

Molecular Vibrations and Mean Amplitudes of Carboxylic Acids

II. Acetic Acid Monomer

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A normal coordinate analysis was performed for the monomeric form of acetic acid. The developed harmonic force constants were used to calculate the mean amplitudes of vibration for CH_3COOH , CD_3COOD , CD_3COOH , and CH_3COOD . For CH_3COOH also the calculated perpendicular amplitude correction coefficients are given.

In the first part¹ a normal coordinate analysis including mean amplitudes of vibration for formic acid monomer was communicated. Similar calculations are reported here for acetic acid monomer and some of its deuterated molecules.

MOLECULAR MODEL

The computations are based on the molecular model as shown in Fig. 1 with the equilibrium structure parameters² $T(\text{C}=\text{O})=1.245 \text{ \AA}$, $S(\text{C}-\text{C})=1.497 \text{ \AA}$, $R(\text{C}-\text{H})=D(\text{C}-\text{H})=1.08 \text{ \AA}$, $U(\text{C}-\text{O})=1.312 \text{ \AA}$, $V(\text{O}-\text{H})=0.95 \text{ \AA}$, $E(\text{CCH}_3)=F(\text{CCH}_6)=2A(\text{H}_6\text{CH}_7)=109.28^\circ$, $B_1(\text{O}=\text{C}-\text{O})=124.30^\circ$, $B_2(\text{C}-\text{C}-\text{O})=116.20^\circ$, and $C(\text{COH})=107.80^\circ$.

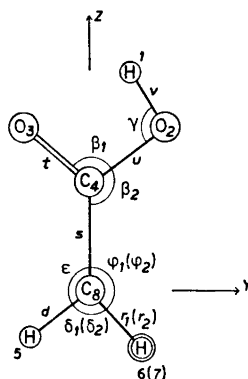


Fig. 1. The CH_3COOH molecular model; symmetry C_s . The H_6 and H_7 atoms are situated above and below the YZ plane, respectively. Valence coordinates not indicated on the figure: τ and ρ for torsions involving the atoms 3-4-8-5 and 1-2-4-8, respectively; θ for the (8,2)-4-3 out-of-plane bending, 3 being the end atom.

SYMMETRY COORDINATES

The valence coordinates are specified in Fig. 1. A complete set of symmetry coordinates, which are distributed among the symmetry species according to

$$\Gamma = 12 A' + 6A''$$

are given in the following.

Species A'

$$S_1 = 2^{-\frac{1}{2}}(r_1 + r_2), S_2 = d, S_3 = s, S_4 = t, S_5 = u, S_6 = v$$

$$S_7 = (RS/2)^{\frac{1}{2}}(\phi_1 + \phi_2), S_8 = (DR/2)^{\frac{1}{2}}(\delta_1 + \delta_2)$$

$$S_9 = (DS)^{\frac{1}{2}}\varepsilon, S_{10} = (TU)^{\frac{1}{2}}\beta_1, S_{11} = (SU)^{\frac{1}{2}}\beta_2, S_{12} = (UV)^{\frac{1}{2}}\gamma$$

Species A''

$$S_1 = 2^{-\frac{1}{2}}(r_1 - r_2), S_2 = (RS/2)^{\frac{1}{2}}(\phi_1 - \phi_2), S_3 = (RD/2)^{\frac{1}{2}}(\delta_1 - \delta_2)$$

$$S_4 = (DT)^{\frac{1}{2}}\tau, S_5 = (SV)^{\frac{1}{2}}\varrho, S_6 = [T(SU)^{\frac{1}{2}}]^{\frac{1}{2}}\theta$$

NORMAL COORDINATE ANALYSIS

An initial valence force field, $F^{(1)}$, was formed by transferring the diagonal force constants from $F^{(1)}$ in formic acid monomer,¹ and including $f(C-C)$ with the value of 4.5 mdyne/Å. The first calculated frequencies for CH₃COOH,

