

# Precise dipole moment and quadrupole coupling constants of benzonitrile

Kirstin Wohlfart <sup>a</sup>, Melanie Schnell <sup>a</sup>, Jens-Uwe Grabow <sup>b</sup>, and Jochen Küpper <sup>a,\*</sup>

<sup>a</sup>*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6, 14195 Berlin, Germany*

<sup>b</sup>*Gottfried-Wilhelm-Leibniz-Universität, Institut für Physikalische Chemie und Elektrochemie, Callinstraße 3a, 30167 Hannover, Germany*

*Key words:* benzonitrile; microwave spectroscopy; rotational spectroscopy; dipole moment; Stark effect; nuclear quadrupole coupling; supersonic-jet; cold molecules  
*PACS:* 33.20.Bx; 33.55.Be; 33.15.-e

---

Cyanobenzenes have recently been suggested as good candidates for the detection of aromatic molecules in interstellar space [1–3], partly due to their large dipole moments. The simplest molecule from this class is benzonitrile ( $C_6H_5CN$ ), which might be detectable, for example, in the proto-planetary nebula CRL 618 [1, 2]. These predictions are based on an assumed abundance of  $10^{-6}$  and a dipole moment of 4.3 D [1], and they are related to the detection of similar molecular species (benzene ( $C_6H_6$ ), diacetylene ( $C_4H_2$ ), and triacetylene ( $C_6H_2$ )) in CRL 618 [4]. Moreover, due to its large dipole moment and therefore its large Stark-effect-to-mass ratio benzonitrile is a prime candidate for the electrostatic deceleration and trapping of large molecules using the Alternate Gradient focusing principle [5].

The value of the benzonitrile dipole moment, however, is still a matter of debate. Due to the  $C_{2v}$  symmetry only a non-zero  $\mu_\alpha$  component of the dipole moment can exist. To our knowledge, only two independent and incompatible values of the dipole moment of benzonitrile in its electronic ground state have been published: From microwave Stark effect measurements a dipole moment of 4.14(5) D was deduced [6] and a similar value based on the same measurements (4.18(8) D) is listed in the CRC Handbook of Chemistry and Physics [7]. Recently, a different value of 4.48(1) D was determined from Stark shift measurements of the rotationally resolved laser-induced-fluorescence spectrum [8].

---

\* Author to whom correspondence should be addressed. Electronic mail: jochen@fhi-berlin.mpg.de

Therefore, we set out for a precise experimental determination of the dipole moment using Fourier-transform microwave spectroscopy (FTMW) in homogeneous electric fields.

The experimental setup of the Hannover COBRA-FTMW-spectrometer has been described in detail elsewhere [9, 10]. In brief, benzonitrile ( $\geq 99\%$  purity) was purchased from Fluka and used without further purification. The sample was co-expanded in 3.5 bar of Ne at a temperature of 300 K through a pulsed nozzle (General Valve Series 9) with a 0.8 mm orifice. The supersonic expansion was pulsed coaxially into the microwave resonator [11], which was specially developed to provide high sensitivity and resolution at low frequencies down to 2 GHz [12]. Some of the lowest rotational transitions of benzonitrile in the range of 2.8–10.9 GHz were recorded with a linewidth (FWHM) of 2.5 kHz and a frequency accuracy of 500 Hz. Homogeneous electric fields for the Stark shift measurements were provided by the Coaxially Aligned Electrodes for Stark effect Applied in Resonators (CAESAR) setup [10] where electric field strengths up to 203 V/cm could be reached. The electric field was calibrated using the  $J = 1 \leftarrow 0$  transition of  $\text{OC}^{36}\text{S}$  (0.02% natural abundance) and a documented dipole moment of 0.71519(3) D [13], see reference [14] for details.

The measured field-free microwave transitions and their estimated experimental uncertainties are listed in table 1. Whereas the frequencies for the  $J = 1 \leftarrow 0$  and  $2 \leftarrow 1$  hyperfine transitions are reported for the first time the accuracy for the  $J = 3 \leftarrow 2$  and  $4 \leftarrow 3$  transitions have been considerably improved with respect to previous measurements [15] and additional hyperfine-splittings could be resolved.

