Microwave Measurements of Rotational Transitions and Nitrogen Quadrupole Coupling for 2-aminopyridine

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Abstract

The high-resolution microwave rotational spectrum was measured for 2-aminopyridine in the 4.5-13.2 GHz range using a pulsed beam Fourier transform microwave spectrometer. The measured transitions for the parent isotopologue in the 0^+ vibrational state of the amino group inversion vibration were used to determine accurate rotational constants and quadrupole coupling constants for the two ^{14}N atoms in the molecule. The molecular parameters determined for the 2-aminopyridine in 0^+ vibrational state have the following values: A = 5780.374~~38~~(1~~3~~) MHz, B = 2733.5017~~0~~(3~~28~~) MHz, C = 1857.6768~~1~~(3~~3~~) MHz, $1.5\chi_{aa}$ ($^{14}N_1$) = 3.5789(45) MHz, $0.25(\chi_{bb} - \chi_{cc})$ ($^{14}N_1$) = 1.5033(24)MHz, $1.5\chi_{aa}$ ($^{14}N_2$) = -0.0958(70) MHz, and $0.25(\chi_{bb} - \chi_{cc})$ ($^{14}N_2$) = -1.1615(21) MHz. The measured quadrupole coupling constants are on excellent agreement with those calculated using different computational methods and basis sets. It is noted that the calculation using the MP2 functional with cc-pvDz basis set closely reproduces the experimental values for quadrupole coupling constants for the two ^{14}N atoms.

Introduction

2-aminopyridine is similar to the nucleic acid base adenine and has two potential hydrogen binding sites. The 2-aminopyridine-2-pyridine complex is an analog of the adenine-uracil base pair and was studied using laser spectroscopy by Leutwyler, et al.[1]

Electronic spectra for the 2-aminopyridine-ammonia complex were reported by Brutschy, et al.[2] Microwave spectra for 2-aminopyridine were measured in the 29-40 GHz range by Kydd and by Mills[3] using a Stark-cell, waveguide spectrometer. The molecule is nonplanar, with the hydrogen atoms of NH_2 out of the plane of the pyridine ring and is shown in Figure 1.

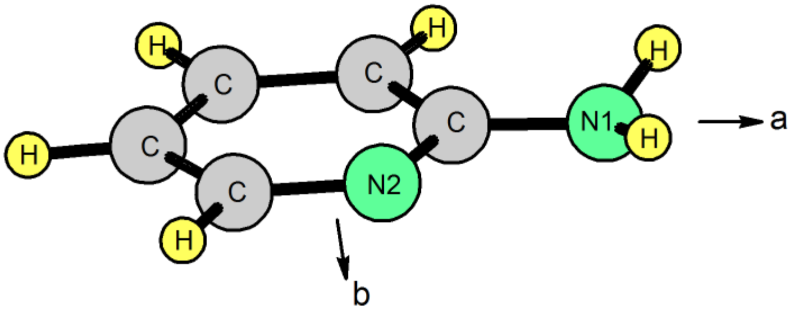

Figure 1. Structure of 2-aminopyridine. N1 is the Nitrogen atom in the amino group, N2 is the Nitrogen in the ring (pyridine)

Due to its feature as a derivatizing reagent, 2-aminopyridine has been utilized as a fluorescent label in various applications such as mass spectrometric analysis, oligosaccharide detection and chromatographic separation.[4,5,6] Similarly 2-aminopyridine and its derivatives have been found to be successful fluorescent chemosensors and are therefore good candidates for molecular sensing applications.[7] It is also effective in inhibiting the corrosions of steels and therefore 2-aminopyridine and its derivatives can serve as excellent anticorrosion agents for industrial usages.[8] Not only does 2-aminopyrdine perform its functions in chemical and industrial fields, it also emerges as a pharmacophore for medical and pharmaceutical applications. A variety of drugs containing 2-aminopyridine available on the market have already been shown to be effective in treating infections caused by microorganisms, tumors, Alzheimer, diabetes and many other medication conditions.[9]

Another principal motivation for the structural investigation of 2-aminopyridine stems from its resemblance to tautomers 2-hyroxypyridine and 2-pyridone for which microwave measurements have been previously reported by our group.[10] In a similar way, 2-aminopyrdine can exhibit hydrogen-bonded interactions to form dimers with its tautomer and other derivatives, which can be compared to basic DNA base pairs interactions.

