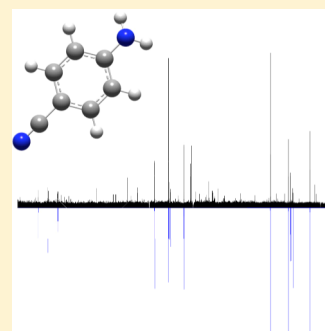


Nuclear Quadrupole Coupling Constants of Two Chemically Distinct Nitrogen Atoms in 4-Aminobenzonitrile

Thomas Betz,^{*,†,‡,§} Sabrina Zinn,^{†,‡,§} Jack B. Graneek,^{†,§} and Melanie Schnell^{*,†,‡,§}[†]Max Planck Institute for the Structure and Dynamics of Matter, Luruper Chaussee 149, D-22761 Hamburg, Germany[‡]The Hamburg Centre for Ultrafast Imaging, Luruper Chaussee 149, D-22761 Hamburg, Germany[§]Center for Free-Electron Laser Science, Notkestrasse 85, D-22607 Hamburg, Germany

Supporting Information

ABSTRACT: The rotational spectrum of 4-aminobenzonitrile in the gas phase between 2 and 8.5 GHz is reported. Due to the two chemically distinct nitrogen atoms, the observed transitions showed a rich hyperfine structure. From the determination of the nuclear quadrupole coupling constants, information about the electronic environment of these atoms could be inferred. The results are compared to data for related molecules, especially with respect to the absence of dual fluorescence in 4-aminobenzonitrile. In addition, the two-photon ionization spectrum of this molecule was recorded using a time-of-flight mass spectrometer integrated into the setup. This new experimental apparatus is presented here for the first time.



INTRODUCTION

4-Aminobenzonitrile (ABN) can be categorized as a para-substituted benzonitrile (Figure 1). This class of molecule has

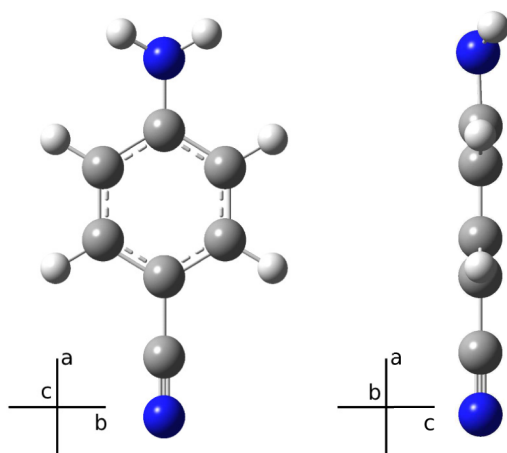


Figure 1. Geometry of 4-aminobenzonitrile. The nitrogen atoms of the nitrile and the amino group lead to a complicated hyperfine structure of rotational transitions. The principal inertial axes are labeled as *a*, *b*, and *c*.

received much attention because some display dual fluorescence, i.e., the solvent-dependent appearance of a second emission at a different frequency from a charge-transfer state upon local excitation.¹ A well-studied example for this effect is dimethylaminobenzonitrile (DMABN).^{2–6} In contrast to this molecule, ABN shows no dual fluorescence.^{7,8} This difference was explained by the additional electron-donating character of

the alkylated amino group in DMABN.⁴ Thus, the electronic environment at the amino-group nitrogen can be decisive for the existence of charge-transfer states and hence dual fluorescence (see, for example, refs 9 and 10).

Here, the rotational spectrum of ABN in the frequency range 2–8.5 GHz measured by broadband microwave spectroscopy is reported. The two chemically distinct nitrogen atoms of the respective amino and nitrile groups of this molecule lead to a hyperfine structure of each rotational transition due to nuclear quadrupole coupling. Determining their individual quadrupole interactions is challenging, due to the complicated, combined splitting effect of the two nuclei. The respective nuclear quadrupole coupling constants are presented here. They allow for the investigation of the electronic environment of the molecule in the vicinity of the nitrogen atoms, which is of particular interest when ABN is compared to other para-substituted benzonitriles showing dual fluorescence. Previous microwave spectroscopy studies investigated the differences between dimethylaniline (DMA) and DMABN.¹¹ Here we extend this comparison to include ABN as well.

