AIP | The Journal of Chemical Physics

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Citation: The Journal of Chemical Physics **78**, 2144 (1983); doi: 10.1063/1.445077
View online: http://dx.doi.org/10.1063/1.445077
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/78/5?ver=pdfcov
Published by the AIP Publishing

Microwave optical double resonance spectroscopy of ND_2 in (000) of $\tilde{X}\,^2B_1$ [a)]

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(Received 26 October 1982; accepted 16 November 1982)

Microwave optical double resonance spectroscopy has been used to observe in excess of 200 microwave transitions involving 21 rotational levels in the (000), $\tilde{X}\,^2B_1$ state of ND_2. The observed transitions have been fitted to two model Hamiltonians. In the first fit, accurate values for the spin rotation constants and ^2D hyperfine constants were determined. The ^2D hyperfine constants are in excellent agreement with those calculated from ^1H parameters in NH_2, (000) $\tilde{X}\,^2B_1$. In the second fit, only the constants of the Hamiltonian describing the spin-rotation effect were determined. The derived spin-rotation parameters for ND_2 (A_s, B_s, C_s, Δ_K^s, Δ_N^s, $\Delta_{NK}^s + \Delta_{KN}^s$, δ_K^s, and δ_N^s) are compared to the appropriate scaled constants of NH_2.

I. INTRODUCTION

As a result of microwave optical double resonance (MODR) spectroscopy, precise values for the spin rotational, spin rotation centrifugal distortion, and ^{14}N and ^1H hyperfine parameters are available for the (000), $\tilde{X}\,^2B_1$ state of NH_2.[1] A similar, but less extensive, MODR study has been reported on the (000) $\tilde{X}$ state of NHD.[2] For the corresponding state of ND_2 the only previous high resolution study was the laser magnetic resonance (LMR) spectrum of ν_2 at 9 μm. This spectrum was analyzed so as to yield precise rotational, centrifugal distortion and spin rotational constants for (000) and (010). The only other report of a spectroscopic study of ND_2 in the gas phase was the classic absorption study of Dressler and Ramsay.[4]

One of the interesting features of free radicals like NH_2 is the spin rotation interaction. Of some interest is the isotopic dependence of the parameters that describe the interaction, the change is particularly large when ^2D is substituted for ^1H since their mass ratio is so large. This subject has recently been considered by Brown *et al.*[5] for the quadratic parameters A_s, B_s, and C_s and the theoretical predictions were applied to NH_2, NHD, and ND_2. No such theoretical considerations of the isotope dependence of the quartic spin rotation parameters appear to have been made, presumably since no large data base exists from experiment upon which to base a comparison.

We report here the application of microwave optical double resonance spectroscopy to the (000), $\tilde{X}\,^2B_1$ state of ND_2 so as to complete studies of ^1H and ^2D isotopic forms of NH_2 at microwave precision. As were the majority of transitions in the $\tilde{X}$ states[1,2] of NH_2 and NHD, the microwave (MW) transitions observed for ND_2 were magnetic dipole in origin, $N_{K_aK_c}$, $F_2(J=N-\frac{1}{2}) \longrightarrow F_1(J=N+\frac{1}{2})$. The analysis of the observed MODR lines reported here yields three quadratic and five quartic parameters describing the spin rotation interaction as well as three ^2D magnetic hyperfine coupling constants. All the determined parameters are compared to values from the equivalent constants of NH_2.

II. EXPERIMENTAL TECHNIQUES

The general experimental approach for MODR studies of NH_2 and NHD have been considered in some detail in previous publications.[1,2] Certain changes specific to the ND_2 experiment are described below.

ND_2 was prepared from the reaction of the products of a 10–30 W microwave discharge in D_2O with N_2H_4. No problem was encountered in obtaining a sufficient concentration of ND_2 for MODR studies by this method although it was apparent that the optimum conditions for maximum NH_2, NHD, or ND_2 in the above chemical scheme did occur at different D_2O partial pressures. Moreover, it was possible to distinguish between NH_2, NHD, and ND_2 by switching rapidly between H_2O and D_2O. Upon this exhange, NH_2 laser induced fluorescence grew in intensity by a factor of 5–10, ND_2 lines disappeared (to the eye) within a few seconds, and NHD lines disappeared over a period of about 30 s. Optimum pressures in the MODR experiment were in the 50–100 mTorr range (measured with an uncalibrated, Hastings DV-6M gauge) at $[D_2O]/[N_2H_4]$ ratios of 1–3.

ND_2 was excited to the (0, 12, 0) and (0, 13, 0) states in $\tilde{A}\,^2A_1$ using 30–100 mW from a Coherent 599-03, single mode, dye laser operated with rhodamine 6G. The particular optical transitions to excite for a desired ground state MODR signal were located using the optical spectrum results of Dressler and Ramsay.[4] Microwave radiation of ≤ 2 W in the 1.5–7.0 GHz range was employed in the study. Resonant cavities were again used[1,2] to produce the necessary magnetic field to pump magnetic dipole transitions effectively. The 1.5–7.0 GHz range studied required the use of three cavities of diameters 19.53, 12.7, and 9.42 cm.

[a)] The work at the University of North Carolina at Chapel Hill was supported by the National Science Foundation, Grant CHF-81111131 and a grant from the Research Corporation.

0021-9606/83/052144-10$2.10

The general procedure to detect a particular $N_{K_aK_c}$, $F_2 \leftarrow F_1$ transition in (000), $\tilde{X}\,^2B_1$ of ND$_2$ was as follows.

(1) The MODR signal for a known microwave transition[1] in NH$_2$, close in frequency to the expected[3] ND$_2$ transition, was optimized using the correct cavity for the MW region of interest. This procedure generally required locating and tuning the TE$_{011}$ mode of the cavity to the appropriate frequency. Occasionally the MW transition predicted for ND$_2$ occurred at the high frequency end of the operational range of a particular cavity. In such circumstances the TE$_{011}$ mode was often either nonobservable, very broad (>10 MHz), or badly coupled. In these cases, other modes of good Q were located and tested to confirm that magnetic dipole transitions in NH$_2$[1] could be adequately pumped prior to the search for the unknown ND$_2$ signals.

