

# Normal Coordinate Analysis of Chloromethyl Formate and its Deuterium Derivatives \*

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Normal coordinate calculations have been carried out for chloromethyl formate ( $\text{HCOOCH}_2\text{Cl}$ ) and its deuterium derivatives ( $\text{DCOOCH}_2\text{Cl}$ ,  $\text{HCOOCD}_2\text{Cl}$ ,  $\text{DCO OCD}_2\text{Cl}$ ) on the basis of the Urey-Bradley force field. In contrast with recent tentative assignments where the skeletal modes  $\delta(\text{C}-\text{O}-\text{C})$ ,  $\delta(\text{O}-\text{C}-\text{Cl})$  and  $\tau(\text{C}-\text{O})$  were located at 420, 325 and 240  $\text{cm}^{-1}$ , respectively, the normal coordinate calculations support that the assignments should be  $\delta(\text{O}-\text{C}-\text{Cl})$  at 420  $\text{cm}^{-1}$ ,  $\tau(\text{C}-\text{O})$  at 325  $\text{cm}^{-1}$  and  $\delta(\text{C}-\text{O}-\text{C})$  at 240  $\text{cm}^{-1}$ . A discussion on the nature of some skeletal modes is included.

The simplest alkylchlorinated ester, chloromethyl formate, has been used for some years as a model when studying conformational effects by vibrational spectroscopy. In two preceding papers the vibrational spectra and the structures of chloromethyl formate and its deuterium derivatives were reported.<sup>1,2</sup> The anomalous infrared carbonyl stretching region of  $\text{DCOOCH}_2\text{Cl}$  and  $\text{DCO OCD}_2\text{Cl}$  was investigated earlier.<sup>3,4</sup>

Only few normal coordinate calculations for formate esters are available in the literature. The normal modes of the basic formate ester, methyl formate, are well known.<sup>5-7</sup> The results of the study of ethyl formate<sup>8</sup> are not comparable to the vibrations of chloromethyl formate, investigated in this work, due to the different set of symmetry coordinates. In the study of *tert*-butyl formate and its deuterium derivatives<sup>9</sup> the contributions of potential energy distribution are given only for the vibrations below 1000  $\text{cm}^{-1}$ . A normal

coordinate analysis for chloromethyl formate and its deuterium derivatives is now carried out in order to confirm the tentative assignment in Ref. 1.

## NORMAL COORDINATE CALCULATIONS

Both experimental<sup>1</sup> and theoretical<sup>2</sup> investigations show that the skeletal ester framework of chloromethyl formate exists in the *Z* conformation with respect to the  $\text{C}(\text{O})-\text{O}$  bond and that the chloromethyl group can oscillate freely about the  $\text{O}-\text{CH}_2\text{Cl}$  bond between the *ap* and  $\pm sc$  conformations. According to *ab initio* calculations<sup>2</sup> the energy curve of this oscillation is very flat and therefore the normal coordinate calculations were carried out for the *Z, ap* conformation (Fig. 1).

Experimental data on the molecular geometry of chloromethyl formate are not available. The bond lengths and bond angles used in this work (Table 1) are taken from an *ab initio* study by Murto.<sup>10</sup> These calculations were carried out with the program GAUSSIAN 80 including the optimization of the internal coordinates with STO-3G basis set.

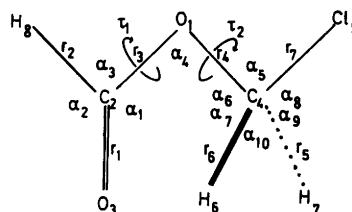


Fig. 1. Internal coordinates of chloromethyl formate (*Z, ap* conformation).

