The Rotational Spectrum of Benzonitrile: Experimental and Theoretical Determination of the Quartic Centrifugal Distortion Constants

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The ground state rotational spectrum of benzonitrile has been reinvestigated in the range 18–160 GHz. High J transitions ($J \leqslant 65$) have been measured and accurate rotational and centrifugal distortion constants have been determined. The experimental quartic centrifugal distortion constants are compared with the values calculated from an ab initio force field. A good agreement is found. © 1989 Academic Press, Inc.

INTRODUCTION

The microwave spectrum of benzonitrile (C_6H_5CN) was first studied simultaneously by Erlandson (*1*) and Lide (*2*), who determined approximate values for the rotational constants. Lide (*2*) determined also the dipole moment: $\mu_a = 4.14$ D.

Later the Copenhagen group analyzed the microwave spectra of the parent species and nine isotopomers and determined a complete and accurate r_s structure (*3*). However, due to their limited frequency range (12–26 GHz) they could not perform a complete centrifugal distortion analysis and the derived rotational constants (particularly A) might be affected by a small systematic error.

Recently the microwave spectrum of benzonitrile was reinvestigated by microwave Fourier transform spectroscopy (MWFT) and the quadrupole coupling constants of the ^{14}N nucleus were accurately determined (*4, 5*).

The aim of the present work is to carry out a complete centrifugal distortion analysis of the rotational spectrum of benzonitrile. This will enable us to see the eventual effects of the centrifugal distortion on the structure. It will also allow us to predict an accurate millimeter-wave spectrum which should allow us to try to detect the presence of ben-

zonitrile in interstellar space or in some planetary atmospheres. Finally as an ab initio force field of benzonitrile has been recently calculated (6), a comparison of the experimental centrifugal distortion constants with the ones calculated from the theoretical force field will be made.

EXPERIMENTAL DETAILS

Some additional centimeter-wave transitions have been measured in the range 12–18 GHz by MWFT spectroscopy (7-10). The spectra were taken at −50 to −60°C and pressures down to 0.3 mTorr. The intensity-weighted mean of the hyperfine components was used for the centrifugal distortion analysis. The accuracy of the measurements is better than 10 kHz.

The other transitions have been measured by a computer-controlled millimeter-wave spectrometer with superheterodyne detection (11). Klystrons or Gunn diodes followed by a harmonic generator are used as sources and Schottky diodes are used both for the detection and for the harmonic generation. The accuracy of the measurements is about 50 kHz.

During the analysis of the millimeter-wave spectrum of a heavy molecule like benzonitrile (i.e., with a dense spectrum due to its small rotational constants), it is often difficult to assign with certainty some transitions because they are more or less masked by nearby stronger lines. To circumvent this difficulty our spectrometer has been slightly modified into a mmw-mmw double-resonance spectrometer. Figure 1 shows a block diagram of the experimental apparatus. A double-square wave modulation of frequency 5 kHz is applied to the frequency synthesizer which is used to stabilize the pump source. Details of the phase stabilization are given in Ref. (12). The modulated pump power is kept from reaching the detector by means of a waveguide filter. The
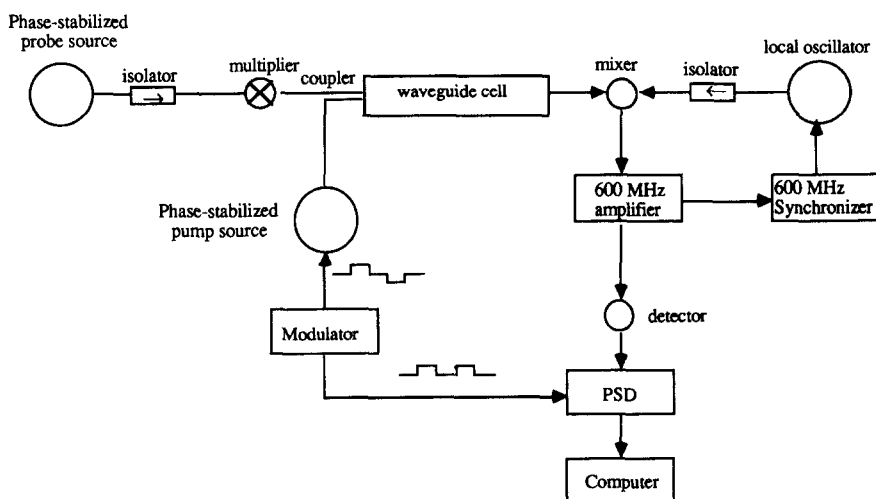

FIG. 1. Block diagram of the superheterodyne millimeter-wave spectrometer adapted for double-resonance measurements.