Several transitions of ND$_2$ fell well below the lowest operating frequency of the TE$_{011}$ mode for our largest cavity (~2000 MHz). It was unrealistic and inconvenient to build the large cylindrical or rectangular cavities needed to go below this frequency. We thus tested many modes that were seen to operate below 2000 MHz in the 19.53 cm diameter cavity. Only one mode (of unknown character) gave moderately strong MODR signals in the 1650–2000 MHz range on magnetic dipole allowed transitions. The low frequency cut off for this mode was determined not by the available microwave sources but rather by the very rapid deterioration and loss of the mode around 1650 MHz.

(2) The particular ND$_2$ optical transitions pumped by the dye laser were easily located using the optical spectrum results of Dressler and Ramsay.[4] The frequencies of the ND$_2$ optical transitions were often confirmed relative to known NH$_2$[4] or NHD[6] features in the same spectral region.

(3) The MW frequencies for the search for the $N_{K_aK_c}$, $F_2 - F_1$ transitions in ND$_2$ were available from the tabulated energy levels obtained from analysis of the LMR results.[3] The calculation of the ^{14}N and ^{2}D hyperfine pattern of each spin rotation transition, using scaled NH$_2$ parameters,[1] greatly speeded up the search once the first hyperfine component had been obtained. In all cases the observation of ground state, magnetic dipole transitions was confirmed by observing the identical signals (frequency and sign) when the $F_1 - F_1$ or $F_2 - F_2$ components of the appropriate optical transition were pumped. All observed signals corresponded to increased fluorescence when the microwave radiation was resonant.

III. OBSERVATIONS

In total, over 200 transitions involving 21 rotational levels were observed and these are given in Table I. The observed linewidth (FWHM) were typically 4–5 MHz. For the para nuclear spin levels $I^D = 1$ [corresponding to (K_aK_c) ee or oo], one would expect nine, fully allowed $(\Delta N = \Delta J = \Delta F)$ hyperfine components for each spin rotation transition. As can be seen, these nine components are generally resolved in our experiment with a characteristic ^{14}N splitting of about 30–70 MHz and about 8–13 MHz for ^{2}D. For ortho levels $I^D = 2$ or 0 (eo or oe rotational states), an 18 line pattern is expected and, as can be seen from Table I, the entire pattern was rarely measured. The reasons for the incomplete patterns are that some components were very weak, that occasionally transitions were unresolved or that, in some situations, the entire pattern was not accurately measured since the extremes of the ^{2}D pattern in each component of the ^{14}N triplet were generally sufficient for the purposes of our fit. As can be seen from Table I, transitions were observed for N_{1N} and N_{1N-1} $(1 \le N \le 6)$, N_{2N-1} $(3 \le N \le 8)$, and N_{2N-2} $(N = 3,\ 4,\ \text{and}\ 7)$.

In most cases the observed ground state MW transitions were far removed from possible overlap with upper state $(\tilde{A})$ MW transitions and thus any assignment ambiguity was removed. For the $\Delta(0,13,0)$ and $\Pi(0,12,0)$ vibrational states of $\tilde{A}\,^2A_1$, the spin rotational splittings are above our maximum operating frequency of 12.4 GHz. For the $N \le 5$ levels of the $\Sigma(0,13,0)$ state the spin splittings of N_{0N} are below our lowest operating range (≤1.6 GHz). One exception was the observation of one component of 6_{06}, $F_1 \leftarrow F_2$, $\Sigma(0,13,0)\ \tilde{A}\,^2A_1$ at around 1770 MHz in the same general region as transitions from 6_{16}, $F_2 \leftarrow F_1$, (000) $\tilde{X}$. We estimate from the observed spin splittings of the optical spectrum that the spin rotational splitting is about 1550 MHz for 6_{06} in $\Sigma(0,13,0)$, $\tilde{A}$ with $F_1 > F_2$. Thus, the 1770 MHz signal can be assigned to the component $J = 6\frac{1}{2} \leftarrow J = 5\frac{1}{2}$, $F^N = 7\frac{1}{2} \leftarrow F^N = 6\frac{1}{2}$ where the F^N quantum number corresponds to the coupling scheme $F^N = J + I^N$, with I^N being the nitrogen hyperfine quantum number. Scaling the ^{1}H parameters obtained from NH$_2$ in the $\tilde{A}$ state[7] one can estimate for this transition that the small ^{2}D hyperfine structure would be unresolved, resulting in a blended line of about 10 MHz width. The other ^{14}N components can be predicted using ^{14}N $\tilde{A}$ state parameters[7] at 1570 and 1410 MHz below our operating range. Extensive unsuccessful searches of the 1650 to 2150 MHz region for additional 6_{06}, $\tilde{A}$ state signals confirmed this view.

To observe the ground state 2_{12} signals listed in Table I, the optical transitions 2_{02}, $\Sigma(0,13,0)\ \tilde{A}\,^2A_1 - 2_{12}$, (000) $\tilde{X}\,^2B_1$, $F_1 - F_1$ or $F_2 - F_2$ were pumped. As expected we observed MODR signals in the range 2341–2493 MHz that corresponded to positive MODR signals, i.e., increased fluorescence with the microwaves on. This is the expected sign of MODR signals in ($\tilde{A}$ or $\tilde{X}$) when the optical transition is partially saturated, the total (spectrally unresolved) fluorescence is monitored and the F_1 and F_2 levels have similar quantum yields. However, the measurement of these positive signals attributable to 2_{12}, $F_2 - F_1$, $\tilde{X}$ was complicated by the presence in roughly the same frequency range, 2250–2400 MHz, of 30 negative MODR signals, i.e., decreased fluorescence with the microwaves on. Such MODR transitions with a negative sign have been observed previously in NH$_2$.[7,8] In such cases, the two levels involved in the MW transition are both in excited vibronic states but have very different quantum yields for fluorescence. The negative signals are not from 2_{02} $F_2 \leftarrow F_1$ in $\Sigma(0,13,0)$ with one of the levels perturbed[7] since the spin splitting for 2_{02} is less than 1 GHz. Subsequently it was found that these same negative transitions occured if other ortho

TABLE I. MODR lines observed in (000) $\tilde{X}\,^2B_1$ of ND_2.