The microwave spectra and rotational constants for 0^- and 0^+ vibrational states of 2-aminopyrdine and several of its deuterium-substituted isotopomers have been reported previously by Kydd and Mills.[3] The two inversion states arise from the NH_2 out of plane motion. Since those rotational spectrum measurements were collected in 1972, with the low resolution of the spectrometer quadrupole hyperfine structure was not resolved in that earlier work. It would also have been more difficult to resolve on the high-J transitions which were measured. Measurements of accurate quadrupole coupling constants can provide information on the electric field gradients and the electronic structure for 2-aminopyrdine. With pulsed-beam, Fourier-transform spectrometers, the quadrupole coupling splitting in 2-aminopyridne for low J transitions be resolved, and the accuracies of rotational constants be significantly improved.

In the present study, we have resolved the hyperfine splitting on low-J transitions due to quadrupole coupling moments of the two nitrogen atoms. Measurements were made on the 2-aminopydine molecule in the 4.5-13.2MHz range by using a pulsed-beam Fourier transform spectrometer. A series of theoretical computations were done to determine the quadrupole coupling strengths of the nitrogen atoms. The comparisons between experimental data and calculated values can serve as an excellent benchmark for the application of computational chemistry in molecules similar to 2-aminopyridine.

Calculations

The rotational constants and quadrupole coupling constants for two ^{14}N atoms in 2-aminopyridine 0^+ vibrational state were calculated using DFT (Minnesota -M11 and B3LYP) and ab initio (Moller-Plesset second-order perturbation theory(MP2)) methods. M11 with Def2QZVPP basis set, B3LYP with cc-pVQZ, and MP2 with cc-pVDZ basis set and MP2 with cc-pVQZ basis set calculations were performed on the high performance computing system (HPC) at University of Arizona. The software used for these calculations is Gaussian 16.[11,12] The condition “output=pickett” was included in the Gaussian script files in order to yield microwave parameters in the Gaussian output files. The results of the calculations are compared with experimental values in Table 1. The excellent agreement of the MP2 calculations, column 3 suggests that the structure is accurately represented by these calculations so the atom Cartesian coordinates are given in Table 2.

Experimental

Rotational transitions were measured for 2-aminopyridine in the 4.5-13.5MHz range at University of Arizona using the Flygare-Balle type pusled-beam Fourier transform microwave spectrometer that was previously described by our group.[13,14] 2-aminopydine (98%) was purchased from Sigma-Aldrich and used without any further purification. In order to successfully carry out the gas phase microwave spectral measurement of 2-aminopyridine, a sublimation test was done to determine the temperature at which it sublimes at as such information is not provided in the study reported by Kydd and Mills. A glass sample cell containing 2-aminopyridine was heated to around 85^{o}C in order to produce the few torr of vapor pressure necessary for microwave measurements. One end of the glass cell was connected to the pulsed valve of the microwave spectrometer while the other end was connected to a gas passing system purified by a Sigma-Aldrich Suppelco OMI-1 purifier.The carrier gas system uses neon as carrier gas and the backing pressure was maintained at around 0.7atm during the measurement. The pressure inside the spectrometer chamber was kept at 10^{-6} to 10^{-7} Torr powered by a diffusion pump system in order to cool molecules through supersonic expansion and populate them at their ground vibrational and rotational states. Other adjustments that include time delay, power, attenuator and cavity mode were made to optimize molecular signal as well as signal to noise ratio. Under these conditions, the molecules were pulsed into the microwave cavity at 2Hz through a General Valve pulsed valve and a FID with 5/1 S/N could be observed for a-type 2_{0212}-1_{0101} (quantum numbers J, K_a, K_c, F_1 and F) transition at 9019.6016MHz in 25 pulsed beam cycles.   Some typical experimental spectra showing the resolved hyperfine splittings are shown in Figure 2.

