

COMPARATIVE CALCULATIONS OF MOLECULAR VIBRATIONS OF SOME ACETYLENIC COMPOUNDS

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Abstract. Normal mode vibrational frequencies of 24 acetylenic hydrocarbons and alcohols were calculated by using MM3, MMFF94, and PM3 methods. The results were compared with experimental data. The best method for the estimation of the frequencies of the stretching vibrations related to the CC triple bond was MM3, which had the relative rms error of 0.3–0.7%.

Key words: molecular vibrations, acetylenic compounds, MM3, MMFF94, PM3.

The synthesis and analysis of acetylenic compounds became very important in recent decades due to their use as convenient starting materials in supramolecular chemistry, nanotechnology, synthesis of drugs, and for other purposes [1]. Among the methods of analysis the vibrational spectroscopy offers a good possibility to characterize the original structure of new compounds (materials) in any state without destroying the sample. Therefore the vibrational spectroscopy of acetylenes has to be investigated. Interpretation of IR as well as Raman spectra is generally empirical, knowledge based, and therefore errors are often possible. Quantum mechanical and molecular mechanics calculations give a possibility to estimate the normal mode vibration frequencies of molecules and interpret them by using animation of vibration.

In the present report we describe the results of comparative calculations of the normal mode vibrations of the following 24 acetylenic hydrocarbons and alcohols: propyne, 1-butyne, 1-pentyne, 1-hexyne, 1-heptyne, 2-butyne, 2-pentyne, 2-hexyne, 2-heptyne, 3-hexyne, 3-decyne, 3,3-dimethyl-1-butyne, 4,4-dimethyl-2-pentyne, 3-methyl-1-pentyne, 5-methyl-1-hexyne, 2-propyn-1-ol, 2-butyne-1-ol, 2-pentyne-1-ol, 2-hexyne-1-ol, 3-butyne-1-ol, 3-butyne-2-ol, 2-methyl-3-butyne-2-ol, 3-pentyne-1-ol, and 3-nonyne-1-ol.

Semiempirical PM3 (HyperChem 5.02 [2]) and two molecular mechanical methods (MM3, TINKER ver. 3.7 [3]; MMFF94, SPARTAN Pro [4]) as the most convenient methods for practical purposes in respect to availability and calculation time were used. Root mean square errors (rms) and relative root mean square errors (rrms) were calculated for the values of the estimated frequencies. From the calculated frequencies the rms values were subtracted and the new rrms values were calculated as described by Dewar et al. [5]. Experimental vibrational frequencies were obtained from the literature [6, 7] and from IR spectra measured by us. Only frequencies of the stretching vibrations related to the CC triple bond as the most useful diagnostic tools for the structure analysis of acetylenes were investigated. Results of the analysis of the calculated frequencies are presented in Table 1.

Table 1. Analysis of calculated vibration frequencies

Type of vibration	No.	Mean value, cm ⁻¹		me, cm ⁻¹	rrms, %	rmse, %
		Observed	Calculated			
PM3 method (HyperChem)						
C≡C (all)	24	2178	2393	-215	9.9	0.6
C≡C (terminal)	12	2120	2325	-205	9.7	0.4
C≡C (internal)	12	2235	2462	-227	10.1	0.2
H-C≡	12	3319	3361	-42	1.3	0.4
C-C≡C	12	924	1046	-122	15.1	7.2
C-C≡C-C (symm.)	12	726	826	-115	16.2	3.6
C-C≡C-C (asymm.)	12	1136	1178	-41	4.1	1.9
MM3 method (TINKER)						
C≡C (all)	24	2178	2198	-20	1.1	0.6
C≡C (terminal)	12	2120	2128	-8	0.5	0.3
C≡C (internal)	12	2235	2268	-33	1.5	0.3
H-C≡	12	3319	3327	-7	0.4	0.4
C-C≡C	12	924	923	1	2.2	2.2
C-C≡C-C (symm.)	12	726	740	-14	3.3	2.6
C-C≡C-C (asymm.)	12	1136	1119	17	2.2	1.5
MMFF94 method (SPARTAN)						
C≡C (all)	24	2178	2165	13	5.7	0.5
C≡C (terminal)	12	2120	2098	22	1.1	0.3
C≡C (internal)	12	2235	2232	3	0.3	0.3
H-C≡	12	3319	3270	-50	1.5	0.4
C-C≡C	12	924	795	129	16.6	8.7
C-C≡C-C (symm.)	12	726	725	2	4.7	4.7
C-C≡C-C (asymm.)	12	1136	1103	34	3.3	1.6

me = mean error, rrms = relative root mean square error, rmse = relative root mean square error after subtraction of mean error.

We established that the best method for the estimation of vibrational frequencies of acetylenes is MM3. MMFF94 and particularly PM3 methods gave remarkably greater rms errors. After subtraction of the systematic rms errors the newly calculated relative mean errors were substantially decreased. It appeared that after such correction all three methods estimate the stretching frequencies of $C\equiv C$ and $H-C\equiv C$ bonds very well – the relative mean errors were 0.3–0.7%. Relative mean errors of the estimated asymmetric $C-C\equiv C-C$ and particularly symmetric $C-C\equiv C-C$ and $C-C\equiv$ stretching frequencies still remained relatively great even after correction. An enormously high value of relative rms was obtained for $C-C\equiv C$ stretching vibration calculated with the MMFF94 and PM3 methods.

To our knowledge the PM3 method has not been systematically tested and compared with other methods in respect to the calculation of normal mode vibrations of acetylenic compounds. Only the scaling factor (0.9761) and the rms error value over all vibrations (159 cm^{-1}) are given by Scott & Radom [8] for other compounds. We confirm that the PM3 method systematically overestimates all frequencies observed, doing so to a greater extent than MM3, whereas MMFF94 underestimates all frequencies except $C-C\equiv C$ stretching.

It is also evident from our data that the use of only one scaling factor for the correction of all calculated frequencies is not possible. Even terminal and internal triple bond vibrations have different rms values and should be therefore handled separately.

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MÕNEDE ATSETÜLEENIREA ÜHENDITE MOLEKULAARVÕNKUMISTE VÕRDLEVAD ARVUTUSED

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On arvutatud 24 atsetüleenirea süsivesiniku ja alkoholi normaalvõnkumiste sagedused, kasutades MM3, MMFF94 ja PM3 meetodit ning võrreldud saadud tulemusi eksperimentaalandmetega. Parimaks osutus MM3 meetod, mis ennustas $C\equiv C$ -sidemega seotud võnkesagedusi täpsusega 0,3–0,7%.