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Table 1. Bond lengths (Å) and bond angles (degrees) used for normal coordinate calculations.<sup>10</sup>

Bond lengths		Bond angles	
H <sub>form.</sub> -C	1.103	H <sub>form.</sub> -C-O	109.23
H-C	1.098	H-C-O	112.22
C=O	1.212	C-O-C	111.55
C(O)-O	1.396	O=C-O	124.19
O-C	1.433	O-C-Cl	107.16
C-Cl	1.809		

The representation of the vibrational modes of chloromethyl formate according to  $C_s$  symmetry is  $14 a' + 6 a''$ . There are two redundant coordinates in the  $a'$  species. The internal coordinates are explained in Fig. 1 and the local symmetry coordinates are given in Table 2. The Urey-Bradley  $Z$ -matrix and Wilson's  $G$ -matrix were constructed by the aid of the computer programs of Schachtschneider<sup>11</sup> and the normal coordinate calculations were carried out by means of a program written by Perttilä.<sup>12</sup> Initial force constants were obtained from normal coordinate calculations of methyl formate<sup>5</sup> and 2-chloroethanol.<sup>13</sup> After several steps of iterations

by a least squares procedure, the values presented in Table 3 for the resulting Urey-Bradley force field were obtained. The observed and calculated wavenumbers, potential energy distributions and assignments for chloromethyl formate and its deuterium derivatives are presented in Tables 4-7. Contributions smaller than 5 % in the potential energy distributions are omitted.

## DISCUSSION

It is seen from the potential energy distributions (Table 4) that the assignment of the vibrational modes of chloromethyl formate is

Table 2. Local symmetry coordinates for chloromethyl formate.

Symmetry coordinates	Description
<b><math>a'</math> species</b>	
$S_1=r_1$	$\nu(\text{C=O})$
$S_2=r_2$	$\nu(\text{CH}_{\text{form.}})$
$S_3=r_3$	$\nu(\text{C-O})$
$S_4=r_4$	$\nu(\text{O-C})$
$S_5=(1/\sqrt{2})(r_5+r_6)$	symm. $\nu(\text{CH}_2)$
$S_6=r_7$	$\nu(\text{C-Cl})$
$S_7=(1/\sqrt{6})(2a_1-a_2-a_3)$	$\delta(\text{O=C-O})$
$S_8=(1/\sqrt{2})(a_2-a_3)$	$\delta(\text{CH}_{\text{form.}})$
$S_9=(1/\sqrt{3})(a_1+a_2+a_3)$	red.
$S_{10}=a_4$	$\delta(\text{C-O-C})$
$S_{11}=(1/2)(a_6+a_7-a_8-a_9)$	wag. $(\text{CH}_2)$
$S_{12}=(1/2\sqrt{5})(4a_{10}-8a_6-a_7-a_8-a_9)$	sciss. $(\text{CH}_2)$
$S_{13}=(1/\sqrt{30})(5a_5-a_6-a_7-a_8-a_9-a_{10})$	$\delta(\text{O-C-Cl})$
$S_{14}=(1/\sqrt{6})(a_5+a_6+a_7+a_8+a_9+a_{10})$	red.
<b><math>a''</math> species</b>	
$S_{15}=(1/\sqrt{2})(r_5-r_6)$	as. $\nu(\text{CH}_2)$
$S_{16}=(1/2)(a_6-a_7-a_8+a_9)$	twist. $(\text{CH}_2)$
$S_{17}=(1/2)(a_6-a_7+a_8-a_9)$	rock. $(\text{CH}_2)$
$S_{18}=\gamma$	$\gamma(\text{CH}_{\text{form.}})$
$S_{19}=\tau_1$	tors. $(\text{C-O})$
$S_{20}=\tau_2$	tors. $(\text{O-CH}_2\text{Cl})$

Table 3. Potential parameters (force constants) of the Urey-Bradley force field for chloromethyl formate.