TABLE I

Newly Measured Transitions of Benzonitrile (in MHz)

J	Kp	Ko<-	J	Kp	Ko	exp.	e.-c.	J	Kp	Ko<-	J	Kp	Ko	exp.	e.-c.
42	8	34	42	8	35	14834.832	-0.005	56	31	25	55	31	24	155272.897	0.017
43	8	35	43	8	36	18714.319	0.044	56	32	24	55	32	23	155229.161	0.022
47	9	38	47	9	39	14135.937	-0.009	56	33	24	55	33	23	155188.495	0.029
49	9	40	49	9	41	22357.066	-0.018	56	35	22	55	35	21	155114.791	-0.041
52	10	42	52	10	43	13290.210	-0.008	57	6	51	56	6	50	154560.145	0.031
53	8	45	52	8	44	152350.242	0.006	57	6	52	56	6	51	151955.763	-0.036
53	9	44	52	9	43	155507.971	-0.035	57	7	51	56	7	50	154540.450	-0.026
53	10	43	52	10	42	154513.123	0.006	57	19	39	56	19	38	159201.448	-0.007
53	10	43	53	10	44	17029.664	-0.008	57	20	37	56	20	36	159026.465	-0.017
54	8	46	53	8	45	154479.766	0.058	57	21	36	56	21	35	158876.512	-0.027
54	8	46	53	10	45	50519.455	-0.093	57	22	35	56	22	34	158746.661	-0.037
54	9	45	53	9	44	158181.005	0.038	57	23	34	56	23	33	158633.205	-0.018
54	11	43	53	11	42	155110.920	0.006	57	24	33	56	24	32	158533.246	0.018
54	8	46	54	8	47	75015.866	0.033	57	25	32	56	25	31	158444.446	0.003
54	9	45	54	9	46	49928.220	0.182	57	26	31	56	26	30	158365.104	0.042
54	10	44	54	10	45	21364.109	0.001	57	27	30	56	27	29	158293.593	-0.036
55	7	48	54	7	47	152710.771	-0.003	57	28	29	56	28	28	158228.961	0.004
55	8	48	54	8	47	152363.010	-0.028	57	29	28	56	29	27	158170.077	0.007
55	8	47	54	8	46	156600.522	-0.023	57	30	28	56	30	27	158116.170	0.011
55	8	47	54	10	44	49225.148	-0.036	57	32	25	56	32	24	158020.677	0.010
55	9	47	54	9	46	154772.436	0.006	57	33	24	56	33	23	157978.021	-0.014
55	10	45	54	12	42	13438.077	0.008	57	34	23	56	34	22	157938.213	-0.029
55	11	44	54	11	43	158484.379	0.001	57	35	22	56	35	21	157900.931	-0.004
55	13	42	54	13	41	155513.868	-0.019	57	36	21	56	36	20	157865.819	0.006
55	14	41	54	14	40	154929.898	0.021	57	37	20	56	37	19	157832.585	-0.029
55	14	42	54	14	41	154925.010	-0.021	57	38	19	56	38	18	157801.100	-0.010
56	6	50	55	6	49	152158.000	-0.025	57	39	18	56	39	17	157771.154	0.050
56	7	49	55	7	48	155035.222	0.005	57	40	17	56	40	16	157742.424	0.002
56	7	50	55	7	49	152129.403	-0.018	57	41	16	56	41	15	157714.930	0.018
56	7	49	55	9	46	13166.291	0.007	57	42	15	56	42	14	157688.449	0.011
56	8	48	55	8	47	158734.847	-0.004	57	43	14	56	43	13	157662.913	0.030
56	8	49	55	8	48	154782.563	0.001	57	44	13	56	44	12	157638.136	-0.004
56	9	48	55	9	47	157278.615	-0.005	57	45	12	56	45	11	157614.111	-0.005
56	9	47	55	11	44	51595.121	-0.278	57	46	11	56	46	10	157590.728	0.002
56	10	47	55	10	46	159017.363	0.026	57	47	10	56	47	9	157567.904	0.008
56	12	45	55	12	44	159101.833	0.004	57	48	9	56	48	8	157545.563	0.005
56	13	43	55	13	42	158512.029	0.021	57	49	9	56	49	8	157523.636	-0.015
56	13	44	55	13	43	158440.282	0.017	57	50	7	56	50	6	157502.101	-0.020
56	14	42	55	14	41	157872.740	0.038	57	11	46	57	11	47	12350.593	-0.003
56	14	43	55	14	42	157865.009	-0.011	58	5	53	57	5	52	154376.018	-0.021
56	15	42	55	15	41	157415.668	0.032	58	6	53	57	6	52	154374.990	-0.027
56	15	41	55	15	40	157416.275	-0.027	58	11	47	58	11	48	15945.457	0.000
56	16	40	55	16	39	157062.525	-0.005	58	13	46	59	11	49	14388.411	0.004
56	17	39	55	17	38	156778.305	0.004	59	5	55	58	5	54	154285.676	0.003
56	18	38	55	18	37	156544.714	-0.029	60	3	57	59	3	56	154240.218	-0.002
56	19	37	55	19	36	156349.478	-0.032	61	3	59	60	3	58	154218.760	0.032
56	20	36	55	20	35	156184.042	0.025	61	4	57	60	4	56	159134.530	0.032
56	21	35	55	21	34	156042.069	0.005	62	1	61	61	1	60	154209.793	0.013
56	22	34	55	22	33	155919.041	-0.003	62	3	59	61	3	58	159093.066	0.022
56	23	33	55	23	32	155811.478	0.021	62	8	54	61	10	51	16325.802	-0.004
56	24	32	55	24	31	155716.576	-0.012	63	0	63	62	0	62	154206.497	-0.027
56	25	31	55	25	30	155632.297	-0.008	63	2	61	62	2	60	159073.226	-0.017
56	26	30	55	26	29	155556.948	0.044	63	12	51	63	12	52	14773.753	0.012
56	27	29	55	27	28	155488.982	-0.031	64	1	63	63	1	62	159064.907	0.001
56	28	28	55	28	27	155427.574	0.062	65	1	65	64	1	64	159061.809	0.004
56	29	27	55	29	26	155371.417	-0.061	65	12	53	64	14	50	13063.041	-0.002
56	30	26	55	30	25	155320.120	-0.027								

