Force fields for nitriles

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Abstract—A valence force field for nitriles based on the force field obtained for hydrocarbons is found to give very good agreement with the observed bands for several mono- and di-nitrile molecules. The average deviation between observed and calculated frequencies for the 238 assigned frequencies is 0.98%. This is a significant improvement over the results obtained previously with a Urey–Bradley force field.

Introduction

A number of studies have been devoted to the analysis of the spectra of small molecules containing the C≡N group. These have included experimental studies and band assignments on molecules with one C≡N group, such as acetonitriles [1–7] and propionitrile [8], as well as on molecules with two C≡N groups, such as malononitrile [9, 10], succinonitrile [11–13], and glutaronitrile [14]. Some of these studies [5, 6, 8–11, 13] have included, and others [15, 16] have been devoted to, normal coordinate calculations of the vibrational frequencies. In the more recent work a Urey–Bradley force field was the basis for this analysis.

Recent studies of hydrocarbons have led to the development of a valence force field [17, 18] which appears to provide a more complete representation of the internal

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potential energy than does the Urey–Bradley force field. This valence force field has been transferred satisfactorily to other small molecules, such as those containing chlorine atoms [19]. We report here its extension to molecules with C≡N groups, and compare the results with those obtained from the Urey–Bradley force field.

Table 1. Nitrile molecules for which normal coordinate calculations were done

Molecule	Formula	Molecular symmetry	Number of fundamentals		Average deviation between observed and calculated frequencies (%)
Acetonitrile	CH_3CN	C_{3v}	$4(A) + 4(E) + 4(E')$	$= 12$	0.28
Acetonitrile-d_3	CD_3CN	C_{3v}	$4(A) + 4(E) + 4(E')$	$= 12$	0.73
Propionitrile	CH_3CH_2CN	C_s	$13(A') + 8(A'')$	$= 21$	0.71
Isobutyronitrile	$CH_3CH(CN)CH_3$	C_s	$17(A') + 13(A'')$	$= 30$	0.56
Malononitrile	$NCCH_2CN$	C_{2v}	$6(A_1) + 2(A_2) + 4(B_1) + 3(B_2)$	$= 15$	0.96
Malononitrile-d_1	$NCCHDCN$	C_s	$9(A') + 6(A'')$	$= 15$	1.25
Malononitrile-d_2	$NCCD_2CN$	C_{2v}	$6(A_1) + 2(A_2) + 4(B_1) + 3(B_2)$	$= 15$	1.09
Succinitrile (trans)	$NCCH_2CH_2CN$ (T)	C_{2h}	$8(A_g) + 5(A_u) + 4(B_g) + 7(B_u)$	$= 24$	1.30
Succinitrile (gauche)	$NCCH_2CH_2CN$ (G)	C_2	$13(A) + 11(B)$	$= 24$	1.08
Glutaronitrile (trans–trans)	$NCCH_2CH_2CH_2CN$ (TT)	C_{2v}	$11(A_1) + 6(A_2) + 9(B_1) + 7(B_2)$	$= 33$	1.13
Glutaronitrile (trans–gauche)	$NCCH_2CH_2CH_2CN$ (TG)	C_2	$17(A) + 16(B)$	$= 33$	1.01
Glutaronitrile (gauche–gauche)	$NCCH_2CH_2CH_2CN$ (GG)	C_1	$33(A)$	$= 33$	1.21

Our force field has provided a useful basis for the analysis of the vibrational spectrum of polyacrylonitrile [20].

CALCULATIONS AND RESULTS

Normal coordinate calculations were done on the 12 molecules listed in Table 1. The Wilson GF matrix method [21] was used, and the torsional coordinate for rotation about the C—C bond was included according to the method of MIYAZAWA and FUKUSHIMA [22]. The computations were performed on an IBM 7090 computer. The molecular constants used in the calculation were as follows: $r(C—C) = 1.54$ Å, $r(C—N) = 1.17$ Å, $r(C—CN) = 1.47$ Å, $r(C—H) = 1.10$ Å, $\measuredangle$ C—C—N $= 180°$, all other angles tetrahedral (standard values of the masses were used).

The procedure which was used was to start with the valence force field constants which had been obtained for the hydrocarbons [17, 18]. To these were added appropriate force constants associated with the C≡N group(s). The values of the latter were determined by seeking a best fit to the observed frequencies, in one case (acetonitrile) by means of a least squares refinement procedure and in the other cases by means of adjustments based on examination of the Jacobian. In some instances

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Table 2. Valence force field constants for nitrile molecules