C=O	stretching	10.161 mdyn/Å <sup>a</sup>
CH <sub>form.</sub>		4.243
C-O		3.469
O-C		2.522
CH		4.449
C-Cl		1.795
O=C-O	bending	1.276 mdyn Å <sup>b</sup>
H <sub>form.</sub> -C=O		0.227
H <sub>form.</sub> -C-O		0.663
C-O-C		0.411
O-C-H		0.369
Cl-C-H		0.415
O-C-Cl		0.823
H-C-H		0.507
CH <sub>form.</sub>	out-of-plane	0.442
C-O	torsion	0.108
O-CH <sub>2</sub> Cl		0.086
O <sub>1</sub> ...Cl	interaction	1.205 mdyn/Å
O <sub>1</sub> ...H <sub>6,7</sub>		0.894
Cl...H <sub>6,7</sub>		0.368
H <sub>6</sub> ...H <sub>7</sub>		-0.037
ρ(CH <sub>2</sub> Cl)	internal tension	-0.048 mdyn Å
O <sub>1</sub> ...H <sub>8</sub>	interaction	0.494 mdyn/Å
O <sub>3</sub> ...H <sub>8</sub>		0.430
O <sub>1</sub> ...O <sub>3</sub>		0.542
C <sub>2</sub> ...C <sub>4</sub>		0.518
O <sub>3</sub> ...C <sub>4</sub>		0.654
C <sub>2</sub> ...H <sub>6,7</sub>		-0.157
H <sub>8</sub> -C <sub>2</sub> -O <sub>1</sub> -C <sub>4</sub>	trans bending	0.061 mdyn Å
C <sub>2</sub> -O <sub>1</sub> -C <sub>4</sub> -Cl		-0.049

<sup>a</sup> 1 mdyn/Å=10 mN m<sup>-1</sup>. <sup>b</sup> 1 mdyn Å=1a J.

straightforward. There are only six normal modes of eighteen which will not fulfill the general rule that not less than 66 % of the potential energy should be associated with a single type of internal coordinate to warrant classification as a localized group frequency. All of these six modes are, typically for esters, due to the vibrations in the skeletal ester framework. On the contrary, the normal modes of the deuteriated species are much less "pure" (Tables 5-7).

Let us examine these skeletal vibrations of chloromethyl formate and its deuterium derivatives more precisely. The so-called "ester peak" is typically a very strong band in the IR spectra of formate esters at the region 1 250-1 000 cm<sup>-1</sup>.<sup>14</sup> The contributions of the potential energy distributions available in literature<sup>5-9</sup> show clearly, that due to the strong couplings, it is difficult to

assign this band to any stretching vibration between two atoms. On the basis of the high intensity of the "ester peak" the commonly used assignment, asymmetric C-O-C stretching vibration, is warranted because the change of the dipole moment is the highest during an asymmetric vibration. The reverse is true for the other strongly coupled skeletal vibration assigned in the literature to the symmetric C-O-C stretching mode. This weak band is located at the region 1 000-800 cm<sup>-1</sup> in the IR spectra of formate esters.<sup>14</sup>

By examining the contributions of the potential energy distributions (Table 4) we can conclude that for chloromethyl formate the "ester peak" is a combination of the C-O and O-C stretching and O=C-O bending modes. Deuteriation of the formyl and/or alkyl hydrogens has no signifi-

Table 4. Observed and calculated wavenumbers ( $\text{cm}^{-1}$ ), potential energy distribution (PED) and assignment for  $\text{HCOOCH}_2\text{Cl}$ .

