Nuclear Quadrupole Effects in the Microwave Spectrum and Dipole Moment of Aniline*

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The quadrupole hyperfine structure was resolved and analyzed for the vibrationally-ground state of the NH_2 species. The quadrupole coupling constants are: $\chi_{aa}=2.34$, $\chi_{bb}=1.86$, and $\chi_{cc}=-4.20$ MHz. The rotational constants obtained from the quadrupole corrected frequencies are as follows: $A=5617.67$, $B=2593.88$, and $C=1777.04$ MHz. The rotational constants of the ND_2 species in the vibrationally-ground state were also determined. By the use of the moments of inertia of both species, the non-planarity of this molecule was ascertained. The dipole moments of the NH_2 and the ND_2 species were determined to be 1.15 ± 0.02 D and 1.13 ± 0.01 D respectively.

In 1966 Lister and Tyler[1)] reported their preliminary findings on the microwave spectra of aniline and its amino-monodeuterated species, and pointed out the non-planarity of the molecules. The detailed results have since been presented by Lister alone.[2)] However, they did not observe the spectra due to the nuclear quadrupole coupling of nitrogen or those for the electric dipole moment.

In order to determine the value of the dipole moment, it seemed necessary to ascertain the effect of the ^{14}N quadrupole coupling on the spectra. For this purpose we have carried out this research.

Experimental

The microwave spectrometer used in this study was improved by adding a stabilized Klystron sweep system, since the longer time constants of 8~20 seconds were required to observe the hyperfine structure due to the ^{14}N quadrupole coupling. The measurements were made in the frequency range from 7.8- to 25-GHz at room temperature by using a 6-m absorption cell.

The sample of aniline, obtained from a commercial source, was purified by vacuum distillation before use. The amino-deuterated aniline, $C_6H_5ND_2$, was prepared by mixing the NH_2 species with D_2O. For measuring the spectrum of the ND_2 species, the waveguide was flushed several times with D_2O.

Results and Discussion

Only the a-type transitions were observed. As is shown in Table 1, the quadrupole hyperfine structures for the NH_2 species could be observed for some of the low-*J* R-branch transitions and all the Q-branch transitions of the vibrationally-ground state. The bracketed transitions in the table could not be well resolved. By using the transitions marked with asterisks in the table, the nuclear quadrupole coupling parameters, χ_{aa}, χ_{bb}, and χ_{cc}, were determined by a least-squares fitting according to the method of Bragg and Golden.[3)] The quadrupole corrected frequencies, $\nu_{obsd}^{correct}$, were calculated by using these parameters. As the rigid-rotor approximation holds for these frequencies, the rotational constants, *A*, *B*, and *C*, were calculated from these frequencies by means of a least-squares fitting. The differences, Δ, between $\nu_{obsd}^{correct}$ and the frequencies calculated from the rotational constants, ν_{calcd}^{rigid}, are given in the last column of the table. It was ascertained that, for the bracketed transitions in the table, the splittings are within 0.3 MHz. The values of the rotational constants and those of χ_{gg} (g=a, b, or c) are listed in Table 2, where the a axis is nearly along the C–N bond and where the c axis is nearly perpendicular to the plane of the C_6H_5N fragment. The rotational constants obtained agreed very well with those reported by Lister and Tyler,[1)] although their values were calculated from the high-*J* R-branch transition frequencies.

For the ND_2 species the low-*J* R-branch transition frequencies of the a-type in the vibrationally-ground state were also observed and assigned as shown in Table 3. By using the rigid-rotor approximation, the rotational constants were calculated by a least-squares fitting from the frequencies of the same transitions as those which are unresolved for the NH_2 species. The results are shown in Table 2.

By using a procedure similar to that of Kraitchman, and by choosing a z axis perpendicular to the plane of the C_6H_5N fragment, the z coordinate of the H or the D atom of the amino group was calculated to be 0.35 Å from the moments of inertia of the two species. The valency angle of ∠H–N–H and the angle between the C–N bond extended and the ∠H–N–H bisector were estimated as 112.3° and 38° respectively, by assuming only the N–H bond length to be 1.00 Å.