Table 1. Observed and calculated vibrational frequencies (in cm⁻¹) for CH₃COOH.*

Approximate description of normal modes	Observed				Calc.	
	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>
<i>A'</i>						
<i>ν</i> (O-H)	3585	3546	3577	3583	3568	3577
<i>ν</i> (C-H)	3030	3027	2997	3051	2946	2997
<i>ν'</i> (C-H)	2944	2935	2961	2944	2830	2961
<i>ν</i> (C=O)	1790	1770	1799	1788	1934	1799
<i>δ</i> (C-C-H)	1441	1403	1401	1430	1807	1401
<i>δ'</i> (C-C-H)	1381	1381	1340	1382	1503	1340
<i>ν</i> (C-C)	1288	1284	1279	1264	1336	1279
<i>δ</i> (C-O-H)	1185	1184	1192	1182	1166	1192
<i>δ</i> (H-C-H)	1053	—	990	989	821	990
<i>ν</i> (C-O)	897	996	846	847	712	846
<i>δ</i> (O=C-O)	626	680	654	642	625	654
<i>δ</i> (C-C-O)	452	564	536	581	381	536
<i>A''</i>						
<i>ν''</i> (C-H)	2985	2983	3048	2996	2949	3048
<i>δ</i> (H-C-H)	1441	1431	1445	1430	1677	1445
<i>δ''</i> (C-C-H)	1112	1082	1068	1048	1487	1068
tors (<i>ρ</i>)	985	650	654	642	815	653
wagg (<i>θ</i>)	597	536	582	534	649	582
tors (<i>τ</i>)	—	—	—	—	331	100

* The here adopted assignment given in italics. The values from Ref. 6 are probably better, but were not accessible to us when the analysis was performed.

a. Ref. 3. *b.* Ref. 4. *c.* Ref. 5. *d.* Ref. 6. *e.* Present calculation with $F^{(1)}$. *f.* Present calculation with $F^{(2)}$.

Table 2. Observed and calculated vibrational frequencies (in cm^{-1}) for CD_3COOD , CD_3COOH , and CH_3COOD .*

CD_3COOD					CD_3COOH					CH_3COOD				
Observed			Calc.		Observed			Calc.		Observed			Calc.	
<i>a</i>	<i>c</i>	<i>g</i>	<i>e</i>	<i>f</i>	<i>a</i>	<i>c</i>	<i>g</i>	<i>e</i>	<i>f</i>	<i>a</i>	<i>c</i>	<i>g</i>	<i>e</i>	<i>f</i>
<i>A'</i>														
2660	<i>2660</i>	2642	2604	2610	—	<i>3640</i>	3582	3568	3577	3021	<i>2957</i>	3039	2946	2997
2270	<i>2237</i>	2275	2207	2250	2296	<i>2225</i>	2285	2208	2251	2942	<i>2929</i>	2952	2830	2961
2119	<i>2111</i>	2116	2056	2138	2116	<i>2111</i>	2118	2056	2138	2653	<i>2640</i>	2642	2604	2610
1760	<i>1760</i>	1775	1892	1753	1760	<i>1760</i>	1783	1896	1756	1770	<i>1792</i>	1775	1930	1797
1280	<i>1280</i>	1300	1507	1298	1335	<i>1335</i>	1338	1509	1326	1445	<i>1430^b</i>	1440	1807	1400
1093	<i>1060</i>	1080	1313	1100	1162	<i>1217</i>	1167	1317	1211	1377	<i>1323</i>	1383	1500	1321
1041	<i>1060</i>	1056	1063	1000	1089	<i>1060</i>	1078	1167	1100	1266	<i>1272</i>	1270	1333	1258
1000	<i>1000</i>	1004	965	994	1043	<i>1060</i>	1055	1063	996	1042	<i>995</i>	990	971	1020
812	<i>812</i>	813	706	815	820	<i>820</i>	819	784	879	953	<i>959</i>	955	762	941
799	<i>785</i>	813	566	667	842	<i>790</i>	819	587	681	856	<i>837</i>	840	696	801
582	—	540	544	593	604	—	615	546	610	596	<i>654</i>	603	593	625
404	—	450	349	485	402	—	478	350	486	434	<i>536</i>	543	379	534
<i>A''</i>														
2244	—	2240	2213	2272	2225	<i>2183</i>	2230	2213	2272	2986	<i>3058</i>	2997	2949	3048
1060	—	1056	1207	1036	1065	<i>1065</i>	1055	1210	1037	1445	<i>1464</i>	1440	1677	1445
925	<i>925</i>	917	1189	852	935	<i>926</i>	918	1190	855	1094	<i>1057</i>	1052	1486	1067
785	—	408	635	555	918	—	560	794	637	—	<i>582</i>	603	693	598
506	—	528	558	467	521	—	560	605	551	—	—	515	563	469
—	—	—	245	74	—	—	—	245	74	—	—	—	331	100

