Theoret. Chim. Acta (Berl.) 53, 327–335 (1979)

THEORETICA CHIMICA ACTA

Calculation of Harmonic Force Constants, Vibrational Frequencies and Integrated Intensities of Some Organic Molecules Using the MINDO/3-Forces Method*

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The harmonic force constants, vibrational frequencies and integrated intensity ratios of CH_2, H_2O, CH_2O, C_2H_2, CO_2, HCN, CH_3, CH_4, and C_2H_4 have been calculated using the MINDO/3-FORCES program and the Pulay method for the calculation of the molecular force constants. The results obtained are in general quite satisfactory when compared with available literature values. The results are, however, not as satisfactory in case of molecules containing heteroatoms, due to the neglect of some dipolar repulsion integrals for the heteroatoms by the MINDO/3 method. Calculated integrated intensities for CH_3 and C_2H_4 agree well with experimental results. The calculated integrated intensities for other molecules are obtained for the first time and no comparison with published data is therefore possible.

Key words: Organic molecules, small ~ , harmonic force constants and vibrational frequencies of

1. Introduction

The wave mechanical evaluation of vibrational force constants was mainly based on *ab initio* SCF calculations [1–9]. Both numerical and analytical evaluations of the Cartesian forces and force constants from the calculated energy functions were applied. Pulay [8] used a combined, analytical, and then numerical evaluation procedure for the calculation of vibrational force constants. His calculated values showed a considerable improvement over previous *ab initio* results. The Pulay *Forces* method included the derivation of the *ab initio* molecular wave functions over the atomic Cartesian coordinates as well as the Hellmann–Feynmann derivatives of the energy expectation value that was used solely for the forces calculation

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* Part of the M.Sc. Thesis of K. H. A. 1978.

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0040-5744/79/0053/0327/$01.80

by other authors [1–7, 10]. Being aware of the limited suitability of the *ab initio* method for the calculation of big molecules, Pulay and Török evaluated the force constants for aromatic and heteroaromatic molecules using a combined CNDO-Forces method [9]. The results were encouraging but far from satisfactory, obviously because of the weakness of the CNDO method in yielding reliable energy values of molecules.

Using the MINDO/3 method and applying the minimization procedure of McIver and Komornicki [11] which did not include the derivation of the molecular wave function, Dewar and Ford [10] calculated the vibration frequencies for a series of molecules. Although the agreement of their values with the experimental frequencies was in many cases quite obvious, their nonconsideration of the wave function derivative should definitely have caused the deviation of their results from the experimental and from our calculated results that are included in the present work. Here we apply our recently developed MINDO/3-Forces method [12] to the evaluation of vibrational force constants and frequencies of a number of molecules. As we pointed out [12], our method includes the evaluation of the wave function-forces in the Pulay sense. We further use the obtained MINDO/3 wave functions to calculate the transition intensities of the corresponding frequencies.

2. Evaluation of Force Constants

The force constants have been calculated from the Cartesian forces obtained from the MINDO/3-Forces program [12]. The geometry of each molecule at which the forces are calculated has been optimized before through the iterative calculation of the MINDO/3-Forces type and is quite near the equilibrium geometry. The Cartesian forces near the equilibrium geometry are used to calculate the internal force constants F_R (or the symmetry force constants) according to Pulay [8]. The differentiations of the forces over the coordinates have been carried out numerically by a variation of 1% or less in the corresponding internal coordinate. The accuracy of the calculation by such a displacement has been checked for a sample case and has been found to be better than 3%. The symmetry force constants can likewise be evaluated using the same formalism as in the case of internal force constants.

3. Evaluation of Frequencies

Once the set of force constants have been obtained for the molecule, then the evaluation of vibrational frequencies becomes a straightforward problem by solving the secular equation [13]

$$|GF - \lambda I| = 0. \tag{1}$$

Having determined the set of frequencies λ, the normalized L vectors can then be obtained algebraically by direct substitution in the eigenvalue equation

$$GF \cdot L = L \cdot \Lambda. \tag{2}$$

The eigenvectors will, later on, be made use of in the calculation of integrated intensities.