The rotational constants of the asymmetric rotor ABN were determined earlier from rotationally resolved electronic spectra.^{12,13} Due to the lower resolution and higher rotational transitions, and therefore smaller hyperfine splittings involved, the quadrupole coupling constants were not accessible. The frequency range of our spectrometer (2–8.5 GHz) together with the high resolution provided by microwave spectroscopy

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facilitates their identification. The two nonvanishing dipole moment components of ABN are 5.46 D along the direction of the weakest moment of inertia (μ_a) and 1.45 D in the direction orthogonal to the benzene ring (μ_c);¹³ hence the spectrum is dominated by a-type asymmetric rotor transitions.

ABN is also a potential candidate for extending the ongoing molecule-deceleration experiments in our group toward larger molecules. We recently demonstrated that the interaction of polar molecules with strong external microwave fields can be used to manipulate their motion, e.g., to guide, focus, and decelerate them.^{14,15} The force on the molecules results from the AC Stark effect of the particular rovibronic states of interest. As it is planned to use ABN in our beam-slowing experiments, a sound knowledge of its rotational spectrum is necessary. ABN is especially suited for this purpose because of its advantageous dipole moment-to-mass ratio and its efficient detection after ionization with a mass spectrometer, which is characterized in this work as well.

The purpose of this paper is 2-fold. First, we present our results on the nitrogen hyperfine splitting of ABN and thus extend recent studies.¹¹ Second, we want to present our new apparatus, a broadband microwave spectrometer equipped with a laser ablation source and a time-of-flight (TOF) mass spectrometer.

EXPERIMENTAL METHODS

The data presented in this work was recorded in our new spectrometer, which is described here for the first time. It was constructed in a modular manner and consists of three vacuum cross-chambers: One for the molecular source, one for the microwave excitation/detection, and one housing a TOF mass spectrometer for beam diagnostics.

In the source chamber the molecules of interest are either coexpanded with a carrier gas through a pulse nozzle or seeded into the expanding carrier gas by ablating them with a laser pulse from a solid sample. The latter method is especially suited for fragile molecules. To measure rotational spectra, the Fourier-transform microwave spectroscopy (FTMW) technique¹⁶ with a broadband chirped-pulse (CP-FTMW) excitation is used.¹⁷ The electronic microwave setup is identical to the one we reported previously.¹⁸ Our accessible frequency range of 2–8.5 GHz is particularly interesting for larger molecular systems like biomolecules and complexes, which have large moments of inertia and thus small rotational constants. Consequently, the main part of the rotational spectrum is located in this low-frequency range. Furthermore, mainly transitions between low-lying rotational states are observed for molecules of the size of ABN. This is advantageous for determining the nuclear quadrupole coupling constants of weakly coupling nuclei, such as nitrogen, because the arising splittings scale inversely with the rotational quantum number J .

In addition to the microwave spectrometer, a commercial TOF ion mass spectrometer (Jordan TOF Products) of Wiley–McLaren type¹⁹ was implemented in the experiment. Together with an ionization laser, this is a highly sensitive tool for monitoring and analyzing our molecular beam and particularly valuable for gaining information about the formation of complexes. The combination with the microwave capabilities of the apparatus will also allow for double-resonance experiments. Furthermore, by scanning the frequency of the ionizing laser pulse the vibrational structure of electronic levels can be investigated, as shown below for ABN.

For the experiments described here, ABN was purchased from Sigma-Aldrich (98% purity) and used without further purification. The sample was heated to 113 °C in a reservoir and the carrier gas neon, with a backing pressure of 2.5 bar, was flowed over it to create a gas mixture. Subsequently, this mixture was expanded into vacuum through a pulse nozzle with an opening time of approximately 400 μ s and a repetition rate of 2 Hz. After an expansion time of 775 μ s, the ABN molecules were excited by a 1 μ s long microwave pulse, which was linearly frequency chirped from 2 to 8.5 GHz. The resulting free induction decay (FID) was recorded for 50 μ s starting 5 μ s after the excitation pulse and then amplified and converted into a digital signal. In total 337 000 FIDs were recorded and digitally averaged. The rotational spectrum was obtained by Fourier transforming the experimental data using a fast Fourier-transform algorithm, without any filters or other treatments. The length of the recorded FID set our frequency resolution to 20 kHz, whereas the full width at half-maximum of our transitions was on the order of 30 kHz. The spectrum of ABN is depicted in Figure 2, together with the results of a fit (see later).

