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## Vibrational spectra of methyl formate and deuterated analogs

**Abstract**—Infrared spectra of  $\text{HCOOCH}_3$ ,  $\text{DCOOCH}_3$  and  $\text{HCOOCD}_3$  have been investigated in the gas phase and in solution from 250 to  $3600\text{ cm}^{-1}$  under moderate resolution. All observed bands except some very weak ones were assigned to fundamental modes, overtones and combinations on the basis of  $C_s$  symmetry and a *cis* configuration. Some modifications are suggested in previous assignments for  $\text{HCOOCH}_3$ . All  $\alpha'$  fundamentals were observed and the assignments checked with the product rule. Some  $\alpha''$  modes appear to be very weak. The results are briefly discussed in the light of recent proposals for distinguishing group and framework vibrations.

WHILE the vibrational spectra of a great number of simple organic molecules, including carboxylic acids [1, 2] have by now been investigated in considerable detail, relatively little has been reported on simple esters. Because of their low symmetry and considerable number of fundamentals, the spectra of even the very simplest esters are difficult to interpret. WILMSHURST has proposed a vibrational assignment for methyl formate and methyl acetate [3]. NOLIN and JONES studied deuterium substituted methyl acetates, but were not able to arrive at a complete interpretation [4]. In conjunction with questions on the validity and limitations of the characteristic frequency concept the spectra of simple esters are of some interest because a number of "groups" such as  $\text{CH}_3$ ,  $\text{CHO}$  and  $\text{COC}$  are directly coupled to each other. This communication discusses the vibrational spectra of methyl formate and deuterium substituted analogs. A complete vibrational assignment is attempted.

### INSTRUMENTATION AND SAMPLES

The spectra of  $\text{HCOOCH}_3$ ,  $\text{DCOOCH}_3$  and  $\text{HCOOCD}_3$  from 250 to  $3600\text{ cm}^{-1}$  were obtained with a Beckman IR-7 prism-grating instrument.† A redistilled sample of commercial  $\text{HCOOCH}_3$  was employed. The spectrum was in very good agreement with published data [3] and is therefore not reproduced. Small samples of the deuterated materials were obtained from Merck and Co. Ltd. (Montreal, Canada)† and used without further purification. No isotopic impurities could be detected by infrared methods.

\* Eastern Utilization Research and Development Division, Agriculture Research Service, U.S. Department of Agriculture.

† Mention of specific companies and/or products does not constitute an endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

[1] R. C. MILLIKAN and K. S. PITZER, *J. Chem. Phys.* **27**, 1305 (1957).

[2] R. C. MILLIKAN and K. S. PITZER, *J. Am. Chem. Soc.* **80**, 3515 (1958).

[3] J. K. WILMSHURST, *J. Mol. Spectrosc.* **1**, 201 (1957).

[4] B. NOLIN and R. N. JONES, *Can. J. Chem.* **34**, 1382 (1956).

## Structural considerations

The structure of methyl formate has been most recently determined by CURL [5] from microwave measurements. The molecule has a planar structure with the double bonded oxygen and the methyl group *cis* to one another, in agreement with earlier infrared [3] and electron diffraction studies [6]. Eighteen fundamental vibrations are divided into twelve *a'* and six *a''* modes, all fundamentals being both infrared and Raman active. Based on the molecular parameters given by CURL [5], the Badger and Zumwalt symmetry parameters  $\rho$  and  $S$  [7] assume the following values:  $\text{HCOOCH}_3$ ,  $\rho = 2.13$ ,  $S = -0.79$ ;  $\text{DCOOCH}_3$ ,  $\rho = 1.97$ ,  $S = -0.75$ ;  $\text{HCOOCD}_3$ ,  $\rho = 2.06$ ,  $S = -0.79$ . The band contours of the three isotopic molecules should within this approximation [7] be quite similar. Type-*A* bands should have a *PQR* structure with a *P-R* separation of about  $20 \text{ cm}^{-1}$ , type-*B* bands a doublet structure with approximately the same separation. Type-*C* bands should exhibit a *PQR* structure with a strong *Q* branch and relatively flat *P* and *R* branches, the latter having ill-defined maxima separated by approximately  $35 \text{ cm}^{-1}$ . The twelve *a'* fundamentals should give rise to type-*A*, type-*B* or type-*AB* hybrid bands. The six *a''* fundamentals should have a type-*C* contour. Inspection of the observed spectra revealed that bands assigned to *a'* modes (see below) generally had the required contours. *P*- and *R*-branches of type-*C* bands were generally very flat; only one type-*C* band could be found for the three molecules with a clearly distinguishable *PQR* structure ( $1032 \text{ cm}^{-1}$ ,  $\text{HCOOCH}_3$ ). In  $\text{DCOOCH}_3$  and  $\text{HCOOCD}_3$  the *a''* fundamentals appeared to exhibit only a sharp *Q* branch.

