

Molecular Vibrations and Mean Amplitudes of Carboxylic Acids

I. Formic Acid Monomer

S. J. CYVIN, INGRID ALFHEIM and G. HAGEN

Institutt for teoretisk kjemi, Norges tekniske høgskole, N-7034 Trondheim, Norway

A normal coordinate analysis is reported for the monomeric form of formic acid. The developed harmonic force constants were used to calculate mean amplitudes of vibration and related quantities. The results are compared with recent experimental mean amplitudes from electron diffraction.

Normal coordinate analyses have been reported previously both for formic¹⁻⁵ and acetic^{3,6} acid. Some mean amplitudes of vibration for formic acid monomer have been reported by Karle and Karle⁷ from an early electron diffraction work using the sector-microphotometer method. Their results are (in Å):

$$\begin{aligned} u(\text{C}=\text{O}) &< 0.030 \\ u(\text{C}-\text{O}) &= 0.044 \pm 0.008 \\ u(\text{O}\cdots\text{O}) &= 0.040 \pm 0.008 \end{aligned}$$

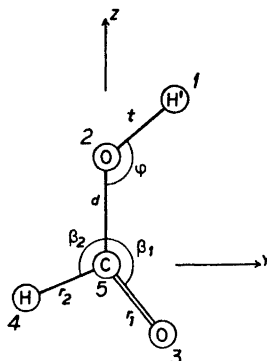
Presumably more accurate results of mean amplitudes were obtained by a recent reinvestigation⁸ of HCOOH in gaseous electron diffraction. This work⁸ also includes the study of formic acid dimer. A similar study of gaseous oxalic acid has also been reported.⁹ No spectroscopic mean amplitudes for carboxylic acids have been reported previously, except some preliminary results⁹ for oxalic acid. It seemed therefore to be of great interest to undertake a systematic spectroscopical study of mean amplitudes of vibration¹⁰ for molecules with carboxylic groups. In the present work the calculated mean amplitudes and perpendicular amplitude correction coefficients for formic acid are reported. Similar results for acetic acid are to be communicated in Part II of this series.

NORMAL COORDINATE ANALYSIS

An initial force field, $F^{(0)}$, was chosen as a valence force field in terms of the internal coordinates given in the legend of Fig. 1. The stretching force

Fig. 1. The HCOOH molecule model; symmetry C_s . Equilibrium parameters: $R_1(\text{C}=\text{O})$, $R_2(\text{C}-\text{H})$, $D(\text{C}-\text{O})$, $T(\text{O}-\text{H})$, $B_1(\angle \text{O}=\text{C}-\text{O})$, $B_2(\angle \text{H}-\text{C}-\text{O})$, $\Phi(\angle \text{C}-\text{O}-\text{H})$. In-plane internal coordinates: r_1 , r_2 , d , t , $(R_1D)^{\frac{1}{2}}\beta_1$, $(R_2D)^{\frac{1}{2}}\beta_2$, $(TD)^{\frac{1}{2}}\phi$. Out-of-plane internal coordinates (not indicated on the figure):

$$[R_1(R_2D)^{\frac{1}{2}}]^{\frac{1}{2}} \gamma_{2453}, (R_2T)^{\frac{1}{2}} \tau_{1254}.$$



constants are shown in Table 1 along with literature values of the corresponding constants. The force constants of the three in-plane bendings (*cf.* Fig. 1) were assumed to be (in mdyne/Å) 1.2, 0.84, and 0.53, respectively, while the

Table 1. Stretching force constants (in mdyne/Å) for HCOOH from different sources.