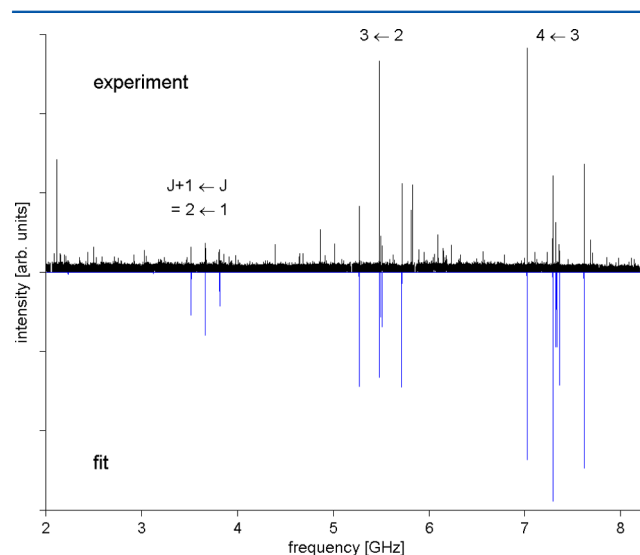


Figure 2. Rotational spectrum of 4-aminobenzonitrile. The upper trace shows the experimental data, and the lower trace represents the result of fitting an asymmetric rotor Hamiltonian to it. Known background lines have been removed.

Note that a number of unassigned lines remain that can be attributed neither to the ABN monomer nor to its isotopologues. They might arise from complexes of ABN. As mentioned, the experimental setup allows us to analyze the molecular beam with the TOF mass spectrometer. The recorded mass spectrum is depicted in Figure 3 and confirms the existence of ABN complexes. Besides the dominant monomer peak, at the mass of 118.4 g/mol, the dimer, trimer, and tetramer of ABN are clearly visible. Also the complex of the ABN dimer with water could be identified. Interestingly, no complex of the ABN monomer and water was observed.

To obtain the mass spectrum of ABN, the molecules were first ionized with a 8 ns long light pulse with a pulse energy of 6 mJ from a tunable Nd:YAG-pumped dye laser (featuring a line width of 0.06 cm^{-1} at a wavelength of 570 nm). The resulting ions were accelerated in an electric field gradient, then they flew through a 1 m long drift tube and finally they were detected by

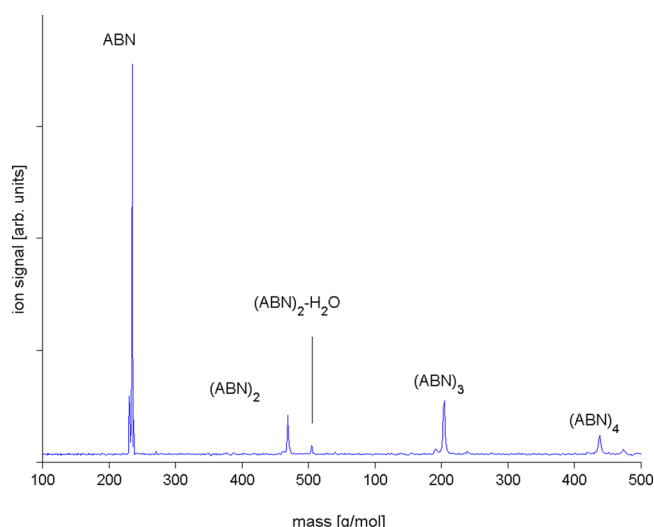


Figure 3. Ion fragments from the molecular beam of ABN analyzed with the TOF mass spectrometer. For each point 36 000 acquisitions were averaged.

a multichannel plate upon their arrival at the end of the tube. The TOF between excitation and detection depends on their mass-to-charge ratio and thus, assuming single ionization, allows for the determination of their mass. During the experiment, the ionization laser frequency was kept resonant for the ABN monomer at a wavelength of 291.5 nm. Even upon complex formation the resonances do not shift much, so that ionization of the complexes was possible. For the final spectrum, 36 000 mass spectra were averaged (Figure 3).