The spectra of  $\text{DCOOCH}_3$  and  $\text{HCOOCD}_3$  are presented in Figs. 1 and 2. Assignments are given in Tables 1 and 2. The fundamentals are collected in Table 3. Fig. 3 presents a schematic correlation of the fundamental modes of  $\text{HCOOCH}_3$ ,  $\text{DCOOCH}_3$  and  $\text{HCOOCD}_3$  in the crowded spectral region below  $1500 \text{ cm}^{-1}$ .

 Table 1. Infrared spectrum of  $\text{DCOOCH}_3$ 

Solution ( $\text{cm}^{-1}$ )	Gas ( $\text{cm}^{-1}$ )	Int.	Type	Assignment
3585	—	vw		$1431 + 2214 = 3645 (1)^*$
3489	3511 3501 3490	vw		
3418	3453 3445 3443 3433	w		$2\nu_{\text{C=O}}$ $\nu_{\text{C=O}} + 304 + 1441$ $2(304 + 1441)$
3378	~3413 ~3400 ~3387	vw		

 [5] R. F. CURL, Jr., *J. Chem. Phys.* **30**, 1529 (1959).

 [6] J. M. O'GORMAN, W. SHAND, Jr. and V. SCHOMAKER, *J. Am. Chem. Soc.* **72**, 4222 (1950).

 [7] R. M. BADGER and L. R. ZUMWALT, *J. Chem. Phys.* **6**, 711 (1938).

## Vibrational spectra of methyl formate and deuterated analogs

Table 1 (cont'd)

Solution ( $\text{cm}^{-1}$ )	Gas ( $\text{cm}^{-1}$ )	Int.	Type	Assignment
3034	3050 } 3041 } 3029 }	s	A	$\alpha'$ fundamental
3005	3011 3007 (Q)	vw s	C	$\alpha''$ fundamental
2957	2979 } 2967 } 2956 }	s	A	$\alpha'$ fundamental
2910	~2920	w		$2 \times 1468 = 2936$
2838	2858 } 2846 } 2840 }	w		$2 \times 1441 = 2882$
2456	2484 } 2473 } 2462 }	vw		$1441 + 1048 = 2489$
2420	2433 } 2423 } 2411 }	w		$2 \times 1213 = 2426$
2355	~2373 } ~2358 }	w		$1213 + 1157 = 2370$
2296		vw		$2 \times 1149 = 2298$ (1)
2257	2269 } 2262 }	w		$1213 + 1048 = 2261$
	—			
2214	2225 } ~2208 }	s	B	$\alpha'$ fundamental
2189	~2203 } 2188 }	w		$1447 + 762 = 2209$ $1157 + 1048 = 2205$
2086	2100 } 2090 } 2081 }	w		$2 \times 1048 = 2096$ $1213 + 878 = 2091$
2017	2040 } 2031 } 2022 }	w		$1157 + 878 = 2035$
1970	1983 } 1972 } 1960 }	w		$1213 + 762 = 1975$

Table I (contd)

Solution ( $\text{cm}^{-1}$ )	Gas ( $\text{cm}^{-1}$ )	Int.	Type	Assignment
1913	1925) 1912)	w		1157 + 762 = 1919 1048 + 878 = 1926
1806	~1820) ~1810) —)	vw		1048 + 762 = 1810
1743	1761) 1751) ~1740)	vs	A	$\alpha'$ fundamental ( $\nu_{\text{C}=\text{O}}$ ) 1441 + 304 = 1745
1699	1724) 1712) 1701)	vs	A	
1633	~1652) 1640) ~1625)	vw		878 + 762 = 1640
~1460	1480) 1468) ~1459)	m	A	$\alpha'$ fundamental
	1456) ~1443)	m		1157 + 304 = 1461
~1440	1447 (Q)	m	C?	$\alpha''$ fundamental
1431	—) 1441) 1431)	m sh	AB?	$\alpha'$ fundamental
1209	1224) 1213) 1201)	vs	A	$\alpha'$ fundamental
1149	1164) 1150)	vs	B	$\alpha'$ fundamental
1045	1059) 1048) ~1039)	m	A	$\alpha'$ fundamental
~1020	1033 (Q)	m	C	$\alpha''$ fundamental
871	888) 870)	s	B	$\alpha'$ fundamental
760	753) 772)	m	B	$\alpha'$ fundamental
	432	vw		304 + 130 = 434
300	~ 314) ~ 304) ~ 290)	s	?	$\alpha'$ fundamental $\alpha''$ fundamental

\* Summation bands marked (1) are calculated from solution spectra.

