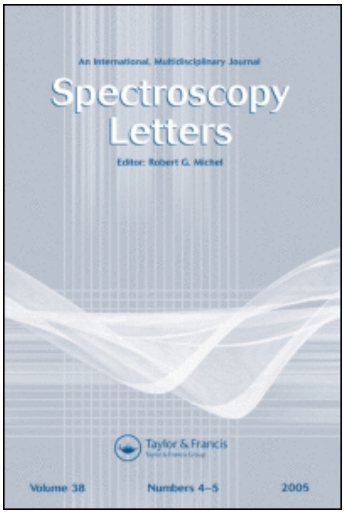

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A Vibrational Force Field For 1-Alkynes and Nitriles

G. A. Crowder[a]
[a] Killgore Research Center West Texas State University Canyon, Texas, USA

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A VIBRATIONAL FORCE FIELD FOR 1-ALKYNES AND NITRILES

Key words: 1-Butyne, 1-Pentyne, Propionitrile, Butyronitrile, Force field, Normal coordinate calculations

G. A. Crowder
Killgore Research Center
West Texas State University
Canyon, Texas 79016 USA

ABSTRACT

Normal coordinate calculations were made for 1-butyne, propionitrile, and the two conformers each of 1-pentyne and butyronitrile, using a thirty-one parameter modified valence force field. Only the triple bond stretching force constant was assumed to be different in the two families of compounds. Twenty force constants were refined to fit 117 frequencies of the six molecules, with the average error being 5.1 cm^{-1}, or 0.65%.

INTRODUCTION

Vibrational assignments have been made for 1-butyne,[1,2] 1-pentyne,[2] propionitrile,[3] and butyronitrile[4] with the aid of normal coordinate calculations. Recently, the fundamentals of 1-butyne and propionitrile were fitted with a common force field, except for the C≡X force constant. The present work was undertaken to see if a common force field could be used for additional alkynes and nitriles.

CALCULATIONS

Normal coordinate calculations were made with a Prime 5500 computer. The computer programs written by Schachtschneider[5,6] were used for calculation of the G matrix (GMAT), for solution of the vibrational secular equation (VSEC), and for the least-squares refinement of selected force constants to fit the calculated frequencies to the observed values (FPERT). The molecular parameters used were C≡N = 0.117 nm, C≡C = 0.1207 nm, C-H = 0.1067 nm, ≡C-C = 0.146 nm, -C-C- = 0.154 nm, -C-H = 0.109 nm, and all angles except for the linear group were assumed to be 109.47^{o}.

RESULTS

Initial values of the force constants were taken from the 1-butyne - propionitrile work.[5] The average

TABLE 1

Observed and calculated wavenumbers for 1-butyne and propionitrile

1-Butyne		Propionitrile	
Obs. cm^{-1}	Calc. cm^{-1}	Obs. cm^{-1}	Calc. cm^{-1}
2116	2123	2261	2255
1470	1466	1463	1466
1462	1462	1463	1462
1446	1441	1434	1441
1385	1383	1382	1384
1322	1314	1324	1314
1261	1258	1265	1258
1090	1090	1090	1091
1070	1070	1074	1071
1008	1015	1008	1015
840	830	837	829
782	776	783	777
634	633	530	532
630	629	371	374
509	512	-	229
344	347	220	220
(225)	225		
208	205		

TABLE 2

Observed and calculated wavenumbers for 1-pentyne

C_s conformer		C_1 conformer	
Obs. cm^{-1}	Calc. cm^{-1}	Obs. cm^{-1}	Calc. cm^{-1}
2127	2123	2127	2123
1465	1465	1465	1466
1465	1462	1465	1462
1460	1451	1460	1451
1435	1429	1435	1440
1385	1384	1385	1383
1341	1349	1328	1337
1282	1284	1253	1258
1253	1257	1253	1249
--	1237	--	1216
1095	1098	--	1108
1095	1090	1077	1074
1040	1032	1050	1042
954	957	925	926
872	864	872	888
840	863	840	852
740	730	762	761
633	632	633	633
628	629	628	629
494	494	530	537
350	349	350	358
340	335	-	327
250	248	250	258
174	166	174	176
-	97	-	94

TABLE 3

Observed and calculated wavenumbers for butyronitrile

C_s conformer		C_1 conformer	
Obs. cm^{-1}	Calc. cm^{-1}	Obs. cm^{-1}	Calc. cm^{-1}
2252	2255	2252	2255
1463	1465	1463	1465
1463	1462	1463	1462
--	1450	--	1451
1428	1431	1428	1436
1385	1385	1385	1384
1342	1343	1329	1323
1278	1285	1278	1277
1261	1256	1261	1257
--	1237	1230	1216
1104	1102	1090	1098
1080	1076	1080	1067
--	1033	1048	1054
942	956	911	925
872	873	872	872
840	861	840	853
740	729	760	737
528	514	557	551
360	366	382	376
360	352	360	353
-	248	-	262
183	178	183	186
-	99	-	96