With the same setup it is possible to study the vibrational structures of electronic levels by a combination of TOF mass spectrometry and ionization techniques, such as resonance enhanced multiphoton ionization (REMPI). To demonstrate

its functionality and to test the detection efficiency of ABN using REMPI for our upcoming beam-slowing experiments, the one-color two-photon ionization spectrum of ABN in the range from 290 to 300 nm was recorded (Figure 4).

The frequency was varied in steps of 0.01 nm and for each point 180 acquisitions were averaged. The line positions were determined by fitting a Lorentzian line shape to each peak. Their assignment was carried out in agreement with refs 9 and 20 and also agrees well with more recent results (Table 1).^{23,24}

Table 1. Line Positions of the One-Color Two-Photon REMPI Spectrum of 4-Aminobenzonitrile

transition ^a	this work	refs 9 and 21
0_0^0 (cm ⁻¹)	33493 ^b	33493
$6a_0^0$ (cm ⁻¹)	382.9(4)	382
$10b_0^2$ (cm ⁻¹)	494.3(3)	494
12_0^1 (cm ⁻¹)	678.0(5)	678
1_0^2 (cm ⁻¹)	806.9(3)	807
1_0^1 (cm ⁻¹)	815.2(2)	815

^aVarsányi notation.²² ^bSet to reported value of ref 9. Errors in parentheses represent the 95% confidence interval of the fit parameters.

ANALYSIS AND DISCUSSION OF THE ROTATIONAL SPECTRUM OF ABN

In the following, the analysis of the microwave spectrum of ABN and especially the results on the nuclear quadrupole coupling in this molecule are discussed in more detail and compared to data for related systems. The differences to DMABN are highlighted and presented with the help of analyzing the occupation numbers of the atomic orbitals of the nitrogen in the amino group.

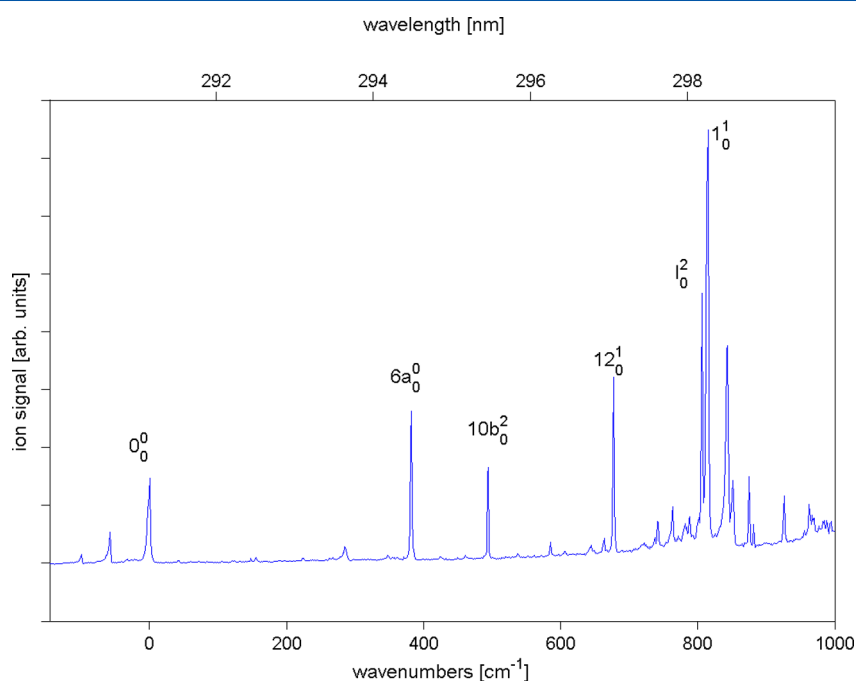


Figure 4. One-color two-photon REMPI spectrum of aminobenzonitrile. The different lines represent resonances of different vibrational levels of the same excited electronic level. The origin was set to the known value of 33 493 cm⁻¹, and the line assignment followed previous work using Varsányi notation.^{20–22}

The microwave spectrum was fitted using an asymmetric rotor Hamiltonian (Watson S-reduction in I' representation) as implemented in the program PGOPHER.²⁵ The fitting results are shown in the lower trace of Figure 2. Rotational quantum numbers involved in the assigned transitions range from $J = 1$ to $J = 4$. A complete line list can be found in the Supporting Information. For the corresponding energy levels the influence of distortion constants was found to be small and thus have been neglected in the fitting procedure. As expected from the dipole moment components, the spectrum of ABN is dominated by a -type transitions. Despite the still significant dipole moment along the c direction, no corresponding transitions were observed. Also no signatures from ^{13}C or other isotopologues of the molecule could be found in the data.