4. Evaluation of Integrated Intensities

The integrated intensities for the various vibrational modes of the molecule can be calculated using the well-known relationship [14]

$$\Gamma_i = N_\pi/3c^2\omega_i \cdot (dP/dQ_i)^2, \tag{3}$$

where Γ_i is the integrated intensity of the normal mode of vibration i, ω_i is the vibrational frequency in cm^{-1} of that particular mode of vibration and dP/dQ_i is the dipole change with respect to the normal coordinate Q_i. One can determine $(dP/dQ_i)^2$ from the changes in three Cartesian dipole derivatives. These Cartesian dipoles are calculated using the atomic charges from the output of the MINDO/3-Forces program. The derivatives with respect to the normal coordinates are then obtained from the transformation relationship between normal and symmetry coordinates

$$S_j = \sum_i L_j^i Q_i. \tag{4}$$

Hence

$$dP^x/dQ_i = \sum_j dP^x/dS_j \cdot dS_j/dQ_i = \sum_j dP^x/dS_j \cdot L_i^j. \tag{5}$$

The summation is over the elements of L_j^i of the normal vibrations of the same symmetry.

5. Results and Discussion

5.1. Molecules Consisting of Carbon and Hydrogen only

5.1.1. $^1CH_2$ Molecule

The results for the singlet carbene molecule, shown in Table 1, seem reasonable in that they compare well with the frequencies of other olefinic systems. Considering the fact that the ground state of the carbene molecule is a triplet [15], no comparison

Table 1. Force constants, vibration frequencies, and integrated intensities ratios of the singlet carbene molecule as calculated using the MINDO/3-Forces method

Force constants of normal vibrations[a]	Frequencies of symmetry adapted vibrations (cm^{-1})	Intensity ratios $\Gamma_\omega/\Gamma_{\omega_2}$
F_r 6.20	ω_1 3134.5	4.79
F_ϑ 0.326	ω_2 981.6	1.00
F_{rr} 0.044	ω_3 3376.7	8.06
$F_{r\vartheta}$ 0.146		

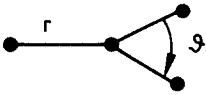
[a] C–H = 1.120 Å; HCH = 102°. Units of force constants in this and in the following tables are: F_r and F_{rr} in mdyne/Å; $F_{r\vartheta}$ in mdyne; F_ϑ in mdyne Å.

Table 2. Force constants, vibration frequencies, and integrated intensity ratios for the methyl radical

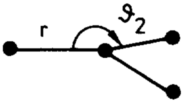
Force constants[a]			Frequencies[b]			Integrated intensity ratios	
	This work	exp. [17]		This work	exp. [17]	This work	exp. [17]
F_r	5.50	5.20	ω_1	3070	—	$\Gamma_{630}/\Gamma_{3132} = 8.75$	8.81
F_ϑ	0.40	0.315	ω_2	630	617		
$F_{r\vartheta}$	-0.18		ω_3	3132	3162	$\Gamma_{630}/\Gamma_{1369} = 9.71$	9.72
$F_{r\vartheta}$	0.51		ω_4	1396	1369	$\Gamma_{3162}/\Gamma_{1369} = 1.11$	1.10
F_{rr}	0.10	0.10					
F_γ	0.11	0.179					

[a] C—H = 1.097; HCH = 120°;
F_γ = out of plane force constant

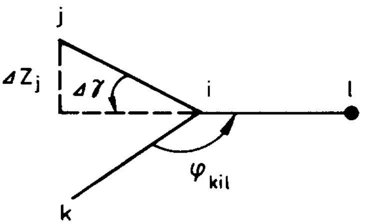
$F_{r\vartheta_1}$



$F_{r\vartheta_2}$



[b] sym. stretch, IR inactive
ω_2 out of plane bending
ω_3 asym. stretch
ω_4 in-plane angle bending



$$\Delta_{\gamma ijkl} = (\Delta Z_j/r_{i,ij})\cdot \sin_{\gamma\,kil}$$

with experimental data is therefore possible. The frequencies and intensity ratios require experimental verification. All frequencies are infrared active since the molecule has a C_{2v} symmetry [13].