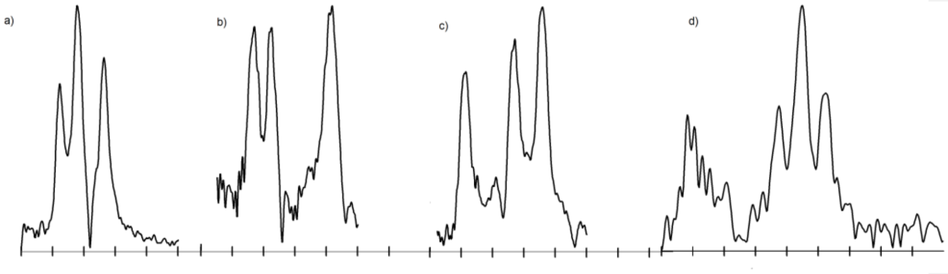

Figure 2. Spectra showing the resolved 14N hyperfine structure, a) 5973 MHz, b) 6781 MHz, c) 7638 MHz and d) 9019 MHz.

The rotational constants from the study by Kydd and Mills as well as the calculated quadrupole coupling constants from Moller-Plesset second-order perturbation theory (MP2) functional with cc-pvDz basis were entered into the SPCAT program in Pickett's program suite[15] to predict the rotational transitions with quadrupole splitting in the 4.5-13.5MHz range. The observed transitions were assigned quantum numbers J, K_a, K_c, F_1 and F, which follow the scheme of angular momentum coupling I_{N1}+J=F_1 and F_1+I_{N2}=F, based on the predictions given by SPCAT. These assigned transitions were used in the SPFIT program contained in Pickett's program suite[15] to fit new and improved rotational constants as well as quadrupole coupling constants.

Results

Searching for molecular signals from 2-aminopyridine in 0^+ vibrational state was direct and efficient since the rotational constants from previous study help us pinpoint the frequency range for rotational transitions with low J's and quadrupole splitting. Rotational transitions for 2-aminopyridine in 0^- state were also predicted and searched for but were not found. The supersonic expansion nozzle of the spectrometer probably cooled the vibrational distribution too much to have sufficient population in the 0^- vibrational state. A total of 66 a-type and b-type transitions were observed for 2-aminopyridne and used in the SPFIT. These rotational transitions are listed in Table 3 and consist exclusively of 0-1, 1-2 and 2-3 transitions as quadrupole coupling tend to blend and collapse for high-J transitions. The best-fit experimental molecular constants are presented in Table 1 along with theoretically calculated parameters.

Discussion

For 0^+ vibrational state 2-aminopyridine, the experimentally measured rotational constants are in excellent agreement with values from previous microwave measurements by Kydd and Mills. Numerical values for rotational constants A, B and C all agree within 1% accuracy.

There were no previous measurements of nuclear quadrupole coupling constants on the two ^{14}N atoms. The present study measured low-J rotational transitions and was able to resolve the quadrupole coupling splitting within those transitions using pulsed-beam Fourier transform microwave spectrometer. Two ^{14}N atoms in 2-aminopyridine have very different quadrupole coupling strengths. By comparing experimentally measured quadrupole coupling constants with theoretically calculated values, it can be seen that calculations based on MP2 (column 3.) and the B3LYP functional (column 3.) yielded better agreements with experimental measurements than M11 functional.

We can compare the quadrupole coupling tensors for 2-aminopyridine and 2-hydroxy~~amino~~pyridine since the principal axes relative the ring nitrogen atom are nearly coincident. Values for the ring nitrogen N2 are given in Table 4. The microwave spectrum and quadrupole coupling for 2-hydroxypyridine were reported by Tanjaroon et al.[10] We note that all values are very similar, indicating a very similar electronic structure for the ring.

Conclusions

Low-J rotational transitions were measured and quadrupole splitting were resolved in the 4.5-13.2 GHz range for 0^+ vibrational state of ~~2-aminopyridne~~2-aminopyridine using a pulsed beam Fourier transform microwave spectrometer. A total of 66 a-type and b-type rotational transitions were assigned and used to determine rotational constants and quadrupole coupling constants for ^{14}N. The measured quadrupole coupling constants were compared to those calculated by different computational methods and basis sets. Calculation using MP2 and B3LYP are in better agreement with the experimentally determined values for quadrupole coupling constants than calculation using M11 functional.

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Break1

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Break2

Table 1. The experimental and calculated molecular parameters for 2-aminopyridine in MHz.