N	K_a	K_c	F_N' [a]	F_N [a]	F'	F	obs.[b] (MHz)	o.−c.[c] (MHz)	Int.[d]	Comment
2	1	1					3245.24		140	e
							3248.81		180	e
							3253.72		160	e
							3258.37		190	e
							3265.21		275	e
							3271.77		130	e
6	1	5	6.5	7.5	5.5	6.5	3973.82	0.83	70	
			6.5	7.5	6.5	7.5	3984.77	1.08	80	
			6.5	7.5	7.5	8.5	3996.47	0.52	100	
			5.5	6.5	4.5	5.5	4017.71	0.96	70	f
			5.5	6.5	5.5	6.5	4028.13	0.89	70	f
			5.5	6.5	6.5	7.5	4040.16	0.68	80	f
			4.5	5.5	3.5	4.5	4054.61	0.76	45	f
			4.5	5.5	4.5	5.5	4065.21	0.89	50	f
			4.5	5.5	5.5	6.5	4077.91	1.11	60	f
4	1	3	4.5	5.5	3.5	4.5	3310.01	−0.57	90	
			4.5	5.5	4.5	5.5	3320.69	−0.3	105	
							3333.73		220	e
			3.5	4.5	3.5	4.5	3344.19	−0.47	110	
			3.5	4.5	4.5	5.3	3356.91	−0.45	120	
			2.5	3.5	1.5	2.5	3353.61	0.42	80	
			2.5	3.5	2.5	3.5	3363.12	−0.11	60	
			2.5	3.5	3.5	4.5	3375.87	−0.45	80	
1	1	1			0.5	1.5	3797.67	0.67	190	
					1.5	2.5	3803.41	0.55	275	
			1.5	2.5	2.5	3.5	3811.84	0.08	320	
					0.5	0.5	8329.92	0.77	60	
					1.5	1.5	3834.18	0.58	100	
					2.5	2.5	3842.36	0.28	160	
					1.5	1.5	3857.49	0.57	45	
					0.5	1.5	3892.89	−0.73	150	
					1.5	2.5	3899.17	−0.14	190	
					0.5	0.5	3907.29	−1.13	100	
					0.5	1.5	3916.11	−0.85	170	
3	1	3	3.5	4.5	2.5	3.5	1898.58	0.19	100	
			3.5	4.5	3.5	4.5	1908.04	0.15	120	
			3.5	4.5	4.5	5.5	1920.15	0.33	150	
			2.5	3.5	1.5	2.5	1994.06	−0.04	80	
			2.5	3.5	2.5	3.5	2003.35	0.52	100	
			2.5	3.5	3.5	4.5	2014.69	0.14	120	
			1.5	2.5	0.5	1.5	2063.59	−0.24	60	
			1.5	2.5	1.5	2.5	2072.26	0.1	70	
			1.5	2.5	2.5	3.5	2085.15	−0.09	90	
5	1	5	5.5	6.5	4.5	5.5	1659.85	0.4		
			5.5	6.5	5.5	6.5	1670.26	0.61		
			5.5	6.5	6.5	7.5	1681.78	0.24		
			4.5	5.5	3.5	4.5	1758.01	−0.13		
			4.5	5.5	4.5	5.5	1768.55	0.52	80	
			4.5	5.5	5.5	6.5	1779.59	−0.27	160	
			3.5	4.5	2.5	3.5	1839.25	0.46	90	
			3.5	4.5	3.5	4.5	1848.18	−1.36	100	
			3.5	4.5	4.5	5.5	1861.69	−0.06	120	
1	1	0					4303.95		70	f
					2.5	3.5	4309.4	−0.85	100	f
					1.5	2.5	4318.01	−0.98	50	f
			1.5	2.5	1.5	2.5	4368.3	0.27	175	f,g
					3.5	4.5	4380.7	−0.32	125	f
5	1	4	5.5	6.5	3.5	4.5	3615.88	0.02	140	
			5.5	6.5	4.5	5.5	3624.46	−0.16	180	
							3629.01			h
			5.5	6.5	5.5	6.5	3634.78	−0.46	240	
			5.5	6.5	5.5	6.5	3640.42	−0.34	280	g
			5.5	6.5	6.5	7.5	3647.45	−0.23	320	

TABLE I (*Continued*)