5.1.2. The Methyl Radical $\cdot CH_3$

The results given in Table 2 are in good agreement with the literature values and the experimental data, especially those of the integrated intensity ratios. All the calculated frequencies are within 2% of the experimental values. Note that the out-of-plane bending angle has been defined according to the IUPAC recommendation [16]. For the calculation of the intensity ratios, the MINDO/3 single-determinant wave function is applied.

5.1.3. Acetylene

The results for acetylene are shown in Table 3. It is to be noted that F_{11}, F_{33} are the asym. and sym. C–H force constants, F_{22} is the C≡C force constant, and F_{44}, F_{55} are the asym. and sym. bending force constants (H—C≡C).

Table 3 clearly shows that our calculated set of force constants are comparable to the accepted literature values and to the values calculated by the *ab initio*-Forces method [18]. A sample calculation for the integrated intensity ratio between $\Gamma\omega_5/\Gamma\omega_3$ is given where no published data is available for comparison.

Table 3. The force constants, vibrational frequencies, and integrated intensity ratios for acetylene as calculated using the MINDO/3-Forces method[a]

Force constants				Frequencies (cm^{-1})		Intensity ratio
	This work	*Ab initio* [18]	exp. [19]	This work	exp. [19]	This work
F_{11}	5.999	6.984	6.381	ω_1 3306	3374	
F_{22}	19.962	18.02	15.953	ω_2 2323.8	1974	
F_{12}	0.552	−0.19	−0.147	ω_3 3295	3287	
F_{33}	5.967	6.970	6.424			$\Gamma_{1096}/\Gamma_{3295} = 14.32$
F_{44}	0.413	0.493	0.359	ω_4 625.7	612	
F_{55}	0.215	0.241	0.159	ω_5 1096.7	729	

[a] The applied distances are, C—H = 1.071 Å and C≡C = 1.196 Å.

ω_1 = C—H asym. stretch, ω_2 = C≡C stretch, ω_3 = C—H sym. stretch, ω_4 = sym. angle bending, ω_5 = asym. angle bending.

5.1.4. Ethylene

Results of our calculation for ethylene are given in Tables 4a and 4b (see Fig. 1). The values in both tables are in pleasing agreement with the experimental data and are nearer to these than Pulay's data, except for the F_R which are better reproduced by his method. The agreement between our calculated integrated

Table 4a. MINDO/3-Forces calculated force constants for the ethylene molecule

Force constants[a]			
	This work	Pulay's calculation [20]	Experimental values [21]
F_r	5.14	5.911	5.168
F_{rR}	0.11	0.096	—
$F_{r\beta,gem.}$	−0.17	−0.161	−0.179
F_R	10.04	9.939	9.305
F_τ	0.128	0.163	0.131
$F_{R\beta}$	0.23	0.296	0.273
F_β	0.977	1.148	0.951
$F_{\beta\beta,trans}$	0.065	0.088	0.071
$F_{\beta\beta,gem.}$	0.394	0.520	0.414
F_ϑ	0.218	0.217	0.167
$F_{\vartheta\vartheta}$	0.026	0.033	0.027

[a] C—H = 1.096; C═C = 1.316 Å; HCH = 110.8°.