Parameter	Experimental	3. MP2(cc-pVQZ)	4. B3LYP(cc-pVQZ)	5. M11(Def2QZVPP)	6. MP2(cc-pVDZ)	Kydd and Mills
A	5780.374~~38~~(1~~3~~)	5827~~6.966~~	5834~~3.744~~	5863~~2.931~~	5699~~.118~~	5780.34
B	2733.5017~~0~~(3~~28~~)	2745~~.465~~	2744~~3.773~~	2757~~.259~~	2699~~8.696~~	2733.57
C	1857.6768~~1~~(3~~3~~)	1869~~.305~~	1868~~.247~~	1877~~6.739~~	1836~~5.766~~	1857.66
1.5 χ_{aa} (N1)*	3.5789(45)	3.455	3.657	4.042	3.119	
0.25(χ_{bb}- χ_{cc})(N1)	1.5033(24)	1.470	1.662	1.797	1.431	
1.5χ_{aa} (N2)*	-0.0958(70)	-0.380	-0.187	-0.219	-0.121	
0.25(χ_{bb}-χ_{cc})(N2)	-1.1615(21)	-1.304	-1.293	-1.427	-1.131	
χ_{aa} (N1)	2.3859(30)	2.303	2.438	2.695	2.079	
χ_{bb}(N1)	1.814(47)	1.788	2.105	2.247	1.822	
χ_{cc} (N1)	-4.120(47)	-4.092	-4.543	-4.941	-3.902	
χ_{aa} (N2)	-0.0639(47)	-0.253	-0.126	-0.146	-0.081	
χ_{bb}(N2)	-2.291(42)	-2.481	-2.524	-2.781	-2.222	
χ_{cc} (N2)	2.355(42)	2.735	2.648	2.927	2.302	

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*N1: Nitrogen in amino group, N2: Nitrogen in the ring (pyridine)

Table 2. Calculated cartesian coordinates in the a,b,c principal axis system from the MP2(cc-pVQZ) calculation, in Å.

Atom	a	b	c
C	1.030002	-1.202934	0.000524
C	-0.895261	0.033715	-0.004740
N	-2.278280	0.036694	0.053188
H	1.468944	-2.192166	0.000878
H	-2.731313	0.826674	-0.371975
H	-2.679278	-0.847594	-0.212993
N	-0.307432	-1.163937	-0.007782
C	1.834095	-0.074849	0.001544
C	-0.169288	1.231371	-0.000290
C	1.211426	1.170263	-0.002006
H	-0.685775	2.180849	0.010455
H	1.794020	2.080535	-0.001592
H	2.909041	-0.168914	0.003503

Table 3. Measured microwave transitions and the deviations from the calculated values for 0^+ vibrational state of 2-aminopyridine. All values are shown in MHz. Measured Transitions (ν_{obs}) (MHz) and deviations of the best-fit calculated frequencies (ν_{o-c})(MHz) The standard deviation for the fit is σ = 0.0062 MHz.

Quantum number assignments		2-Aminopyridine	
$J' K_a' K_c' F_1' F'$	$J'' K_a'' K_c'' F_1'' F''$	ν_{obs}	ν_{o-c}
1 0 1 0 1	0 0 0 1 1	4589.9780	-0.0075
1 0 1 0 1	0 0 0 1 2	4589.9910	0.0055
1 0 1 2 2	0 0 0 1 1	4591.0410	-0.0069
1 0 1 2 2	0 0 0 1 2	4591.0560	0.0081
1 0 1 2 3	0 0 0 1 2	4591.0700	0.0076
1 0 1 1 0	0 0 0 1 1	4591.7570	-0.0019
1 0 1 1 2	0 0 0 1 2	4591.7700	-0.0035
1 0 1 1 2	0 0 0 1 1	4591.7800	0.0065
1 0 1 1 1	0 0 0 1 2	4591.7910	0.0075
1 1 1 0 1	0 0 0 1 0	7636.9204	-0.0045
1 1 1 2 2	0 0 0 1 2	7637.4668	-0.0016

