Z. Phys. D 38, 35–40 (1996)

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New Dunham coefficients of the $A^1\Sigma^+$-State of NaH and NaD

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Received: 1 March 1996 / Final version: 28 May 1996

Abstract. We determined new Dunham coefficients of the $A^1\Sigma^+$-State of NaH and NaD from degenerate Four-Wave-Mixing (DFWM) spectra in the near UV and in the blue spectral region. In the case of NaH we combined these data with results of Rafi et al. and Orth et al.. The new set of coefficients describes the vibrational dependence of the rotational constants B and D and of the band origins from $v' = 0$ up to 25. The spectral positions of the lines in our DFWM-spectra can be reproduced by this coefficients with an accuracy better than $0.3\,\mathrm{cm}^{-1}$ for J-values ≤ 15 and $2\,\mathrm{cm}^{-1}$ for J-values ≤ 25. Especially for high J-values this is an improvement up to 30 times in comparison to Dunham coefficients recommended before. A RKR-potential of the $A^1\Sigma^+$-state was calculated with the new coefficients. The Dunham coefficients of NaD were obtained by scaling the NaH coefficients with the reduced masses of the molecules. A comparison of our results to molecular constants determined from the measured NaD-spectra shows good agreement.

PACS: 33.15.Mt; 33.20.Kf; 42.65.Hw

1 Introduction

Since 1930 the spectrum of NaH was investigated by several groups [2, 4–6]. Olsson [7] established for the first time a correct numbering of the vibrational levels of the first electronic excited state, the $A^1\Sigma^+$-state of NaH, and Pankhurst [5] determined from his emission spectra a set of Dunham coefficients [8] which was improved since then several times [2, 9].

NaH is the subject of many theoretical studies because of the interesting anomalous behaviour of the $A^1\Sigma^+$-state and the simplicity of the molecule [10–13]. Spectroscopic investigations of NaH with high accuracy are necessary to test the results of these studies and the methods used therein.

Since 1990 our group [14] has investigated the formation of NaH via collisions of excited sodium atoms with molecular hydrogen in the gas phase by resonance coherent anti-Stokes-Raman-Scattering (RECARS) and DFWM. Although the spectroscopic features of NaH seemed to be well known unexpected difficulties appeared in assigning new spectral lines, which we identified later as NaH-lines. Line positions calculated with Dunham coefficients recommended by Stwalley et al. [3] did not fit the measured spectra. Especially for high rotational levels the experimentally determined line positions differ from the calculated ones up to $60\,\mathrm{cm}^{-1}$ (see line P_{23} (15, 0) in Fig. 1; the band is characterized by (v', v''). For this reason the calculations led for many cases to a wrong ordering of neighbouring lines. For example the R_{16} (12, 0)-line in the spectrum was found at a shorter wavelength than the P_2 (10, 0)-line in contradiction to the calculations (see Fig. 1).

The main reason for this is the following: Stwalley et al. recommend molecular coefficients derived by comparing and analyzing data from the existing literature. The main source of information for the constants of the $A^1\Sigma^+$-state are the measurements of Pankhurst [5]. However, he derived the centrifugal distortion constant D for only a few vibrational levels. The resulting Dunham coefficients Y_{12} correctly describe the vibrational dependence of D only up to $v' = 7$ (see Fig. 2). Therefore Stwalley and co-workers [2, 3] did not recommend specific values for the related Dunham coefficients.

For this reason the assignment of many NaH-lines based on the comparison of spectral positions taken from their spectra with calculated ones may be ambigious. Therefore we measured overview spectra of NaH between 436 nm and 470 nm and between 370 nm and 405 nm to cover the whole branches and to identify the lines step by step proceeding from the band heads.