Vibrational spectra of methyl formate and deuterated analogs

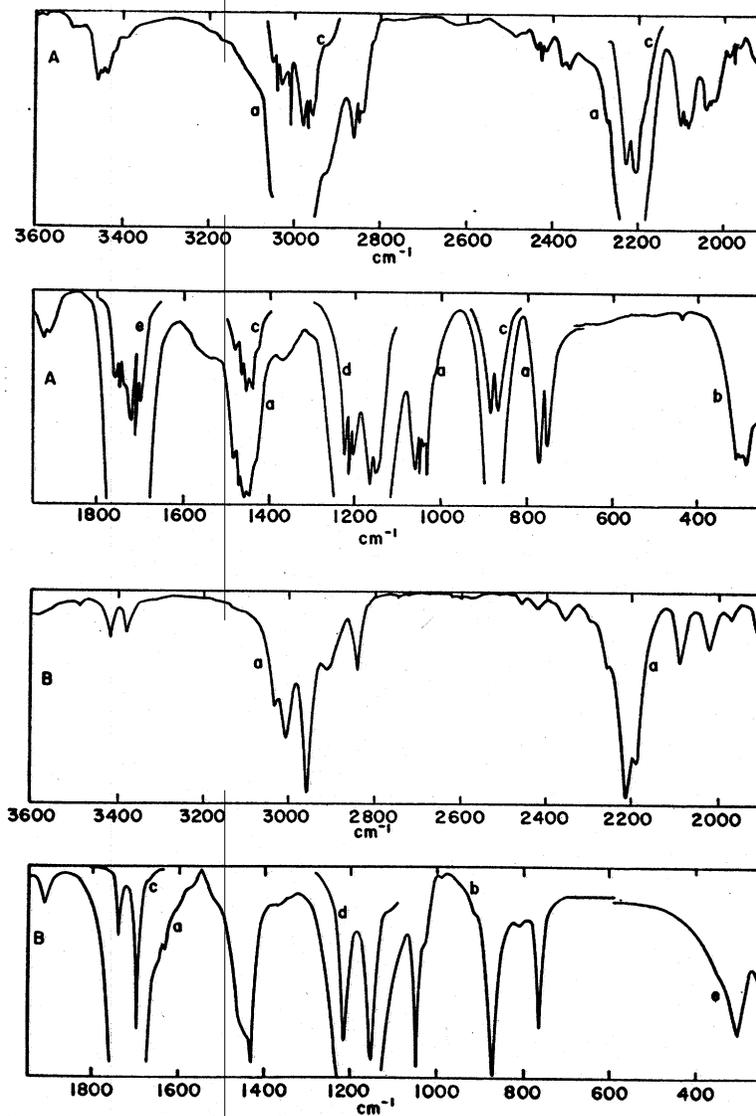


Fig. 1. Infrared spectrum of DCOOCH<sub>3</sub>

A. Vapor in 10 cm cell. Pressure: a, 200 mm; b, 70 mm; c, 30 mm; d, 5 mm; e, 2 mm.

B. Solution in CCl<sub>4</sub> (3600–1100 cm<sup>-1</sup>, 600–250 cm<sup>-1</sup>) and CS<sub>2</sub> (1100–600 cm<sup>-1</sup>). Concentration: a, 1:25; b, 1:50; c, 1:200; d, 1:300 in 0.4 mm cell; e, ca. 1:10 in 0.1 mm cell.