By using transition frequencies which are hardly affected at all by the ^{14}N quadrupole coupling, the dipole moments were measured for both the NH_2 and the ND_2 species. For the transitions used, the Stark energies are 10~20 times larger than the quadrupole coupling energies. Therefore, the Stark levels were calculated as in a strong-field case[4,5)] and are those

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Table 1. Transition frequencies of $C_6H_5NH_2$ in the vibrationally-ground state (in MHz)

Transition		ν_{obsd}[a]	$\nu_{\text{obsd}}-\nu_{\text{calcd}}$	$\nu_{\text{obsd}}^{\text{correct}}$	Δ[b]
$J' \leftarrow J$	$F' \leftarrow F$				
R-branch					
$2_{12} \leftarrow 1_{11}$	3 ← 2[c]	7924.80[d]	0.02	7924.98	−0.01
	1 ← 0		−0.07		
	2 ← 1	7925.54[d]	−0.03		
$2_{02} \leftarrow 1_{01}$	3 ← 2	8597.52	0.07	8597.6	0.1
	2 ← 1		−0.19		
	1 ← 0	8598.0	0.0		
	2 ← 2	8598.4	0.0		
$2_{11} \leftarrow 1_{10}$	2 ← 2	9558.	0.0	9558.66	−0.01
	3 ← 2	9558.57[d]	−0.02		
	2 ← 1	9559.26[d]	0.01		
	1 ← 1	9560.2	0.0		
$3_{13} \leftarrow 2_{12}$	4 ← 3	11804.06	0.12	—	
	2 ← 1		0.05		
	3 ← 2		−0.19		
$3_{03} \leftarrow 2_{02}$	4 ← 3	12563.08	0.09	—	
	2 ← 1		0.01		
	3 ← 2		−0.23		
$3_{22} \leftarrow 2_{21}$	2 ← 1	13112.2	0.0	13112.75	0.01
	4 ← 3	13112.57[d]	−0.01		
	3 ← 2	13113.35[d]	0.02		
$3_{21} \leftarrow 2_{20}$	4 ← 3	13662.30	0.00	13662.38	−0.01
	3 ← 2	13662.74	−0.02		
$3_{12} \leftarrow 2_{11}$	2 ← 1	14238.38	0.29	—	
	4 ← 3		0.08		
	3 ← 2		−0.17		
Q-branch					
$4_{13} \leftarrow 4_{14}$	4 ← 4	8055.43[d]	0.04	8056.88	0.03
	5 ← 5	8057.40[d]	0.02		
	3 ← 3	8057.87	−0.02		
$5_{14} \leftarrow 5_{15}$	5 ← 5	11821.12	−0.18	11822.52	−0.16
	6 ← 6	11823.08	−0.13		
$6_{15} \leftarrow 6_{16}$	6 ← 6	15945.65	−0.23	15946.90	−0.23
	7 ← 7	15947.50	−0.13		
	5 ← 5		−0.42		
$7_{25} \leftarrow 7_{26}$	7 ← 7	10637.68	0.00	10638.62	0.00
	8 ← 8	10639.07	0.06		
	6 ← 6		−0.13		
$8_{26} \leftarrow 8_{27}$	8 ← 8	14930.60	−0.12	14931.54	−0.12
	9 ← 9	14931.95	−0.11		
	7 ← 7		−0.28		
$9_{36} \leftarrow 9_{37}$	9 ← 9	8447.28	0.09	8447.94	0.09
	10 ← 10	8448.30	0.17		
	8 ← 8		0.06		
$10_{37} \leftarrow 10_{38}$	10 ← 10	12614.45	−0.15	12615.18	−0.14
	11 ← 11	12615.58	−0.06		
	9 ← 9		−0.16		

a) Maximum experimental uncertainties in frequency measurements are ±0.05 MHz for R-branches and ±0.1 MHz for Q-branches. b) $\Delta=\nu_{\text{obsd}}^{\text{correct}}-\nu_{\text{calcd}}^{\text{rigid}}$. c) Braces indicate unresolved lines. d) Quadrupole coupling constants were determined by using the differences of these transition frequencies.