1 1 1 1 0	0 0 0 1 1	7637.9414	0.0104
1 1 1 2 3	0 0 0 1 2	7638.0786	0.0041
1 1 1 1 2	0 0 0 1 1	7638.5313	-0.0003
1 1 1 1 1	0 0 0 1 2	7639.3188	-0.0124
2 0 2 1 2	1 0 1 1 2	9017.8291	0.0038
2 0 2 3 3	1 0 1 2 3	9018.9316	-0.0036
2 0 2 3 3	1 0 1 2 2	9018.9629	0.0131
2 0 2 3 4	1 0 1 2 3	9019.1250	0.0053
2 0 2 2 2	1 0 1 1 1	9019.2676	-0.0095
2 0 2 2 3	1 0 1 1 2	9019.3711	-0.0051
2 0 2 1 2	1 0 1 0 1	9019.6016	-0.0117
2 0 2 2 3	1 0 1 2 3	9020.0872	-0.0071
2 0 2 1 0	1 1 1 1 1	5970.4204	-0.0076
2 0 2 3 2	1 1 1 1 1	5970.9219	0.0058
2 0 2 1 2	1 1 1 1 2	5971.0635	0.0019
2 0 2 2 2	1 1 1 1 1	5971.7422	0.0006
2 0 2 2 1	1 1 1 1 1	5971.8960	0.0015
2 0 2 3 4	1 1 1 2 3	5972.1045	-0.0031
2 0 2 3 2	1 1 1 2 1	5972.1821	-0.0019
2 0 2 3 3	1 1 1 2 2	5972.5352	0.0060
2 0 2 2 3	1 1 1 1 2	5972.6172	0.0046
2 0 2 1 2	1 1 1 0 1	5972.6704	-0.0034
2 0 2 2 2	1 1 1 2 1	5973.0190	0.0095
2 0 2 2 3	1 1 1 2 3	5973.0684	-0.0068
2 0 2 2 1	1 1 1 1 0	5973.2778	-0.0048
2 0 2 2 2	1 1 1 2 2	5973.5972	0.0050
2 0 2 2 1	1 1 1 2 2	5973.7372	-0.0055
3 1 2 3 2	3 0 3 3 2	6778.6372	0.0005
3 1 2 3 4	3 0 3 3 4	6778.9922	0.0049
3 1 2 3 2	3 0 3 3 3	6779.0757	-0.0031
3 1 2 5 4	3 0 3 3 4	6779.2778	-0.0177
3 1 2 4 3	3 0 3 3 3	6779.3262	-0.0006
3 1 2 2 3	3 0 3 3 3	6779.6660	0.0055
3 1 2 3 3	3 0 3 3 4	6779.7627	-0.0004
3 1 2 2 2	3 0 3 3 2	6779.9316	-0.0022
3 1 2 3 3	3 0 3 3 3	6780.0825	0.0068
3 1 2 4 3	3 0 3 4 3	6780.2275	0.0004
3 1 2 3 2	3 0 3 2 1	6780.3657	-0.0029
3 1 2 4 5	3 0 3 4 5	6780.5920	-0.0002
3 1 2 3 4	3 0 3 4 4	6780.7285	0.0051
3 1 2 2 3	3 0 3 2 3	6781.1636	0.0028
3 1 2 4 4	3 0 3 4 5	6781.2817	0.0117
3 1 2 3 3	3 0 3 2 3	6781.5679	-0.0081
3 1 2 4 4	3 0 3 4 4	6781.7036	-0.0027
3 1 2 2 2	3 0 3 2 2	6782.2310	-0.0002
3 0 3 2 2	2 0 2 1 2	13154.7710	0.0067

3 0 3 4 4	2 0 2 3 3	13154.8660	-0.0024
3 0 3 4 5	2 0 2 3 4	13155.0580	0.0049
3 0 3 4 3	2 0 2 3 2	13155.0820	-0.0050
3 0 3 4 3	2 0 2 3 3	13155.3200	-0.0045
3 0 3 3 4	2 0 2 2 3	13155.3980	0.0127
3 0 3 2 1	2 0 2 1 1	13155.4330	-0.0001
3 0 3 3 2	2 0 2 2 1	13155.4550	0.0041
3 0 3 3 2	2 0 2 2 2	13155.6100	0.0062

Table 4. Comparison of ^{14}N quadrupole coupling values for 2-aminopyridne and 2-hydroxypyridne. The N2 nitrogen is in the ring.

	2-aminopyridne	2-hydroxypyridne
χ_{aa} (N2)	-0.0639(47)	-0.076(11)
χ_{bb}(N2)	-2.291(42)	-2.2828(64)
χ_{cc} (N2)	2.355(42)	2.3588(64)

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