Reference	2	4	5	11	Present $F^{(0)}$
C=O	13.20	9.609	12.43	11.65	11.6
C-H	—	4.728	4.69	—	4.65
C-O	6.91	5.203	6.18	5.96	6.1
O-H	—	7.162	7.16	—	7.2

two out-of plane force constants were set equal to 0.27 and 0.215. With this very simple harmonic force field the observed vibrational frequencies for the four H and D isotopic species of formic acid monomer were reproduced surprisingly well, the average deviation between observed and calculated values being 2.8 %; *cf.* Tables 2 and 3. The approximate description of normal modes as given in Table 2 emerged from the calculation of potential energy distribution coefficients. For the in-plane modes it is consistent with the description of Wilmshurst's¹⁵ assignment, but partly contradicted by other authors.^{3,13}

Let L_0 be the normal-coordinate transformation matrix from the initial calculations, *i.e.*

$$GF^{(0)}L_0 = L_0A_0$$

where A_0 represents the calculated frequencies. A refined force field, $F^{(1)}$, was obtained by adjusting the frequencies to the observed values for HCOOH (see Table 2). If these frequencies are represented by the matrix A , one assumed

$$F^{(1)} = \tilde{L}_0^{-1} A L_0^{-1}$$

Table 2. Observed and calculated vibrational frequencies (in cm^{-1}) for HCOOH and DCOOD.*

Approximate description of normal modes	HCOOH					DCOOD			
	Observed			Calc.		Obs.		Calc.	
	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
<i>A'</i>									
$\nu(\text{O}-\text{H})$	3567	<i>3570</i>	—	3593	3570	<i>2632</i>	—	2621	2605
$\nu(\text{C}-\text{H})$	2943	<i>2943</i>	—	2939	2943	<i>2232</i>	—	2233	2228
$\nu(\text{C}=\text{O})$	1794	<i>1770</i>	—	1897	1770	<i>1742</i>	—	1805	1698
$\delta(\text{H}-\text{C}-\text{O})$	1346	<i>1387</i>	—	1303	1387	<i>1171</i>	—	1172	1189
$\nu(\text{C}-\text{O})$	1200	<i>1229</i>	—	1208	1229	<i>1040</i>	—	1017	1066
$\delta(\text{C}-\text{O}-\text{H})$	1105	<i>1105</i>	—	1191	1105	<i>945</i>	—	901	850
$\delta(\text{O}=\text{C}-\text{O})$	658	636	<i>625</i>	634	625	538	<i>558</i>	573	564
<i>A''</i>									
wagg	1033	<i>1033</i>	1033	1135	1033	873	<i>873</i>	884	808
tors	919	<i>636</i>	638	585	536	489	<i>491</i>	479	518

* The here adopted assignment given in italics.

a. Ref. 12.

b. Ref. 13.

c. Ref. 14.

d. Present calculation with $F^{(0)}$.

e. Present calculation with $F^{(1)}$.

Table 3. Observed and calculated vibrational frequencies (in cm^{-1}) for DCOOH and HCOOD.*

	DCOOH				HCOOD			
	Obs.		Calc.		Obs.		Calc.	
	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
<i>A'</i>								
<i>3570</i>	—	—	3593	3570	<i>2948</i>	—	2939	2943
<i>2220</i>	—	—	2235	2229	<i>2632</i>	—	2621	2604
<i>1756</i>	—	—	1808	1701	<i>1772</i>	—	1894	1767
<i>1220</i>	—	—	1200	1203	<i>1360</i>	—	1300	1384
<i>1143</i>	—	—	1171	1129	<i>1178</i>	—	1203	1220
<i>970</i>	—	—	987	1021	<i>990</i>	—	936	876
629	<i>620</i>	—	618	610	541	<i>562</i>	582	572
<i>A''</i>								
<i>870</i>	—	—	948	864	<i>~1000</i>	—	1085	991
629	<i>629</i>	—	599	629	512	<i>508</i>	479	519

* Adopted assignment in italics.

b–*e*. See footnotes to Table 2.

Tables 2 and 3 include the calculated frequencies for the four isotopic molecules with the refined force field. A slight over-all improvement is achieved as to the agreement between observed and calculated frequencies; the average deviation is reduced to 2.0 %. This improvement may not be real, however; it should be noted that differences of about 1.7 % occur between observed values of frequencies from different sources.