We applied the *D*egenerate-*F*our-*W*ave-*M*ixing (DFWM) method, a non-linear optical technique, which has attracted much attention recently [15 and references therein]. DFWM is now widely used for kinetic studies

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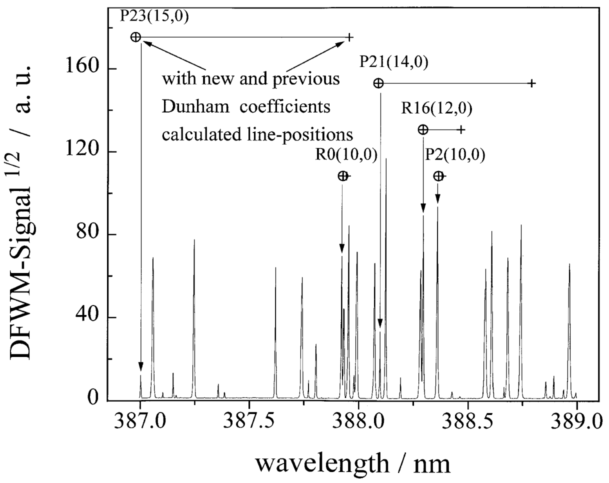

Fig. 1. Small part of the DFWM-spectrum of NaH with the assignment of some exemplary lines. The *crosses* indicate the line positions calculated by Dunham coefficients recommended in [3]. The *circles with crosses* show the calculated positions if the new set of coefficients for the $A^1\Sigma^+$-state given in Table 2 is used. The improvement of the accuracy is obvious especially for high J-values

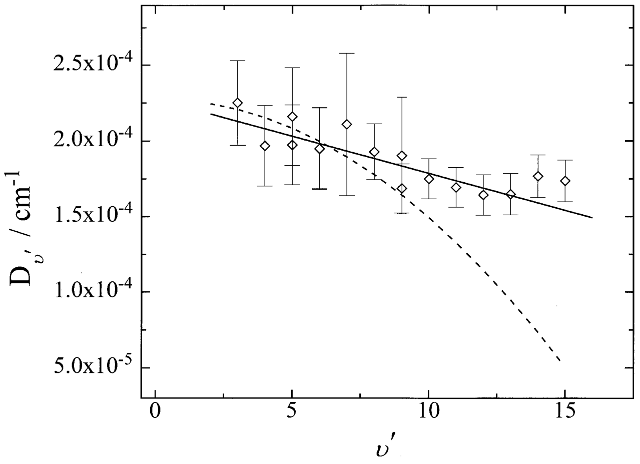

Fig. 2. The centrifugal distortion constant $D_{v'}$ of the $A^1\Sigma^+$-state of NaH is plotted versus the vibrational level v'. The experimental values (*diamonds*) are obtained from the measured DFWM-spectra. The *dashed line* depicts a calculation of D by Dunham coefficients which R.C. Pankhurst got from his emission measurements [5]. These coefficients do not lead to reasonable values at high v'-levels. Therefore Stwalley et al. do not recommend them [3]. However, the new Dunham coefficients Y_{02} and Y_{12} given in Table 2 describe the dependence of D on v' within the experimental uncertainty (see *solid line*)

[16, 17], investigations of combustion processes [18], and ultrashort time dynamics [19–21]. Some features of DFWM are of considerable interest for molecular structure investigations. Besides its sensitivity it is the subDoppler line resolution together with the phase conjugate nature of the signal [22] which make this technique very attractive. Using pulsed dye lasers with narrow bandwidth one obtains, even at high temperatures, narrow linewidths governed by the natural or collision-induced lifetimes of the involved states. It has been shown previously [23] that this technique is also suitable to observe NaH.

Meanwhile Rafi et al. had measured the absorption spectrum at shorter wavelengths and reported the band origins and rotational constants for $v' = 12$ to 25 [1] while our data covers the region $v' = 2$ to 15 and Orth et al. [2] give experimental values for $v' = 0$ and 1. By using all this data it was possible to fit a set of Dunham coefficients (see Table 2) which describes the vibrational dependence of the molecular constants of the $A^1\Sigma^+$-state for $v' = 0$ to 25.