TABLE II

Double-Resonance Connections

measured pump transition	used probe transition
$54_{9,45} \leftarrow 54_{9,46}$	$54_{9,46} \leftarrow 53_{9,45}$
$54_{8,46} \leftarrow 53_{10,43}$	$55_{8,47} \leftarrow 54_{8,46}$
$55_{8,47} \leftarrow 54_{10,44}$	$55_{8,47} \leftarrow 54_{8,46}$
$56_{9,47} \leftarrow 55_{11,44}$	$55_{11,44} \leftarrow 54_{11,45}$

harmonic frequencies of the pump source have no spurious effects because the local oscillator is kept at a constant frequency difference of 600 MHz from the probe oscillator. The intermediate frequency is then filtered and amplified by a narrowband amplifier. Either the probe or the pump may be tuned over a wide range of fixed frequency steps while the phase-demodulated signal is digitally averaged. When the pump is swept the accuracy of the measurements is about 100 kHz.

The sample of benzonitrile was obtained commercially and was used without further purification.

ANALYSIS

The assignment was relatively easy because the spectrum is strong and there are only μ_a-type transitions (due to the C_{2V} symmetry of benzonitrile). Double-resonance experiments were also of great help. First an approximate spectrum was calculated using the constants derived from a fit of the microwave transitions (3–5). Higher J transitions were identified by the "bootstrap" method as described by Kirchhoff (13). The newly measured transitions are listed in Table I and the double-resonance connections are given in Table II. One hundred thirteen new transitions with $J \leqslant 65$ and $K_- \leqslant 50$ have been measured. In order to derive the molecular parameters a weighted least-squares program based on the Hamiltonian of Watson (14) was used. The microwave data of Refs. (3–5) were also taken into account. The Hamiltonian matrix was directly diagonalized and the I^r representation in the A re-