Force constant	Hydro-carbons[17]	Aceto-nitriles	Propio-nitrile	Isobutyro-nitrile	Malono-nitriles	Succino-nitriles	Glutaro-nitriles
K_r	4.699	4.881	4.860	4.880			
K_d	4.554		4.677		4.737	4.760	4.690
K_s	4.588			4.588			
K_R	4.387		4.387	4.387		4.387	4.387
$K_{R'}$	4.337						
$K_{R''}$	4.534						
K_{sN}		5.260	5.260	5.260	5.200	5.200	5.200
K_{CN}		17.730	17.450	17.270	17.850	17.550	17.410
H_α	0.540	0.550	0.540	0.540			
H_β	0.645	0.695	0.645	0.695			
H_δ	0.550		0.550		0.503	0.540	0.540
H_γ	0.656		0.656			0.656	0.656
$H_{\gamma N}$			0.680		0.680	0.680	0.680
H_ζ	0.657			0.657			
H_ω	1.130		1.130		1.130	1.130	1.130
H_φ	1.084			1.084			
H_Δ	1.086						
H_τ	(0.024)		0.102	0.100		0.102	0.102
H_ϕ		0.304	0.319	0.304	0.319	0.329	0.329
F_r	0.043	0.068	0.078	0.068			
F_d	0.006		0.065		0.055	0.055	0.055
F_R	0.101		0.101	0.101	0.101	0.101	0.101
$F_{R\gamma}$	0.328	0.328	0.328	0.328	0.328	0.328	0.328
$F_{R\gamma}'$	0.079		0.079	0.079	0.079	0.079	0.079
$F_{R\omega}$	0.417		0.417	0.417	0.417	0.417	0.417
F_β	−0.012	−0.012	−0.012	−0.012			
F_γ	−0.021		−0.021		−0.021	−0.021	−0.021
F_γ'	0.012		0.013	0.013	0.013	0.012	0.012
F_φ	−0.041			−0.041			
$F_{\gamma\omega}$	−0.031		−0.031	−0.031	−0.031	−0.031	−0.031
f_γ^t	0.127		0.127	0.127		0.127	0.127
f_γ^g	−0.005		−0.005	−0.005		−0.005	−0.005
$f_\gamma'^t$	0.002		0.002			0.002	0.002
$f_\gamma'^g$	0.009		0.009			0.009	0.009
$f_\gamma''^t$	−0.014					−0.014	−0.014
$f_\gamma''^g$	−0.025					−0.025	−0.025
$f_{\gamma\omega}^t$	0.049		0.049	0.049		0.049	0.049
$f_{\gamma\omega}^g$	−0.052		−0.052	−0.052		−0.052	−0.052
f_ω^t	−0.011					−0.011	−0.011
f_ω^g	0.011					0.011	0.011
Number of force constants	37	9	29	24	15	28	28

slight modifications in the diagonal valence force field constants were necessary in order to obtain optimum agreement between observed and calculated frequencies. The final sets of force constants are given in Table 2. The notation follows that previously used [17, 18], except for K_{sN}, K_{CN}, H_ϕ, and $H_{\gamma N}$ which represent force constants for C—CN stretching, C≡N stretching, C—C≡N bending, and C—C—H bending in the —CH$_2$—CN group, respectively.

The calculated frequencies are compared with observed frequencies in Tables 3–8. The potential energy distributions in the normal modes are also given, only contributions greater than 15% being listed.

DISCUSSION

1. *Acetonitrile*

Normal coordinate calculations on acetonitrile have been made using a valence force field [5], a Urey–Bradley force field [6], and an orbital valency force field [16].

Table 3. Observed and calculated frequencies of acetonitriles

	$\bar{\nu}_{\mathrm{obs}}$ [6]	$\bar{\nu}_{\mathrm{calc}}$ [6]	$\bar{\nu}_{\mathrm{obs}}$ [16]	$\bar{\nu}_{\mathrm{calc}}$ [16]	$\bar{\nu}_{\mathrm{calc}}$ [5]	$\bar{\nu}_{\mathrm{calc}}$(VFF)	
CH$_3$CN							
ν_1	2954	3003	2954.2	2947.6	2980	2953	ν_s(CH$_3$)(99)
ν_2	2267	2276	2266.7	2267.3	2231	2268	ν(CN)(89)
ν_3	1385	1361	1389	1388.5	1396	1387	δ_s(CH$_3$)(93)
ν_4	920	916	920.3	921.7	920	920	ν(CCN)(88)
ν_5	3009	2961	3009.1	3035.0	3009	3009	ν_a(CH$_3$)(99)
ν_6	1453	1470	1454.2	1451.6	1454	1452	δ_a(CH$_3$)(91)
ν_7	1041	1041	1040.8	1041.6	1041	1048	r(CH$_3$)(89)
ν_8	362	359	361.0	361.6	361	357	δ(CCN)(98$_1$)
ζ_5	0.062	0.065	0.073	0.14		0.15	
ζ_6	−0.384	−0.363	−0.39	−0.41		−0.37	
ζ_7	0.422	0.423	0.422	0.45		0.33	
ζ_8	0.945	0.913	0.93	0.91		0.92	
CD$_3$CN							
ν_1			2125.6	2114.2		2121	ν_s(CD$_3$)(95)
ν_2			2277.6	2277.5		2273	ν(CN)(84)
ν_3			1110	1110.5		1103	δ_s(CD$_3$)(67), ν(CCN)(30)
ν_4			831.3	829.3		833	ν(CCN)(66), δ_s(CD$_3$)(24)
ν_5			2256.6	2247.1		2244	ν_a(CD$_3$)(98)
ν_6			1046.4	1049.1		1042	δ_a(CD$_3$)(95)
ν_7			846.4	846.2		826	r(CD$_3$)(89)
ν_8			331.2	330.2		335	δ(CCN)(94)
ζ_5			0.14	0.25		0.27	
ζ_6			−0.40	−0.46		−0.43	
ζ_7			0.45	0.47		0.37	
ζ_8			0.86	0.83		0.85	

