

Scaled quantum mechanical (SQM) force field and theoretical vibrational spectrum for benzonitrile

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(Received 6 January 1989; in final form 20 February 1989; accepted 23 February 1989)

Abstract—The complete harmonic force field of benzonitrile has been determined by *ab initio* Hartree-Fock calculations using a 4-21 Gaussian basis set. As force constants are systematically over-estimated at this level, the directly calculated force field was scaled by empirical factors previously optimized for benzene and HCN. Frequencies calculated from this scaled quantum mechanical (SQM) force field confirm the published experimental assignments for benzonitrile, benzonitrile-*p-d* and benzonitrile-*d₅*. Aside from the C-H (and C-D) stretching frequencies, which are strongly affected by anharmonicity, the mean deviation between the observed and calculated frequencies is below 9 cm^{-1} for each isotopomer. Theoretical i.r. intensities reproduce the main features of the spectra semiquantitatively.

INTRODUCTION

The quantum chemical calculation of molecular harmonic force fields, even within the Hartree-Fock SCF scheme and using the relatively small 4-21 Gaussian basis set [1], has proved to be successful for many different compounds [2], including several benzene derivatives (see benzene [3], fluorobenzene [4], aniline [5] and toluene [6]). After an empirical scaling, the final results of these calculations, the so-called scaled quantum mechanical (SQM) force fields [7], give very good predictions for the vibrational normal modes: the *a priori* [8] reproduction of the fundamental frequencies is excellent (mean deviations are below 10 cm^{-1} , with maximum deviations usually below 20 cm^{-1}), and the i.r. intensities are correct semiquantitatively. As a natural continuation of these gratifying works, we report here similar calculations on another simple substituted aromatic system: benzonitrile, $\text{C}_6\text{H}_5\text{CN}$.

Although the structure [9-11], vibrational spectrum [12-16] and vibrational force field [16-18] of benzonitrile have been studied several times, there are still some unresolved questions.

Values of the small structural changes accompanying an introduction of the electron-withdrawing CN group into the benzene ring, measured by different techniques, are somewhat contradictory. Works by NYGAARD and co-workers [9], based on the investigation of the microwave spectra of benzonitrile and nine isotopic species, resulted in accurate rotational constants [9b], but the calculated substitution (r_s) and average (r_z) structures are quite different, with the r_s and r_z CC distances deviating in opposite directions from an undistorted benzene skeleton. DIEHL *et al.* [10] measured the r_z structure of benzonitrile by liquid-crystal NMR spectroscopy, and obtained appreciably different, in most cases smaller, structural effects. Very recently an electron diffraction investigation [11] was made with the purpose of resolving some of these problems. Unfortunately, the effect of

the differences between the ring CC distances proved to be too small to measure. Furthermore, the use of an external constraint for the relation of the *ipso* and *ortho* CCC angles may have introduced some artifact into the analysis. There are geometry optimizations for benzonitrile at the Hartree-Fock level using different basis sets [19-20], the largest being a 6-31G** calculation by BOCK *et al.* [20b]. These authors, based on careful geometry optimizations of different benzene derivatives, made some interesting comments on the structural features of benzonitrile, and claim that there are "perhaps unsuspected uncertainties in the analysis of the experimental data". Although the geometry is not a subject of the present study, selection of the reference geometry does influence the force constants; our results on the geometry will thus be presented in the section on computational details.

After incomplete early studies, assignment of the vibrational spectra of benzonitrile has been made by BAK and NIELSEN [12], GREEN [13], JAKOBSEN [14], GREEN and HARRISON [15], and KUWAE and MACHIDA [16]. The choice of fundamentals by BAK and NIELSEN was based on data obtained for pyridine, and turned out to be in conflict with the assignment of other monosubstituted benzenes. (Note that they also gave a tentative assignment for several fundamentals of benzonitrile-*p-d*, which was further developed by KUWAE and MACHIDA.) GREEN's first discussion of the vibrational spectrum of benzonitrile was already mainly correct; his treatment of the low-frequency region, however, used some erroneous data. JAKOBSEN studied benzonitrile-*d₅* and gave a detailed discussion of it in order to substantiate the assignment of the low frequency region. Critically evaluating the available data and re-measuring the i.r. and Raman spectra of the vapour, GREEN and HARRISON proposed a new, reliable assignment, which was later confirmed by KUWAE and MACHIDA. The latter authors also gave a full assignment for the fundamentals of benzonitrile-*p-d* and reassigned five low frequency fundamentals of benzonitrile-*d₅*, correcting the work of JAKOBSEN.

Note that KOSTYUCHENKO and SVERDLOV [18] gave several fundamentals of *o*- and *m*-C₆H₄DCN, but since these data are far from complete, no attempt will be made to include the results in the present analysis.

There are only a few simplified harmonic force fields of benzonitrile, based on experimental frequencies. DANCHINOV *et al.* [17] carried out a normal coordinate analysis for the in-plane vibrations, but refined only force constants related to the substituent. The valence type force field of KUWAE and MACHIDA [16] was fitted to the frequencies of C₆H₅CN, *p*-D-C₆H₄CN and C₆D₅CN, but many parameters had to be fixed during the refinement procedure. KOSTYUCHENKO and SVERDLOV [18] published only diagonal constants of a harmonic force field for benzonitrile, so that their results are of limited value.

Consequently, calculation of the harmonic force constants of benzonitrile in accord with present-day standards seems to be of interest and will be presented in this paper. Trends in the force field will be discussed, followed by a brief review of the assignments for benzonitrile and two of its isotopomers.