We have simultaneously fit the newly measured lines together with previously published microwave transitions [15, 16] using the QStark program package [17, 18]. A weighted analysis of all these lines was performed assuming for the transition frequencies from Fliege et al. [15] measurement accuracies of 20 kHz and for the transition frequencies from Vormann et al. [16] measurement accuracies of 5 kHz. The resulting rotational constants, centrifugal distortion constants, and nitrogen nuclear quadrupole coupling constants of benzonitrile are given in table 2. The values of the rotational constants are in good agreement with literature values [15, 16, 20]. The nitrogen nuclear quadrupole coupling constants agree with those determined by the Kiel group using perturbation theory [15, 16] within the published error limits, and, moreover, the accuracy of these nuclear quadrupole coupling constants could be improved considerably in our study. The centrifugal distortion constants agree within error limits with those of large- $J$  microwave transition measurements [20]. The resulting value of the inertial defect  $\Delta I = 0.0801(12) \text{ u}\text{\AA}^2$  is small and confirms the planarity of benzonitrile.

In order to determine the dipole moment of benzonitrile, Stark effect mea-

$J'_{K'_a K'_c} \leftarrow J''_{K''_a K''_c}$	$F' \leftarrow F''$	frequency (MHz)	uncertainty (MHz)	obs.-calc. (MHz)
1 <sub>01</sub> ← 0 <sub>00</sub>	1 ← 1	2760.22090	0.00050	0.00030
1 <sub>01</sub> ← 0 <sub>00</sub>	2 ← 1	2761.49318	0.00150	0.00154
1 <sub>01</sub> ← 0 <sub>00</sub>	0 ← 1	2763.39853	0.00050	-0.00011
2 <sub>02</sub> ← 1 <sub>01</sub>	1 ← 0	5502.12082	0.00100	-0.00095
2 <sub>02</sub> ← 1 <sub>01</sub>	1 ← 1	5505.30033	0.00100	0.00052
2 <sub>02</sub> ← 1 <sub>01</sub>	3 ← 2	5503.27585	0.00100	0.00009
2 <sub>02</sub> ← 1 <sub>01</sub>	2 ← 1	5503.19315	0.00100	0.00092
2 <sub>02</sub> ← 1 <sub>01</sub>	1 ← 2	5504.02800	0.00100	-0.00077
2 <sub>02</sub> ← 1 <sub>01</sub>	2 ← 2	5501.92073	0.00100	-0.00046
2 <sub>02</sub> ← 1 <sub>01</sub>	3 ← 2	5503.27579	0.00100	0.00003
2 <sub>11</sub> ← 1 <sub>10</sub>	1 ← 0	5856.56986	0.00100	-0.00059
2 <sub>11</sub> ← 1 <sub>10</sub>	1 ← 1	5855.10867	0.00150	-0.00070
2 <sub>11</sub> ← 1 <sub>10</sub>	2 ← 1	5853.96436	0.00100	-0.00029
2 <sub>11</sub> ← 1 <sub>10</sub>	1 ← 2	5855.69296	0.00100	-0.00073
2 <sub>11</sub> ← 1 <sub>10</sub>	2 ← 2	5854.54929	0.00100	0.00032
2 <sub>11</sub> ← 1 <sub>10</sub>	3 ← 2	5855.28522	0.00100	0.00073
2 <sub>12</sub> ← 1 <sub>11</sub>	1 ← 0	5191.71753	0.00050	0.00000
2 <sub>12</sub> ← 1 <sub>11</sub>	1 ← 1	5190.00134	0.00050	-0.00017
2 <sub>12</sub> ← 1 <sub>11</sub>	2 ← 1	5189.02665	0.00150	0.00008
2 <sub>12</sub> ← 1 <sub>11</sub>	1 ← 2	5190.68619	0.00150	0.00170
2 <sub>12</sub> ← 1 <sub>11</sub>	3 ← 2	5190.33981	0.00100	0.00062
3 <sub>03</sub> ← 2 <sub>02</sub>	4 ← 3	8206.82990	0.00100	0.00066
3 <sub>03</sub> ← 2 <sub>02</sub>	3 ← 2	8206.79124	0.00100	0.00102
3 <sub>03</sub> ← 2 <sub>02</sub>	2 ← 1	8206.56481	0.00100	0.00051
4 <sub>04</sub> ← 3 <sub>03</sub>	5 ← 4	10855.26125	0.00150	0.00071
4 <sub>04</sub> ← 3 <sub>03</sub>	4 ← 3	10855.24427	0.00150	0.00092
4 <sub>04</sub> ← 3 <sub>03</sub>	3 ← 2	10855.13590	0.00100	0.00043
4 <sub>04</sub> ← 3 <sub>03</sub>	3 ← 3	10857.01706	0.00050	-0.00008
4 <sub>04</sub> ← 3 <sub>03</sub>	3 ← 4	10855.62177	0.00200	-0.00178
4 <sub>04</sub> ← 3 <sub>03</sub>	4 ← 4	10853.84943	0.00050	-0.00032