The comparison of NaH and NaD should give information about the influence of the mass of the nuclei on potential surfaces and reaction kinetics. However, only very few spectroscopic data are available for the $A^1\Sigma^+$-state of NaD. Therefore Stwalley et al. recommend to scale the Dunham coefficients of NaH with the reduced masses to get appropriate coefficients for NaD [3]. To validate this procedure a set of NaD coefficients (see Table 4) was calculated from the new NaH coefficients and compared with molecular constants obtained directly from NaD spectra which were measured in the same spectral regions as the NaH spectra.

2 Experiment

The Na + H_2 collision system is prepared in a heat pipe oven filled with sodium and 100 mbar of hydrogen ($n = 1.2{\cdot}10^{18}$ cm^{-3}) and heated up to 600 K. A detailed description of the heat pipe oven is given elsewhere [24]. The sodium atoms in the gas phase ($n = 6{\cdot}10^{14}$ cm^{-3}) are excited in the $3p_{3/2}$ level by a flashlamp-pumped dye laser. Via collisions between excited sodium atoms and hydrogen molecules sodium hydride is produced [14, 16]. The concentration of NaH-molecules in vibrational levels up to $v'' = 3$ is sufficient for our spectroscopic study.

The spectra of sodium hydride are recorded via degenerate Four-Wave-Mixing in a phase conjugated geometry with two crossed polarized and counterpropagating pump beams. A p-polarized probe beam crosses them at an angle of about 2°. All beams have a waist of 2 mm, measured with a beam profile analyzer. The energy of the pump beams is 20 μJ per pulse while the probe beam is five times weaker. The source of these beams is an excimer pumped dye laser, which delivers laser pulses of 10 ns time duration. The signal beam, which arises due to the interaction of the probe and pump beams with the sample, is s-polarized and counterpropagating to the probe beam. It is split off the probe beam by a polarizer and guided through a computer controlled attenuator to a photomultiplier. The attenuator is necessary to adapt the dynamic range of the signal (1 : 10000) to the photomultiplier. The spectra are obtained by tuning the wavelength of the DFWM-laser in steps of 0.002 nm and recording the signal of the photomultiplier via a boxcar amplifier by a personal computer. For further details see [23] and [17].

Adequate wavelength calibration of the DFWM-laser beam is achieved with the help of an optogalvanic cell (OG505, LAS) filled with neon or argon. A small fraction of the radiation is sent through this cell and induces changes of the lamp discharge current. These changes are measured at a resistor, processed by another boxcar amplifier, and stored simultaneously with the DFWM-signal in the computer. An optogalvanic calibration spectrum is recorded for each DFWM-spectrum. Linear extrapolation between the wavelengths of the features of the optogalvanic spectra, tabulated in [25], allows the determination of the absolute NaH-line positions with an uncertainty of the order of the laser linewidth, which is 0.2 cm^{-1}.

3 Results

3.1 NaH

The measured DFWM-spectra of NaH show *R*- and *P*-lines of bands of the $A^1\Sigma^+ \rightarrow X^1\Sigma^+$ transition with upper vibrational levels $v' = 2$ to 15 and rotational numbers up to 25. As discussed for example by Herzberg [26] the analysis was carried out by calculating the differences ΔF between the wave numbers of the *R*- and *P*-lines belonging to the same ground state level. $\Delta F_{v'}(J)$ depends only on the rotational constant $B_{v'}$, the centrifugal distortion constant $D_{v'}$ and higher order rotational terms of the vibronic level v' of the $A^1\Sigma^+$-state:

$$\Delta F_{v'}(J) = 4B_{v'}(J + \tfrac{1}{2}) - D_{v'}((2J + 1)^3 + 3(2J + 1)) + \text{h.o.}. \tag{1}$$

We obtained the constants *B* and *D*, dependent on the vibronic level v', by fitting this function with a least square method to the experimental determined $\Delta F_{v'}(J)$ values. The constants are listed in Table 1.

Values of the *B* and *D* coefficients for the ground state were obtained by applying the same procedure to *R*- and *P*-lines which belong to the same excited state level. These constants were found to be in excellent agreement with published values [3] within the accuracy of the measurements. For the determination of the band origins the rotational part of the transition energies of the lines was calculated from the obtained *B* and *D* values and subtracted from the transition energies. For each band the mean value and the standard deviation of these results were calculated for all observed lines of the band (see Table 1).