N	K_a	K_c	F_N'[a]	F_N[a]	F'	F	obs.[b] (MHz)	o.−c.[c] (MHz)	Int.[d]	Comment
5	1	4					3652.98			h
							3657.52			h
			5.5	6.5	7.5	8.5	3661.57	−0.46	360	
			4.5	5.5	4.5	5.5	3667.55	0.55	230	
			4.5	5.5	4.5	5.5	3673.93	−0.42	280	g
			4.5	5.5	5.5	6.5	3680.29	−0.24	290	
			3.5	4.5	3.5	4.5	3694.63	−0.26	360	e
			4.5	5.5	6.5	7.5	3694.63	−0.47	368	e
			3.5	4.5	3.5	4.5	3701.07	−1.07	195	g
			3.5	4.5	4.5	5.5	3707.21	−0.5	140	
			3.5	4.5	5.5	6.5	3722.29	−0.57	180	
3	1	2	3.5	4.5	1.5	2.5	3121.72	0.18	100	
			3.5	4.5	2.5	3.5	3128.56	0.05	120	
							3133.27		140	
							3139.41		200	
			3.5	4.5	3.5	4.5	3146.98	−0.26	250	g
			3.5	4.5	4.5	5.5	3151.18	−0.09	250	
							3158.73		275	
			2.5	3.5	1.5	2.5	3162.72	−0.18	280	e
			2.5	3.5	2.5	3.5	3162.72	0.27	280	e,g
							3166.51		285	
			1.5	2.5	1.5	2.5	3173.42	−0.35	260	g
			2.5	3.5	4.5	5.5	3181.71	−0.11	170	
			1.5	2.5	0.5	4.5	3193.14	−0.17	150	
4	1	4	4.5	5.5	2.5	3.5	1714.01	0.98	70	
			4.5	5.5	3.5	4.5	1720.96	−0.01		
			4.5	5.5	4.5	5.5	1731.18	0.26		
			4.5	5.5	4.5	5.5	1737.81	0.93		g
			4.5	5.5	5.5	6.5	1743.16	0.29		
			4.5	5.5	6.5	1.5	1756.37	−0.44	150	
			3.5	4.5	1.5	2.5	1809.89	−0.2	50	
			3.5	4.5	2.5	3.5	1817.52	0.34	70	
			3.5	4.5	3.5	4.5	1827.44	0.79	80	
			3.5	4.5	3.5	4.5	1833.58	−0.12	90	g
			3.5	4.5	4.5	5.5	1837.91	−0.6	95	
			3.5	4.5	5.5	6.5	1852.77	0.02	130	
			2.5	3.5	2.5	3.5	1901.22	−0.45		
			2.5	3.5	2.5	3.5	1910.66	−0.05		g
			2.5	3.5	3.5	4.5	1913.69	−0.46		
			2.5	3.5	4.5	5.5	1929.59	0.03		
6	1	6	6.5	7.5	7.5	8.5	1660.17	0.39	60	
							1673.34		70	
			5.5	6.5	3.5	4.5	1729.29	0.07	70	
			5.5	6.5	4.5	5.5	1737.26	−0.44	70	
			5.5	6.5	5.5	6.5	1747.97	0.13	60	
			5.5	6.5	5.5	6.5	1752.52	−0.25	80	g
			5.5	6.5	6.5	7.5	1758.93	−0.71	180	i
							1767.44		220	i
							1770.93		240	i
							1813.01		60	
							1821.81		80	
			4.5	5.5	6.5	7.5	1858.19	−0.75	120	
2	1	2			1.5	2.5	2341.43	0.44	140	j
							2344.51			h, j
					2.5	3.5	2249.52	0.04	140	j
					3.5	3.5	2354.56	0.41	160	j
					3.5	4.5	2361.24	0.27	380	j
							2367.29		100	j
					4.5	5.5	2375.99	0.42	360	j
					3.5	3.5	2397.58	−0.13	100	j
					3.5	2.5	2410.89	0.3	70	j
							2433.66		70	j
					0.5	1.5	2435.92	0.14	90	j
					1.5	2.5	2442.94	0.39	110	j

TABLE I (*Continued*)

N	K_a	K_c	F_N'[a]	F_N[a]	F'	F	obs.[b] (MHz)	o.−c.[c] (MHz)	Int.[d]	Comment
2	1	2					2446.65		100	j
					2.5	3.5	2453.61	0.37	280	j
							2459.86		110	j
					3.5	4.5	2468.33	0.2	260	j
							3472.46		60	j
							2492.49		60	j
4	2	2			3.5	4.5	5899.35	0.65	120	
							5903.95		80	f
							5909.47		250	
					3.5	4.5	5920.72	1.94	325	
					2.5	3.5	5928.11	1.14		f, h
					3.5	4.5	5940.49	1.01	180	
					4.5	5.5	5931.44	0.24	225	
3	2	2	3.5	4.5	2.5	3.5	6720.43	−0.75	160	
			3.5	4.5	3.5	4.5	6729.61	−0.35	190	
			3.5	4.5	4.5	5.5	6740.48	−0.68	220	
			2.5	3.5	1.5	2.5	6752.49	−0.92	100	
			2.5	3.5	2.5	3.5	6760.73	−0.83	120	
			2.5	3.5	3.5	4.5	6772.12	−0.55	125	
			1.5	2.5	1.5	2.5	6784.21	−0.47		
			1.5	2.5	2.5	3.5	6796.01	−0.49		
5	2	4	5.5	6.5	4.5	5.5	5294.27	0.07	170	
			5.5	6.5	5.5	6.5	5304.03	−0.26	225	
			5.5	6.5	6.5	7.5	5315.77	−0.36	250	
			4.5	5.5	3.5	4.5	5344.77	−0.23	150	
			4.5	5.5	4.5	5.5	5354.66	−0.14	180	
			4.5	5.5	5.5	6.5	5366.07	−0.52	200	
			3.5	4.5	2.5	3.5	5386.69	−0.11	140	
			3.5	4.5	3.5	4.5	5396.43	−0.15	150	
			3.5	4.5	4.5	5.5	5408.51	−0.19	160	
7	2	6					4969.65			f
					8.5	9.5	4982.55	−0.3		f
					7.5	8.5	5044.39	−0.12		f
					5.5	6.5	5086.61	0.11		f
					6.5	7.5	5097.61	−0.89		f
4	2	3	4.5	5.5	2.5	3.5	5759.44	0.51	130	
			4.5	5.5	3.5	4.5	5767.05	0.49	175	
			4.5	5.5	4.5	5.5	5776.21	0.04	280	
			4.5	5.5	4.5	5.5	5781.76	−0.46	350	g
			4.5	5.5	5.5	6.5	5787.59	−0.22	300	
							5801.49		350	e
			3.5	4.5	2.5	3.5	5809.22	−0.25	175	
			3.5	4.5	3.5	4.5	5818.65	−0.03	225	
							5824.73		275	e
			3.5	4.5	4.5	5.5	3830.37	0.1	260	
			2.5	3.5	0.5	1.5	5836.35	0.15	175	
							5843.46		300	e
			2.5	3.5	2.5	3.5	5852.01	0.36	160	
							5862.98		230	
			2.5	3.5	4.5	5.5	5878.61	−0.17	230	
3	2	1					6750.6		100	f, k
					3.5	4.5	6760.65	0.75	250	e, f, k
					1.5	2.5	6760.65	1.41	250	e, f, k
			3.5	4.5	3.5	4.5	6768.85	0.22	140	f, g, k
							6772.01		140	f, k
			2.5	3.5	2.5	3.5	6778.35	0.92	300	f, g, k
							6787.1		350	f, k
					4.5	5.5	6795.3	−0.04	210	f, k
					3.5	4.5	6802.6	0.28	200	f, k
6	2	5			8.5	9.5	5092.2	−0.66		
					7.5	8.5	5149.12	0.06		
							5166.01			f, h
			4.5	5.5	4.5	5.5	5176.69	−0.46		g