COMPUTATIONAL DETAILS

In performing these calculations we have followed exactly the standard scheme described in detail in Ref. [1]. The actual calculations have been carried out by the force method of PULAY [21], using TEXAS, an *ab initio* gradient program [22]. The Gaussian basis set used throughout the calculations is denoted as 4-21 [1]. Scaling of the force constants was also as described previously [7]. Infrared intensities were calcu-

lated from the theoretical dipole moment derivatives and the scaled force field.

The internal coordinates, selected in accordance with the recommendations of Ref. [1], are basically the same as those used for benzene [3], and are listed in Table 1.

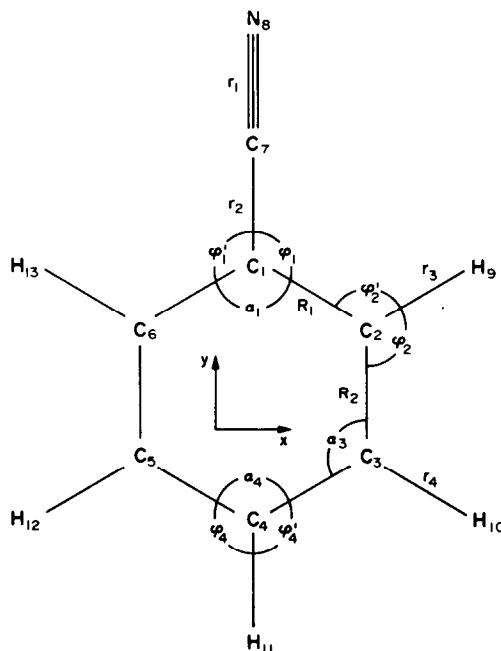


Fig. 1. Numbering of atoms and individual internal coordinates in benzonitrile.

Table 1. Internal coordinates for benzonitrile*

No.	Internal coordinate	Description
In-plane		
1	r_1	CN stretching (CN)
2	r_2	CC stretching (CC')
3-7	r_3, \dots, r_7	CH stretchings (CH)
8-13	R_1, \dots, R_6	CC stretchings (CC)
14	λ_1	CCN linear bending (λ_1)
15	$\beta_1 = 2^{-1/2}(\varphi_1 - \varphi_1')$	CC deformation ($\beta CC'$)
16-20	β_2, \dots, β_6	CH deformations (βCH)
21	$q_{21} = 6^{-1/2}(\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6)$	b_{1u} ring deformation
22	$q_{22a} = 12^{-1/2}(2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6)$	e_{2g} ring deformation
23	$q_{22b} = 1/2(\alpha_2 - \alpha_3 + \alpha_5 - \alpha_6)$	e_{2g} ring deformation
Out-of-plane		
24	λ_2	CCN linear bending (λ_2)
25	γ_1	CC wagging ($\gamma CC'$)
26-30	$\gamma_2, \dots, \gamma_6$	CH waggings (γCH)
31	$q_{31} = 6^{-1/2}(\delta_1 - \delta_2 + \delta_3 - \delta_4 + \delta_5 - \delta_6)$	b_{2g} ring deformation
32	$q_{32a} = 1/2(-\delta_1 + \delta_3 - \delta_4 + \delta_6)$	e_{2u} ring deformation
33	$q_{32b} = 12^{-1/2}(-\delta_1 + 2\delta_2 - \delta_3 - \delta_4 + 2\delta_5 - \delta_6)$	e_{2u} ring deformation

*See Fig. 1. γ_1 is the angle of the C-C' bond with the C₆C₁C₂ plane, etc. All waggings are positive if the X (X=C/H) atom moves toward the positive Z direction. δ_1 is the C₆C₁C₂C₃ dihedral angle, and so on cyclically; the signs of these torsional coordinates are defined according to E. B. WILSON JR, J. C. DECIUS and P. C. CROSS, *Molecular Vibrations*. McGraw-Hill, New York (1955). λ_1 and λ_2 are defined as $\pi - \alpha$ (CCN); their signs are such that the N atom moves in the positive X direction in λ_1 and in the positive Z direction in λ_2 .

Table 2. Structural results for benzonitrile*

Parameter	Experimental†			Theoretical	
	MW [9] r_s	ED [11] r_z	NMR [10] r_g	4-21‡	6-31G** [20b]
$r(C_1C_2)$	1.388	1.396	1.400	1.408	1.390
$r(C_2C_3)$	1.396	1.391		1.398	1.391
$r(C_3C_4)$	1.397	1.399		1.400	1.395
$r(C_1C_7)$	1.451	1.444	1.438	1.434	1.445
$r(C_7N_8)$	1.158	1.156	1.168	1.166	1.137
$r(C_2H_9)$	1.080	1.088	1.086	1.073	1.074
$r(C_3H_{10})$	1.082	1.087		1.089	1.076
$r(C_4H_{11})$	1.080	1.084		1.083	1.077
$\angle(C_6C_1C_2)$	121.8		121.9	120.8	120.4
$\angle(C_1C_2C_3)$	119.0		118.6	119.4	119.6
$\angle(C_2C_3C_4)$	120.1		120.5	119.7	120.1
$\angle(C_3C_4C_5)$	120.1		120.0	121.0	120.2
$\angle(C_1C_2H_9)$	120.6		—§	120.0	119.7
$\angle(C_2C_3H_{10})$	120.0		—§	120.0	119.8

*Distances (r) in Ångstroms, angles (\angle) in degrees. For numbering of atoms see Fig. 1.

