Extended Analysis of the $K = 3$ Inversion-Rotation Doublets for $^{14}ND_3$ and $^{15}ND_3$ in the $\nu_2 = 1$ Excited State

J. Doose, W. Neustock, and A. Guarnieri

Institut für Physikalische Chemie der Universität Kiel, Abteilung Chemische Physik, Kiel, FRG

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Several $K = 3$ doublets of $^{14}ND_3$ and $^{15}ND_3$ in the $\nu_2 = 1$ excited vibrational state have been observed. With the new lines we were able to obtain improved values for the η_3^0 and η_3^J constants. For $^{14}ND_3$ $\eta_3^0 = 2.3517(15) \cdot 10^{-5}$ MHz, $\eta_3^J = -1.068(8) \cdot 10^{-8}$ MHz, and for $^{15}ND_3$ $\eta_3^0 = 2.3548(23) \cdot 10^{-5}$ MHz, $\eta_3^J = 1.061(10) \cdot 10^{-8}$ MHz.

Introduction

In two preceding investigations [1, 2] the pure inversion spectrum of the ammonia isotopomers $^{14}ND_3$ and $^{15}ND_3$ in the $\nu_2 = 1$ excited vibrational state has been investigated. In a further publication [3] these microwave data have been used together with high resolution IR-data to perform a more general fitting of the molecular parameters.

A fit of the $K = 3$ doublets measured in the millimeter wave range has also been performed in [1] and [2] but the values of the obtained η_3 parameters had a large error and did not show complete agreement with the values obtained in [3] because of the limited number of available $K = 3$ doublets. To get a better information about these parameters and also as complementary data of recent publications [4, 5], we have now considered and measured a sufficient number of $K = 3$ doublets for both isotopomers up to $J = 15$.

Experimental

Ammonia $^{14}ND_3$ has been purchased from Merck, Sharp & Dohme (Canada) with a D concentration of 99 atom% and used without purification.

The $^{15}ND_3$ sample was prepared from $^{15}ND_4Cl$ purchased from Rohstoff Einfuhr GmbH, Düsseldorf with a declared D concentration of 99% and ^{15}N concentration of 95%. Oki and Okaya klystrons, used to produce millimeter wave frequencies in the region 45–100 GHz, were phase locked to a PTS 500 signal generator through a double-loop stabilisation. Source modulation of the Klystron is provided by phase modulating the 10 MHz of the Schomandl FDS 30 synchronizer.

The PTS synthesizer is controlled by a TI-Personal Computer which generates the digitally controlled sweep for the klystron. When Stark modulation was used, the cell was a conventional Hughes-Wilson type Stark cell of 1,5 m length. 33 kHz square wave modulation was applied to the septum.

The range of the sample pressures was between 3 and 7 Pa. Measurements were made partially at room temperature and partially at 400 K. The accuracy of the measurements is believed to be $\pm$ 10 kHz except for very weak lines.

Results and Discussion

All measured lines are listed in Table 1. The lines of the $K = 3$ doublets have an intensity ratio of 10:1 because of the spin statistics, and thus lines with $J > 10$ (absolute energy level higher than 1500 cm^{-1}) were sometimes very weak and only measurable with Stark spectroscopy and an averaging procedure. The transition $A_1'-A_1''$ is strong, the $A_2'-A_2''$ is weak and the sequence strong-weak or weak-strong is dependent of the J quantum number. The symmetry species of the levels are those corresponding to the permutation inversion group isomorphous to the D_{3h} point group.

It should here be remembered that the $K = 3$ doublets originate from an operator

$$H_3' = H_i(\varrho)\,(\hat{J}_+^6 + \hat{J}_-^6)\,,$$

Reprint requests to Prof. Dr. A. Guarnieri, Institut für Physikalische Chemie der Universität Kiel, Abteilung Chemische Physik, Olshausenstraße 40, D-2300 Kiel 1.