$\nu_\mathrm{s,a}$: (symmetric, antisymmetric) stretching; $\delta_\mathrm{s,a}$: (symmetric, antisymmetric) bending; r: rocking.

Table 4. Observed and calculated frequencies of propionitrile

$\bar{\nu}_{\mathrm{obs}}$ [8]			
Infrared	Raman	$\bar{\nu}_{\mathrm{calc}}$ (VFF)	
2999 vs		3001 A'	ν_a(CH$_3$)(99)
	3001 s dp	3001 A''	ν_a(CH$_3$)(99)
2958 s	2949 vs p	2952 A'	ν_s(CH$_3$)(99)
2958 s		2947 A''	ν_a(CH$_2$)(99)
2900 s	2898 s p	2912 A'	ν_s(CH$_2$)(99)
2252 s	2251 vs p	2252 A'	ν(CN)(88)
1461 vs		1457 A'	δ_a(CH$_3$)(58), δ(CH$_2$)(33)
	1466 m dp	1451 A''	δ_a(CH$_3$)(92)
1431 s	1436 m p	1445 A'	δ(CH$_2$)(66), δ_a(CH$_3$)(30)
1386 m	1374 vw p	1364 A'	δ_s(CH$_3$)(83)
1316 m	1322 w p	1308 A'	w(CH$_2$)(65)
1260 vw	1270 vw dp	1261 A''	t(CH$_2$)(83)
1090 vvw		1092 A''	r_a(CH$_3$)(38), r(CH$_2$)(34)
1075 s	1078 m p	1061 A'	r_s(CH$_3$)(48), ν(CC)(16)
1004 m	1010 s p	1025 A'	ν(CC)(66), ν(CCN)(19)
836 w	838 s p	831 A'	ν(CCN)(50), r_s(CH$_3$)(23)
784 s	784 vw dp	776 A''	r(CH$_2$)(51), r_a(CH$_3$)(39)
545 m	548 m p	528 A'	δ(CCC)(52), δ_i(CCN)(34)
	378 m dp	375 A''	δ_o(CCN)(83)
(236?)		236 A'	δ_i(CCN)(63), δ(CCC)(34)
	226 m dp	226 A''	τ(81)

vs: very strong; s: strong; m: medium; w: weak; p: polarized; dp: depolarized. Symbols for internal coordinates same as in Table 3, plus: w: wagging; t: twisting; $\delta_{i,o}$: (in-plane, out-of-plane) bending; τ: torsion.

Table 5. Observed and calculated frequencies of isobutyronitrile

$\bar{\nu}_{obs}$	$\bar{\nu}_{calc}$(VFF)	
2990	3012 A'	$\nu_a(CH_3)(99)$
	3011 A'	$\nu_a(CH_3)(99)$
	3011 A''	$\nu_a(CH_3)(99)$
	3009 A''	$\nu_a(CH_3)(99)$
2943	2952 A'	$\nu_s(CH_3)(99)$
	2952 A''	$\nu_s(CH_3)(99)$
2882	2904 A'	$\nu(CH)(99)$
2243	2243 A'	$\nu(CN)(88)$
1477	1465 A'	$\delta_a(CH_3)(65)$
1463	1459 A''	$\delta_a(CH_3)(82)$
1456	1456 A'	$\delta_a(CH_3)(72)$
1452	1453 A''	$\delta_a(CH_3)(87)$
1391	1394 A'	$\delta_s(CH_3)(94)$
1372	1393 A''	$\delta_s(CH_3)(93)$
1324	1328 A'	$\delta(CH)(47)$
1320	1318 A''	$\delta(CH)(62)$
1172	1182 A'	$r(CH_3)(48)$
1118	1127 A''	$\nu_a(CC)(45), r(CH_3)(31)$
1108	1111 A'	$r(CH_3)(41), \delta(CH)(37)$
970	979 A''	$r(CH_3)(54), \nu_a(CC)(37)$
936	945 A''	$r(CH_3)(69), \delta(CH)(20)$
916	928 A'	$\nu_s(CC)(38), r(CH_3)(34), \nu(CCN)(22)$
755	775 A'	$\delta(CCN)(37), \nu_s(CC)(34)$
547	542 A''	$\delta(CCCN)(57), \delta(CCN)(34)$
510	512 A'	$\delta(CCCN)(49), \delta(CCN)(30)$
362	379 A'	$\delta(CCC)(70)$
280	270 A'	$\delta(CCN)(42), \tau_a(28), \delta(CCCN)(21)$
220	233 A''	$\tau_s(95)$
	218 A'	$\tau_a(69), \delta(CCN)(23)$
	207 A''	$\delta(CCN)(59), \delta(CCCN)(31)$