†The following abbreviations are used: MW = microwave spectroscopy; ED = electron diffraction; NMR = liquid-crystal NMR spectroscopy, using ZLI 1167 liquid crystal solvent. The standard deviations of the MW parameters are less than 0.0006 Å and 0.05° [9b]. In the ED analysis (refinement A of Ref. [11]) the differences between the C–C and C–H bond length were ignored; the maximum total error reported in Ref. [11] is 0.005 Å and 1.4° for the distances and angles, respectively. The appropriate errors reported for the NMR results are 0.006 Å and 0.9° [10].

‡Present results, corrected theoretical geometry used as reference in the force constant calculations, see text. For comparison, the corresponding corrected theoretical values in benzene, taken from Ref. [3], are: $r(CC) = 1.395$ Å, $r(CH) = 1.077$ Å.

§The five C–H bonds were assumed to bisect the respective C–C–C angles.

In Table 2, various experimental and some of the theoretical results for the geometry of benzonitrile are compiled. The sixth column is the geometry used in this study for the evaluation of the force constants. This reference configuration was obtained in the following way. Using the same theoretical model as for the calculation of the force constants (Hartree–Fock model, 4-21 basis set) the theoretical equilibrium geometry was determined by complete optimization. Then empirical corrections were applied on the bond distances using the following offset values [1]: +0.010 Å for ring CC bonds, +0.005 Å for CH bonds, +0.003 Å for C–CN and +0.016 Å for the CN bond. After these corrections, the final geometry is considered a good estimate of the true equilibrium structure. Note that the trends within the ring CC and CH distances—these are not affected by the corrections—are the same as in the larger basis set results. Also, the (uncorrected) 4-21 bond angles agree excellently with the 6-31G** values.

As to the scale factors (used in the SQM scheme to correct for the deficiencies of the calculated force fields), they were taken over from benzene (Set II of Table 8 of Ref. [3]) and from HCN. We determined the latter factors from a comparison of theoretical [23] and experimental [24] force fields in the following way. In Ref. [24b], harmonized frequencies were used to calculate the best empirical force constants for HCN. In order to get a scale factor for CN stretching, we had to use the originally measured frequency, i.e. to

lower the empirical CN stretching force constant by about 3%, and compare the calculated 4-21 value of Ref. [23] with this. This gave a scale factor of 0.85 for the CN stretching motion. For the linear bending in HCN a scale factor of 0.65 was obtained, which was used for both the in-plane and out-of-plane linear bending motions of benzonitrile. For $CC'(C_1C_7)$ stretching and CC' wagging, the same scale factors were used as for the ring CC stretchings (0.911) and CH waggings (0.739), respectively.

RESULTS AND DISCUSSION

Force field

Our results for the complete harmonic in-plane and out-of-plane force fields of benzonitrile are compiled in Tables 3 and 4. To conserve space several columns which follow from symmetry have been omitted.

We start the discussion with the substituent group. The corrected theoretical CN bond length in benzonitrile (1.156 Å)—which should approximate the “ideal experimental” value as far as possible—is in close agreement with the best experimental results for HCN (1.153 Å [25]) and CH_3CN (1.157 Å [26]). As expected from the small lengthening of the bond, there is a slight decrease in the CN stretching force constant of benzonitrile as compared to HCN. As to the CC' bond, the bond length of 1.437 Å and the diagonal force constant of 5.39 aJ Å⁻² suggest a partial double bond character.

Table 3. In-plane SQM force field of benzonitrile*

No.†	1 (rCN)	2 (rCC)	3 (rCH)	4 (rCH)	5 (rCH)	8 (rCC)	9 (rCC)	10 (rCC)	14 (λ_1)	15 (β_{CC})	16 (β_{CH})	17 (β_{CH})	18 (β_{CH})	21 (ring)	22 (ring)	23 (ring)
1	17.574															
2	0.008	5.390														
3	0.005	0.011	5.217													
4	0.004	0.005	0.013	5.204												
5	0.001	0.001	0.003	0.013	5.188											
6	0.004	0.005	0.001	0.003	0.013											
7	0.005	0.011	0.002	0.001	0.003											
8	-0.077	0.382	0.063	-0.007	-0.023	6.474										
9	0.025	-0.019	0.068	0.077	-0.003	0.696	6.657									
10	-0.022	-0.055	-0.002	0.079	0.077	-0.423	0.729	6.558								
11	-0.022	-0.055	-0.022	-0.004	0.077	0.388	-0.414	0.719								
12	0.025	-0.019	-0.019	-0.024	-0.003	-0.396	0.413	-0.414								
13	-0.077	0.382	-0.008	-0.020	-0.023	0.697	-0.396	0.388								
14	0.0	0.0	0.000	0.001	0.0	0.017	0.004	-0.005	0.298							
15	0.0	0.0	-0.012	0.006	0.0	0.239	0.019	-0.026	0.080	0.703						
16	-0.003	0.014	-0.007	-0.005	0.006	-0.189	0.161	0.011	-0.001	0.004	0.515					
17	-0.003	-0.010	0.005	-0.002	-0.005	-0.009	-0.176	0.170	-0.003	-0.010	0.007	0.513				
18	0.0	0.0	-0.006	0.005	0.0	0.020	-0.013	-0.167	-0.000	-0.002	-0.010	0.008	0.512			
19	0.003	0.010	0.000	-0.006	0.005	-0.020	0.019	-0.009	-0.003	-0.010	-0.001	-0.010	0.008			
20	0.003	0.014	0.006	0.000	-0.006	0.006	-0.020	0.015	-0.001	0.004	-0.011	-0.001	-0.010			
21	-0.018	-0.238	0.095	-0.097	0.099	-0.021	-0.011	0.016	0.0	0.0	-0.002	-0.000	0.0	1.268		
22	-0.035	-0.256	0.047	0.050	-0.094	0.073	-0.242	0.124	0.0	0.0	-0.067	0.067	0.0	0.018	1.280	
23	0.0	0.0	-0.078	0.080	0.0	0.176	-0.007	-0.168	0.018	0.079	-0.034	-0.039	0.078	0.0	0.0	1.252

*Units are consistent with energy measured in aJ, stretching coordinates in Å and bending coordinates in radians. The values listed are *ab initio* 4-21 values scaled with empirical factors taken over from benzene and HCN (see text). Columns which follow from symmetry have been omitted.