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Table 1. Frequencies of the doublet lines in MHz for $^{14}ND_3$ and $^{15}ND_3$. Sign + on K corresponds to the spin statistical weight 1 ($A_2'-A_2''$) and sign − to the spin statistical weight 10 ($A_1'-A_1''$).

J	K	$^{14}ND_3$	$^{15}ND_3$
5	+3	101 321.365 [c]	
5	−3	101 323.215 [c]	92 462.707 [b]
6	+3	97 821.14 [c]	89 139.720 [b]
6	−3	97 815.54 [c]	89 134.098 [b]
7	+3	93 883.70 [c, a]	85 406.47 [b]
7	−3	93 897.59 [c, a]	85 422.54 [b]
8	+3	89 618.67 [a]	81 375.59 [b]
8	−3	89 588.34 [a]	81 344.65 [b]
9	+3	84 994.25 [d, a]	77 006.30 [d]
9	−3	85 054.41 [d, a]	77 066.04 [d]
10	+3	80 277.50 [a]	72 566.77 [a]
10	−3	80 165.94 [a]	72 455.79 [d, a]
11	+3	75 169.43 [d, a]	67.755.07 [a]
11	−3	75 360.71 [d, a]	67 946.83 [a]
12	+3	70 376.50 [a]	63 275.52 [a]
12	−3	70 061.66 [a]	62 961.17 [a]
13	+3	64 898.53 [a]	58 126.44 [a]
13	−3	65 396.24 [a]	58 624.78 [a]
14	+3	60 486.22 [a]	54 056.20 [a]
14	−3	59 728.21 [a]	53 296.49 [a]
15	+3	54 591.46 [a]	48 509.24 [a]
15	−3	55 711.94 [a]	49 632.29 [a]

[a] This work. — [b] Measured in Kiel, see [2]. — [c] Measured in Kiel, see [1]. — [d] Measured in Cologne, see [3].

where $H_i(\varrho)$ is a function of the large amplitude inversion coordinate ϱ defined in [6, 7] and $\hat{J}_\pm$ are rotational step operators. Suitable wave functions are obtained by multiplying inversion wave functions $\Psi(^{s}_{a})_{J,K}(\varrho)$ with a linear combination of symmetric top wave functions:

$$|A_\pm\rangle = 2^{-1/2}(|J, k\rangle \pm |J, -k\rangle) \quad \text{as it follows}$$

$$|\Psi(^{s}_{a})_{J,K}(\varrho)\rangle\, |A_\pm\rangle = |^{\pm}\varphi(^{s}_{a})_{J,K}(\varrho)\rangle\,.$$

For $K = 3$ follows with the use of the given operator:

$$\begin{aligned}\langle^{\pm}\varphi(^{s}_{a})_{J,3}|\, H_3'\, |^{\pm}\varphi(^{s}_{a})_{J,3}\rangle &= \langle\Psi(^{s}_{a})_{J,3}|\, H_i(\varrho)\, |\Psi(^{s}_{a})_{J,3}\rangle\langle A_\pm|\, \hat{J}_+^6 + \hat{J}_-^6\, |A_\pm\rangle \\ &= \pm\, \hbar^6 \langle\Psi(^{s}_{a})_{J,3}|\, H_i(\varrho)\, |\Psi(^{s}_{a})_{J,3}\rangle\,. \\ &\quad\cdot \prod_{r=1}^{3} [J(J+1) - r(r-1)]\,.\end{aligned}$$

The matrix element $\langle\Psi(^{s}_{a})_{J,3}|\, H_i(\varrho)\, |\Psi(^{s}_{a})_{J,3}\rangle$ represents a ϱ-independent parameter which depends parametrically upon J and is called $\eta_3^{(^{s}_{a})}$ [6, 7].