Table 1

Measured hyperfine-resolved field-free transition frequencies, estimated experimental uncertainties, and fit residuals. See text for details.

measurements in homogeneous electric fields were performed on the  $J'_{K'_a K'_c} F' \leftarrow J''_{K''_a K''_c} F'' = 1_{01}1 \leftarrow 0_{00}0$ ,  $1_{01}1 \leftarrow 0_{00}1$ , and  $4_{04}3 \leftarrow 3_{03}3$  transitions. For our deceleration experiments we are especially interested in the Stark effect of the absolute rovibronic ground state of benzonitrile. Moreover, that  $0_{00}$  state is the most polar rotational state for all molecules, and, therefore, exhibits the largest Stark shift in strong electric fields [5]. Additionally, the selected transition had good intensities. The applied high voltages were calibrated and electric field strengths calibration measurements for OCS were done, as described in reference [14]. From these measurements an error estimate for the

$A$ (MHz)	5655.2654 (72)
$B$ (MHz)	1546.875864 (66)
$C$ (MHz)	1214.40399 (10)
$\chi_{aa}$ (MHz)	-4.23738 (36)
$\chi_{bb} - \chi_{cc}$ (MHz)	0.3397 (10)
$\chi_{bb}$ (MHz)	2.2886 (11)
$\chi_{cc}$ (MHz)	1.9488 (11)
$\Delta_J$ (kHz)	0.0456 (15)
$\Delta_{JK}$ (kHz)	0.9381 (56)
$\Delta_K$ (kHz)	0.50(38)
$\delta_J$ (kHz)	0.01095 (41)
$\delta_K$ (kHz)	0.628 (53)
$\Delta I$ ( $\mu\text{\AA}^2$ )	0.0801 (12)
number of measurements	93
$\sigma$ (MHz)	0.00524
$\hat{\sigma}$	0.675
$\mu_a$ (D)	4.5152 (68)
number of measurements	78
$\sigma$ (MHz)	0.00228
$\hat{\sigma}$	0.709

Table 2

Upper part: Rotational constants,  $^{14}\text{N}$  quadruple coupling constants, centrifugal distortion constants, inertial defect, the number of hyperfine-resolved components included in the fit, overall standard deviation, and weighted standard deviation from the fit of the field-free lines of benzonitrile. Lower part: Dipole moment, number of measurements at different electric field strengths, overall standard deviation, and weighted standard deviation from the fit of the Stark-shifts at various electric field strengths. See text for details.

electric field strengths was specified. For electric fields up to 203 V/cm the frequencies of the transitions in the electric field could be determined with uncertainties between 0.5 kHz–8 kHz, depending on the  $J$ -complexity of the Stark-split and -shifted spectra and the electric field strength. The dipole moment and its error estimate are given in table 2. This value is in agreement ( $3\sigma$ ) with the value from Stark-shift measurements of the rotationally resolved laser-induced-fluorescence spectrum [8], but differs considerably from previous

microwave measurements [6, 7].<sup>1</sup>

In conclusion, we have simultaneously determined the rotational constants, nitrogen nuclear quadrupole coupling constants, and centrifugal distortion constants of benzonitrile from Fourier transform microwave spectroscopy in a supersonic jet. The value of the dipole moment of benzonitrile is determined precisely to  $\mu_a = 4.5152(68)$  D from Stark-shift measurements. This should settle the issue regarding the value of the dipole moment of benzonitrile.