†See Table 1 for the definition of internal coordinates.

Table 4. Out-of-plane SQM force field of benzonitrile*

No.	24 (λ_2)	25 ($\gamma_{CC'}$)	26 (γ_{CH})	27 (γ_{CH})	28 (γ_{CH})	31 (ring)	32 (ring)	33 (ring)
24	0.327							
25	-0.062	0.462						
26	0.011	-0.071	0.439					
27	-0.002	-0.000	-0.071	0.438				
28	0.003	-0.019	-0.004	-0.068	0.443			
29	-0.002	-0.000	-0.016	-0.001	-0.068			
30	0.011	-0.071	0.003	-0.016	-0.004			
31	0.027	-0.146	0.141	-0.144	0.140	0.365		
32	-0.026	0.146	-0.073	-0.071	0.143	-0.003	0.302	
33	0.0	0.0	-0.123	0.129	0.0	0.0	0.0	0.309

*See footnotes to Table 3.

It is then puzzling to observe that the force field of benzonitrile shows the CN group to be fairly well isolated: all the couplings between the CN stretching and the ring stretchings (q_8 - q_{10} in Table 3) or ring deformations (q_{21} - q_{23}) are small, well below 0.1. (The largest value is -0.077 aJ \AA^{-2} for the CN/CC^{ortho} coupling.) One may be inclined to draw from this the conclusion that the CN triple bond participates very little in the conjugation. However, it should be realized that second (and further) neighbour interactions are also surprisingly small in a typical conjugated system, as for hexatriene [27].

The fact, however, that even the nearest neighbour CN/CC' interaction is negligible in benzonitrile, which would thus support, at first sight, the above conclusion, deserves discussion. Experimentally, both the magnitude and the sign of this structurally important interaction remained uncertain. In their attempt to fit a force field to the experimental frequencies, KUWAE and MACHIDA [16] pointed out that trial values for CN/CC' ranging from -0.3 to $+0.9$ aJ \AA^{-2} gave essentially the same fit (with corresponding changes, of course, in the CN and CC' diagonal constants). Their conclusion was that a coupling constant near zero is the most probable choice because this gives the most reasonable diagonal constants (as expected from the effects of conjugation), but only further isotope data could solve the uncertainty. Our calculated value is 0.008 aJ \AA^{-2} (Table 3), supporting the above assumption. This very small, practically zero, interaction constant is, however, in striking contrast to the corresponding values in HCN or CH₃CN, which, calculated at the same theoretical level, are *negative*, -0.3 aJ \AA^{-2} [23] and -0.1 aJ \AA^{-2} [26], respectively. (There is some doubt about CH₃CN, since the thorough experimental work of DUNCAN *et al.* [26] gave a significant positive value of $+0.2$ aJ \AA^{-2} , but we tend to believe that the theoretical results are basically correct, implying a considerable negative interaction constant.) It is also known, however, that in conjugated systems the nearest neighbour stretch-stretch interaction is definitely a large *positive* constant (its value ranges from $+(0.3-0.4)$ aJ \AA^{-2} in butadiene [7] and hexatriene [27] to $+0.7$ aJ \AA^{-2} in benzene [3]).

Accepting the theoretical result for CH₃CN, the negligible CN/CC' coupling in benzonitrile can then be rationalized as follows: the N \equiv C'-C unit in benzonitrile is *not* a simple analogue of HCN or CH₃CN, since it is part of a larger conjugated system; thus the near-zero CN/CC' interaction is the result of the above two counteracting factors.

Another point worth mentioning about the substituent is the relation of the two CCN bendings, $\lambda_1 = q_{14}$ and $\lambda_2 = q_{24}$. The corresponding force constants do split significantly ($F_{14,14} = 0.298$ aJ rad^{-2} , $F_{24,24} = 0.327$ aJ rad^{-2}), but the effect is not as dramatic as one may expect on the basis that the two modes — which form a degenerate pair in HCN or CH₃CN — now describe an in-plane and an out-of-plane motion, respectively. This has its consequences on the assignment, see below.

After the substituent force field, we turn now to the effects of the substituent on the benzene ring. (Force constants of benzene are those obtained by the Set II scale factors of Ref. [3].)

Starting with changes *inside* the ring, the CC stretching force constants (see q_8 - q_{10} in Table 3) have changed by -1.6% , $+1.2\%$ and -0.3% in the *ortho*, *meta* and *para* positions, respectively, as compared to the benzene value of 6.578 aJ \AA^{-2} . Not surprisingly, these changes are smaller than in fluorobenzene, where the largest change was about 3% [4]. The trend in the CC force constants is what can be expected from the bond length variation: a shorter bond length (see Table 2) involves stronger force constant. (One may add, however, that, as was already noted in fluorobenzene [4], the changes in the force constants are smaller than expected from the simplest estimate based on the bond length change and the cubic force constant.)