TABLE 4

Force constants for 1-alkynes and nitriles

Force Constant	Group	Coordinates Involved	Atom(s) Common	Initial Value[a]	Final Value[a]	Standard Error
Stretch						
K_r	CH_3	C-H	-	4.835	4.835	-
K_d	CH_2	C-H	-	4.663	4.663	-
$K_R(I)$	≡C-C	C-C	-	5.130	5.130	-
$K_R(II)$	-C-C-	C-C	-	4.223	4.223	-
$K_X(I)$	C≡C	C≡C	-	15.087	15.087	0.072
$K_X(II)$	C≡N	C≡N	-	17.645	17.549	0.073
K_S	≡C-H	C-H	-	5.933	5.923	0.015
Stretch-stretch						
F_r	CH_3	CH,CH	C	0.039	0.039	-
F_d	CH_2	CH,CH	C	0.016	0.016	-
F_R	C-C-C	CC,CC	C	0.177	0.158	0.047
Bend						
H_α	CH_3	H-C-H	-	0.541	0.537	0.002
H_β	C-CH_3	C-C-H	-	0.617	0.653	0.010
H_δ	CH_2	H-C-H	-	0.532	0.535	0.003
$H_\gamma(I)$	-C-CH_2	C-C-H	-	0.647	0.634	0.004
$H_\gamma(II)$	≡C-CH_2	C-C-H	-	0.689	0.660	0.008
H_ω	C-C-C	C-C-C	-	0.984	0.930	-
H_ϕ	X≡C-C	X≡C-C	-	0.305	0.311	0.006
H_ξ	C≡C-H	C≡C-H	-	0.211	0.211	0.002

Table 4 (continued)

Force Constant	Group	Coordinates Involved	Atom(s) Common	Initial Value[a]	Final Value[a]	Standard Error
Stretch-bend						
$F_{R\gamma}$	$C\text{-}CH_2\text{-}CH_3$	CC,CCH	C-C	0.261	0.257	0.019
$F'_{R\gamma}$	$C\text{-}CH_2\text{-}C$	CC,CCH	C	0.034	0.005	0.020
$F_{R\omega}$	$C\text{-}CH_2\text{-}CH_3$	CC,CCC	C-C	0.212	0.413	0.032
Bend-bend						
F_{β}	$C\text{-}CH_3$	CCH,CCH	C-C	-0.005	-0.018	0.005
F_{γ}	$C\text{-}CH_2\text{-}C$	CCH,CCH	C-C	-0.028	-0.020	0.004
F'_{γ}	$C\text{-}CH_2\text{-}C$	CCH,CCH	C-H	0.023	0.023	-
$F_{\gamma\omega}$	$C\text{-}CH_2\text{-}C$	CCH,CCH	C-C	-0.091	-0.091	-
$F_{\omega\phi}$	$X\equiv C\text{-}C\text{-}C$	XCC,CCC	$\equiv$C-C	-0.048	-0.048	0.010
f^t_{γ}	$C\text{-}CH_2\text{-}CH_3$	HCC,CCH [trans]	C-C	0.016	0.107	0.008
f^g_{γ}	$C\text{-}CH_2\text{-}CH_3$	HCC,CCH [gauche]	C-C	-0.017	-0.035	0.005
$f^t_{\gamma\omega}$	$C\text{-}CH_2\text{-}CH_3$	HCC,CCC [trans]	C-C	0.072	0.072	-
$f^g_{\gamma\omega}$	$C\text{-}CH_2\text{-}CH_3$	HCC,CCC [gauche]	C-C	-0.037	-0.068	0.013
Torsion						
H_{τ}	$CH_2\text{-}CH_2\text{-}CH_3$	C-C	-	0.0116	0.0116	-

[a]Stretching constants are in units of mdyn/Å; stretch-bend constants are in units of mdyn/rad; bending constants are in units of mdyn Å$(rad)^{-2}$

error for the two conformers of 1-pentyne and the two conformers of butyronitrile was ca. 10 cm^{-1} in the initial calculation. Three FPERT runs were made, and in the final run, twenty of the thirty-one force constants were adjusted to fit 117 assigned frequencies of the six molecules (excluding the C-H stretching frequencies), with the average difference between observed and calculated values being 5.1 cm^{-1}, or 0.65%. The observed and calculated wavenumbers below the C-H stretch region are given in Tables 1-3. In order to conserve space, the potential energy distributions are not given here, but they are available from the author. The force constant definitions, initial values, and final values are given in Table 4.

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REFERENCES

1. G. A. Crowder and H. Fick, J. Mol. Struct., 147, 17 (1986).
2. G. A. Crowder, J. Mol. Struct. 172, 151 (1988).
3. G. A. Crowder, Spectrochim. Acta 42A, 1229 (1986).
4. G. A. Crowder, J. Mol. Struct. 158, 229 (1987).

5. J. H. Schachtschneider and R. G. Snyder Spectrochim. Acta 19, 117 (1963).

6. J. H. Schachtschneider, Shell Development Co. Tech. Rept., Nos. 231-64 (1964) and 57-65 (1965).

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