The obtained rotational and nuclear quadrupole constants are listed in Table 2. They show good agreement with the

previously reported rotational constants and predictions of *ab initio* calculations. Concerning the quantum chemical methods, the overall best agreement is obtained by density functional theory using the M06-2X functional and a 6-31+G(d,p) basis set. The differences in the results obtained at the MP2 level of theory mainly arise from different equilibrium positions of the hydrogen atoms in the amino group.

Note that no line splitting arising from the inversion motion of the amino group is observed under the cold conditions of a molecular jet. Similar to the case for the related molecule aniline, the splittings of the respective energy levels are so large that the thermal population of the excited modes becomes negligible at low temperatures (compare, e.g., refs 26 and 27).

The nuclear quadrupole splitting of the rotational transitions arising from the different nitrogen nuclei is nicely resolved for the two lower rotational transitions ($J + 1 \leftarrow J = 3 \leftarrow 2$ and $2 \leftarrow 1$), whereas for the transitions with $J + 1 \leftarrow J = 4 \leftarrow 3$ the groups of lines become quite congested. This underlines the need for observations in this low-frequency range. Typical nuclear quadrupole splitting patterns are presented in Figure 5.

The nuclear quadrupole coupling in molecules is very sensitive to the local electric field gradient, and a comparison of the results with a series of related molecules highlights their differences. To relate the nuclear quadrupole coupling constants measured in the inertial principal axis system of ABN (a , b , c) to other molecules, the nuclear quadrupole coupling tensors have to be transferred to their principal axis system (x , y , z). In the case of the molecules described herein, the transformation between the two coordinate systems is given by a rotation around the b axes by an angle θ .¹¹ Because the off-diagonal elements of the nuclear quadrupole coupling tensors are not determined in the experiment, this angle was estimated from quantum chemical calculations at the M06-2X/6-31+G(d,p) level of theory. For this purpose the eigenvectors of the calculated nuclear quadrupole tensor were expressed in the

Table 2. Spectroscopic Constants of 4-Aminobenzonitrile

parameter	this work	ref 12	M06-2X ^c	B3LYP ^c	MP2 ^c
A (MHz)	5581.0(4)	5579.3(5)	5589.84	5565.3	5572.2
B (MHz)	990.3627(7)	990.26(9)	990.5	984.7	981.1
C (MHz)	841.4827(6)	841.39(8)	841.8	837.0	834.9
χ_{aa}^a (MHz)	2.48(1)		2.315	2.416	2.225
χ_{bb}^a (MHz)	1.87(2)		2.038	2.115	1.800
χ_{cc}^a (MHz)	−4.352(2)		−4.389	−4.531	−4.024
χ_{aa}^b (MHz)	−4.138(9)		−3.712	−3.476	−2.868
χ_{bb}^b (MHz)	2.40(2)		2.259	2.172	1.464
χ_{cc}^b (MHz)	1.74(2)		1.475	1.304	1.405
assigned lines	114				
mean error (kHz)	11.64				

^aAmino nitrogen. ^bNitrile nitrogen. ^c6-31+G(d,p) basis set.