Concerning the ring deformations, among the in-plane force constants (corresponding to coordinates q_{21} - q_{23}), the one related with the b_{1u} deformation, $F_{21,21}$, is perfectly stable (1.269 aJ \AA^{-2} in benzene [3], 1.263 aJ \AA^{-2} in fluorobenzene [4] and 1.268 aJ \AA^{-2} in benzonitrile). The other two diagonal constants, $F_{22,22}$ and $F_{23,23}$, can be considered as an interesting measure of the substituent effect, as their counterparts in benzene form the degenerate e_{2g} pair

here split by the substituent. The e_{2g} force constant in benzene was $1.247 \text{ aJ rad}^{-2}$ [3], while the two components in benzonitrile are $1.280 \text{ aJ rad}^{-2}$ and $1.252 \text{ aJ rad}^{-2}$ (Table 3). The observed splitting of 2.6% may again be compared to that of fluorobenzene [4]: there the perturbation was larger, causing a splitting of $\approx 6\%$. There seems to be, however, no simple relation between the electronic nature of the substituent and its effect on these diagonal constants. Concerning the out-of-plane deformations, all three force constants in benzonitrile (q_{31} – q_{33}) are slightly smaller than in benzene. There is again a small splitting, of about 2%, between $F_{32,32}$ and $F_{33,33}$.

Among the coupling force constants the structurally important ring CC/CC couplings show no significant change as compared to benzene. As was observed for all the investigated benzene derivatives (fluorobenzene [4], aniline [5], toluene [6]), they show the trend *ortho* > –*meta* \approx *para* [28].

While substituent effects in fluorobenzene were significant even *outside* the ring, they are hardly noticeable in benzonitrile. The CH stretching force constants are 5.22, 5.20 and 5.19 aJ \AA^{-2} in the *ortho*, *meta* and *para* positions, respectively, which means that all of them increased very slightly from the value of 5.18 aJ \AA^{-2} in benzene [3]. The changes are in line with the small bond length variations (see Table 2). Variation of the CH in-plane bendings (from 0.515 to $0.512 \text{ aJ rad}^{-2}$, Table 3) is hardly significant as compared to the benzene value of $0.514 \text{ aJ rad}^{-2}$. No significant changes are present for the out-of-plane CH waggings (γCH 's), which vary from 0.439 to $0.443 \text{ aJ rad}^{-2}$, as compared to $0.439 \text{ aJ rad}^{-2}$ in benzene [3].

In summary, substituent effects in benzonitrile are noticeable but significantly smaller than those in fluorobenzene. The excellent reproduction of the vibrational frequencies (see next section) gives confidence that even the fine details of the force field discussed above should have physical reality.

Frequencies and assignment

The theoretical frequencies obtained from the SQM force field of Tables 3 and 4 are compared with assignments of the experimental spectrum of $\text{C}_6\text{H}_5\text{CN}$ in Table 5. Similar results for the *p*-deutero and pentadeutero isotopomers are compiled in Table 6. The vibrational modes are numbered simply according to the order of frequencies obtained in this study. Characterization is based on the present theoretical results (using the M matrix criterion $M_{ip} = L_{ip}^{-1} L_{pi}$ [29], where i refers to a normal mode and p to an internal coordinate). The dominant internal coordinates are indicated by their serial numbers defined in Table 1.

It has been relatively easy to assign the vibrational spectra of mono-substituted benzenes ($\text{C}_6\text{H}_5\text{X}$) on a purely experimental basis since the overwhelming majority of frequencies are almost independent of the nature of the substituent X. Spectroscopic observa-

tions on a number of benzene derivatives could thus be combined to give reliable assignments. (The stability of most frequencies is, of course, well reproduced by our calculations [3–6].) To give a clearer overview, we indicated the X-sensitive frequencies by bold type in Table 5. The rest of the frequencies—altogether 25 fundamentals—agree with fluorobenzene [4] within about 20 cm^{-1} . Consequently, the only uncertainties in the early experimental assignments for benzonitrile had been those concerning the few X-sensitive modes.

In the a_1 species there are three X-sensitive modes: ν_1 , ν_2 and ν_6 in our notation (Table 5). The assignment of ν_1 was tentative in the first study by GREEN [13]; later, the i.r. band contour gave definite support to it [15]. The present calculated result clearly shows that the lowest a_1 fundamental is indeed around 460 cm^{-1} in benzonitrile. Concerning ν_2 , our theoretical results confirm that the Raman band at 762 cm^{-1} and the i.r. band at 756 cm^{-1} , rather than being counterparts of the same mode, represent two different normal modes, belonging to species $a_1(\nu_2)$ and $b_1(\nu_{28})$, in close coincidence. This was assumed from the beginning by GREEN [13], while BAK and NIELSEN [12] assigned, erroneously, a frequency at 1070 cm^{-1} as the a_1 fundamental. The third a_1 frequency, ν_6 , is calculated to be at 1190 cm^{-1} , and—although strongly mixed—may be considered in simplified terms as the CC' stretching frequency, but it should be kept in mind that the other two X-sensitive modes—even the lowest frequency a_1 mode—contain significant contributions from CC' stretching. In connection with ν_6 it should also be noticed that in its vicinity, at 1180 cm^{-1} , there is another normal mode: this band was first given as depolarized, so that its placement in species a_1 needed some explanation [13]. In the later study [15] this band was already listed, without comment, as polarized. It is reassuring that the calculation indeed predicts two close-lying frequencies in this region.