TABLE 2. ROTATIONAL CONSTANTS, PRINCIPAL MOMENTS OF INERTIA, AND QUADRUPOLE COUPLING CONSTANTS OF ANILINE IN THE VIBRATIONALLY-GROUND STATE

$C_6H_5NH_2$	
$A=5617.67\pm0.15$ MHz	$I_a=89.962$ amu·Å^2
$B=2593.88\pm0.02$	$I_b=194.834$
$C=1777.04\pm0.02$	$I_c=284.391$
$\chi_{aa}=2.34\pm0.06$ MHz,	$\chi_{bb}=1.86\pm0.06$ MHz,
$\chi_{cc}=-4.20\pm0.06$ MHz	
$C_6H_5ND_2$	
$A=5521.15\pm1.90$ MHz	$I_a=91.534$ amu·Å^2
$B=2403.82\pm0.07$	$I_b=210.238$
$C=1679.01\pm0.07$	$I_c=300.996$

Conversion factor: 505375 amu·Å^2·MHz

TABLE 3. TRANSITION FREQUENCIES OF $C_6H_5ND_2$ IN THE VIBRATIONALLY-GROUND STATE (in MHz)

Transition	ν_{obsd}[b]	$\nu_{\text{obsd}}-\nu_{\text{calcd}}$
$2_{02} \leftarrow 1_{01}$	8053.44	0.11
$2_{11} \leftarrow 1_{10}$	8890.34	−0.12
$3_{03} \leftarrow 2_{02}$[a]	11815.88	−0.11
$3_{13} \leftarrow 2_{12}$[a]	11095.90	0.12
$3_{12} \leftarrow 2_{11}$[a]	13259.20	0.05
$3_{22} \leftarrow 2_{21}$	12248.45	−0.03
$3_{21} \leftarrow 2_{20}$	12680.88	−0.10
$4_{04} \leftarrow 3_{03}$[a]	15339.89	−0.22
$4_{14} \leftarrow 3_{13}$[a]	14686.35	−0.02
$4_{13} \leftarrow 3_{12}$[a]	17520.57	0.14
$4_{23} \leftarrow 3_{22}$	16243.50	0.07
$4_{22} \leftarrow 3_{21}$[a]	17233.95	0.23
$4_{32} \leftarrow 3_{31}$	16526.87	0.23
$4_{31} \leftarrow 3_{30}$	16591.70	−0.09
$5_{05} \leftarrow 4_{04}$[a]	18693.14	0.12
$5_{14} \leftarrow 4_{13}$	21615.28	−0.03
$5_{24} \leftarrow 4_{23}$	20164.83	−0.22
$5_{23} \leftarrow 4_{22}$[a]	21878.79	−0.26
$5_{33} \leftarrow 4_{32}$	20698.94	0.41
$5_{32} \leftarrow 4_{31}$	20918.79	0.18
$5_{41} \leftarrow 4_{40}$	20670.53	0.21

a) Rotational constants were determined from these transition frequencies. b) Maximum experimental uncertainties in frequency measurements are ±0.2 MHz.

TABLE 4. STARK EFFECT AND DIPOLE MOMENTS OF ANILINE[a]

Transition	Shift MHz(kV/cm)$^{-2}$	
	Obsd	Calcd
$C_6H_5NH_2$		
$2_{02} \leftarrow 1_{01}$ $M_J=0$	-11.47 ± 0.85	-11.75
$3_{12} \leftarrow 2_{11}$ $M_J=2$	-10.86 ± 0.35	-10.54
$3_{13} \leftarrow 2_{12}$ $M_J=0$	-0.548 ± 0.024	-0.503
$C_6H_5ND_2$		
$3_{12} \leftarrow 2_{11}$ $M_J=0$	-0.436 ± 0.153	-0.523
$M_J=2$	-11.53 ± 0.37	-11.52
$3_{03} \leftarrow 2_{02}$ $M_J=2$	3.67 ± 0.39	3.68

Dipole moment	
$C_6H_5NH_2$	$C_6H_5ND_2$
$\mu_a^2=1.33\pm0.04$	$\mu_a^2=1.27\pm0.02$
$\mu=1.15\pm0.02$D	$\mu=1.13\pm0.01$D

a) Electric-field calibration was made with OCS for which $\mu=0.7152$ D.

determined for the asymmetric rotor without the quadrupole coupling effects. The value of the dipole moment of the NH_2 species agreed with that of the ND_2 species within the range of experimental uncertainty. As was expected, the component, μ_c, which is nearly perpendicular to the plane of the phenyl group, is zero for the NH_2 or the ND_2 species within the range of experimental uncertainty.

The value of the dipole moment of the NH_2 species is markedly different from that of 1.48 D obtained from the dielectric constant measurements at the temperature of 459 K in vapor.(6) It is certain that the value of this study is more accurate, for the difference between the values of the moment is probably due to the incorrect value of the sum of the atomic and the electric polarization as estimated from the molar refraction. The atomic polarization of this molecule may be anomalously large.

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