TABLE I (*Continued*)

N	K_a	K_c	$F_N'^{a}$	F_N^{a}	F'	F	obs.[b] (MHz)	o.−c.[c] (MHz)	Int.[d]	Comment
					5.5	4.5	5183.51	0.11		
					6.5	7.5	5196.8	−0.63		
8	2	7			8.5	9.5	4943.99	0.35		
							4947.01			f,h
					9.5	10.5	4955.86	0.41		
							4969.29			
					5.5	6.5	4990.36	0.19		
							5012.37			
					8.5	9.5	5022.64	0.99		
					9.5	10.5	5034.18	−0.55		
7	2	5			5.5	6.5	5836.24	0.13	140	
					6.5	7.5	5845.28	0.6	175	
					7.5	8.5	5855.7	−1.13	275	f,k
							5861.87		325	
							5868.88		325	
					6.5	7.5	5874.71	0.47	300	
					4.5	5.5	5878.69	0.31	375	
			7.5	8.5	9.5	10.5	5882.95	−0.33	275	
							5893.78		200	
					8.5	9.5	5900.6	−0.01	300	
					7.5	8.5	5915.68	−0.28	170	

[a] Intermediate hyperfine quantum "number" given only when assignment is unambiguous.

[b] Measurement uncertainty ±0.5 MHz unless noted in Comment column.

[c] Residuals of fit II.

[d] Relative intensity. Use only for comparison between lines of a given $N_{K_aK_c}$.

[e] Blended transitions.

[f] Measurement uncertainty ±1.0 MHz .

[g] Ortho level, $I_D=0$ component.

[h] Weak feature.

[i] Upper state transition (see the text), anomalous intensity.

[j] Complicated by presence of negative (upper state) signals in same region, see the text and Ref. 9.

[k] Broad features, hard to locate line center.

levels in (0, 13, 0) $\tilde{A}\,^2A_1$, were optically excited. The negative signals were strongest when 5_{24}, F_2 was optically excited and thus were of a collisional (four-level) type for 2_{02}, F_1 or F_2. A detailed consideration of these negative signals and other collisional effects in both NHD and ND_2 can be found elsewhere.[9]

IV. ANALYSIS

The ND_2 data of Table I was analyzed using a similar method to that used for NH_2.[1] The basic form of the Hamiltonian was

$$\hat{H}=\hat{H}_{\mathrm{ROT}}+\hat{H}_{\mathrm{SR}}+\hat{H}^{\mathrm{N}}_{\mathrm{HF}}+\hat{H}^{\mathrm{D}}_{\mathrm{HF}}\ ,$$

where the four terms represent the rotational, spin-rotational, ^{14}N-hyperfine, and ^{2}D-hyperfine contributions, respectively. Since the observed MODR transitions frequencies depend almost entirely on the latter three contributions to $\hat{H}$, the appropriate parameters in $\hat{H}_{\mathrm{ROT}}$ were not fitted. $\hat{H}_{\mathrm{ROT}}$ was set up in Watson's A-reduced form[10] and included the three quadratic and five quartic parameters. One sectic term, $H_K N_a^6$, was also included. Values for all nine parameters in $\hat{H}_{\mathrm{ROT}}$ were taken from the infrared LMR results.[3]

The spin-rotational Hamiltonian $\hat{H}_{\mathrm{SR}}$ was set up in the A-reduced form of Brown and Sears.[11] This formalism includes the three quadratic parameters (A_S, B_S, C_S) and six quartic parameters, set up in form analogous to Watson's rotational Hamiltonian.[10] So as to preserve continuity with our previous work[1] we chose to define the quartic contributions to $\hat{H}_{\mathrm{SR}}$ to have the *opposite* signs to those used by Brown and Sears.[11] Inspection of the appropriate matrix elements for $\hat{H}_{\mathrm{SR}}$[11] indicated that the independent determination of both Δ^S_{NK} and Δ^S_{KN} might prove difficult. $(\Delta^S_{NK}+\Delta^S_{KN})$ makes a contribution to the diagonal matrix elements ($\Delta N=\Delta K=0$) while Δ^S_{NK} alone contributes to $\Delta K=0$, $\Delta N=-1$ matrix elements. Simple calculations indicated that the off-diagonal contributions from Δ^S_{NK} would be less than our typical line measurement uncertainty of 0.5 MHz. We thus decided to determine only the linear combination $\Delta^S_{NK}+\Delta^S_{KN}$, arising from the diagonal contribution, in the least squares fit.

The hyperfine Hamiltonians included magnetic contributions for ^{14}N and ^{2}D (dipole–dipole and Fermi contact) and electric quadrupole terms for ^{14}N. No electric quadrupole terms for ^{2}D were included since its effect should be much less than that for ^{14}N and since the ^{14}N quadrupole parameters were barely determined from MODR results for NH_2.[1]

The energy levels were calculated by setting up and diagonalizing the Hamiltonian matrix. The coupling

TABLE II. Fine and hyperfine parameters for ND_2 (in MHz).

Parameter	Fit I[a,b]	Fit II[b,c]
A_S	−5127.7(8)	−5127.6(8)
B_S	−669.1(2)	−669.1(2)
C_S	+3.8(8)	+3.7(2)
Δ_N^S	−0.083(6)	−0.083(6)
Δ_K^S	−9.3(3)	−9.3(3)
$(\Delta_{NK}^S + \Delta_{KN}^S)$	0.88(6)	+0.88(6)
δ_N^S	−0.040(3)	−0.040(3)
δ_K^S	−0.26(6)	−0.26(6)
a_D	−10.1(3)	−10.32[d]
T_{aa}^D	3.3(7)	+2.86[d]
T_{cc}^D	−1.0(4)	−0.80[d]
σ_{FIT}	0.54[e]	0.56[e]

[a] In fit I, ^{14}N hyperfine parameters fixed at those of NH_2 (Ref. 1) rotational and centrifugal distortion parameters from Ref. 3.

[b] Uncertainties are three standard deviations.