The results of these calculations are given in Table 3, together with the frequencies calculated from our valence force field for acetonitrile and acetonitrile-d_3. The average deviation between observed and calculated frequencies, viz., 0.28%, (cf. Table 1), compares favorably with that obtained from the orbital valency force field [16], viz., 0.22%, is better than that from the earlier valence force field [5], which gives 0.38%, and is much better than what is obtained from the Urey–Bradley force field, viz., 0.98%. Using our force constants we have also computed Coriolis coupling constants for acetonitrile and acetonitrile-d_3, using the C-matrix method of MEAL and POLO [23]. These are listed in Table 3, and are in reasonable agreement with the observed values.

2. *Propionitrile*

The vibrational spectrum of propionitrile has been studied both in the infrared and Raman [8]. The observed frequencies, as well as the polarizations of the Raman bands are listed in Table 4 together with our calculated frequencies. The assignments suggested in Table 4 are in good agreement with the symmetry species of the bands determined from the polarizations of the Raman lines. In those cases (2999 and 3001, 1461 and 1466) where assignments of apparently single bands are made to two predicted modes, such assignments are indicated by the contour of the vapor phase bands [8]. The band at 1090 is weakly indicated in the spectrum; and the band at 236 cm^{-1} is hypothesized from the presence in the infrared spectrum of a

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Table 6. Observed and calculated frequencies of malononitriles

$\tilde{\nu}_{obs}$ [10]		$\tilde{\nu}_{calc}$ [10]			$\tilde{\nu}_{calc}$ (VFF)		
Infrared	Raman						
NC CH$_2$ CN							
2968 vs	2960(1)	2952	B_2	$\nu_a(CH_2)$	2968	B_2	$\nu_a(CH_2)(100)$
2935 vs	2929(5)	2941	A_1	$\nu_s(CH_2)$	2928	A_1	$\nu_s(CH_2)(99)$
2275 ms		2269	A_1	$\nu_s(CN)$	2277	B_1	$\nu_a(CN)(88)$
	2263(7)	2269	B_1	$\nu_a(CN)$	2270	A_1	$\nu_s(CN)(89)$
1395 vs	1386(4)	1381	A_1	$\delta(CH_2)$	1398	A_1	$\delta(CH_2)(98)$
1318 vw	1310(2)	1347	B_1	$w(CH_2)$	1320	B_1	$w(CH_2)(79)$
1220 vw	1214(3)	1186	A_2	$t(CH_2)$	1229	A_2	$t(CH_2)(100)$
982 s	975(1)	950	B_1	$\nu_a(CCN)$	976	B_1	$\nu_a(CCN)(76)$
933 m		929	B_2	$r(CH_2)$	936	B_2	$r(CH_2)(93)$