* Adopted assignment in italics. *a, c, e, f*. See footnote to Table 1. *g*. Ref. 2.

CD_3COOD , CD_3COOH , and CH_3COOD did not agree quite well with observed values;²⁻⁶ the average deviation from the values of the adopted assignment (*cf.* Tables 1 and 2) was 13 %. Nevertheless the initial force field seemed suitable as the starting point for refinements of the force constants. Through several steps of iterations, of which the details need not to be reported here, a force field, $F^{(2)}$, was produced, which reproduces the adopted assignments for the four isotopic molecules with an average deviation of 1.9 %. This force field was adjusted to reproduce exactly the observed frequencies for CH_3COOH . The approximate description of normal modes (Table 1) is set up on the basis of calculated potential energy distribution coefficients from $F^{(2)}$. This description is consistent with the one of Nakamoto *et al.*⁷ except for the two lowest frequencies in A' .

Table 3 shows the symmetry force constants of the force field $F^{(2)}$.

MEAN AMPLITUDES OF VIBRATION

The developed force field $F^{(2)}$ was used to calculate the mean amplitudes of vibration⁸ for the four isotopic molecules of acetic acid monomer. The results at 298.16°K are shown in Table 4. The mean amplitudes for the various

Table 3. Symmetry force constants (mdyne/Å) of $F^{(2)}$.

A'	1	2	3	4	5	6
1	4.97					
2	0.14	4.82				
3	-0.01	-0.02	5.06			
4	0.05	-0.02	1.04	9.41		
5	0.00 ₂	-0.01	1.00	0.59	6.57	
6	0.00 ₃	0.00 ₃	0.01	-0.03	0.01	7.13
7	-0.00 ₃	0.01	0.12	-0.08	-0.09	-0.00 ₁
8	-0.01	-0.00 ₂	-0.15	0.11	-0.19	-0.00 ₄
9	0.01	-0.01	-0.04	0.02	-0.11	-0.01
10	-0.01	0.00 ₄	-0.18	0.88	0.57	0.01
11	0.00 ₄	-0.00 ₂	-0.06	0.32	0.41	-0.00 ₃
12	0.01	-0.00 ₃	0.09	0.05	0.17	-0.00 ₃
A'	7	8	9	10	11	12
7	0.74					
8	0.20	0.65				
9	0.00 ₂	0.21	0.68			
10	-0.02	-0.02	-0.03	1.65		
11	-0.01	0.01	-0.04	0.55	1.58	
12	-0.01	-0.01	-0.02	0.03	-0.02	0.59
A''	1	2	3	4	5	6
1	4.94					
2	-0.01	0.56				
3	-0.01	-0.05	0.33			
4	0.00 ₀	-0.01	0.01	0.03		
5	-0.00 ₀	0.00 ₂	0.00 ₀	-0.00 ₃	0.13	
6	0.00 ₂	-0.05	-0.05	0.05	-0.01	0.20

isotopic molecules are seen to have characteristic magnitudes for every type of interatomic distances; the secondary isotope effects are negligible.