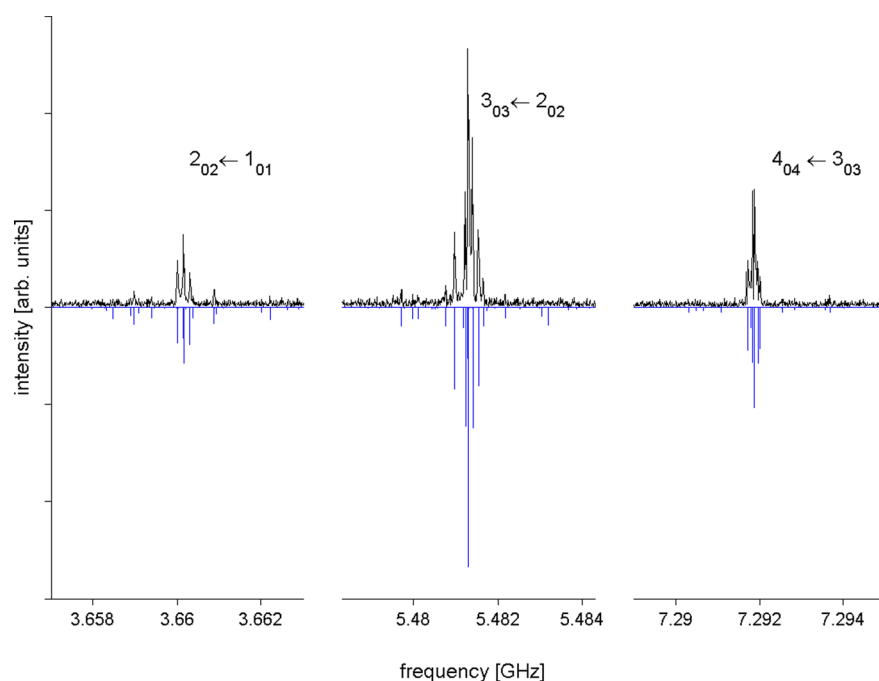


Figure 5. Nuclear quadrupole coupling splitting due to the two nitrogen atoms in ABN for three different rotational transitions. For higher rotational quantum numbers the splitting is smaller and the transition groups are more congested and more difficult to resolve. The transitions are labeled according to the scheme $J'_{K'_a K'_c} \leftarrow J_{K_a K_c}$.

coordinates of the inertial principal axis system. θ is then given by the angle between the axes x and a or equivalently between the axes z and c . The axes y and b coincide. The transformed values of the nuclear quadrupole coupling components are then derived from the experimental results by a coordinate rotation, as discussed in ref 11.

For the nuclear quadrupole coupling constants of the nitrile-nitrogen atom, the corresponding corrections are very small and thus have been neglected. In Table 3, the obtained nuclear

Table 3. Nitrile Quadrupole Coupling in ABN, DMABN, and Benzonitrile

parameter	ABN	DMABN ¹¹	benzonitrile ²⁸
χ_{aa} (MHz)	−4.138(9)	−4.11(30)	−4.2574(4)
χ_{bb} (MHz)	2.40(2)	2.40(13)	2.289(1)
χ_{cc} (MHz)	1.74(2)	1.71(13)	1.949(1)

quadrupole coupling constants for ABN, DMABN, and benzonitrile are compared. Both the amino and the dimethylamino group are known to have a strong electron-donating effect on the aromatic ring. The very similar nuclear quadrupole coupling constants for ABN and DMABN compared to that of the reference molecule benzonitrile confirm this result.

The comparable nuclear quadrupole coupling constants of the amino nitrogen resulting from these rotations are presented in Table 4. In molecules with methylated amino groups

Table 4. Nuclear Quadrupole Coupling Constants of the Nitrogen in the Amino Group^a

parameter	aniline ^{11,27,29}	ABN	DMABN ¹¹	DMA ¹¹
χ_{xx} (MHz)	2.72	2.69(2)	2.56	2.61
χ_{yy} (MHz)	1.86	1.87(2)	2.8	2.8
χ_{zz} (MHz)	−4.59	−4.559(2)	−5.35	−5.41
θ (deg) ^b	13.3	9.7	2.8	3.6

^aValues are given in the principle axis system of χ . ^bRotation angle.

(DMABN, DMA), the nuclear quadrupole coupling of the amino-nitrogen atom is enhanced because of the electron-donating character of the methyl groups. However, the nitrile group is known to be electron withdrawing. This property leads to a reduction of the amine nuclear quadrupole coupling, as can be seen for DMABN when compared to DMA. ABN features significantly lower nuclear quadrupole coupling constants than DMA or DMABN. Together these results indicate a lower electron density close to the nitrogen atom in the amino group and thus a lower tendency for the existence of charge-transfer states. In addition, the similarity between ABN and aniline is strengthened by the comparison in Table 4.