890 s	892(5)	928	A_1	$\nu_s(CCN)$	904	A_1	$\nu_s(CCN)(62), \delta(CCC)(25)$
582 m	574(3)	553	A_1	$\delta(CCC)$	570	A_1	$\delta(CCC)(43), \delta_i(CCN)(30), \nu_s(CCN)(24)$
367 s		369	B_1	$\delta(CCN)$	366	B_1	$\delta_i(CCN)(99)$
	367(10)	364	A_2	$\delta(CCN)$	360	A_2	$\delta_o(CCN)(100)$
337 s		356	B_2	$\delta(CCN)$	351	B_2	$\delta_o(CCN)(94)$
	167(10)	165	A_1	$\delta(CCN)$	164	A_1	$\delta_i(CCN)(66), \delta(CCC)(33)$
NC CHD CN							
2948 s		2946	A'	$\nu(CH)$	2948	A'	$\nu(CH)(99)$
2272 ms		2271	A'	$\nu(CN)$	2277	A'	$\nu(CN)(88)$
2272 ms		2268	A''	$\nu(CN)$	2275	A''	$\nu(CN)(84)$
2194 ms		2150	A'	$\nu(CD)$	2171	A'	$\nu(CD)(93)$
1282 mw		1294	A''	$\delta(CH)$	1291	A''	$\delta(CH)(75)$
1247 s		1245	A'	$\delta(CH)$	1246	A'	$\delta(CH)(70)$
1063 ms		1023	A''	$\nu(CCN)$	1070	A''	$\nu_a(CCN)(45), \delta(CD)(34)$
937 m		937	A'	$\nu(CCN)$	903	A'	$\nu_s(CCN)(55), \delta(CCC)(19)$
856 ms		837	A''	$\delta(CD)$	838	A''	$\delta(CD)(67), \nu_a(CCN)(27)$
816 m		807	A'	$\delta(CD)$	815	A'	$\delta(CD)(51)$
582 ms		548	A'	$\delta(CCC)$	569	A'	$\delta(CCC)(38), \delta_i(CCN)(30), \nu_s(CCN)(24)$
374 w		367	A''	$\delta(CCN)$	365	A''	$\delta_i(CCN)(90)$
357 s		350	A''	$\delta(CCN)$	355	A''	$\delta_o(CCN)(90)$
320 m		332	A'	$\delta(CCN)$	331	A'	$\delta_o(CCN)(90)$
		161	A'	$\delta(CCN)$	164	A'	$\delta_i(CCN)(67), \delta(CCC)(29)$
NC CD$_2$ CN							
2272 m	2273(8)	2282	A_1	$\nu_s(CN)$	2277	A_1	$\nu_s(CN)(84)$
2272 m	2273(8)	2266	B_1	$\nu_a(CN)$	2277	B_1	$\nu_a(CN)(88)$
2230 ms	2228(2)	2187	B_2	$\nu_a(CD_2)$	2213	B_2	$\nu_a(CD_2)(98)$
2146 ms	2146(4)	2124	A_1	$\nu_s(CD_2)$	2132	A_1	$\nu_s(CD_2)(93)$
1165 m	1162(0.5)	1141	B_1	$w(CD_2)$	1170	B_1	$\nu_a(CCN)(51), w(CD_2)(42)$
1037 s	1033(3)	1046	A_1	$\delta(CD_2)$	1026	A_1	$\delta(CD_2)(83)$
892 vw	892(1)	862	A_2	$t(CD_2)$	893	A_2	$t(CD_2)(98)$
858 m	854(5)	841	A_1	$\nu_s(CCN)$	862	A_1	$\nu_s(CCN)(57), \delta(CCC)(23)$
829 ms	828(1)	824	B_1	$\nu_a(CCN)$	810	B_1	$w(CD_2)(60), \nu_a(CCN)(34)$
795 w		790	B_2	$r(CD_2)$	786	B_2	$r(CD_2)(86)$
577 ms	581(2)	548	A_1	$\delta(CCC)$	569	A_1	$\delta(CCC)(43), \delta_i(CCN)(30), \nu_s(CCN)(23)$
356 ms		369	B_1	$\delta(CCN)$	362	B_1	$\delta_i(CCN)(98)$
	356(4)	356	A_2	$\delta(CCN)$	352	A_2	$\delta_o(CCN)(98)$
	302(1)	318	B_2	$\delta(CCN)$	317	B_2	$\delta_o(CCN)(87)$
	163(4)	157	A_1	$\delta(CCN)$	163	A_1	$\delta_i(CCN)(66), \delta(CCC)(33)$