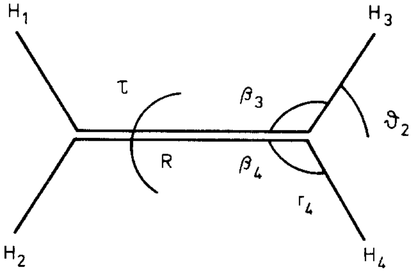


Fig. 1. Internal normal coordinates of the ethylene molecule

Table 4b. MINDO/3-Forces calculated vibrational frequencies and integrated intensity ratios for ethylene

Type of frequencies	This work cm^{-1}	Experimental [22, 23] cm^{-1}	Integrated intensity ratios This work	observed [24]
ω_1 A_{1g}	3077	3019		
ω_2 A_{1g}	1697	1623		
ω_3 A_{1g}	1414	1344		
ω_4 A_u	821	825		
ω_5 B_{1g}	3221	3272		
ω_6 B_{1g}	1104	1050		
ω_7 B_{2g}	946	949	$\Gamma\omega_7/\Gamma\omega_9 = 8.823$	10.474
ω_8 B_{2u}	877	943	$\Gamma\omega_7/\Gamma\omega_{10} = 115.070$	129.231
ω_9 B_{2u}	3146	3106	$\Gamma\omega_7/\Gamma\omega_{11} = 18.750$	18.584
ω_{10} B_{1u}	968	995	$\Gamma\omega_7/\Gamma\omega_{12} = 11.110$	12.426
ω_{11} B_{3u}	3014	2990		
ω_{12} B_{3u}	1401	1444		

intensity ratios and the experimentally observed ones is quite good in spite of the large variation in experimental intensities from 130 to one.

5.1.5. Methane

The results for methane are given in Table 5; see also Fig. 2. The calculated force constants are close to those of Pulay and the accepted literature values. The calculated frequencies are better than those of Dewar *et al.* [10]. The calculated intensity ratios are not comparable with the experimental ratios due to the overlap of the experimental spectral bands (see the note in Table 5).

Table 5. MINDO/3-Forces calculated force constants, vibrational frequencies and internal intensity ratios for methane

Force constants	This work	Pulay [25]	exp. [26]	Frequencies $(cm^{-1})^c$	This work	Dewar [10]	exp. [27, 28]
$F_{11}{}^a$	5.290	5.770	5.842	ω_1 (A)^b	2985	3505	3137
F_{22}	0.530	0.593	0.486	ω_2 (E)	1500	1567	1326
F_{33}	5.240	5.626	5.385	ω_3 (F_2)	3097	3551	3158
F_{34}	0.285	0.215	0.206	ω_4 (F_2)	1322	1597	1270
F_{44}	0.534	0.559	0.458				

[a] C—H = 1.091 Å; HCH = 109.5°. The diagonal force constants are designated in the same way as in the Pulay's paper.

[b] ω_1 = sym. stretch, ω_2 = angle bend, degenerate, ω_3 = asymmetric stretch, triply degenerate, ω_4 = angle bend, triply degenerate.

[c] The calculated intensity ratios are, $\Gamma_{1500}/\Gamma_{3097} = 4.971$, $\Gamma_{1500}/\Gamma_{1322} = 0.404$, $\Gamma_{1322}/\Gamma_{3097} = 12.310$. Due to the overlap of the bands in the experimental spectra no correlation of the theoretical with the experimental intensity ratios is possible (see J. Heicklen, Spectrochim. Acta **17**, 201 (1961)).

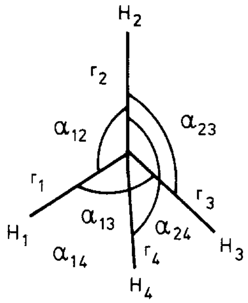


Fig. 2. Internal coordinates of the methane molecule

5.2. Molecules Consisting of Carbon, Hydrogen, Oxygen, or Nitrogen

5.2.1. Formaldehyde

Tables 6a and 6b show our calculated force constants and frequencies together with the calculated values of Pulay [29], that were empirically scaled, and the values of Dewar *et al.* [10]. Inspecting the values one finds that our calculation reproduces the formaldehyde force constants quite well. They are comparable with the *ab initio* values [29], but show some quantitative deviation from the experimental result. Of particularly good agreement with the experimental values are the non-diagonal force constants, which seem even better than the *ab initio* values. Note