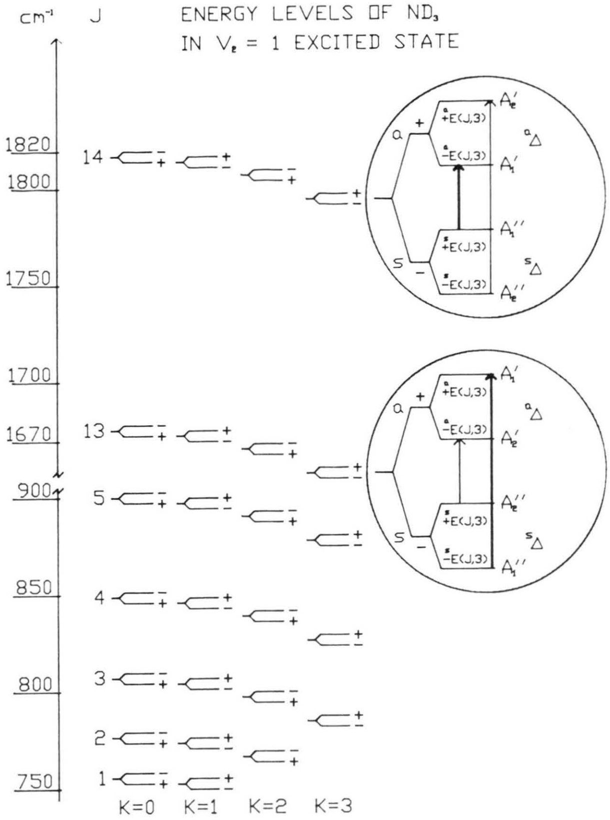

Fig. 1. Inversion-rotation levels of the $\nu_2 = 1$ excited state (after [8]). $K = 3$ levels are blown-up showing the splitting and the characteristics of the doublets whose frequency difference is given by

$$\Delta\nu = 4\,\eta_3 \prod_{r=1}^{3} [J(J+1) - r(r-1)]\,.$$

The measured frequencies do not allow a separate determination of $\eta_3^{(a)}$ and $\eta_3^{(s)}$ but only an average value of $\eta_3 = (\eta_3^{(s)} + \eta_3^{(a)})/2$. It follows that the interaction energy is given by

$$^{(^{s}_{a})}E(J, 3) = \eta_3[J(J+1)] \cdot [J(J+1) - 2] \cdot [J(J+1) - 6]\,,$$

where a and s indicate the parity of the inversion wave functions. Following the nomenclature of the D_{3h} group, the a-inversion level splits into A_2' and A_1' sublevels and the s-inversion level accordingly into A_1'' and A_2'' sublevels. Only $A_2'-A_2''$ and $A_1'-A_1''$ transitions are allowed. Because of spin statistics the $A_2'-A_2''$ transition is 10 times weaker than the $A_1'-A_1''$ transition (see Figure 1). The splitting

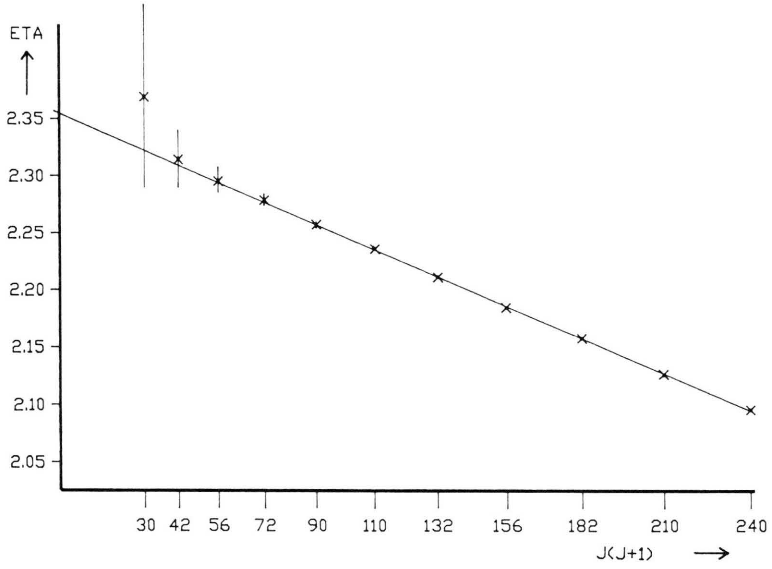

Fig. 2. Plot of the η_3 constant against $J(J+1)$ showing the J-dependence and the corresponding measurement error given by the length of the error bars. The large error for $J = 5$ is due to the corresponding small distance between the lines of the doublet.