TABLE III

Rotational, Centrifugal Distortion Constants, and Correlation Coefficients for Benzonitrile

A(MHz)	5655.2647 (20)	1.000									
B(MHz)	1546.875885(161)	0.489	1.000								
C(MHz)	1214.404344(138)	0.015	0.866	1.000							
Δ_J(kHz)	0.045287 (22)	0.197	0.917	0.937	1.000						
Δ_{JK}(kHz)	0.93268 (29)	0.868	0.250	-0.160	-0.066	1.000					
Δ_K(kHz)	0.3175 (112)	0.973	0.376	-0.090	0.113	0.823	1.000				
δ_J(kHz)	0.0110056(51)	0.751	0.567	0.203	0.326	0.551	0.749	1.000			
δ_K(kHz)	0.60649 (24)	0.408	-0.084	-0.334	-0.174	0.502	0.362	-0.223	1.000		
Φ_{KJ}(Hz)	-0.005523(145)	0.857	0.220	-0.190	-0.075	0.990	0.817	0.511	0.554	1.000	
Φ_K(Hz)	0.200 (24)	0.931	0.224	-0.224	-0.054	0.912	0.959	0.609	0.490	0.910	1.000
Number of lines	166										

TABLE IV

Derived Constants

Determinable combinations

A	5655.2648	(21)
B	1546.87567	(16)
C	1214.40660	(14)
T_{aa}	-1.295	(11)
T_{bb}	-0.06730	(3)
T_{cc}	-0.02328	(2)
T_1	-1.06855	(29)
$T_2/(A+B+C)$	-1.7389	(5)

Derived $T_{\alpha\beta}$ constants

T_{ab}	-1.026
T_{ac}	-0.00505
T_{bc}	-0.0374
$\overset{.}{T}_{ab}$	-0.5574

Rotational constants independent of centrifugal distortion

A'	5655.2636
B'	1546.87455
C'	1214.40622

Rotational constants in MHz, T constants in kHz.

duction gives the best fit. The derived parameters are listed in Table III, together with their standard deviations and their correlation coefficients. The constant Δ_K is not very well determined: $\Delta_K/\sigma(\Delta_K) = 28$. It is further highly correlated with A, Φ_{KJ}, and Φ_K. This behavior is normal for a near-prolate top ($\kappa = -0.85$) with only A-type selection rules. The least well determined parameter is Φ_K with $\Phi_K/\sigma(\Phi_K) = 8.3$. In fact Φ_K is determined mainly by the high-J weak lines measured from Fourier spectroscopy. Its greatest contribution is only -1.34 MHz for the $65_{12,53} \leftarrow 64_{14,50}$ line. It is furthermore highly correlated with A, Δ_{JK}, Δ_K, and Φ_{KJ}. On the other hand the sextic constant Φ_{KJ} is relatively well determined with $\Phi_{KJ}/\sigma(\Phi_{KJ}) = 38$. Its contribution is the greatest for the $57_{50,7} \leftarrow 56_{50,6}$ line with -3.93 MHz and it is greater than 100 kHz for 49 lines.

Benzonitrile is planar. Indeed the inertial defect is very small:

$$\Delta = I_c - I_a - I_b = 0.07919(5) \text{ u\AA}^2.$$

The planarity defect defined by (13-16)

$$\Delta\tau = \tau_{cccc} - \frac{\tau_2 - C\tau_1}{A+B} = 4\left(T_{cc} - \frac{T_2 - CT_1}{A+B}\right) = -0.957(69) \text{ Hz}$$

although significantly determined is also very small (see, for instance, Table 8.31 of

TABLE V

Comparison of Experimental and Ab Initio Centrifugal Distortion Constants

	exp.	calc.	deviation
Δ_J	0.04529(2)	0.04490	0.9%
Δ_{JK}	0.9327(3)	0.96156	3.1%
Δ_K	0.32(1)	0.24305	23%
δ_J	0.011006(5)	0.01084	1.5%
δ_K	0.6065(5)	0.61372	1.2%
$-T_{aa}$	1.30(1)	1.2495	3.5%
$-T_{bb}$	0.06730(3)	0.0666	1.0%
$-T_{cc}$	0.02328(2)	0.0232	0.3%
$-T_1$	1.0686(3)	1.0963	2.6%
$-T_2/(A+B+C)$	1.7389(5)	1.7771	2.2%