weak band at 471 cm^{-1}, which is taken to be an overtone. It will be seen that our force field is in quite satisfactory agreement with the observed spectrum.

3. *Isobutyronitrile*

A further check of our valence force field for molecules with one C≡N group is provided by a calculation of the frequencies of isobutyronitrile. These are shown in Table 5. The spectrum of this molecule has not been reported on, and in Fig. 1 we show an infrared spectrum of this material in the liquid state (obtained on a Beckmann

Table 7. Observed and calculated frequencies of succinonitriles

ν_obs [13] Infrared	Raman	gauche [13]	ν_calc [13] (gauche)	ν_calc [13] (trans)	trans [13]	ν_calc (VFF) (gauche)	gauche (VFF)	ν_calc (VFF) (trans)	trans (VFF)
2985	2985	A ν(CH$_2$)	—	2982	A_u ν(CH$_2$)	2979	A ν_a(CH$_2$)(99)	2981	B_g ν_a(CH$_2$)(99)
2982	2982	B ν(CH$_2$)	2958	2944	B_u ν(CH$_2$)	2975	B ν_a(CH$_2$)(99)	2972	A_u ν_a(CH$_2$)(100)
2965	2965	B ν(CH$_2$)	2922	2925	B_u ν(CH$_2$)	2935	B ν_s(CH$_2$)(99)	2937	A_g ν_s(CH$_2$)(99)
2947	2947	A ν(CH$_2$)	—	2903	A_g ν(CH$_2$)	2934	A ν_s(CH$_2$)(99)	2932	B_u ν_s(CH$_2$)(99)
2255	2255	B ν(CN)	2275	2277	B_u ν(CN)	2257	B ν(CN)(88)	2258	B_g ν(CN)(88)
2254	2254	A ν(CN)	2275	2277	A_g ν(CN)	2257	A ν(CN)(88)	2257	A_g ν(CN)(88)
1431 vs	1430*(8)	B δ(CH$_2$)	1424	1429	B_u δ(CH$_2$)	1439	B δ(CH$_2$)(93)	1444	B_u δ(CH$_2$)(97)
1420* vs	1425†(8)	A δ(CH$_2$)	1421	1424	A_g δ(CH$_2$)	1436	A δ(CH$_2$)(98)	1429	A_g δ(CH$_2$)(96)
1339 s	1359†(2)	B w(CH$_2$)	1365	1312	A_g w(CH$_2$)	1350	B w(CH$_2$)(75)	1374	A_g w(CH$_2$)(99)
1322* w	1331†(4)	A w(CH$_2$)	1287	1321	B_u w(CH$_2$)	1332	A w(CH$_2$)(45),t(CH$_2$)(29)	1288	B_g t(CH$_2$)(94)
1272† m		B t(CH$_2$)	1178	1178	A_u t(CH$_2$)	1218	A w(CH$_2$)(53),ω(CH$_2$)(29)	1257	B_u w(CH$_2$)(89)
1232 s	1232(2)	A t(CH$_2$)	1168	1166	B_g t(CH$_2$)	1189	B t(CH$_2$)(86)	1193	A_u t(CH$_2$)(93)
1200 m	1202(0)	A ν(CC)	1072	1073	A_g ν(CC)	1052	A ν(CC)(52),r(CH$_2$)(22)	1036	A_g ν(CC)(76)
1028 w	1180†(0)				B_g ν(CC)	1012	A r(CH$_2$)(53)	1030	B_g r(CH$_2$)(88)
1002 s	1025(6)	B ν(CCN)	971	986	B_g r(CH$_2$)	987	B ν(CCN)(39),δ(CCC)(23)	957	A_g ν(CCN)(39),δ(CCC)(34)
962 s	1005(2)	A r(CH$_2$)	980	975	A_g ν(CCN)	822	A ν(CCN)(50),ν(CC)(22)	930	B_u ν(CCN)(85)
917† s	975*(4)	A ν(CCN)	833	894	B_u ν(CCN)	802	B r(CH$_2$)(52),ν(CCN)(35)	753	A_u r(CH$_2$)(83)
818 s	951†(4)	B τ(CCN) / r(CH$_2$)	802	794	A_u r(CH$_2$)				
812* sh	812*(8)								
780† s									
604 s	603(1)	B δ(CCC)	594	522	B_u δ(CCC)	585	B δ(CCC)(49),δ(CCN)(26)	516	B_u δ(CCN)(49),δ(CCC)(45)
529† m	510†(1)	A δ(CCN)	461	480	A_g δ(CCC)	467	A δ(CCN)(50),δ(CCC)(37)	480	A_g δ(CCN)(36),δ(CCC)(29)
480 s	478(4)	A δ(CCN)	358	367	A_u δ(CCN)	383	A δ(CCN)(85)	388	A_u δ(CCC)(87)
388 m	384(4)	B δ(CCN)	356	355	B_g δ(CCN)	361	B δ(CCN)(91)	358	B_g δ(CCN)(97)
368 s	357(4)	B δ(CCN)	260	241	A_g δ(CCN)	255	B δ(CCN)(70)	249	A_g δ(CCN)(63),δ(CCC)(30)
247 m	240†(8)	A δ(CCN)	222	153	B_u δ(CCN)(?)	196	A δ(CCC)(42),δ(CCN)(41)	153	B_u δ(CCC)(52),δ(CCN)(40)(?)
230 m	170(0)	A τ	—	—	A_u τ	72	A τ(70)	77	A_u τ(82)
180 m									

* Present only, or much stronger, at low temperature.
† Absent, or much weaker, at low temperature.