### Acknowledgments

We would like to thank Gerard Meijer for his continuous support and Zbigniew Kisiel for updating QStark to allow weighted fits. Financial support from the *Land Niedersachsen* and the *Deutsche Forschungsgemeinschaft*, also within the priority program 1116 “Interactions in ultracold gases”, is acknowledged.

### References

- [1] P. M. Woods, T. J. Millar, A. A. Zijlstra, and E. Herbst, *Astrophys. J.* **574**, L167 (2002).
- [2] P. M. Woods, T. J. Millar, A. A. Zijlstra, and E. Herbst, *IAU SYMPOSIA: Planetary Nebulae: Their Evolution and Role in the Universe* pp. 279–280 (2003).
- [3] E. Herbst, private communication with J.-U. Grabow (2007).
- [4] J. Cernicharo, A. M. Heras, A. G. G. M. Tielens, J. R. Pardo, F. Herpin, M. Guélin, and L. B. F. M. Waters, *Astrophys. J.* **546**, L123 (2001).
- [5] H. L. Bethlem, M. R. Tarbutt, J. Küpper, D. Carty, K. Wohlfart, E. A. Hinds, and G. Meijer, *J. Phys. B* **39**, R263 (2006).
- [6] D. R. Lide, *J. Chem. Phys.* **22**, 1577 (1954).
- [7] D. R. Lide, ed., *CRC Handbook of Chemistry and Physics*, vol. 71 (CRC Press, Boca Raton, 1990).
- [8] D. R. Borst, T. M. Korter, and D. W. Pratt, *Chem. Phys. Lett.* **350**, 485 (2001).
- [9] J.-U. Grabow, W. Stahl, and H. Dreizler, *Rev. Sci. Instrum.* **67**, 4072 (1996).
- [10] M. Schnell, D. Banser, and J.-U. Grabow, *Rev. Sci. Instrum.* **75**, 2111 (2004).
- [11] J.-U. Grabow and W. Stahl, *Z. Naturforsch. A* **45**, 1043 (1990).
- [12] J.-U. Grabow, *Habilitationschrift*, Gottfried-Wilhelm-Leibniz-Universität Hannover, Germany (2004).

---

<sup>1</sup> It should be noted, that in the original publication the author himself states that “attempts to study the Stark effect of benzonitrile encountered a number of difficulties.” See reference [6] for details.

- [13] J. M. L. J. Reinartz and A. Dymanus, *Chem. Phys. Lett.* **24**, 346 (1974).
- [14] F. Filsinger, K. Wohlfart, M. Schnell, J.-U. Grabow, and J. Küpper, *Phys. Chem. Chem. Phys.* (2007), accepted, available as advance articles on the web: DOI: 10.1039/b711888k.
- [15] E. Fliege, G. Bestmann, R. Schwarz, and H. Dreizler, *Z. Naturforsch. A* **36**, 1124 (1981).
- [16] K. Vormann, U. Andresen, N. Heinsing, and H. Dreizler, *Z. Naturforsch. A* **43**, 283 (1988).
- [17] Z. Kisiel, J. Kosarzewski, B. A. Pietrewicz, and L. Pszczółkowski, *Chem. Phys. Lett.* **325**, 523 (2000).
- [18] Z. Kisiel, B. A. Pietrewicz, P. W. Fowler, A. C. Legon, and E. Steiner, *J. Phys. Chem. A* **104**, 6970 (2000).
- [19] C. Unterberg, A. Gerlach, A. Jansen, and M. Gerhards, *Chem. Phys.* **304**, 237 (2004).
- [20] G. Włodarczak, J. Burie, J. Demaison, K. Vormann, and A. G. Császár, *J. Mol. Spec.* **134**, 297 (1989).