Ref. (*15*)). This allows us to use the planarity relations to determine the order of magnitude of the $T\alpha\beta$ centrifugal distortion constants and to estimate the influence of the centrifugal distortion on the rotational constants. The formulas used for the calculations are summarized in the Appendix and the results are given in Table IV. The effect of the centrifugal distortion on the rotational constants (Eqs. (A1) and (A6)) is negligibly small and can hardly have any effect on a structure determination. On the other hand our constant A differs by 200 kHz from that of Ref. (*3*). This is due to the fact that A is difficult to determine accurately for a near-prolate top with only A-type transitions. Although this discrepancy is small for the parent species, it could be greater for some isotopic species where fewer lines have been measured. In conclusion the difficulty of determining A might be at the origin of a small uncertainty in the structure.

Ab initio quantum chemical methods may now calculate reliable harmonic force fields, even for fairly complex molecules (*17–20*). Basis sets of modest size overestimate the force constants, but the errors are mainly systematic and can be corrected by an empirical scaling. The resulting scaled force field may be used for successful predictions of vibrational spectra and was already used to calculate with a good accuracy the quartic centrifugal distortion constants of furan, pyrrole, and pyridine (*21*). The force field of benzonitrile was recently calculated by the ab initio gradient method at the Hartree–Fock level using a 4-21 Gaussian basis set (*6*). This allows us to compare theoretical and experimental centrifugal distortion constants. The reference geometry and the internal coordinates were taken from the original work on the calculation of the force field. The results are shown in Table V. The agreement is very satisfactory, both for the Δ constants and for the T constants. For the Δ_K constant (or the T_{aa} constant) the deviation is relatively great, but in this case, this is probably the experimental determination which is not accurate enough. In fact, fixing Δ_K at the ab initio value has a negligible influence on the quality of the fit.

A fit with all quartic constants fixed at their ab initio values (A, B, C, Φ_{KJ}, and Φ_K free) gives a standard deviation of only 342 kHz, the greatest residue being only 1.74 MHz for the $56_{9,47} \leftarrow 55_{11,44}$ line. This indicates that the ab initio quartic constants may be of great help when starting a centrifugal distortion analysis.

APPENDIX

Determinable Combinations in Terms of Constants of the A Reduction

$$A = A^{(A)} + 2\Delta_J$$

$$B = B^{(A)} + 2\Delta_J + \Delta_{JK} - 2\delta_J - 2\delta_K$$

$$C = C^{(A)} + 2\Delta_J + \Delta_{JK} + 2\delta_J + 2\delta_K \tag{A1}$$

Planarity Relations

$$T_{ac} = \frac{1}{2} A^2 C^2 \left\{ \frac{T_{aa}}{A^4} - \frac{T_{bb}}{B^4} + \frac{T_{cc}}{C^4} \right\}$$

$$T_{bc} = \frac{1}{2} B^2 C^2 \left\{ -\frac{T_{aa}}{A^4} + \frac{T_{bb}}{B^4} + \frac{T_{cc}}{C^4} \right\} \tag{A2}$$

with

$$T_{\alpha\alpha} = \frac{1}{4} \tau_{\alpha\alpha\alpha\alpha}$$

$$T_{\alpha\beta} = \frac{1}{4} (\tau_{\alpha\alpha\beta\beta} + 2\tau_{\alpha\beta\alpha\beta}) \tag{A3}$$

from $T_1 = T_{ac} + T_{bc} + T_{ab}$ follows

$$T_{ab} = T_1 - T_{ac} - T_{bc} \tag{A4}$$

and

$$T_{ab}^* = \frac{\tau_{abab}}{4} = \frac{1}{2} T_{ab} - \frac{1}{4} A^2 B^2 \left\{ -\frac{T_{aa}}{A^4} - \frac{T_{bb}}{B^4} + \frac{T_{cc}}{C^4} \right\} \tag{A5}$$

Rotational Constants Independent of Centrifugal Distortion

$$A' = A + 2T_{bc} + 2T_{ab}^*$$

$$B' = B + 2T_{ac} + 2T_{ab}^*$$

$$C' = C + 2T_{ab} - 3T_{ab}^* \tag{A6}$$

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