Together with published data from Orth et al. [2] and Rafi et al. [1] (see Fig. 3) the newly derived values represent a complete set of experimental values for the rotational constants and band origins of the excited state for $v' = 0$ up to 25. It was found that the Dunham coefficients recommended in [3] reproduce the $B_{v'}$- and $\Delta G(v')$-values [$\Delta G(v') =$ band origin $(v' + 1)$-band origin (v')] very well up to $v' = 10$ but for higher v' there are increasing discrepancies (see Fig. 3).

A new set of Dunham coefficients Y_{kl} was obtained by fitting the functions

$$\Delta G(v') = \sum_{k=1} Y_{k0}((v' + \tfrac{3}{2})^k - (v' + \tfrac{1}{2})^k), \tag{2}$$

$$B_{v'} = \sum_{k=0} Y_{k1}(v' + \tfrac{1}{2})^k \tag{3}$$

and

$$D_{v'} = -\sum_{k=0} Y_{k2}(v' + \tfrac{1}{2})^k \tag{4}$$

to the data. They are listed in Table 2. The coefficients correlate partly. Within the given errors (Table 2) different sets can be found, which reproduce the data with the same accuracy.

Good agreement between (2) and the experimental values of $\Delta G(v')$ is achieved only if the coefficients Y_{k0} recommended in [3] with $2 \leq k \leq 6$ are modified and an additional coefficient Y_{70} is introduced (see Fig. 3). To adapt (3) to the data for the rotational constant $B_{v'}$ it was necessary to modify the coefficients Y_{k1} given in [3] with $k \geq 2$. The values for the coefficients Y_{02} and Y_{12}, which

Table 1. Rotational constants of the $A^1\Sigma^+$-state and band origins determined by DFWM-spectra of NaH. For the band (2, 1) there is no value for $D_{v'}$ given because in this case too few lines were observed to get a reasonable fit

Band: (v', v'')	$B_{v'}$/cm^{-1}	$D_{v'} \cdot 10^4$/cm^{-1}	Band origin/cm^{-1}
(2, 1)	1.869 ± 0.014	–	21812.4 ± 0.4
(3, 1)	1.913 ± 0.012	2.25 ± 0.28	22149.6 ± 0.3
(4, 1)	1.924 ± 0.012	1.97 ± 0.26	22493.2 ± 0.4
(5, 1)	1.937 ± 0.012	1.97 ± 0.26	22842.9 ± 0.3
(6, 1)	1.940 ± 0.012	1.95 ± 0.26	23197.1 ± 0.3
(5, 2)	1.942 ± 0.013	2.16 ± 0.32	21747.9 ± 0.3
(6, 2)	1.939 ± 0.012	1.95 ± 0.27	22101.8 ± 0.3
(7, 2)	1.946 ± 0.017	2.11 ± 0.47	22459.3 ± 0.4
(9, 3)	1.915 ± 0.013	1.90 ± 0.38	22120.9 ± 0.3
(8, 0)	1.928 ± 0.011	1.93 ± 0.18	25046.5 ± 0.5
(9, 0)	1.908 ± 0.011	1.69 ± 0.16	25407.2 ± 0.3
(10, 0)	1.897 ± 0.010	1.75 ± 0.10	25767.4 ± 0.3
(11, 0)	1.878 ± 0.010	1.69 ± 0.10	26126.7 ± 0.3
(12, 0)	1.856 ± 0.010	1.64 ± 0.10	26484.5 ± 0.4
(13, 0)	1.834 ± 0.010	1.65 ± 0.10	26839.4 ± 0.3
(14, 0)	1.814 ± 0.010	1.77 ± 0.10	27191.2 ± 0.4
(15, 0)	1.784 ± 0.011	1.74 ± 0.10	27539.7 ± 0.4