MEAN AMPLITUDES OF VIBRATION

The derived force field $F^{(1)}$ was used to calculate the mean amplitudes of vibration for HCOOH. The results at 448.16°K are shown in Table 4, and correspond to the value of h equal to zero.

Table 4. Calculated and observed mean amplitudes of vibration (\AA units) for HCOOH. Temperature: 448.16°K.

Distance	Atom pair ^a	(Equil.) ^b	Calculated		Obs. ^c
			$h=0$	0.5 mdyne/ \AA	
O—H'	1—2	(0.984)	0.071	0.071	0.068 ^c
C—H	4—5	(1.106)	0.079	0.079	0.077 ^c
C—O	2—5	(1.361)	0.045	0.047	0.042
C—O	3—5	(1.217)	0.039	0.039	0.032
C···H'	1—5	(1.902)	0.110	0.101	0.09 ^c
O···O	2—3	(2.271)	0.058	0.061	0.054
O···H	2—4	(2.016)	0.099	0.102	0.09 ^c
O···H	3—4	(2.083)	0.096	0.099	0.09 ^c
O···H'	1—3	(2.325)	0.145	0.120	0.12 ^c
H···H'	1—4	(2.829)	0.125	0.122	—

^a According to the numbering of atoms in Fig. 1.

^b Interatomic separations (in \AA) as calculated from the structural data⁸ used as equilibrium parameters.

^c Unrefined during the least-squares procedure of interpretation of electron diffraction data. See also Ref. 16.

Table 5. Final results of calculated mean amplitudes (u) and perpendicular amplitude corrections (K) for HCOOH; \AA units.

Distance	u		K	
	0°K	298.16°K	0°K	298.16°K
O—H'	0.070 ₅	0.070 ₈	0.017 ₈	0.018 ₈
C—H	0.078 ₈	0.078 ₈	0.013 ₁	0.013 ₄
C—O	0.045 ₅	0.045 ₉	0.001 ₂	0.001 ₃
C—O	0.039 ₀	0.039 ₁	0.001 ₅	0.001 ₈
C···H'	0.099 ₄	0.099 ₅	0.006 ₆	0.007 ₀
O···O	0.053 ₉	0.056 ₂	0.000 ₁	0.000 ₁
O···H	0.100 ₃	0.100 ₇	0.005 ₅	0.005 ₅
O···H	0.096 ₇	0.097 ₃	0.004 ₉	0.005 ₀
O···H'	0.116 ₂	0.117 ₂	0.005 ₅	0.005 ₀
H···H'	0.121 ₄	0.121 ₅	0.008 ₃	0.008 ₇

The potential parameter h was introduced in order to modify the mean amplitudes according to the method of specific imposing of potential parameters. The constant h corresponds to a stretching coordinate for the hydrogen bond. The procedure and its application to HCOOH within a range of h values from -0.1 to 0.9 mdyne/Å is described elsewhere.¹⁶ It was found¹⁶ that $h=0.5$ mdyne/Å gives the best fit to an estimated value used in the electron-diffraction investigation, viz. $u(\underline{\text{O}}\cdots\text{H})=0.12$ Å, pertaining to a nozzle temperature of $175\pm 10^\circ\text{C}$. The appropriate spectroscopic u values at 175°C are included in Table 4 along with the electron diffraction results.⁸ These modified mean amplitudes are based on another force field, which, as well as $F^{(1)}$, reproduces exactly the observed vibrational frequencies.

In the present normal coordinate analysis the force field based on $h=0.5$ mdyne/Å and adjusted to the observed frequencies for HCOOH is considered as the final result. The mean amplitudes of vibration for HCOOH at the standard temperatures of 0°K and 298.16°K as calculated from the final force field are shown in Table 5. Also included are the perpendicular amplitude correction coefficients or K -values¹⁰ at the same temperatures.

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