Normal coordinate analysis of deuterated benzonitriles

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Abstract : A zero-order normal coordinate analysis of both in-plane and out-of-plane vibrations was made for benzonitrile, benzonitrile-p-d, benzonitrile-o-d and benzonitrile-d₃ by transferring the force constants from our earlier work The observed and calculated frequencies agree with an average error of 10 4 cm⁻¹ On the basis of calculated potential energy distributions and eigen vectors, several assignments suggested by earlier workers have been revised

keywords   Normal coordinate analysis, potential energy distribution

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1. Introduction

We have been investigating the vibrational spectra of substituted benzenes by recording their IR and Raman spectra and subjecting them to normal coordinate analysis. We have already reported the vibrational spectra and results of normal coordinate analysis of monohalogenated benzonitriles [1]. The transferability of force constants obtained above have been demonstrated to some substituted benzonitriles [2–4]. In continuation of this work, now, we made a normal coordinate analysis of benzonitrile (BN), benzonitrile-p-d (BN-p-d), benzonitrile-m-d (BN-m-d), benzonitrile-o-d (BN-o-d) and benzonitrile-d₅ (BN-d₅), whose vibrational frequencies were reported by Varsanyi [5].

2. Zero-order calculations and results

The molecules under investigation possess different point group symmetries. The symmetry of BN, BN-p-d and BN-d₅ is C_{2v} point group and that of BN-m-d and BN-o-d is C_s. In the C_{2v} structure, the 33 fundamentals are distributed as $12a_1 + 3a_2 + 7b_1 + 11b_2$, whereas in the C_s structure the 33 fundamentals fall into 23 vibrations of a' species and 10 vibrations of a'' species. All the modes belonging to

a_1, b_1 and b_2 species of the C_{2v} point group are allowed in IR and Raman spectra, whereas the a_2 modes are allowed in the Raman but forbidden in the IR spectra. Similarly, all the modes belonging to a' and a'' species of the C_s point group are active both in IR and Raman spectra.

A zero-order vibrational analysis of both in-plane and out-of-plane vibrations was made for BN, BN-p-d, BN-m-d, BN-o-d and BN-d₅ using the molecular parameters, internal coordinates and symmetry coordinates employed in our earlier work [1]. All the zero-order force constants were transferred from monohalogenated benzonitriles [1]. The average error between the observed and calculated frequencies is 12.7, 6.3, 9, 9 and 13 cm⁻¹ for BN, BN-p-d, BN-m-d and BN-o-d and BN-d₅, respectively. These should be considered as good since the force constants are not refined in the zero-order calculation. This demonstrates the transferability of force constants presented in reference 1. The observed and calculated frequencies, potential energy distributions (PED) and vibrational assignments of these molecules are summarised in Table 1. Potential energy distributions below 10% are not shown.

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Table 1. Observed and calculated frequencies (in cm⁻¹) and vibrational assignments of benzonitrile and its deuterated species.

Mode	BN		BN-p-d		BN-m-d		BN-o-d		BN-d₅		Vibrational assignments[a]
	Obs. Freq	Cal Freq	Obs. Freq	Cal. Freq.	Obs Freq	Cal. Freq.	Obs. Freq	Cal. Freq.	Obs.	Cal.	
ν(CH/CD)2	3027	3038	–	3043	.	3047	–	3051	–	2258	102(2)
ν(CH/CD)7a	3042	3078	2285	2285	–	3075	–	3086	2283	2283	100(7a)
ν(CH/CD)7b	3039	3071	–	3071	2270	2285	–	3077	-	2275	100(7b)
ν(C–CN)13	1192	1193	1190	1193	1196	1187	1192	1187	1123	1133	34(13)+21(18a)+21(12)+18(
ν(CH/CD)20a	3071	3100	3080	3093	3095	3093	2280	2285	2286	2300	98(20a)
ν(CH/CD)20b	3080	3115	.	3115	–	3107	3100	3109	2305	2311	97(20b)
ν(CC)1	769	772	755	766	757	757	756	767	718	729	41(6a)+20(1)+19(13)+10(18
ν(CC)8a	1599	1600	1595	1597	1592	1597	1593	1592	1568	1570	76(8a)+25(9a)
ν(CC)8b	1584	1574	1564	1567	1573	1568	1573	1569	–	1542	83(8b)+21(9b)
ν(CC)14	1289	1272	1284	1263	1277	1260	1271	1271	1289	1258	75(14)+25(9b)
ν(CC)19a	1492	1487	1482	1478	1474	1470	1472	1472	1378	1384	58(18a)+42(19a)
ν(CC)19b	1448	1443	1408	1412	1421	1422	1442	1432	1330	1325	57(18b)+41(19b)
β(CCC)6a	461	459	456	456	449	459	457	457	452	451	42(6a)+26(13)
β(CCC)6b	629	639	–	638	617	632	–	633	599	616	72(6b)+17(9b)
β(CCC)12	1001	995	980	976	999	997	985	982	959	950	60(1)+30(12)
β(CH/CD)3	1337	1330	1305	1310	1328	1317	1297	1280	1040	1038	93(3)
β(CH/CD)9a	1178	1164	1178	1163	840	859	1163	1170	838	837	80(9a)+20(8a)
β(CH/CD)9b	1163	1172	862	852	1174	1168	1115	1111	845	843	68(9b)+32(14)
β(C–CN)15	172	187	–	186	-	186	–	185	170	180	48 β(C=N) + 48(15)
β(CH/CD)18a	1027	1020	1023	1019	1037	1035	1042	1032	830	818	41(19a)+29(18a)+25(12)
β(CH/CD)18b	1071	1065	1105	1116	1102	1079	863	851	823	808	45(19b)+43(18b)
ν(C≡N)	2232	2232	2230	2232	2230	2232	2230	2232	2226	2232	86ν(C≡N)+14(13)
β(C≡N)	551	539	–	537	–	537	–	535	552	528	50β(C≡N)+39(15)
π(CH/CD)5	987	982	970	964	–	975	958	981	871	866	86(5)
π(CH/CD)10a	848	829	840	837	670	653	627	616	695	645	99(10a)
π(C–CN)10b	162	149	–	146	–	149	–	148	160	142	65(10b)+23(16b)+15ω(C≡N)
π(CH/CD)11	758	740	613	620	810	797	778	775	572	531	103(11)
π(CH/CD)17a	978	964	–	829	913	924	–	862	780	793	98(17a)
π(CH/CD)17b	925	889	–	953	876	888	906	945	769	734	103(17b)
τ(CCCC)4	686	694	727	719	688	695	746	732	638	621	76(4)+14(5)
τ(CCCC)16a	401	411	–	411	–	383	–	381	357	354	110(16a)
τ(CCCC)16b	381	393	–	378	–	399	–	400	382	363	75(16b)+28ω(C≡N)
ω(C≡N)	548	558	545	543	529	538	540	558	488	507	48ω(C≡N)+35(4)+25(10b)