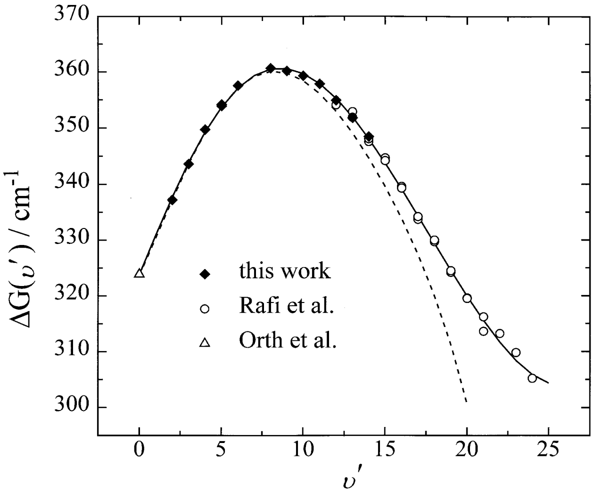

Fig. 3. The difference $\Delta G(v')$ between the vibrational energies of successive levels of the $A^1\Sigma^+$-state of NaH is plotted against the vibrational level v'. The experimental values are obtained from the DFWM-spectra (this work, *diamonds*) and references [2, 1] (*triangle*, *circles*). The size of these symbols corresponds to the experimental uncertainty. The *dashed line* depicts the values calculated from the Dunham coefficients given in [3]. For v'-values > 10 there is an increasing discrepancy between the measurements and the calculations. Therefore new Dunham coefficients Y_{k0} were fitted (*solid line*) to the data points

Table 2. Dunham coefficients of the $A^1\Sigma^+$-state of NaH. Values without errors are the same as in [3] and did not have to be changed. Since the coefficients are partly correlated a variation within the given errors conserves the accuracy of calculated transition energies only if several coefficients are changed simultaneously

Y_{kl}/cm^{-1}	$l = 0$	$l = 1$	$l = 2$
$k = 0$	0.86	1.7121	$(-2.30 \pm 0.10)\cdot 10^{-4}$
$k = 1$	317.56	0.09152	$(4.9 \pm 0.4)\cdot 10^{-6}$
$k = 2$	2.701 ± 0.001	$(-12.09 \pm 0.01)\cdot 10^{-3}$	
$k = 3$	$(27.31 \pm 0.01)\cdot 10^{-2}$	$(6.50 \pm 0.02)\cdot 10^{-4}$	
$k = 4$	$(-43.29 \pm 0.01)\cdot 10^{-3}$	$(-1.80 \pm 0.05)\cdot 10^{-5}$	
$k = 5$	$(21.59 \pm 0.05)\cdot 10^{-4}$	$(1.9 \pm 0.1)\cdot 10^{-7}$	
$k = 6$	$(-5.25 \pm 0.05)\cdot 10^{-5}$		
$k = 7$	$(5.3 \pm 0.3)\cdot 10^{-7}$		

describe the v'-dependence of the centrifugal distortion constant $D_{v'}$, were derived by fitting (4) to the experimental results (see Fig. 2). The value $-2.30 \cdot 10^{-4}$ cm^{-1} of Y_{02} does not coincide with the prediction $-1.99 \cdot 10^{-4}$ cm^{-1} from the Kratzer relation (5) [26].

$$Y_{02} = -4 \cdot Y_{01}^3 / Y_{10}^2 \tag{5}$$

But this formula is strictly valid only for a harmonic or a Morse potential. The bottom of the $A^1\Sigma^+$-potential is more shallow than in the case of these potentials (see Fig. 4) and the retractility nearby the equilibrium distance is weaker than indicated by Y_{10} leading to a larger centrifugal distortion. This anomalous behavior of the potential results also in increasing vibrational spacings $\Delta G(v')$ with increasing vibrational quantum number up to $v' = 9$ (see Fig. 3) whereas a harmonic potential shows equidistant and a Morse potential decreasing spacings.