To further support this argument, a population analysis of the amino-nitrogen p-orbitals was carried out according to the Townes–Dailey model^{30,31} and in close analogy to refs 11 and 32. It allows for the determination of the following indicators from the nuclear quadrupole coupling constants: $i_o(\text{NX})$, the ionic character of the amino-group N–H bonds, $i_o(\text{NC})$, the ionic character of the N–C bond between the amino group and the aromatic ring, and $\pi_c(\text{NC})$, the covalent character of the latter. From these quantities the orbital occupancies of the nitrogen p-orbitals (N_x , N_y , N_z) were calculated. The corresponding formulas are given in the Supporting Information. Note that N_z corresponds to the lone-pair occupation of

the nitrogen atom. Furthermore, the angle between the two N–H bonds φ is linked to the amount of s-type hybridization and thus to $i_o(\text{NX})$ (see refs 30 and 33, page 234 ff). Its value is needed for the computations above and was taken from quantum chemical calculations for ABN and from the corresponding references for the compared molecules. Note that in ref 11, discussing DMA and DMABN, there is some confusion with the coordinate system labels, so that our values deviate from the published ones.

The interpretation of the resulting numbers, listed in Table 5, follows closely the arguments given in ref 11. It stands out that

Table 5. Bond Characters and Nitrogen p-Orbital Occupancies

parameter	aniline	ABN	DMA	DMABN
φ	113.1	113.9	114.7	118
$i_o(\text{NC})$	0.38	0.38	0.27	0.29
$i_o(\text{NX})$ X = H, X = CH ₃	0.28	0.29	0.29	0.32
$\pi_c(\text{NX})$	0.12	0.11	0.04	0.00
N_x	1.33	1.34	1.28	1.31
N_y	1.28	1.29	1.29	1.32
N_z	1.88	1.89	1.96	2.00

ABN has the lowest occupation of the lone-pair orbital N_z of the amino-nitrogen and a high covalent character π_c of the amino-group bonds. The combination of the high ionic character of the nitrogen aromatic-carbon bond $i_o(\text{NC})$ in ABN and the low ionic character of this bond in DMABN suggests that less charge is concentrated at this location. This could represent a barrier for charge-transfer states and thus explain the absence of dual fluorescence in ABN. In general, this finding adds microscopic details of the electron distribution to the discussion of dual emission in aminobenzonitrile-like molecules, which can be related to the dynamics of the molecule upon electronic excitation.¹⁰

CONCLUSIONS

We investigated the broadband rotational and the REMPI spectrum of ABN with our new experimental apparatus, which combines the power of a broadband microwave spectrometer with the analytic advantages of a mass spectrometer. The obtained information on vibronic transitions is particularly interesting with respect to future beam-slowing experiments.

The assigned rotational constants were determined to higher precision and agree very well with previous findings from rotationally resolved electronic spectra. These high-resolution results were used to benchmark quantum chemical calculations. We find that density functional theory using the M06-2X functional showed the best agreement for ABN.

The hyperfine structure due to the nuclear quadrupole coupling of the two chemically distinct nitrogen atoms in ABN was resolved. The experimentally determined nuclear quadrupole coupling constants allowed for the analysis of the electronic environment of the nitrogen locations. It was found that DMABN and ABN have a similar electronic environment at the nitrile-nitrogen atom and hence that the influence of the methyl groups through the aromatic ring is negligible compared to the effect of the amino group itself.

By calculating the occupancies of the hybrid orbitals of the amino-group nitrogen, we showed that there is a significantly lower charge density in ABN compared to other para-substituted benzonitriles like DMABN. This result is

particularly interesting with respect to the occurrence of dual fluorescence because it can be interpreted as a possible barrier to charge-transfer states.

■ ASSOCIATED CONTENT

■ Supporting Information

Table listing all assigned lines of ABN and equations used to calculate the orbital occupancies. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

■ AUTHOR INFORMATION

Corresponding Authors

*T. Betz: e-mail: thomas.betz@mpsd.mpg.de.

*M. Schnell: e-mail: melanie.schnell@mpsd.mpg.de.

Notes

The authors declare no competing financial interest.

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