(obs)	(calc)	PED	assignment
2987	2989	99(5)	symm. $\nu(\text{CH}_2)$
2960	2959	98(2)	$\nu(\text{CH})$
1740	1739	66(1)+23(8)+6(3)	$\nu(\text{C}=\text{O})$
1439	1432	74(12)+21(11)	$\delta(\text{CH}_2)$
1370	1374	72(8)+23(1)	$\delta(\text{CH})$
1336	1346	70(11)+20(12)	w( $\text{CH}_2$ )
1120	1115	39(3)+28(7)+26(4)	as. $\nu(\text{C}-\text{O}-\text{C})$
937	945	45(4)+26(3)+18(13)+8(10)	symm. $\nu(\text{C}-\text{O}-\text{C})$
750	759	60(6)+18(13)+14(10)+5(4)	$\nu(\text{C}-\text{Cl})$
720	702	65(7)+12(4)+9(10)+6(3)	$\delta(\text{O}=\text{C}-\text{O})$
420	406	57(13)+23(6)+15(3)	$\delta(\text{O}-\text{C}-\text{Cl})$
240	241	69(10)+15(13)+10(6)	$\delta(\text{C}-\text{O}-\text{C})$
3061	3062	100(15)	as. $\nu(\text{CH}_2)$
1261	1256	85(16)+8(17)+5(18)	$\tau(\text{CH}_2)$
1049	1049	76(18)+15(16)+7(17)	$\gamma(\text{CH})$
1003	973	69(17)+16(18)+9(16)	$\rho(\text{CH}_2)$
325	344	62(19)+19(20)+15(17)	$\tau(\text{C}-\text{O})$
68	83	66(20)+14(17)+9(16)+9(19)	$\tau(\text{O}-\text{C})$

Table 5. Observed and calculated wavenumbers ( $\text{cm}^{-1}$ ), potential energy distribution (PED) and assignment for  $\text{DCOOCH}_2\text{Cl}$ .

(obs)	(calc)	PED	assignment
2989	2989	99(5)	symm. $\nu(\text{CH}_2)$
2236	2195	91(2)+6(1)	$\nu(\text{CD})$
1694	1676	74(1)+9(3)+9(8)+5(2)	$\nu(\text{C}=\text{O})$
1438	1432	74(12)+21(11)	$\delta(\text{CH}_2)$
1333	1346	71(11)+21(12)	w( $\text{CH}_2$ )
1108	1109	39(4)+30(3)+24(7)	as. $\nu(\text{C}-\text{O}-\text{C})$
1052	1070	58(8)+20(3)+8(1)+5(4)+5(7)	$\delta(\text{CD})$
886	900	32(4)+21(3)+20(8)+18(13)+7(10)	symm. $\nu(\text{C}-\text{O}-\text{C})$
745	759	63(6)+17(13)+13(10)+5(4)	$\nu(\text{C}-\text{Cl})$
720	695	66(7)+13(4)+10(10)+5(3)	$\delta(\text{O}=\text{C}-\text{O})$
410	402	55(13)+24(6)+15(3)	$\delta(\text{O}-\text{C}-\text{Cl})$
200	239	68(10)+16(13)+10(6)	$\delta(\text{C}-\text{O}-\text{C})$
3062	3062	100(15)	as. $\nu(\text{CH}_2)$
1257	1253	87(16)+8(17)	$\tau(\text{CH}_2)$
1000	997	62(17)+21(16)+9(18)+5(20)	$\rho(\text{CH}_2)$
866	866	84(18)+14(17)	$\gamma(\text{CD})$
318	316	65(19)+20(18)+14(17)	$\tau(\text{C}-\text{O})$
a	83	67(20)+14(17)+9(16)+9(19)	$\tau(\text{O}-\text{C})$

<sup>a</sup> Not detected.

cant effect on the couplings of the asymmetric C–O–C stretching mode. The couplings of the symmetric C–O–C stretching mode, on the other hand, seem to be very sensitive both to the

alkyl group and to the deuteration of the formyl hydrogen. In the case of chloromethyl formate the C–O–C symmetric stretching vibration is coupled to C–O–C and O–C–Cl bending

Table 6. Observed and calculated wavenumbers ( $\text{cm}^{-1}$ ), potential energy distribution (PED) and assignment for  $\text{HCOOCD}_2\text{Cl}$ .