[c] Fit II, all hyperfine parameters fixed at those of NH_2 (Ref. 1) ^2D parameters appropriately scaled, other parameters as fit I.

[d] Scaled from ^1H parameters of Ref. 1, fit II and used here as fixed parameters. Experimental uncertainties for a_D, T_{aa}^D and T_{aa}^D are ±0.07, ±0.19, and ±0.09 MHz, respectively.

[e] Standard deviation of the fit.

scheme used was $\mathbf{J}=\mathbf{N}+\mathbf{S}$, $\mathbf{F}^N=\mathbf{J}+\mathbf{I}^N$, and $\mathbf{F}=\mathbf{F}^N+\mathbf{I}^D$, where F is strictly the only good quantum number but where F^N is still a good label for energy states. The basis functions used in the matrix elements were $|NKSJI^NFM_F\rangle$ for $I^D=0$ and $|NKSJI^NF^NI^DFM_F\rangle$ for $I^D>0$. For the para levels, ee or oo in K_aK_c, I^D is 1. For the ortho levels (eo or oe) the resultant deuterium nuclear spin is 0 or 2. Even using a Wang basis, the resultant matrix for a given value of F could be quite large when $I^D=2$. For instance, for $F=21/2$, the size of the $\hat{H}$ matrix was 165×165. However the diagonalization algorithm was efficient and the calculation of all $I^D=2$ energy levels with $F\leq 21/2$ required only 1.5 min CPU time on an IBM 3033.

The initial calculation of the energy levels and transitional frequencies used the LMR quadratic spin-rotational constants[3] and the ^{14}N and ^2D hyperfine parameters scaled from NH_2.[1] Once definite assignments were obtained, a standard, least squares fit was performed on all the transitions in Table I deemed to be well determined, i.e., not blended, sufficiently intense, or unambiguously assignable. All the parameters to be determined were fitted simultaneously for all three spin states.

The fitting was done using two approaches. In fit I the parameters in $\hat{H}_{HF}^N$ were fixed at the ^{14}N values of NH_2, (000) $\tilde{X}\,^2B_1$,[1] and the parameters in $\hat{H}_{SR}$ and $\hat{H}_{HF}^D$ were determined by fitting 167 transitions with a standard deviation of 0.54 MHz. The values obtained for the parameters are given in Table II. The derived ^2D magnetic hyperfine coupling constants, a_D (Fermi contact) and T_{aa}^D, T_{cc}^D (dipole–dipole), are in excellent agreement with those scaled from the equivalent ^1H parameters in NH_2 (see entries under fit II in Table II).

Since the ^1H hyperfine effects in NH_2 are appreciable and thus better determined than the ^2D parameters in ND_2, it appeared better to fix the ^2D parameters at the scaled ^1H values. Thus in fit II the ^2D parameters in $\hat{H}_{HF}^D$ (scaled from ^1H), as well as all parameters in $\hat{H}_{ROT}$ and $\hat{H}_{HF}^N$, were fixed and only the parameters in $\hat{H}_{SR}$ were varied. Using this second method, the same 167 transitions were fitted to a standard deviation of 0.56 MHz, a figure comparable to our estimated measurement uncertainty of ±0.5 MHz. Table II presents the parameters obtained from fit II and compares them to those of fit I. As can be seen none of the spin-rotational parameters determined in fit II show any significant difference from the equivalent parameter of fit I.

The residuals of fit II are given in Table I. Evidence of any systematic trends in these residuals was checked. For instance, prior experience with NH_2^1 had shown that certain spin-rotational splittings were sensitive to the $\hat{H}_{ROT}$ used because of off-diagonal elements of N in $\hat{H}_{SR}$. So even though rotational parameters are not determined in this study, care must be taken to reproduce accurately the rotational splittings between levels relatively close in energy and interacting through off-diagonal ($\Delta N=\pm 1$, $\Delta K=0$ or ± 2) elements of the spin-rotational interaction. Such situations occur in ND_2 for some MODR observed levels, e.g., 5_{14}, F_2 (4_{32}, F_1 64 GHz below), 7_{25}, F_2 (6_{43}, F_1 40 GHz below), and 3_{22}, F_1 (4_{04}, F_2 169 GHz above). Any significant miscalculation of the rotational energies of these sensitive levels will produce a systematic offset in the observed–calculated MODR frequencies. As can be seen in Table I no such trends are apparent for 3_{22}, 5_{14}, or 7_{25}.

The results of fit II are most satisfactory. Approximately 80% of the observed MODR transitions were deemed sufficiently resolved, unambiguously assignable, and of sufficient strength to be included in the fit. Transitions from 20 of the 21 rotational levels observed were fitted upon. None of the transitions observed for F_2–F_1, 2_{11} were fitted since all lines were badly blended primarily as a result of the small ^{14}N hyperfine splittings for this level. Of the entire group of 167 transitions fitted, only six transitions (3.6%) have residuals more than $2\sigma_{FIT}$ (i.e., >1.12 MHz) and only one transition (0.6%) has a residual more than $3\sigma_{FIT}$. A comparison of the residuals for fits I and II showed no significant differences. It was therefore deemed unnecessary to display the fit I residuals in Table I.

V. DISCUSSION

A. Quadratic spin rotational parameters

All three quadratic spin rotation parameters are well determined for ND_2 from the MODR results. The A_s and B_s constants are in excellent agreement with the same parameters determined from a fit of the LMR data[3] (see Table III). This result is gratifying for future infrared

TABLE III. Comparison of ND_2 spin rotational parameters (MHz).

	MODR[a]	LMR[b]
A_s	$-5127.6(8)$[c]	$-5120(26)$
B_S	$-669.1(2)$	$-649(23)$
C_S	$+3.7(2)$	$+6.3$

[a] This work, fit II, Table II.
[b] Reference 3; C_S fixed at $+6.3$ MHz.
[c] Uncertainty three standard deviations.

TABLE IV. Quadratic spin rotational parameters in ND_2 compared to NH_2 (in MHz).