Table 8. Observed and calculated frequencies of glutaronitriles

Solid (S)*	$\bar{\nu}_{obs}$ [14] Solid (M)	Liquid			GG (Solid S)			$\bar{\nu}_{calc}$ (VFF) TG (Solid M)			TT (Liquid)
2950 s	2950 ms	2959 s	2959	B	$\nu_a(CH_2)(99)$	2961	A	$\nu_a(CH_2)(99)$	2962	B_2	$\nu_a(CH_2)(99)$
			2956	A	$\nu_a(CH_2)(99)$	2955	A	$\nu_a(CH_2)(99)$	[2954	A_2	$\nu_a(CH_2)(99)$]
			2951	B	$\nu_a(CH_2)(100)$	2950	A	$\nu_a(CH_2)(99)$	2949	B_2	$\nu_a(CH_2)(100)$
2890 w	2874 w	2890 m	2914	A	$\nu_s(CH_2)(99)$	2916	A	$\nu_s(CH_2)(98)$	2917	A_1	$\nu_s(CH_2)(99)$
			2913	B	$\nu_s(CH_2)(99)$	2914	A	$\nu_s(CH_2)(99)$	2913	B_1	$\nu_s(CH_2)(99)$
			2912	A	$\nu_s(CH_2)(99)$	2910	A	$\nu_s(CH_2)(95)$	2909	A_1	$\nu_s(CH_2)(100)$
2247 s	2245 s	2249 s	2249	A	$\nu(CN)(88)$	2249	A	$\nu(CN)(88)$	2250	A_1	$\nu(CN)(88)$
			2249	B	$\nu(CN)(88)$	2249	A	$\nu(CN)(88)$	2249	B_1	$\nu(CN)(88)$
1460 ms	1451 ms	1458 ms	1445	A	$\delta(CH_2)(91)$	1449	A	$\delta(CH_2)(95)$	1453	A_1	$\delta(CH_2)(93)$
			1441	B	$\delta(CH_2)(95)$	1440	A	$\delta(CH_2)(94)$	1438	B_1	$\delta(CH_2)(94)$
1433 s	1420 s	1429 vs	1438	A	$\delta(CH_2)(90)$	1434	A	$\delta(CH_2)(92)$	1431	A_1	$\delta(CH_2)(99)$
	1364 m	1366 m				1375	A	$w(CH_2)(62)$	1385	B_1	$w(CH_2)(56), \nu(CC)(32)$
1350 s		1355 m	1358	A	$w(CH_2)(78)$						
			1344	B	$w(CH_2)(53), t(CH_2)(25)$						
	1328 m	1333 m				1342	A	$w(CH_2)(60)$			
1316 ms		1314 m	1332	B	$w(CH_2)(40)$				1323	A_1	$w(CH_2)(73)$
	1300 w	1299 m				1292	A	$w(CH_2)(43), t(CH_2)(42)$			
1287 w		1289 vw	1262	A	$t(CH_2)(76)$				[1293	A_2	$t(CH_2)(93)$]
	1282 ms	1272 m				1282	A	$t(CH_2)(70)$	1277	B_2	$t(CH_2)(85)$
	1224 m	1224 ms				1203	A	$t(CH_2)(42), w(CH_2)(42)$	1225	B_1	$w(CH_2)(94)$
1190 ms		1193 vw	1181	B	$t(CH_2)(62), w(CH_2)(20)$						
	1181 m	1181 m				1170	A	$t(CH_2)(81)$			
	1174 m	1170 vw							[1169	A_2	$w(CH_2)(62), t(CH_2)(28)$]?
1125 w		1120 vw	1161	A	$t(CH_2)(70), w(CH_2)(24)$						
1065 m	1060 m	1066 w	1089	B	$\nu(CC)(65)$	1068	A	$\nu(CC)(44), r(CH_2)(35)$	1068	B_2	$r(CH_2)(80)$
		1056 w							1039	B_1	$\nu(CC)(79)$
	1045 m	1047 m				1054	A	$\nu(CC)(43), r(CH_2)(30)$	1035	A_1	$\nu(CC)(70)$
1026 m		1022 m	1042	A	$r(CH_2)(38), \nu(CC)(20)$						
1010 m	1009 ms	1008 ms	1020	B	$r(CH_2)(39), w(CH_2)(23)$	1020	A	$\nu(CC)(25)$			
		998 w							968	A_1	$\nu(CCN)(53)$
	943 ms	945 m				955	A	$\nu(CCN)(58)$			
903 ms		904 ms	907	A	$\nu(CCN)(39), r(CH_2)(35)$						
		888 w							900	B_1	$\nu(CCN)(70)$
873 ms		870 ms	895	B	$\nu(CCN)(40), r(CH_2)(36)$						
	859 ms	860 ms				868	A	$\nu(CCN)(43)$			
837 ms	839 ms	835 ms	840	A	$\nu(CC)(54), \nu(CCN)(21)$	847	A	$r(CH_2)(45)$	[842	A_2	$r(CH_2)(77)$]
768 ms	757 s	757 s	746	B	$r(CH_2)(68), \nu(CCN)(17)$	742	A	$r(CH_2)(75)$			
		737 ms							722	B_2	$r(CH_2)(84)$
588 w	586 ms	583 ms	576	A	$\delta(CCCN)(41)$	564	A	$\delta(CCCN)(46), \delta(CCN)(23)$			
		565 w							571	B_1	$\delta(CCCN)(61), \delta(CCN)(28)$
537 ms		535 w	517	B	$\delta(CCCN)(46), \delta(CCN)(33)$						
	511 ms	507 m				490	A	$\delta(CCN)(38), \delta(CCCN)(31)$			

Table 8 (cont.)

Solid (S)*	$\bar{\nu}_{obs}$ [14] Solid (M)	Liquid			GG (Solid S)			$\bar{\nu}_{calc}$ (VFF) TG (Solid M)				TT (Liquid)
		481 vw							451	A_1	δ(CCN)(55), δ(CCCN)(24)	
									[374	A_2	δ(CCN)(89)]	
		373† m	378	A	δ(CCN)(53), δ(CCC)(20)	375	A	δ(CCN)(72)	373	B_2	δ(CCN)(93)	
			374	B	δ(CCN)(87)	374	A	δ(CCN)(90)				
		347† sh	348	A	δ(CCN)(64), δ(CCC)(32)							
		338† ms				341	A	δ(CCC)(43), δ(CCN)(40)	331	A_1	δ(CCC)(60)	
			260	B	δ(CCN)(57), δ(CCCN)(23)	223	A	δ(CCN)(41), δ(CCCN)(27)	235	B_1	δ(CCN)(66)	
			170	A	δ(CCCN)(41), δ(CCN)(40)	188	A	δ(CCN)(41), δ(CCCN)(35)	115	A_1	δ(CCCN)(45), δ(CCN)(32)	
			106	B	τ_a(66)	86	A	τ(71)	[105	A_2	τ_s(89)]	
			43	A	τ_s(87)	64	A	τ(71)	86	B_2	τ_a(80)	