Mostly because Y_{02} and Y_{12} are missing in the set of coefficients recommended up to now the spectral line positions are reproduced with a much higher accuracy, in particular for high J-values, if they are calculated with the new coefficients instead the previously recommended ones (see Fig. 1). Apart from the Dunham coefficients of the $A^1\Sigma^+$-state the coefficients of the ground state inclusive the centrifugal distortion [3, 27] and an electronic energy of 22713.0 cm^{-1} [3] were used to obtain the transition energies.

By means of the new coefficients a Rydberg-Klein-Rees (RKR) potential for the $A^1\Sigma^+$-state was calculated up to $v' = 25$ using an algorithm reported by Tellinghuisen [28]. The result is depicted in Fig. 4 and the RKR turning points are listed in Table 3. The potential is in good agreement with the one published by Orth et al. [2]. However, it includes five additional vibrational levels.

3.2 NaD

The spectra of NaD were recorded in the region between 371–405 nm and 430–468 nm and were analyzed in the same way as the NaH-spectra in order to get the band origins and rotational constants for the vibrational levels $v' = 4$ to 17 of the $A^1\Sigma^+$-state. The results are given in Table 4.

The constants of the levels $v' = 4$, 5 and 6 were, to our knowledge for the first time, directly derived from NaD-spectra. For $v' \geq 7$ the obtained values are in good agreement with data of Olsson [7] (see Fig. 5).

As discussed by several authors [e.g. 8, 26, 29] the Dunham coefficients of two isotopic molecules A, B with

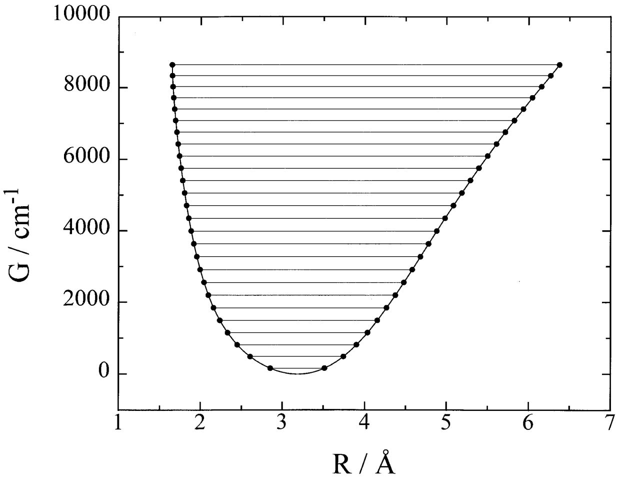

Fig. 4. The RKR potential energy curve of the $A^1\Sigma^+$-state of NaH. G is the vibrational energy inclusive the Dunham correction and equals $\sum_{k=0} Y_{k0}(v' + 1/2)^k$

Table 3. Turning points of the RKR potential energy curve of the $A^1\Sigma^+$-state of NaH. $G(v')$ is the vibrational energy inclusive the Dunham correction and equals $\sum_{k=0} Y_{k0}(v' + 1/2)^k$

v'	$G(v')$/cm^{-1}	R_-/Å	R_+/Å
0	160.34	2.8529	3.5154
1	483.99	2.6065	3.7425
2	814.41	2.4478	3.9011
3	1151.66	2.3293	4.0343
4	1495.28	2.2358	4.1541
5	1844.46	2.1596	4.2659
6	2198.19	2.0959	4.3727
7	2555.33	2.0416	4.4765
8	2914.70	1.9947	4.5784
9	3275.16	1.9535	4.6793
10	3635.63	1.9168	4.7798
11	3995.13	1.8840	4.8805
12	4352.78	1.8542	4.9815
13	4707.83	1.8270	5.0831
14	5059.65	1.8021	5.1855
15	5407.70	1.7792	5.2890
16	5751.56	1.7580	5.3935
17	6090.89	1.7386	5.4992
18	6425.45	1.7209	5.6062
19	6755.10	1.7047	5.7144
20	7079.78	1.6902	5.8239
21	7399.59	1.6775	5.9345
22	7714.79	1.6666	6.0458
23	8025.85	1.6577	6.1572
24	8333.54	1.6511	6.2677
25	8639.05	1.6472	6.3758

