33.341(34)	32.83(50)
Y_{22}	-2.69(20) x 10^{-3}	-
Y_{31}	-1.0517(55)	-0.96(7)

(a) All constants given in MHz.

(b) Quoted uncertainties are two standard errors in the fit.

(c) Scaled from the measured value for NaD.

(d) Derived from optical spectra.

The structure of the data set dictates which of the Dunham coefficients are legitimately determined. The observation of high rotational transitions in several vibrational states requires that the coefficients Y_{01}, Y_{02}, and Y_{03} be fit (essentially a fit to B, D, and H within each vibrational state). Since the effective B, D, and H values vary with vibrational state, however, vibrational corrections to the above constants are necessary to accurately describe the energy levels. For Y_{01}, the largest of the Dunham coefficients determined, an additional vibrational correction term is needed to fit the data for each successive vibrational level (i.e., the fits require the terms corresponding to Y_{11}, Y_{21}, and Y_{31}). For Y_{02}, only the linear and quadratic vibrational correction (Y_{12} and Y_{22}) have been found necessary, while for Y_{03}, whose contributions to the observed frequencies are comparatively small, no vibrational corrections were needed. Hence, the data were fit using the eight coefficients Y_{01}, Y_{11}, Y_{21}, Y_{31}, Y_{02}, Y_{12}, Y_{22}, and Y_{03}. A weighted linear least-squares routine in which the weights were taken as inversely proportional to the square of the estimated experimental uncertainties was used to determine the optimum values for the Dunham coefficients Y_{lm}.

Initial fits were performed by combining the measurements of the $J = 1 \leftarrow 0$ transitions from Ref. (8) with the data obtained here. The results, however, were somewhat disappointing in that the calculated values for the $J = 1 \leftarrow 0$ transitions were 400 to 600 kHz below the reported values for each of the vibrational levels involved, while the estimated uncertainties for those measurements were only 200 kHz. Moreover, omission of these frequencies gave rise to an excellent fit with considerably improved residuals for all transitions included, but the constants thus derived similarly failed to acceptably reproduce the lowest rotational transition of each vibrational level. In an effort to isolate the problem, individual fits to Bv, Dv, and Hv were performed for the $v = 0$ and $v = 1$ data separately and yielded similar results. Hence, while our measurements are internally consistent (as evidenced by the quality of the fits produced) there appear to exist small but observable systematic differences between our data and those of Ref. (8), causing our extrapolated values of the $J = 1 \leftarrow 0$ transitions to differ from the reported numbers. The internal consistency of our measurements suggests that such an error, if present, is not of the form of a constant (or random) offset, but rather one whose magnitude is proportional to the frequency of the transition. In this regard, a Doppler shift in the measured frequencies resulting from the bulk flow velocity of the gas through the absorption cell requires some attention. We have, however, carefully checked for the presence of such shifts in our data but conclude (not unexpectedly) that within our experimental uncertainties, no such effects are observable.[3] There are, of course, a number of other possible explanations for the

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[3] To investigate this possibility, we very carefully measured the frequency of the $v = 2, J = 6 \leftarrow 5$ transition with the far-infrared radiation propagating along and against the direction of the gas flow. In separate runs, the values obtained were 1 634 433.23(20) and 1 634 433.32(20) MHz with the radiation and gas copropagating, and 1 634 433.35(20) and 1 634 433.14(20) MHz for the frequency with the radiation and gas counterpropagating. Each of these measurements, which were performed after the installation of a computer signal averaging system, is the average of two bidirectional scans, under conditions in which the measured linewidth for the transition was ~6 MHz (the expected Doppler width at 600 K). From the agreement between these measurements, we conclude that within the experimental uncertainty, our data are free from contamination by Doppler shifts resulting from bulk flow velocity. In addition, independent mass flow measurements give a bulk flow velocity of the gas through the absorption cell of ~4 m/s, corresponding to a Doppler shift of only 1 part in 10^8 (20 kHz at 1.6 THz), thus independently confirming this conclusion.

observed discrepancy including a small offset in the reported $J = 1 \leftarrow 0$ frequencies due to sodium nuclear quadrupole coupling (see note below), a small Doppler shift in the data of Ref. (8), overly optimistic estimates of the experimental uncertainties, or, quite possibly, some combination of these effects. Whatever the causes, the effects they produce are small and do not alter the parameter values of Sastry *et al.* We have, nonetheless, chosen to report the Dunham coefficients determined from a fit to our data alone, and the results are presented in Table II.

The second column of Table II gives the constants as determined by Sastry *et al.* Where comparison is possible the agreement is seen to be excellent. The coefficient Y_{02} is determined directly and is seen to be in good agreement with the value obtained by isotopically scaling the NaD value, but is 40 times more accurate. The observed agreement confirms the earlier analysis based on limited rotational data used in conjunction with optical data and isotopic scaling laws. In light of this agreement, no transitions of NaD were measured since the pure rotational data for that species were already more abundant than for the protonated form. It is unfortunate that in the case of NaH, isotopic substitution of the heavy atom is not possible, as such substitution would enable a more rigorous test of theoretical treatments of Born–Oppenheimer breakdown. Nonetheless, the agreement between our results employing an extensive set of pure rotational data and those of previous studies should provide some measure of confidence in the constants derived from analyses in which only limited rotational data are available.

Note added in proof: Sundholm, Pyykkö, and Laaksonen have recently calculated the ^{23}Na nuclear quadrupole coupling constant for NaH to be -4.11 MHz in its hypothetical vibrationless state [*Mol. Phys.* **55**, 627–635 (1985)]. Using this value, the $J = 1 \leftarrow 0$ transitions are readily shown to consist of triplets with displacements from line center equal to -0.8, 0.2, and 1.0 MHz in an intensity ratio of 2:3:1. Hence, observation of this transition, if neither fully resolved nor completely blended, could be in error by several hundred kilohertz, thus supporting hyperfine structure in the lowest rotational lines as a significant contributor to the discrepancies discussed above. The higher J lines are, of course, less susceptible to such an effect. We gratefully acknowledge Dr. Eric Herbst for bringing this to our attention.

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