Table 2. Measured and calculated frequency difference in MHz between lines of the doublets for $^{14}ND_3$.

J	Measured (MHz)	Calculated (MHz)	Meas.-Calc. (kHz)
5	1.91	1.87	40 [c]
6	5.60	5.58	20 [c]
7	13.89	13.86	30 [c]
8	30.33	30.27	60 [a]
9	60.07	60.03	40 [d, a]
10	110.56	110.44	120 [a]
11	191.28	191.23	50 [d, a]
12	314.94	315.02	−80 [a]
13	497.71	497.62	90 [a]
14	758.21	758.37	−160 [a]
15	1120.48	1120.41	70 [a]

[a] This work. – [c] Measured in Kiel, see [1]. – [d] Measured in Cologne, see [3].

Table 3. Measured and calculated frequency difference in MHz between lines of the doublets for $^{15}ND_3$.

J	Measured (MHz)	Calculated (MHz)	Meas.-Calc. (kHz)
5	–		
6	5.72	5.59	130 [b]
7	14.06	13.88	−180 [b]
8	30.55	30.31	240 [a]
9	60.34	60.12	220 [d, a]
10	110.82	110.61	210 [a]
11	191.76	191.55	210 [d, a]
12	315.57	315.58	−10 [a]
13	498.40	498.57	−170 [a]
14	759.71	759.94	−230 [a]
15	1123.05	1122.89	160 [a]

[a] This work. – [b] Measured in Kiel, see [2]. – [d] Measured in Cologne, see [3].

Table 4. Values for the η_3^0 and η_3^J constants in MHz compared with those obtained in preceding investigations.

	This work	[3] (IR + MW data)	[1] and [2]
η_3^0 ($^{14}ND_3$)	$2.3517(15) \cdot 10^{-5}$	$2.365(10) \cdot 10^{-5}$	$2.33(5) \cdot 10^{-8}$
η_3^J ($^{14}ND_3$)	$-1.068(7) \cdot 10^{-8}$	$-1.15(8) \cdot 10^{-8}$	–
η_3^0 ($^{15}ND_3$)	$2.3548(23) \cdot 10^{-5}$	$2.455(10) \cdot 10^{-5}$	$2.408(24) \cdot 10^{-5}$
η_3^J ($^{15}ND_3$)	$-1.061(10) \cdot 10^{-8}$	$-2.05(12) \cdot 10^{-8}$	$-1.57(30) \cdot 10^{-8}$

between the doublet lines is therefore given by

$$\Delta\nu = 4\eta_3 \prod_{r=1}^{3} [J(J+1) - r(r-1)] .$$

It has been shown that the J dependence of the η_3 parameter should be of the kind

$$\eta_3 = \eta_3^0 + J(J+1)\,\eta_3^J + \text{higher terms.}$$

In Tables 2 and 3 the measured and calculated frequency differences inside a doublet are listed together with the deviation obtained by the fitting procedure. The smaller deviations in the case of $^{14}ND_3$ are due to the better measurement possibilities because of the stronger intensity of the lines due to the better experimental conditions.

In Table 4 the values obtained for the constants η_3^0 and η_3^J for both isotopomers are compared with those given in the preceding publications. It can be seen that the present values are i) more precise than the literature values and ii) that the discrepancy between $^{14}ND_3$ and $^{15}ND_3$ data is now below the error level of the measurements, as expected.

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