The only really difficult task in the experimental assignments was to identify the lowest five frequencies, appearing in species b_2 and b_1 . Basically, this concerns the in-plane and out-of-plane bending motions of the CCN group (two CC' and two CN bendings, q_{15} , q_{25} and q_{14} , q_{24} in our Table 1), from which a fifth mode (ν_{26}) cannot be separated. GREEN's original study [13], based on some mistaken old data, selected the following five frequencies as fundamentals: in-plane modes—325 and 263 (or 380) cm^{-1} ; out-of-plane modes—548, 380 (or 263) and 170 cm^{-1} . JAKOBSEN, in connection with his study on the d_5 -isotopomer [14], emphasized that the 325 and the 263 cm^{-1} bands could not be observed in his spectra; instead of these frequencies he suggested two near-coincidences around 550 and 170 cm^{-1} , respectively. With this he had found the correct fundamentals but their distribution between species b_1 and b_2 was still erroneous: apparently led by the assumption that the lowest frequencies should correspond to out-of-plane modes, he put both low frequencies (162 and 172 cm^{-1}) into species b_1 (then assigning the 381 cm^{-1} band as a b_2 mode).

Table 5. Fundamental vibrational frequencies of benzonitrile (in cm^{-1})

No.	Calculated (SQM)*			Experimental†		
	frequency	i.r. int. (km/mol)	Characterization	i.r.	Raman	JAKOBSEN [14]
<i>A</i> ₁ (in-plane)						
1	457	0.1	22 (ring); 2 (CC')	462 w	456	461
2	752	4.0	22 (ring); 2 (CC'); 8, 13 (CC)	—	762	769
3	997	0.1	21 (ring)	1002 m	1001	1001
4	1025	2.3	10, 11 (CC)	1029 s	1027	1027
5	1182	1.0	16, 20 (β CH)	1179 s	1180	1178
6	1190	0.6	17, 19 (β CH); 9, 12 (CC); 2 (CC')	—	1193	1192
7	1492	18.8	17, 19, 16, 20 (β CH)	1496 s	—	1492
8	1606	0.9	9, 12 (CC)	1602 s	1602	1599
9	2262	28.2	1 (CN)	2242 vs	2239	2232
10	3064	≈ 0.0	5, 4, 6 (CH)	3033 w	—	3042
11	3082	10.9	5, 3, 7 (CH)	3051 s	—	3062
12	3098	5.4	4, 6, 3, 7 (CH)	3081	3083	3080
<i>B</i> ₂ (in-plane)						
13	159	4.8	14 (λ_1); 15 (CC')	(163) s	163	381
14	536	≈ 0.0	14 (λ_1); 15 (CC')	—	544	551
15	623	0.1	23 (ring)	(615) w	621	629
16	1078	2.1	9, 12 (CC); 16, 20 (β CH)	(1070) s	—	1071
17	1171	0.9	18, 17, 19 (β CH)	(1160) m	—	1163
18	1269	6.3	8, 13, 9, 12 (CC)	(1280) m	—	1289
19	1331	0.8	16, 20 (β CH)	(1332) m	—	1337
20	1445	11.6	18, 17, 19 (β CH); 9, 12 (CC)	(1450) s	—	1448
21	1589	0.6	10, 11, 8, 13 (CC)	(1587) m	—	1584
22	3075	2.2	4, 6, 3, 7 (CH)	—	—	3027
23	3091	12.6	3, 7, 4, 6 (CH)	—	—	3072
<i>B</i> ₁ (out-of-plane)						
24	136	2.1	25 (γ CC'); 24 (λ_2); 32 (ring)	141 sh	(145)	162
25	366	0.8	32 (ring); 24 (λ_2)	372 m	—	172
26	537	16.1	24 (λ_2); 25 (γ CC')	542 vs	544	548
27	679	54.4	31 (ring)	688 vs	—	686
28	754	34.2	31 (ring); 28, 27, 29 (γ CH)	756 vs	—	758
29	928	3.1	26, 30, 28 (γ CH)	922 s	—	925
30	993	0.2	28, 27, 29 (γ CH); 31 (ring)	—	990	(989)
<i>A</i> ₂ (out-of-plane)						
31	397	0.0	33 (ring)	—	—	401
32	839	0.0	27, 29, 26, 30 (γ CH)	—	—	848
33	973	0.0	26, 30, 27, 29 (γ CH)	—	—	978

* Results of the present study, obtained from the force field given in Tables 3 and 4. For a clearer overview, the substituent-sensitive frequencies are given in bold type. In the approximate characterization of a normal mode, coordinates dominant according to the *M*-matrix [29] criterion are indicated by their serial number defined in Table 1.

† The normal frequencies of GREEN and HARRISON were measured in the gas phase; in blocks *B*₂ and *B*₁, parentheses indicate estimated centres. JAKOBSEN's fundamentals are gas phase values, when available. Qualitative i.r. intensities are indicated by the usual notation; they were measured in the liquid phase.

GREEN and HARRISON [15] accepted JAKOBSEN's fundamentals (with minor modifications in the exact frequency values, based on vapour measurements) but, induced by some preliminary empirical force field calculations [17, 30] and the band contour of the absorption at 380 cm^{-1} , interchanged the distribution between symmetry species for one pair: they put one of the frequencies around $150\text{--}170\text{ cm}^{-1}$ into the in-plane species *b*₂ and replaced it in species *b*₁ by the 380 cm^{-1} band. This final assignment is definitely supported by the present quantum chemical results. Specifically, both near-coincidences (at $\approx 540\text{ cm}^{-1}$ and at $\approx 160\text{ cm}^{-1}$, see Table 5) are clearly confirmed.

The somewhat unexpected result that there is a very low frequency mode not only in species *b*₁ but also in *b*₂ can be understood if it is realized that the out-of-plane and in-plane linear CCN bending force constants (q_{24} and q_{14} , respectively) have fairly close values, as discussed above. The complete assignment by GREEN and HARRISON [15], also accepted by KUWAE and MACHIDA [16], is thus confirmed in every respect by the present quantum chemical results.

Once the assignment for the parent molecule has been settled, the deuterated isotopomers need only a brief discussion.