Table 5 shows the calculated mean amplitudes for CH_3COOH at absolute zero and 298.16°K, along with the corresponding perpendicular amplitude correction coefficients (K -values).⁸

MODIFIED FORCE FIELD AND MEAN AMPLITUDES

In the above normal coordinate analysis the existence of a hydrogen bond has not been taken specifically into account. The similar studies of formic acid monomer^{1,9} indicated the relevance of making some corrections which would lead to a smaller $\text{O}\cdots\text{H}$ mean amplitude pertaining to the hydrogen bond. Therefore a modification of the force field along the same line was performed also for the acetic acid monomer in the present work. The procedure has been referred to as "specific imposing of a potential parameter".^{1,9}

The force field $F^{(2)}$ of the above analysis is augmented by one row and column by inclusion of a stretching coordinate p , which corresponds to the

Table 4. Mean amplitudes of vibration (\AA units) for isotopic acetic acid monomer at 298.16°K .

Distance	Atom pair	(Equil.)	CH_3COOH	CD_3COOD	CD_3COOH	CH_3COOD
O—H	1—2	(0.950)	0.071		0.07 ₀	
O—D	1—2	(0.950)		0.06 ₀		0.06 ₀
C—H	5—8	(1.080)	0.078			0.07 ₈
C—H	6—8	(1.080)	0.078			0.07 ₈
C—D	5—8	(1.080)		0.06 ₇	0.06 ₇	
C—D	6—8	(1.080)		0.06 ₆	0.06 ₆	
C—O	2—4	(1.312)	0.044	0.04 ₄	0.04 ₄	0.04 ₄
C—O	3—4	(1.245)	0.040	0.04 ₀	0.04 ₀	0.04 ₀
C— $\bar{\text{C}}$	4—8	(1.497)	0.049	0.04 ₈	0.04 ₈	0.04 ₈
C \cdots H	1—4	(1.840)	0.102		0.10 ₁	
C \cdots H	4—5	(2.115)	0.105			0.10 ₄
C \cdots H	4—6	(2.115)	0.104			0.10 ₄
C \cdots D	1—4	(1.840)		0.08 ₈		0.08 ₈
C \cdots D	4—5	(2.115)		0.09 ₁	0.09 ₁	
C \cdots D	4—6	(2.115)		0.09 ₀	0.09 ₀	
C \cdots H	1—8	(3.190)	0.095		0.09 ₅	
C \cdots D	1—8	(3.190)		0.08 ₄		0.08 ₄
C \cdots O	2—8	(2.387)	0.057	0.05 ₆	0.05 ₆	0.05 ₆
C \cdots $\bar{\text{O}}$	3—8	(2.372)	0.059	0.05 ₉	0.05 ₉	0.05 ₉
O \cdots $\bar{\text{O}}$	2—3	(2.261)	0.050	0.04 ₉	0.04 ₉	0.04 ₉
O \cdots $\bar{\text{H}}$	2—5	(3.278)	0.099			0.09 ₉
O \cdots H	2—6	(2.671)	0.242			0.24 ₄
O \cdots D	2—5	(3.278)		0.08 ₇	0.08 ₇	
O \cdots D	2—6	(2.671)		0.23 ₇	0.23 ₇	
$\bar{\text{O}}\cdots$ H	1—3	(2.307)	0.128		0.12 ₇	
$\bar{\text{O}}\cdots$ H	3—5	(2.468)	0.132			0.13 ₁
$\bar{\text{O}}\cdots$ H	3—6	(3.068)	0.176			0.17 ₆
$\bar{\text{O}}\cdots$ D	1—3	(2.307)		0.11 ₁		0.11 ₁
$\bar{\text{O}}\cdots$ D	3—5	(2.468)		0.11 ₆	0.11 ₆	
$\bar{\text{O}}\cdots$ D	3—6	(3.068)		0.17 ₀	0.17 ₀	
$\bar{\text{H}}\cdots$ H	5—6	(1.768)	0.132			0.13 ₂
$\bar{\text{H}}\cdots$ H	6—7	(1.762)	0.144			0.14 ₃
D \cdots D	5—6	(1.768)		0.11 ₂	0.11 ₂	
D \cdots D	6—7	(1.762)		0.12 ₃	0.12 ₃	
H \cdots H	1—5	(3.951)	0.138			
H \cdots H	1—6	(3.525)	0.201			
D \cdots D	1—5	(3.951)		0.11 ₈		
D \cdots D	1—6	(3.525)		0.18 ₈		
H \cdots D	1—5	(3.951)			0.12 ₈	0.12 ₈
H \cdots D	1—6	(3.525)			0.19 ₈	0.19 ₇