–, not observe

[a]Results in this column correspond to BN. The number before the parentheses is % PED and that inside the parentheses is mode notation as given by Wilson [6]. Results of other molecules can be obtained from the authors.

3. Vibrational assignments

The vibrational assignments presented in Table 1 are self-explanatory. Hence the discussion is confined to certain important modes only. The following points of disagreement with Varsanyi [5] are note-worthy.

1. In BN, the frequencies now attributed to modes 2, 20a, 7b, 20b, 14, 3, 15, 10b, 16b and $\omega(C\equiv N)$ were thought to be 7b, 2, 20b, 20a, 3, 14, 10b, $\gamma(C\equiv N)$ 15 and 16b, respectively, by Varsanyi [5].

2. In BN-p-d, the bands now ascribed to the vibrations 14, 3, 9b and $\omega(C\equiv N)$ were considered to be arising from 3, 14, 17b and 16b, respectively, by Varsanyi [5].

3. In BN-m-d, the bands now identified as 7b, 14, 3, 9a, 11, 17a, 17b, 10a and $\omega(C\equiv N)$ were expected to be 7a, 3, 14, 10a, 17b, 5, 9a, 11 and 16b, respectively, by Varsanyi [5].

4. In BN-o-d, the fundamentals now attributed to 20b, 7a, 14, 3, 18b, 9b, 11, 17b, 10a and $\omega(C\equiv N)$ were expected to be 2, 20a, 3, 14, 9b, 18b, 17b, 17a, 11 and 16b, respectively, by Varsanyi [5].

5. In BN-d$_5$, the observed frequencies now identified as 7a, 20a, 9a, 18a, 20b, 9b, 15, 5, 10b, 16b, $\omega(C\equiv N)$ and 16a were expected to be 20b, 2, 9b, 5, 20a, 18a, 10b, 9a, $\gamma(C\equiv N)$, 16a, 16b and 15, respectively, by Varsanyi [5].

3.1. C-C Stretching vibrations :

Vibrations 8a and 8b are expected around 1600 cm^{-1} in the molecules investigated. The higher frequency has a large amount of C–C stretching character ranging from 76 to 86% in the five molecules studied. It mixes with C–H in-plane bending modes. In the lower frequency C–C stretching character ranges from 83 to 94%. This also mixes with C–H in-plane bending modes. The present calculations establish that mode 8a is greater in frequency than 8b.

Modes 19a and 19b are expected in the range 1400–1500 cm^{-1}. The higher frequency is a C–C stretching mode to the extent of 41–60%, whereas the lower frequency is a C–C stretching vibration to the extent of 38–63%. They mix with C–H in-plane bending modes. Present computations establish that the frequency of 19a is greater than that of 19b.

Mode 14, which is known as the kekule mode can be assigned to the fundamentals near 1289, 1284, 1277, 1271 and 1289 cm^{-1} in BN, BN-p-d, BN-m-d, BN-o-d and BN-d$_5$, respectively, on the basis of calculations.

3.2. Ring vibrations :

The four ring vibrations 1, 6a, 6b and 12 were identified and assigned from careful consideration of their characteristics eigen vector distributions.

Let us consider the modes 6a and 6b corresponding to the benzene band at 606 cm^{-1}. According to normal coordinate treatment the bands at 461, 456, 449, 457 and 452 cm^{-1} are attributed to mode 6a, whereas those at 629, 638 (calculated value), 617, 633 (calculated value) and 599 cm^{-1} are ascribed to the vibration 6b in BN, BN-p-d, BN-m-d, BN-o-d and BN-d$_5$, respectively.

The mode 12 comes near 1010 cm^{-1} in benzene. According to normal coordinate analysis it should appear around 1001, 980, 999, 985 and 959 cm^{-1} in BN, BN-p-d, BN-m-d, BN-o-d, BN-d$_5$, respectively. A large contribution of PED from mode 1 to this vibration is note-worthy.

In benzene mode 1 is a pure C–C stretching vibration as it is totally symmetric and separated from C–H stretching vibrations by a large extent. As these restrictions are removed in substituted benzenes, mode 1 mixes with several other vibrations. On the basis of the calculations mode 1 is ascribed to the fundamental at 769, 755, 757, 756 and 718 cm^{-1} in BN, BN-p-d, BN-m-d, BN-o-d and BN-d$_5$, respectively.

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