	ND_2[a]	NH_2 scaled[b]	NH_2[c]
A_S	$-5127.6(8)$	$-5219(1)$	$-9266.82(107)$
B_S	$-669.1(2)$	$-678.6(2)$	$-1354.09(40)$
C_S	$+3.7(2)$	$6.2(1)$	$+11.81(16)$

[a] This work, uncertainties are three standard deviations.
[b] Scaled from the results of column 3 using the relationships (Ref. 5). $A_S^*/A^* = A_S/A$ (and similarly B_S, C_S), where the starred quantities refer to ND_2. ND_2 rotational constants were those of Hills and McKellar (Ref. 3) and for NH_2 those of Kawaguchi *et al*. (Ref. 12). The quoted errors are purely statistical and do not reflect the approximations of the scaling model (Ref. 5).
[c] MODR results of Ref. 1, fit II.

LMR studies as the LMR analysis[3] of ν_2 simultaneously fitted 25 parameters in (000) and (010) using no other spectral data in the fit. As expected the MODR determined quadratic spin rotational parameters are 30–100 times more precise than the LMR ones since the MODR experiment measures spin rotational splittings directly and at a 20 times better resolution than the infrared experiment.

Table IV compares the ND_2 spin rotational parameters with the experimentally determined parameters of NH_2.[1] As can be seen the absolute errors in the ND_2 parameters are similar to those in NH_2. Such agreement is expected since the NH_2 and ND_2 MODR experiments measured similar rotation levels. The slight difference is that the NH_2 study had a larger range of N and included $K_a = 0$ levels.

Also included in Table IV is the comparison between quadratic parameters for ND_2 and those of ND_2 scaled from the equivalent parameters in NH_2. The scaling method used the established relationship[5]

$$A_s^* = (A_s A^*)/A \tag{1}$$

and similar expressions for parameters about the b and c axes, and where starred parameters refer to ND_2, unstarred to NH_2. As input to these relationships, the A_s, B_s, and C_s for NH_2 of Hills and Cook[1] were used, as were the LMR determined rotational constants for NH_2[12] and ND_2.[3] As can be seen the scaled A_s and B_s values for ND_2 are in good agreement with the experimentally determined parameters, with errors of about 1.5%. This is slightly worse than the situation in NHD,[2,5] where the calculated and experimental A_s and B_s agreed to within 0.9% and 0.5%, respectively. Previously Eq. (1) had been very successful in scaling isotopic forms of ClO_2[13] and NO_2.[14] For $^{37}ClO_2$ the experimental and scaled (from $^{35}ClO_2$) A_s, B_s, and C_s agree to the <0.1%, <0.1%, and 5%, respectively.[13] A similar comparison[14] can be made between the $^{15}NO_2$ observed and calculated (from $^{14}NO_2$) A_s, B_s, and C_s where the agreement is good to 0.2%, 0.5%, and 0.1%, respectively. Thus the reliability of Eq. (1) is well founded, with the current A_s and B_s parameters for ND_2 being the least well predicted of the species considered so far. This present comparison also represents the most stringent test of the scaling relationship.

In the light of the above consistent success of the model it is rather surprising that there is such poor agreement between the observed C_s for ND_2 of 3.5 MHz and the calculated C_s of 6.2 MHz. In NHD[2,5] the isotopic relationship is valid to about 2% for C_s although it should be remarked that this excellent agreement is probably fortuitous since the C_s parameter for NHD is essentially undetermined[2] at $+8.6 \pm 11.7$ MHz, where the error quoted is three standard deviations. The reason for the apparent breakdown of Eq. (1) for C_s in ND_2 is unclear. Not only is the parameter C_s small for ND_2 but the ratio $C_{s/c}$ is very small for ND_2 in comparison to another Π radical for which the relationship does work, namely, ClO_2.[13] Presumably the neglect of the vibrational contributions to C_s in (000), a vibrational averaging effect, or other approximations made in deriving Eq. (1), strictly valid only for the equilibrium, nonvibrating geometry, are causing this disagreement.

B. Quartic spin rotational parameters

For ND_2 a set of five quartic spin rotational constants is determined in this work and comparison to the equivalent parameters in NH_2 is possible, as shown in Table V. As expected, the absolute errors in the NH_2 and ND_2 parameters are again comparable in magnitude. All constants show decreases in magnitude of factors of between 2–5 upon going from NH_2 to ND_2.

Attempts[10,15] have been made for NH_2 to derive from the Δ_K^S, Δ_N^S, etc., the corresponding $\eta_{\alpha\beta\gamma\delta}$ terms, the coefficient of the general quartic term $\hat{N}_\alpha \hat{N}_\beta \hat{N}_\gamma \hat{S}_\delta$ in the spin rotational Hamiltonian.[16] Unfortunately there are

TABLE V. Quartic spin rotational parameters in ND_2 compared to NH_2 (in MHz).

	ND_2[a]	Scaled NH_2[b]	NH_2[c]
Δ_N^S	$-0.083(6)$	$-0.081/-0.070$	$-0.310(5)$
Δ_K^S	$-9.3(3)$	$-10.2/-10.04$	$-32.80(31)$
$\Delta_{KN}^S + \Delta_{NK}^S$	$+0.88(6)$	$+0.95/+0.79$	$+3.31(12)$
δ_N^S	$-0.040(3)$	$-0.032/-0.069$	$-0.153(3)$
δ_K^S	$-0.26(6)$	-0.033	$-0.50(4)$

[a] This work, fit II. Errors are three standard deviations.
[b] Scaled from NH_2 parameters; see the text for methods.
[c] Reference 1, fit II.

more η's than Δ^S's and the previous attempt[15] at reducing the number of η's by applying planarity conditions has both theoretical and practical limitations.[10] We thus chose not to pursue this approach for ND_2 in any depth. However, it is interesting that ND_2 does exhibit the same property as NH_2, namely, $\Delta_N^S = 2\delta_N^S$ quite accurately. This formula has previously been derived[15] by invoking planarity conditions and the assumption that $\eta_{cccc} = 0$.