hydrogen bond. The modified force field F_h contains one additional nonvanishing constant, namely the potential parameter h , as is indicated on Fig. 2. In the present calculations the value of $h=0.5$ mdyne/ \AA was transferred from formic acid monomer.^{1,9} It should be noted that the force constant matrix F_h is based on a set of internal coordinates with one redundancy. But the F_h matrix may be converted to an F matrix in terms of standard symmetry coordinates without redundancy. The here developed force field, as represented

Table 5. Mean amplitudes of vibration (u) and perpendicular amplitude correction coefficients (K) for CH_3COOH from the force field $F^{(2)}$; cf. also Table 4. Units: Å.

	u		K	
	0°K	298.16°K	0°K	298.16°K
O—H	0.070 ₅	0.070 ₅	0.022 ₄	0.024 ₇
C—H ₅	0.078 ₁	0.078 ₁	0.033 ₂	0.102 ₄
C—H ₆	0.077 ₆	0.077 ₆	0.036 ₄	0.113 ₁
C—O	0.044 ₁	0.044 ₄	0.002 ₆	0.005 ₃
C—O	0.040 ₀	0.040 ₃	0.002 ₃	0.002 ₅
C—C	0.048 ₅	0.049 ₀	0.001 ₈	0.002 ₇
C ₄ ···H ₁	0.101 ₇	0.102 ₀	0.010 ₄	0.011 ₆
C ₄ ···H ₅	0.104 ₃	0.104 ₃	0.018 ₉	0.063 ₂
C ₄ ···H ₆	0.103 ₆	0.104 ₁	0.017 ₃	0.052 ₉
C ₃ ···H ₁	0.094 ₄	0.095 ₂	0.005 ₅	0.006 ₀
C···O	0.054 ₃	0.056 ₇	0.000 ₆	0.000 ₉
C···O	0.056 ₇	0.059 ₅	0.000 ₅	0.000 ₇
O···O	0.048 ₈	0.049 ₉	0.000 ₈	0.001 ₃
O···H ₅	0.098 ₈	0.099 ₅	0.009 ₀	0.027 ₇
O···H ₆	0.154 ₈	0.242 ₁	0.012 ₃	0.039 ₉
O···H ₁	0.126 ₁	0.127 ₇	0.007 ₀	0.007 ₃
O···H ₅	0.128 ₁	0.131 ₃	0.014 ₃	0.049 ₅
O···H ₆	0.128 ₇	0.176 ₅	0.010 ₄	0.033 ₃
H ₅ ···H ₆	0.130 ₈	0.132 ₁	0.052 ₀	0.184 ₁
H ₄ ···H ₇	0.143 ₁	0.144 ₄	0.054 ₉	0.198 ₁
H ₁ ···H ₅	0.137 ₇	0.138 ₄	0.012 ₁	0.031 ₄
H ₁ ···H ₆	0.157 ₂	0.200 ₃	0.014 ₁	0.035 ₇

by F , was adjusted to fit exactly the adopted assignment of observed frequencies (Table 1) according to

$$\text{GFL}_h = L_h \lambda_h, \quad F_a = \tilde{K}_h \lambda K_h$$

where $L_h = K_h^{-1}$ and λ_h are calculated on the basis of F_h , λ represents the observed frequencies, and F_a is the adjusted, final force constant matrix.

Table 6 shows the calculated mean amplitudes and perpendicular amplitude corrections for CH_3COOH at absolute zero and 298.16°K, as calculated from the force field F_a .