(obs)	(calc)	PED	assignment
2985	2959	99(2)	$\nu(\text{CH})$
2205	2167	98(5)	symm. $\nu(\text{CD}_2)$
1735	1738	66(1)+23(8)+6(3)	$\nu(\text{C}=\text{O})$
1372	1373	74(8)+23(1)	$\delta(\text{CH})$
1150	1115	39(3)+29(7)+25(4)	as. $\nu(\text{C}-\text{O}-\text{C})$
1076	1096	69(11)+10(6)+9(4)+5(12)	w( $\text{CD}_2$ )
1005	1040	69(12)+8(13)+6(6)+5(11)	$\delta(\text{CD}_2)$
892	921	39(4)+26(3)+14(13)+9(10)+8(12)	symm. $\nu(\text{C}-\text{O}-\text{C})$
698	696	55(7)+23(6)+8(4)+6(3)	$\delta(\text{O}=\text{C}-\text{O})$
680	685	35(6)+16(7)+15(10)+15(13)+10(4)+9(11)	$\nu(\text{C}-\text{Cl})$
408	404	57(13)+23(6)+15(3)	$\delta(\text{O}-\text{C}-\text{Cl})$
235	235	69(10)+15(13)+9(6)	$\delta(\text{C}-\text{O}-\text{C})$
2305	2259	99(15)	as. $\nu(\text{CD}_2)$
1020	1073	85(18)+7(16)+5(17)	$\gamma(\text{CH})$
983	930	51(16)+22(17)+20(18)+5(19)	$\tau(\text{CD}_2)$
800	768	50(17)+45(16)	$\rho(\text{CD}_2)$
293	316	55(19)+20(17)+19(20)+5(16)	$\tau(\text{C}-\text{O})$
a	78	66(20)+13(17)+11(19)+9(16)	$\tau(\text{O}-\text{C})$

<sup>a</sup> Not detected.

Table 7. Observed and calculated wavenumbers ( $\text{cm}^{-1}$ ), potential energy distribution (PED) and assignment for  $\text{DCOOCD}_2\text{C}$ .

(obs)	(calc)	PED	assignment
2238	2195	89(2)+6(1)	$\nu(\text{CD})$
2210	2166	96(5)	symm. $\nu(\text{CD}_2)$
1692	1676	74(1)+9(3)+9(8)+5(2)	$\nu(\text{C}=\text{O})$
1145	1110	42(4)+24(3)+20(7)+6(11)+5(12)	as. $\nu(\text{C}-\text{O}-\text{C})$
1083	1094	66(11)+10(6)+6(7)+5(3)	w( $\text{CD}_2$ )
1038	1073	47(8)+21(3)+8(1)+6(12)+5(7)+5(13)	$\delta(\text{CD})$
1005	1030	71(12)+13(8)+5(6)	$\delta(\text{CD}_2)$
870	884	30(4)+22(3)+18(8)+16(13)+9(10)	symm. $\nu(\text{C}-\text{O}-\text{C})$
698	693	48(6)+32(7)+7(13)	$\nu(\text{C}-\text{Cl})$
680	681	36(7)+16(6)+16(10)+14(4)+9(13)+6(11)	$\delta(\text{O}=\text{C}-\text{O})$
413	400	55(13)+23(6)+15(3)	$\delta(\text{O}-\text{C}-\text{Cl})$
200	233	68(10)+16(13)+9(6)	$\delta(\text{C}-\text{O}-\text{C})$
2310	2259	99(15)	as. $\nu(\text{CD}_2)$
971	1000	37(16)+33(18)+21(17)	$\tau(\text{CD}_2)$
856	845	63(18)+32(16)	$\gamma(\text{CD})$
800	764	56(17)+35(16)	$\rho(\text{CD}_2)$
290	290	57(19)+19(17)+18(20)+5(16)	$\tau(\text{C}-\text{O})$
a	78	66(29)+13(17)+10(19)+9(16)	$\tau(\text{O}-\text{C})$

<sup>a</sup> Not detected.

vibrations with the percentage of 8 and 18 %, respectively. This is in agreement with the studies of methyl formate and *tert*-butyl formate taking into account the additional coupling in case of

chloromethyl formate due to the C-Cl bond.