For benzonitrile-*d*₅, we quote in Table 6 the assign-

Table 6. Fundamental vibrational frequencies of *p*-C₆H₄DCN and C₆D₅CN (in cm⁻¹)*

No.	<i>p</i> -C ₆ H ₄ DCN		C ₆ D ₅ CN		
	calc.	exp. [16]	calc.	experimental [14]	[16]
<i>A</i> ₁ (in-plane)					
1	453	455	448	452	449
2	749	755	709	710	707
3	980	983	836	840	837 [†]
4	1023	1024	869	871	871
5	1182	1178	954	966	957
6	1190	1190	1123	1138	1122
7	1485	1481	1369	1380	1370
8	1601	1593	1570	1568 [†]	1565
9	2262	2223	2262	2238	2220
10	2276	2282	2260	2295 [‡]	2271 [†]
11	3073	3070	2280	2295 [‡]	2271 [†]
12	3094	3070	2300	2295 [‡]	2308
<i>B</i> ₂ (in-plane)					
13	158	170	153	357	162
14	536	544 [†]	524	552	531
15	617	613 [†]	600	599	599
16	873	866 [†]	824	819	822 [†]
17	1112	1104	847	838	837 [†]
18	1264	1284	1041	1040	1037
19	1318	1304	1263	1285	1284
20	1404	1411	1315	1331	1326
21	1578	1585	1549	1568 [†]	1557
22	3075	3066	2272	2295 [‡]	2271 [†]
23	3091	3066	2290	2295 [‡]	2282
<i>B</i> ₁ (out-of-plane)					
24	132	156	130	160	150
25	354	367	341	170	351
26	534	544 [†]	478	488	491
27	600	613 [†]	543	572	558
28	730	729	632	643	640
29	863	866 [†]	772	770	768
30	966	962	841	(830)	822 [†]
<i>A</i> ₂ (out-of-plane)					
31	397	414	345	(382)	351
32	839	843 [§]	652	682	656
33	973	974 [§]	793	792	789

* See footnotes to Table 5.

[†] Frequency used twice, assuming coincidence.[‡] There was just one assigned band in the i.r. vapour spectrum.[§] The same frequency is assumed as the corresponding value of benzonitrile-*h*₅._{||} Estimation of an unperturbed frequency, the measured frequency is at 716 cm⁻¹.

ment given by JAKOBSEN [14] and by KUWAE and MACHIDA [16]. The most significant difference between them is the interchange of the frequencies at around 350 and 160 cm⁻¹, between species *b*₂ and *b*₁. This is the same problem as was discussed for benzonitrile-*h*₅ above, and is again confirmed by our calculations. It is also confirmed that the 552 cm⁻¹ band selected by JAKOBSEN for *v*₁₄ is slightly high (its strong intensity also suggests that it is an out-of-plane mode), and the band at 531 cm⁻¹ (weak shoulder) suggested in Ref. [16] is a better choice. For all the other slight revisions (*v*₂₇, *v*₃₁, *v*₃₂) the present results support KUWAE and MACHIDA [16].

As to the *p-d*-isotopomer, worth mentioning are the cases where one frequency was assigned to two normal modes, assuming accidental near-degeneracy. Beyond the frequency around 540 cm⁻¹, which was already present and discussed in the parent molecule, two new coincidences were assumed between species *b*₂ and *b*₁ by KUWAE and MACHIDA [16], those at 613 and 866 cm⁻¹ (Table 6). Both are confirmed by the calculations: the *b*₁ frequency calculated at 600 cm⁻¹ (*v*₂₇), which is new as compared to -*h*₅ and involves mainly the C-D wagging deformation, is fairly close to *v*₁₅ in *b*₂ (calculated value 617 cm⁻¹, mainly a ring deformation); also, the new *b*₂ frequency around 870 cm⁻¹

(ν_{16} , predominantly C–D deformation) is close to ν_{29} (with significant CD wagging contribution) in species b_1 (calculated values 873 and 863 cm^{-1} , respectively).

In conclusion, the calculated and experimental frequencies are in very satisfactory agreement for all three isotopomers, if the right assignments are selected. Omitting the C–H(C–D) stretching frequency region, which we have not considered in detail because it is strongly affected by anharmonicity and Fermi resonances, mean deviations are below 9 cm^{-1} in each case.

Infrared intensities

We list, as part of Table 5, the i.r. intensities of the normal modes of benzonitrile, calculated from the theoretical (unadjusted) dipole moment derivatives and the scaled theoretical force fields of Tables 3 and 4. To give a better overview we have compared the theoretical and measured spectra in Fig. 2.

Directly, quantum chemical calculations yield, not intensities but dipole moment derivatives with respect to internal coordinates. Determination of these derivatives from the observed i.r. spectrum is, however, rather difficult: for benzonitrile none of them is avail-

able. The only experimental data with which the present results can be compared are some dipole moment derivatives for acetonitrile [31], those connected with the CN and CC stretchings, and the CCN bending. Our calculated benzonitrile dipole gradients, compared in parentheses with the corresponding measured and 4-31G* theoretical values in acetonitrile [31], are as follows: CN = $-2.5(-0.9; -2.1)$ D/Å, CC = $-0.6(-0.4; -1.1)$ D/Å and CCN = $1.0(1.8; 2.0)$ D/rad. The signs indicate the following partial charges in terms of the bond moment hypothesis, valid for all three derivatives: $\delta^+ \text{C} - \delta^+ \text{C} - \delta^- \text{N}$.