Table 4. Rotational constants of the $A^1\Sigma^+$-state of NaD and band origins determined by DFWM-spectra of NaD. For some bands there are no values for $D_{v'}$ given because in these cases too few lines were observed to get a reasonable fit

Band: (v', v'')	$B_{v'}$/cm^{-1}	$D_{v'}\cdot 10^4$/cm^{-1}	Band origin/cm^{-1}
(10, 0)	1.010 ± 0.011	–	24877.0 ± 0.4
(11, 0)	1.007 ± 0.010	0.51 ± 0.15	25136.4 ± 0.4
(12, 0)	1.004 ± 0.010	0.52 ± 0.13	25396.5 ± 0.4
(13, 0)	0.997 ± 0.010	0.49 ± 0.13	25656.7 ± 0.4
(14, 0)	0.991 ± 0.010	0.48 ± 0.13	25916.8 ± 0.4
(15, 0)	0.983 ± 0.010	0.47 ± 0.13	26176.3 ± 0.4
(16, 0)	0.977 ± 0.010	0.47 ± 0.13	26435.3 ± 0.4
(17, 0)	0.969 ± 0.010	0.47 ± 0.13	26693.2 ± 0.5
(5, 1)	1.006 ± 0.008	0.68 ± 0.14	22778.1 ± 0.4
(6, 1)	1.003 ± 0.006	0.50 ± 0.06	23028.2 ± 0.3
(7, 1)	1.009 ± 0.005	0.52 ± 0.04	23280.6 ± 0.3
(8, 1)	1.004 ± 0.013	0.41 ± 0.10	23536.5 ± 0.4
(4, 2)	0.993 ± 0.009	–	21725.7 ± 0.3
(5, 2)	1.002 ± 0.007	0.58 ± 0.11	21972.1 ± 0.3
(6, 2)	1.008 ± 0.007	0.59 ± 0.06	22221.9 ± 0.3
(7, 2)	1.011 ± 0.005	0.54 ± 0.04	22474.6 ± 0.3
(8, 2)	1.012 ± 0.005	0.52 ± 0.04	22729.5 ± 0.3
(9, 2)	1.014 ± 0.005	0.55 ± 0.04	22986.7 ± 0.3
(10, 2)	1.009 ± 0.006	0.51 ± 0.06	23244.9 ± 0.4
(11, 2)	0.994 ± 0.023	–	23504.2 ± 0.4
(7, 3)	1.013 ± 0.008	0.66 ± 0.19	21688.1 ± 0.3
(8, 3)	1.013 ± 0.008	0.54 ± 0.14	21943.2 ± 0.3
(12, 3)	1.006 ± 0.012	–	22978.1 ± 0.4
(10, 4)	1.015 ± 0.011	–	21691.6 ± 0.3
(11, 4)	1.004 ± 0.010	–	21951.2 ± 0.3

identical potential functions scale to a very good approximation with the reduced masses μ of the molecules:

$$Y_{klB} = \left(\frac{\mu_A}{\mu_B}\right)^{k/2+l} Y_{klA} \tag{6}$$

$B_{v'}$, $D_{v'}$ and $\Delta G(v')$-values were calculated via Dunham coefficients which were obtained by this formula from the new determined NaH-coefficient of the $A^1\Sigma^+$-state. Then they were compared with the data derived from the spectra (see Fig. 5). The agreement is within the experimental accuracy of 0.007 cm^{-1} for $B_{v'}$ and $6\cdot 10^{-6}$ cm^{-1} for $D_{v'}$.

A determination of Dunham coefficients from experimental data which are available only for a limited number of vibrational levels ($v' = 4$ to 17) of NaD would lead to very inaccurate molecular constants for vibrational levels outside of the observed region. Thus the scaling of the NaH-coefficients leads to the more suitable set of Dunham coefficients of the $A^1\Sigma^+$-state of NaD. This set is given in Table 5.