* Solid (S) = stable solid, Solid (M) = metastable solid.
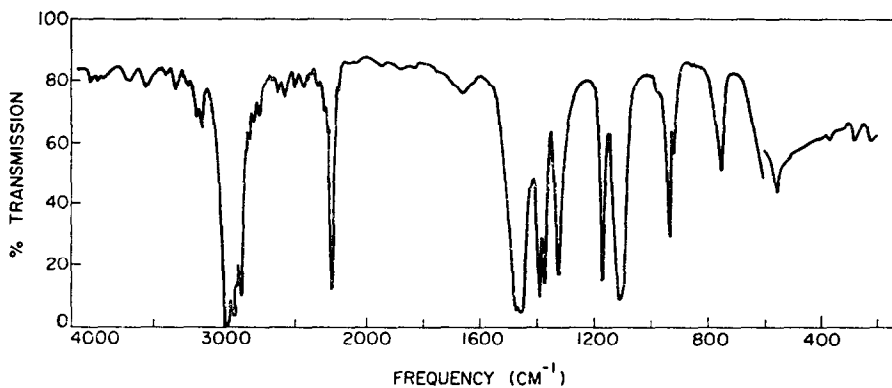† New bands observed in present work.

Fig. 1. Infrared spectrum of isobutyronitrile.

IR-12 spectrometer). The observed bands are listed in Table 5, and an assignment based on frequency correlation is suggested. This of course is not decisive, and other evidence for band assignments is desirable (for example, polarization of Raman lines). It will be seen, however, that reasonable agreement is achieved between observed and calculated frequencies with force constants which are essentially transferred from the hydrocarbons and acetonitrile.

4. Malononitrile

Malononitrile is the simplest example of a nitrile with two C≡N groups. Because of the attachment of the two C≡N groups to the same carbon atom, some of the force constants have had to be modified slightly as compared to their values in molecules with one C≡N group (cf. Table 2). Calculations have been done on malononitrile, malononitrile-d_1, and malononitrile-d_2, for which infrared and Raman data are available [10]. The observed and calculated frequencies are given in Table 6, where they are compared with calculations based on a Urey–Bradley force field [10].

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The latter calculations give average deviations between observed and calculated frequencies of 1.89%, 1.61%, and 2.07% for the above three molecules respectively, compared to our values of 0.96%, 1.25%, and 1.09%. This again suggests that the valence force field may provide a better representation of the internal potential energy of a molecule than the Urey–Bradley force field.

5. *Succinonitrile*

The vibrational spectrum of succinontrile has been the subject of three recent papers [11–13]. This molecule can exist in two rotationally isomeric forms, a *trans* and a *gauche* conformation. Both are present at room temperature, but only the *gauche* form is stable below −50°C [11]. The latter form can also be stabilized in a copper nitrate coordination compound [12], and this as well as the temperature study have permitted an assignment of bands to be made to the *trans* and *gauche* structures. A recent calculation of the predicted spectrum has been made using a Urey–Bradley force field [13]. In Table 7 we compare the observed infrared and Raman bands with these calculations and with the results obtained using our valence force field. The results are substantially the same as obtained previously [13], although our calculations suggest some modifications in assignments. The overall agreement using the valence force field is again somewhat better (giving average deviations of 1.30% and 1.08% for the *trans* and *gauche* structures respectively) than is obtained with the Urey–Bradley field (which gives average deviations of 2.41% and 2.22% for these two structures).

6. *Glutaronitrile*

Glutaronitrile can exist in three rotationally isomeric forms, *trans–trans* (TT), *trans–gauche* (TG), and *gauche–gauche* (GG). (The fourth form, GG', is sterically and electrically unfavorable.) Experimental studies of this molecule [14] indicate that the GG form is the stable structure in the crystalline solid. A metastable crystalline form is obtained by rapid cooling to −60°C, and it has been suggested that the molecule is in the TG conformation in this case [14]. The TT form is believed to exist in the liquid state together with the other two forms.

A normal coordinate analysis of each isomer has been done on the assumption that the CH_2 group is a point mass [14]. We have computed the normal vibrations for the three isomers, with inclusion of all hydrogen atoms and with the valence force field which was used for the other nitriles. The calculated frequencies are compared with the observed bands in Table 8. (We have observed the infrared spectrum of the liquid down to 200 cm^{-1}, and find the three new low-frequency bands listed in Table 8.) It will be seen that the bands can be assigned quite well on the basis of the structural assignments to solid and liquid phases made by MATSUBARA [14]. The average deviations in frequencies of 1.13%, 1.01% and 1.21% for the TT, TG, and GG isomers respectively are in the same range as those obtained for the other nitrile molecules, and suggest a satisfactory assignment.