As to the other dipole derivatives of benzonitrile, the gradients connected with the CH stretchings are (in parentheses the corresponding theoretical values of fluorobenzene [4]): *ortho* = $-0.21(-0.21)$, *meta* = $-0.40(-0.42)$, *para* = $-0.40(-0.45)$ D/Å. The benzonitrile values differ very little from those of fluorobenzene. The negative signs indicate that, similarly to fluorobenzene [4] or ethylene [32], and as was first suggested by SCHMID [33], the polarity of the C–H bonds is $\text{C}^+ \text{H}^-$ in stretchings, i.e. the direction of the dipole change is opposite to the hydrogen displacement (with a definition of the dipole moment vector showing from negative to positive charge). Derivatives for the in-plane CH bendings are (again in parentheses the respective values of fluorobenzene): *ortho* = $0.32(0.31)$, *meta* = $0.24(0.26)$, *para* = $0.26(0.23)$ D/rad. Derivatives for the out-of-plane CH bendings are: *ortho* = $0.76(0.92)$, *meta* = $0.70(0.69)$, *para* = $0.65(0.72)$ D/rad. The positive values show that, contrary to the stretchings, the polarity of the C–H bonds is $\text{C}^- \text{H}^+$ in both the in-plane and out-of-plane bendings. The stability of the calculated dipole derivatives is remarkable. It should be added to the above discussion that the dipole change in stretchings is not exactly along the CH bond, and in bendings not exactly perpendicular to it; for example, in the *ortho* position the deviations are about 4–5°.

To our best knowledge no accurate gas phase integrated intensities, A_k , are available for benzonitrile. For a few bands A_k values have been measured in CCl_4 solution [34, 35]. (It is well known that intensities measured in solutions tend to be somewhat higher than gas phase intensities [36], but this can be neglected without consequence in the following comparison of data.) For the 1606 and 1589 cm^{-1} bands (calc.) the summed-up calculated intensity of 1.56 km mol^{-1} agrees remarkably well with the measured value, 2.28 km mol^{-1} [34]. However, intensities of 18.8 and 11.6 km mol^{-1} are calculated for the 1492 cm^{-1} and 1445 cm^{-1} bands respectively, while the measured values [35] are 4.3 and 3.4 km mol^{-1} , respectively. Thus the agreement between the measured and calculated intensities, as usual, is far from being quantitative; the over-estimation of the intensities of these bands by the calculation is also apparent by inspection of Fig. 2.

Some other observations in Fig. 2 are worth mentioning. Calculations predict, in agreement with exper-

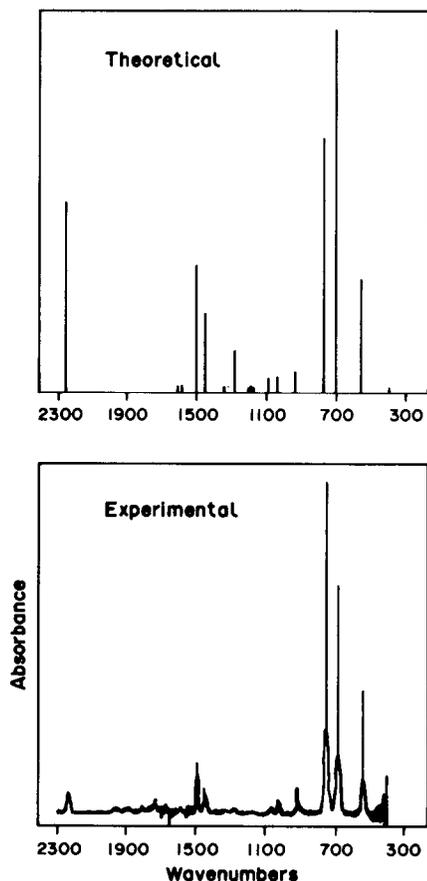


Fig. 2. Experimental and theoretical i.r. spectrum of benzonitrile.

iment, the high intensities of most of the out-of-plane bands. Although the present calculation correctly predicts the 679 and 754 cm^{-1} bands (calc.) to be the most intense, it reverses their relative intensities. Another notable feature of the theoretical spectrum is the significant over-estimation of the intensity of the CN stretching mode. Nevertheless, with all these limitations, the main features of the spectrum—relative intensities on a semiquantitative scale as normally used in spectroscopy—are reasonably reproduced by the present calculation.

CONCLUSION

The present study serves as another example of the great practical virtue of *ab initio* quantum chemical calculations for the interpretation of the vibrational spectra of ground state molecules. The scaled quantum mechanical (SQM) harmonic force field of benzonitrile, obtained from the *ab initio* 4-21 values by scaling them with empirical scale factors taken over from benzene and HCN, may be considered as the best harmonic force field available for this molecule. This SQM force field of benzonitrile shows all the expected features resulting from the introduction of the electron-withdrawing $-\text{CN}$ group into the benzene ring. The normal frequencies of the parent molecule, calculated from the SQM force field, support the results of the detailed experimental work of GREEN and HARRISON. Calculations are also in complete agreement with assignments for two deuterated isotopomers ($p\text{-D-C}_6\text{H}_4\text{CN}$ and $\text{C}_6\text{D}_5\text{CN}$) given by KUWAE and MACHIDA. Agreement between the measured and calculated i.r. intensities is semiquantitative.

Acknowledgements—This work was supported in part by the Hungarian Academy of Sciences and the U.S. National Science Foundation under grant No. INT-7819341, as part of a co-operative research program of the Eötvös L. University and the University of Texas. The quantum chemical calculations were performed during a visit by one of us (G.F.) to the Chemistry Department of the University of Texas at Austin, staying with Prof. JAMES E. BOGGS. Support from the Robert A. Welch Foundation is also acknowledged. We thank Dr SÁNDOR HOLLY for recording the i.r. spectrum of benzonitrile.

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