4 Discussion and conclusions

A comparison between the measured NaH-spectra and line positions calculated with the new Dunham-coefficients shows an agreement better than 0.3 cm^{-1} for J-values below 15. For higher angular momenta up to $J = 25$ the differences are still less than 2 cm^{-1} (see Fig. 1). Thus these coefficients lead to a reliable identification of NaH-lines, although one studies only a small part of the spectrum which does not contain any band head.

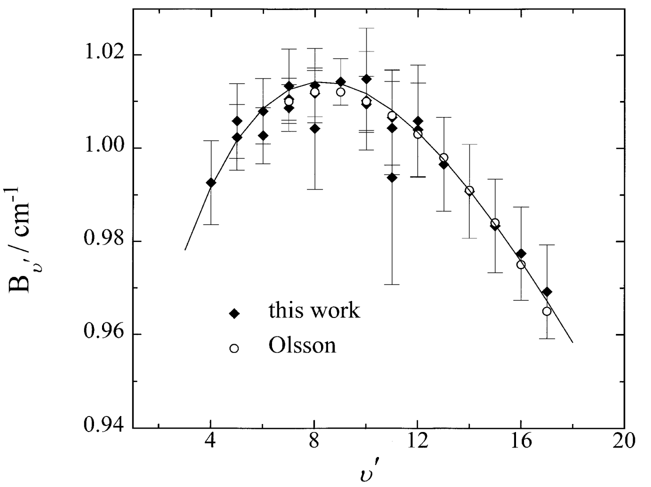

Fig. 5. Experimental values for the rotational constant $B_{v'}$ of the $A^1\Sigma^+$-state of NaD obtained from DFWM-spectra (this work, *diamonds*) and from [7] (*circles*) are compared to values which were calculated by scaling the new Dunham coefficients of NaH with the reduced masses (*solid line*)

Table 5. Dunham coefficients of the $A^1\Sigma^+$-state of NaD calculated by means of the reduced mass-method from the coefficients of NaH

Y_{kl}/cm^{-1}	$l = 0$	$l = 1$	$l = 2$
$k = 0$	0.86	0.8926	$-6.3\cdot 10^{-5}$
$k = 1$	229.30	0.03445	$9.6\cdot 10^{-7}$
$k = 2$	1.408	$-3.286\cdot 10^{-3}$	
$k = 3$	$10.28\cdot 10^{-2}$	$1.28\cdot 10^{-4}$	
$k = 4$	$-11.78\cdot 10^{-3}$	$-2.55\cdot 10^{-6}$	
$k = 5$	$4.238\cdot 10^{-4}$	$1.9\cdot 10^{-8}$	
$k = 6$	$-7.44\cdot 10^{-6}$		
$k = 7$	$5.4\cdot 10^{-8}$		

The results presented above show also that DFWM is a suitable method to investigate the structure of molecules particularly if it is combined with an optogalvanic calibration.

The DFWM-signal varies with the dephasing time T_2 depending on the intensity of the laser beams [30]. In our experiment T_2 is given by the coherence-time of the laser which is 0.3 ns (corresponding to a bandwidth of 0.01 cm^{-1} for one mode) and independent on the lifetime of any involved level as long as this lifetime is larger than the laser-coherence-time. The signal of LIF or of emission spectroscopy might be suppressed by quenching or reactive processes, which may depopulate the irradiating levels. Therefore in some cases a transient species can still be investigated by DFWM while other techniques may fail due to an inadequate signal level. In addition the DFWM-signal arises as a laser like beam. This is a great advantage if the sample has reactive components-like in our case of sodium- which would destroy collecting optics if they are in contact with the sample.

By using a laser with a smaller linewidth it is possible to measure the spectral DFWM-profiles of the observed transitions. With the help of the existing knowledge about DFWM [31] the analysis of these profiles should yield information on interaction potentials and on the live times as well as on the coherence times of the states involved.

We like to thank A. Klamminger for his experimental data of the NaH-spectrum in the blue spectral region, L. Lehr and H. Bauer for their helpful support with the experiments and R. de Vivie-Riedle and S. Rutz for using their RKR-programm.

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