Table 6a. MINDO/3-Forces calculated force constants of the formaldehyde molecule[a]

Designation	This work	Pulay [29]	Experiment [30]
F_{11} C=O	13.600	13.900	12.910
F_{12} C=O/C—H	0.905	0.675	0.811
F_{13} C=O/sym. bend	0.321	0.414	0.388
F_{22} sym. C—H	5.145	4.999	4.999
F_{23} C—H/sym. bend	−0.120	−0.106	−0.122
F_{33} sym. bend	0.502	0.645	0.572
F_{44} sym. C—H	5.396	4.909	4.872
F_{55} rock	0.697	0.946	0.858
F_{45} C—H/rock	0.152	0.157	0.212
F_{66} wagging	0.415	0.514	0.403

[a] The applied distances are: C—H = 1.12 Å; C=O = 1.21 Å and HCO = 121°.

Table 6b. Calculated vibrational frequencies of the formaldehyde molecule

Frequencies (cm^{-1})				
Designation	This work	Pulay [29]	Dewar [10]	Experiment [30]
ω_1 (A_1)	2756.8	2799	3332	2766
ω_2 (A_1)	1816	1722	2006	1746
ω_3 (A_1)	1580	1474	1374	1501
ω_4 (B_1)	3016	2879	3301	2843
ω_5 (B_1)	1116.4	1207	1046	1247
ω_6 (B_2)	1170	1186	1076	1164

Table 7. MINDO/3-Forces calculated force constants and vibration frequencies of H_2O

	Force constants				Frequencies (cm^{-1})		Intensity
	This work	*ab initio* [25]	exp. [14]		This work	exp. [22]	ratio
F_r	8.817	9.138	8.450	ω_1	3888	3833	$\Gamma_{3833}/\Gamma_{3942}$
F_{rr}	−0.142	−0.172	−0.09	ω_2	1540	1649	
$F_{r\vartheta}$	0.348	0.301	0.250	ω_3	4013	3942	
F_ϑ	0.677	0.851	0.700				

also the correct sign of the F_{23} element. Bigger deviations are encountered by the sym. and asym. C–H force constants, 29% and 9.3% respectively. The big values of both force constants and their relatively big deviations should influence the calculated vibration frequencies. The values of Table 6b meet this expectation. It is seen that our calculated frequencies deviate more from the experimental frequencies than those of Pulay [29]. However, they are still nearer to the experiment than the values of Dewar *et al.* [10]. The improvement in the MINDO/3 calculated IR frequencies is definitely due to the inclusion of the wave function derivative in the evaluation of the molecular forces and force constants.

5.2.2. The H_2O Molecule

The calculated O—H force constants of H_2O, Table 7, are quite acceptable in that they fall near the existing literature values [14]. They even compare better with these than the *ab initio* results [25]. Also, a good agreement is found for the deformation and O—H stretching frequencies with the experimental values. The applied bond angle for the calculation was 103°, compared with the experimental value of 103.5° [32]. The applied bond distance was 0.967 Å.

Table 8. MINDO/3-Forces calculated force constants of CO_2 and HCN

	Force constants	
	This work	Experiment
CO_2		
F_r	18.400	15.900 [14]
F_{rr}	2.800	2.200
F_ϑ	0.694	0.780
$R_{C=Z}$	1.175 Å	1.162 Å[a]
HCN		
F_r	6.400	6.251 [32]
F_R	18.330	18.703
F_{Rr}	0.550	−0.200
F_ϑ	0.292	0.260
r_{C-H}	1.059 Å	1.063 Å[b]
$R_{C\equiv N}$	1.157 Å	1.155 Å

[a] C.-P. Courtoy, Ann. Soc. Sci. Bruxelles, Ser. 1, 73, 5 (1959).

[b] C. C. Costain and B. P. Stoicheff, J. Chem. Phys. **30**, 777 (1959).