An interesting phenomenon is observed in the contributions of the potential energy distributions of the symmetric C-O-C stretching vibra-

tion when the formyl hydrogen of the formate esters is replaced by a deuterium atom. It is seen from Tables 5 and 7 that there is an additional coupling with the CD in-plane bending mode compared with the non-deuteriated compounds. Due to this coupling, the frequency of the symmetric (C–O–C) stretching mode is shifted to lower wavenumbers. On the other hand, the phenomenon, described above, clarifies the frequency shift of the (C=O) stretching mode of deuterioformates to lower frequencies (Tables 5 and 7) because the strong coupling between the  $\delta(\text{CH})$  mode and the  $\nu(\text{C}=\text{O})$  mode fails in the case of the deuterioformates.

The two intense bands in the IR spectra of chloromethyl formate and its deuterium derivatives at the region 750–680  $\text{cm}^{-1}$  are due to the C–Cl stretching and O=C–O bending vibrations. Both of these vibrations are highly mixed and have a marked frequency shift upon deuteration of the hydrogen atoms in the chloromethyl group. It is seen from Tables 4 and 5 that these modes are not coupled to each other in the case of the compounds  $\text{HCOOCH}_2\text{Cl}$  and  $\text{DCOOCH}_2\text{Cl}$  but a strong coupling exists between these modes in the case of the compounds  $\text{HCOOCD}_2\text{Cl}$  and  $\text{DCO OCD}_2\text{Cl}$  (Tables 6 and 7). From this change in the couplings it follows that the frequencies at 750–745  $\text{cm}^{-1}$  [ $\nu(\text{C}-\text{Cl})$ ] for the compounds  $\text{HCOOCH}_2\text{Cl}$  and  $\text{DCOOCH}_2\text{Cl}$  are shifted to 698  $\text{cm}^{-1}$  [ $\delta(\text{O}=\text{C}-\text{O})$ ] and 680  $\text{cm}^{-1}$  [ $\nu(\text{C}-\text{Cl})$ ] in the case of the compounds  $\text{HCOOCD}_2\text{Cl}$  and  $\text{DCO OCD}_2\text{Cl}$ , respectively. It is seen, however, from the contributions in the potential energy distributions that these two modes for the former compounds are so delocalized that it is somewhat arbitrary to assign them to any group frequency.

The O–C–Cl bending vibration is a low frequency band located at the region 420–410  $\text{cm}^{-1}$  for all the compounds investigated in this work. The constant place of this band is an indication on the unchanged couplings upon deuteration. The same is true for the C–O torsional and C–O–C bending modes located in the IR spectra at the region 325–290 and 240–200  $\text{cm}^{-1}$ , respectively. It has to be pointed out, that this assignment, supported by normal coordinate calculations for the  $\delta(\text{O}-\text{C}-\text{Cl})$ ,  $\delta(\text{C}-\text{O}-\text{C})$  and  $\tau(\text{C}-\text{O})$  modes, differs from the tentative assignment, presented in Ref. 1. There is, however, no reason to doubt the results of the

normal coordinate calculations, because the assignment in Ref. 1 was made by analogy conclusions with related esters not including chlorine atoms in the skeletal ester framework. As was mentioned in the beginning of this chapter, all the other bands in the IR spectra of chloromethyl formate are localized group frequencies and do not need any discussion.

The agreement of the observed and calculated frequencies (Table 4) is quite satisfactory for the compound  $\text{HCOOCH}_2\text{Cl}$ . The bigger differences in the case of the deuteriated species (Tables 5–7) are probably an indication of the anharmonicity during the vibrations of these compounds.<sup>15</sup>

After this manuscript was finished, the article "Normal Coordinate Analysis & Thermodynamic Functions of Chloromethyl Formate" by R. Prasad<sup>16</sup> became available to us.

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