If one wishes to consider the isotopic dependence of the quartic parameters, one finds no detailed theoretical development, unlike the case for the quadratic terms. If one could generate meaningful $\eta_{\alpha\beta\gamma\delta}$ from the Δ^S it would be possible to consider the isotopic dependence of the $\eta_{\alpha\beta\gamma\delta}$ from the approximate relationship,[11]

$$\eta_{\alpha\beta\gamma\delta} = \sum_{\zeta} \frac{\tau_{\alpha\beta\gamma\zeta}\epsilon_{\zeta\delta}}{2B_{\zeta}} \quad , \tag{2}$$

where the τ are the centrifugal distortion constants, $A_s \equiv \epsilon_{aa}$, etc. Unfortunately the validity of this equation is questionable for the absolute determination of $\eta_{\alpha\beta\gamma\delta}$. For example, consider Eq. (2) relating the η_{aaaa} and τ_{aaaa} terms. For ND_2 and NH_2 $\tau_{aaaa} = -715$ and -2260 MHz, respectively, while the corresponding observed η_{aaaa} parameters are 8.27 and 29.8 MHz. The use of Eq. (2) predicts for ND_2 and NH_2, η_{aaaa} values of 4.58 and 14.7 MHz, respectively. For the η_{bbbb} and τ_{bbbb} relationship Eq. (2) is somewhat more successful. The observed τ_{bbbb} [η_{bbbb}] for ND_2 and NH_2 are (in MHz) -73 [$+0.136$] and -225 [$+0.620$]. The calculated η_{aaaa} are 0.125 and 0.392 MHz, respectively, with errors of 8% and 37%. However the use of Eq. (2) as a predictive method for the isotopic dependence of the $\eta_{\alpha\beta\gamma\delta}$ might still be meaningful. For example, from Eq. (2) we have for the simplest case,

$$\eta_{bbbb} = \frac{\tau_{bbbb}\epsilon_{bb}}{2B}$$

and, since $\epsilon_{bb} = B_s$ and $B_s \propto B$ one would expect

$$\eta^*_{bbbb} = \eta_{bbbb}\tau^*_{bbbb}/\tau_{bbbb} \, . \tag{3}$$

For NH_2 and ND_2, $\tau_{bbbb} = -225$ and -73 MHz, respectively, and since $\Delta_N^S = -\frac{1}{2}\tau_{bbbb}$,[15] Eq. (3) predicts $\Delta_N^S = -0.101$ MHz for ND_2 compared to the observed value of $-0.083(6)$ MHz. Similarly, Eq. (3) with b replaced by a gives reliable calculation of η_{aaaa} for ND_2 of 9.49 MHz, an error of only ~15%. So apparently for the isotopic dependence of the $\eta_{\alpha\beta\gamma\delta}$, Eq. (2) appears to be moderately successful.

Jones and Brown[13] in treating the Δ_K^S parameter for isotopic forms of ClO_2 adopted the empirical relationship

$$(\Delta_K^S)^* = \Delta_K^S A^* A_s^* / A A_s$$

to relate $^{37}ClO_2(*)$ to $^{35}ClO_2$. Adopting such an expression for NH_2 predicts $\Delta_K^S = -10.2$ MHz for ND_2, which is within 10% of the observed value of $-9.3(3)$ MHz. Indeed since A_S is proportional to A, scaling Δ_K^S for NH_2 by the ratio of (D/H) of A^2, AA_S, or A_S^2 give predictions of Δ_K^S for ND_2 of -10.40, -10.22, and -10.04 MHz, respectively, all close to the observed value.

Following this same empirical approach, it would appear that Δ_N^S, $(\Delta_{NK}^S + \Delta_{KN}^S)$, and δ_N^S should scale as $(B+C)^2$, $A(B+C)$, and $(B-C)^2$, respectively. Such relationships predict Δ_N^S, $(\Delta_{NK}^S + \Delta_{KN}^S)$, and δ_N^S for ND_2 of -0.081, $+0.95$, and -0.032 MHz compared to the observed of $-0.083(6)$, $+0.88(6)$, and $-0.040(3)$ MHz. Whether such empirical relationships are indeed valid will probably have to await a thorough theoretical development as well as the further determination of quartic parameters for other pairs of low mass, isotopic species (e.g., PH_2, PD_2; AsH_2, AsD_2; H_2O^+, D_2O^+.

The form of Eqs. (2) and (3) and the similarity between the quartic rotational and quatic spin rotational Hamiltonians suggests other possible empirical relationships,

$$(\Delta_K^S)^* = \Delta_K^S \Delta_K^* / \Delta_K \tag{4}$$

and similarly for Δ_N^S, $(\Delta_{NK}^S + \Delta_{KN}^S)$, δ_K^S, and δ_K^S. The use of Eq. (4) predicts for the Δ_N^S, Δ_K^S $(\Delta_{NK}^S + \Delta_{KN}^S)$, δ_N^S, and δ_K^S parameters (in MHz) of ND_2 -0.070, -10.04, $+0.79$, -0.069, and -0.033, respectively. As can be seen from the observed parameters of Table V, Eq. (4) gives reasonable agreement (better than 20%) for the Δ_N^S, $(\Delta_{NK}^S + \Delta_{KN}^S)$, and Δ_K^S but poor agreement for δ_K^S and δ_N^S. Again a though derivation of the form of the Δ^S parameters, as well as further isotopic data, will be required before any definitive conclusions can be drawn about possible isotopic relationships for the Δ^S's

VI. CONCLUSION

As a result of these studies precise quadratic and quartic spin rotational parameters are now available for ND_2 in (000), $\tilde{X}\,^2B_1$. This is the first time that the set of three quadratic and five quartic parameters is available for two isotopic forms of a free radical. The parameters in ND_2 can be directly compared with the equivalent parameters in NH_2 so as to gain insight into the isotopic dependence of the spin rotation interaction. Reliable isotopic scaling was confirmed for A_s and B_s but surprisingly not for C_s. Several empirical relationships were investigated for the quartic parameters. A detailed theory of the dependence of the quartic parameters is required to gain further insight.

ACKNOWLEDGMENTS

One of us (G. W. H.) would like to thank Mr. Tim Van Slambrouck of Spectra Physics for the loan of an argon ion laser for part of the period in which the experimental work at UNC was undertaken. Critical comments on an earlier version of the manuscript by Dr. J. M. Brown are also gratefully acknowledged.

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