5.2.3. The CO_2 and HCN Molecules

Finally we report our calculated force constants of both CO_2 and HCN molecules, Table 8. The literature values for CO_2 are well reproduced; F_ϑ and the nondiagonal F_{rr} showing the better agreement with the literature values [14]. As for HCN, both stretching force constants compare well with the available experimental values [31].

References

1. Janoscheck, R., Diercksen, G., Preuss, H.: Intern. J. Quantum Chem. **1**, 373 (1967)
2. Body, R. G., McClure, D. S., Clementi, E.: J. Chem. Phys. **49**, 491 (1968)
3. Haas, J., Janoscheck, R., Preuss, H., Diercksen, G.: J. Mol. Structure **3**, 165 (1969)
4. Peyerimhoff, S. D. Buenker, R.: J. Chem. Phys. **49**, 312 (1968)
5. Meyer, W.: Arbeitsberichte der Gruppe Quantenchemie, MPI Astrophysik, Nr. 10, 1968
6. Schoenborn, M., Csizmadia, I. G.: Acta Phys. (Budapest) **27**, 377 (1969)
7. Klaus, K.: Arbeitsberichte der Gruppe Quantenchemie, MPI Astrophysik, Nr. 11, 97 (1968)
8. Pulay, P.: Mol. Phys. **17**, 197 (1969)
9. Pulay, P., Török, F.: Mol. Phys. **25**, 1153 (1973)
10. Dewar, M. J. S., Ford, G. P.: J. Am. Chem. Soc. **99**, 1685 (1977)
11. McIver, J. W., Jr., Komornicki, A.: Chem. Phys. Letters **10**, 303 (1977)
12. Khalil, S. M., Shanshal, M.: Theoret. Chim. Acta (Berl.) **46**, 23
13. Wilson, E. B., Jr., Decius, J. C., Cross, R. C.: Molecular vibrations. New York: McGraw-Hill 1955
14. Davies, M.: Infrared spectroscopy and molecular structure. New York: Elsevier 1963
15. Bernheim, R. A., Bernard, H. W., Wang, P. S., Wood, L. S., Skell, P. S.: J. Chem. Phys. **53**, 1280 (1970)
16. Shimanuchi, M.: IUPAC communication on vibrational spectroscopy, Dec. 1976
17. Snelson, A.: J. Chem. Phys. **74**, 537 (1970)
18. Pulay, P., Meyer, W.: Mol. Phys. **29**, 473 (1974)
19. Suzuki, I., Overend, J.: Spectrochim. Acta **25**, 977 (1969)
20. Pulay, P., Meyer, W.: J. Mol. Spectry. **40**, 59 (1971)
21. Swanstrom, P., Janoscheck, R., Preuss, H.: Intern. J. Quantum Chem. **3**, 881 (1969)
22. Herzberg, G.: Molecular spectra and molecular structure. New York: Van Nostrand 1945
23. Gallaway, W. S., Barker, E. F.: J. Chem. Phys. **7**, 455 (1939)
24. Golike, R. C., Mills, I. M., Person, W. B., Crawford, B., Jr.: J. Chem. Phys. **25**, 1266 (1956)
25. Pulay, P.: Mol. Phys. **21**, 329 (1971)
26. Duncain, J. L. Mills, I. M.: Spectrochim. Acta **20**, 523 (1964)
27. Mills, I.: Spectrochim. Acta **16**, 35 (1960)
28. Jones, L. H., McDowall, R.: J. Mol. Spectry. **3**, 632 (1959)
29. Pulay, P.: Theoret. Chim. Acta (Berl.) **32**, 253 (1974)
30. Blau, H. H., Nielsen, H. H.: J. Mol. Spectry. **1**, 24 (1957)
31. Strey, G., Mills, I.: Mol. Phys. **26**, 129 (1973)
32. Bingham, R. C., Dewar, M. J. S., Lo, D. H.: J. Am. Chem. Soc. **97**, 1302 (1975)

Received September 4, 1978/March 1, 1979