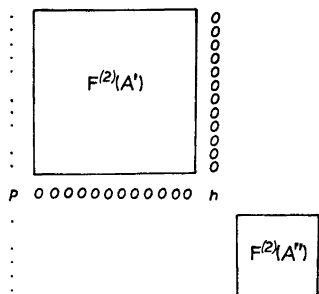


Fig. 2. Schematic representation of the modified force field F_h .

Table 6. Mean amplitudes of vibration (u) and perpendicular amplitude correction coefficients (K) for CH_3COOH from the modified force field F'_2 ; units: \AA .

Distance	u		K	
	0°K	298.16°K	0°K	298.16°K
O—H	0.070 ₅	0.070 ₅	0.021 ₃	0.023 ₅
C—H ₅	0.078 ₁	0.078 ₁	0.033 ₅	0.103 ₁
C—H ₆	0.077 ₆	0.077 ₆	0.036 ₇	0.113 ₉
C—O	0.044 ₇	0.044 ₉	0.002 ₆	0.005 ₃
C—O	0.040 ₂	0.040 ₅	0.002 ₃	0.002 ₃
C—C	0.049 ₉	0.050 ₁	0.001 ₈	0.002 ₇
C ₄ ···H ₁	0.096 ₆	0.096 ₈	0.010 ₀	0.011 ₂
C ₄ ···H ₅	0.105 ₅	0.106 ₂	0.019 ₀	0.063 ₂
C ₄ ···H ₆	0.104 ₃	0.104 ₉	0.017 ₄	0.053 ₂
C ₈ ···H ₁	0.092 ₄	0.093 ₄	0.005 ₃	0.005 ₇
C···O	0.055 ₇	0.057 ₃	0.000 ₆	0.000 ₉
C···O	0.057 ₀	0.059 ₃	0.000 ₅	0.000 ₁
O···O	0.048 ₅	0.049 ₃	0.000 ₈	0.001 ₂
O···H ₅	0.099 ₅	0.100 ₅	0.009 ₁	0.027 ₉
O···H ₆	0.155 ₅	0.243 ₂	0.012 ₄	0.040 ₁
O···H ₁	0.113 ₁	0.113 ₆	0.007 ₀	0.007 ₇
O···H ₅	0.129 ₄	0.133 ₀	0.014 ₃	0.049 ₇
O···H ₆	0.129 ₂	0.177 ₂	0.105 ₁	0.033 ₈
H ₅ ···H ₆	0.131 ₄	0.132 ₇	0.052 ₃	0.185 ₃
H ₆ ···H ₇	0.144 ₃	0.145 ₃	0.055 ₁	0.199 ₁
H ₁ ···H ₅	0.134 ₄	0.135 ₂	0.012 ₀	0.031 ₄
H ₁ ···H ₆	0.157 ₆	0.201 ₅	0.013 ₈	0.035 ₅

An electron diffraction experiment might be decisive as to the preference of the values in Table 5 or 6. For the time being the results of Table 6 are considered as the final values of the present spectroscopical analysis.

Finally it should be noted that special uncertainties are attached to the present results of calculation due to the unobserved lowest (A'') frequency, here assumed as 100 cm^{-1} .

REFERENCES

1. Cyvin, S. J., Alfheim, I. and Hagen, G. *Acta Chem. Scand.* **24** (1970) 3038.
2. Tabor, W. J. *J. Chem. Phys.* **27** (1957) 974.
3. Sverdlov, L. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **17** (1953) 567.
4. Weltner, W., Jr. *J. Am. Chem. Soc.* **77** (1955) 3941.
5. Wilmshurst, J. K. *J. Chem. Phys.* **25** (1956) 1171.
6. Haurie, M. and Novak, A. *J. Chim. Phys.* **62** (1965) 141.
7. Nakamoto, K. and Kishida, S. *J. Chem. Phys.* **41** (1964) 1554.
8. Cyvin, S. J. *Molecular Vibrations and Mean Square Amplitudes*, Universitetsforlaget, Oslo, and Elsevier, Amsterdam 1968.
9. Alfheim, I., Cyvin, S. J., Hagen, G. and Motzfeldt, T. *To be published*.

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