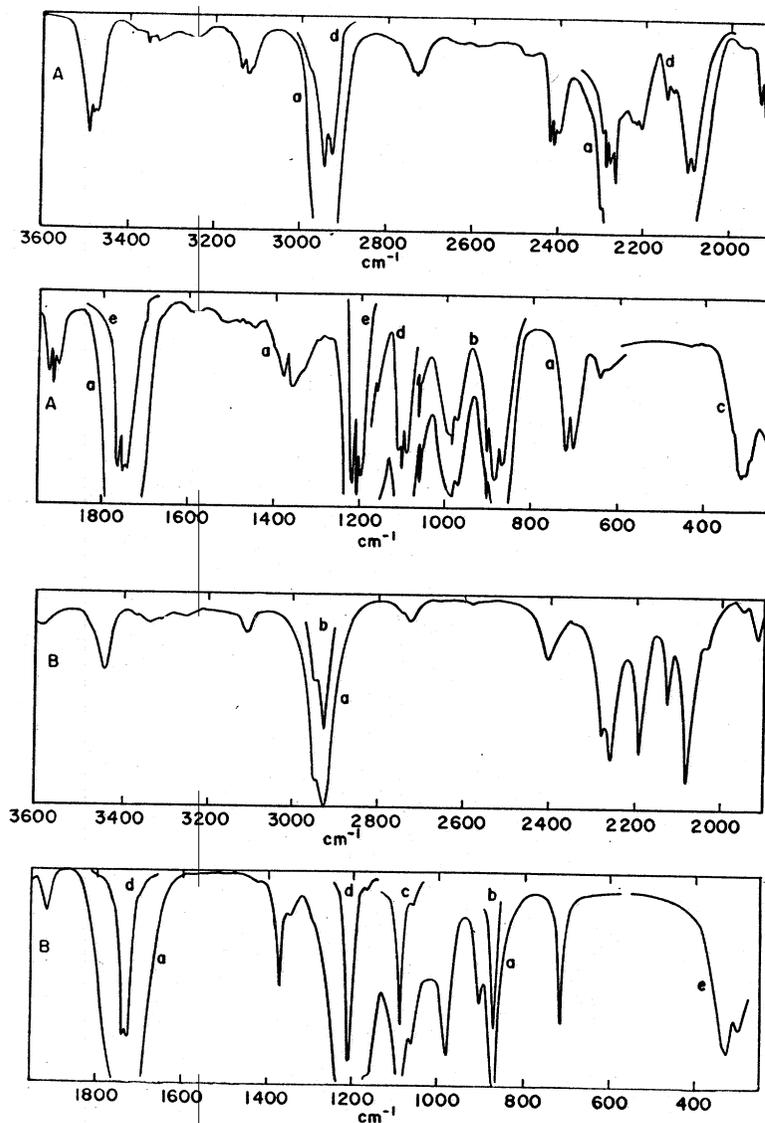


Fig. 2. Infrared spectrum of  $\text{HCOOCD}_3$

- A. Vapor in 10 cm cell. Pressure: a, 180 mm; b, 75 mm; c, 50 mm; d, 25 mm; e, 5 mm.
- B. Solution in  $\text{CCl}_4$  ( $3600\text{--}950\text{ cm}^{-1}$ ;  $600\text{--}250\text{ cm}^{-1}$ ) and  $\text{CS}_2$  ( $950\text{--}600\text{ cm}^{-1}$ ). Concentration: a, 1:16; b, 1:50; c, 1:100; d, 1:300 in 0.4 mm cell; e, ca. 1:10 in 0.1 mm cell.

Table 2. Infrared spectrum of HCOOCD<sub>3</sub>

Solution (cm <sup>-1</sup> )	Gas (cm <sup>-1</sup> )	Int.	Type	Assignment
3442	3493) 3477)	w		2 × 1754 = 3508
3360	~3360	vw		1102 + 2258 = 3360
3335	~3333	vw		1060 + 2284 = 3344
~3105	3136) 3120)	w		2258 + 877 = 3135
2947	~2975	vw		2258 + 714 = 2972
2926	2940) 2931) 2921)	s	AB	α' fundamental
2726	2734) 2727) 2717)	w		2 × 1368 = 2736 1754 + 985 = 2739
2578	2588) 2577) 2568)	vw		1368 + 1210 = 2578
2460	~2470	vw		1102 + 1368 = 2470
2404	2414) 2403) 2393)	w		2 × 1210 = 2420
2279	2291) 2284) 2272)	s	A	α' fundamental
2258	2258 (	s	C	α" fundamental
2193	2221) 2214) 2201)	m		2 × 1102 = 2204 1368 + 877 = 2245
2127	2143) 2135) 2127)	m		1102 + 1063 = 2165
2082	2093) 2081)	s	B	α' fundamental
~2036	—	vw		1736 + 300 = 2036 (1)*
1950	1978) 1971) 1960)	vw		2 × 985 = 1970

Table 2 (contd)

Solution ( $\text{cm}^{-1}$ )	Gas ( $\text{cm}^{-1}$ )	Int.	Type	Assignment
1916	1928 1918 1908	w		$1210 + 714 = 1924$
1736	1766 1754	vs	AB	$a'$ fundamental $2 \times 877 = 1754$
1726	~1747 1743			
1425	—	vw		$2 \times 712 = 1424$ (1)*
1374	1378 1358	m	B	$a'$ fundamental
1347	—	vw		$1057 + 300 = 1357$ (1)*
1208	1220 1210 1197	vs	A	$a'$ fundamental
1162	1160	vw		$877 + 305 = 1182?$
1086	1109 1102 1090	s	A	$a'$ fundamental
1057	~1075 ~1055	m	B?	$a'$ fundamental
	1060 (Q)	m	C	$a''$ fundamental
979	994 985 973	m	AB	$a'$ fundamental
900	906 (Q)	w	C	$a''$ fundamental
869	884 869	s	B	$a'$ fundamental
712	721 706	m	B	$a'$ fundamental
	638	w		$2 \times 324 = 648$ (1)*
324	~ 330 ~ 310	s	?	$a''$ fundamental $a'$ fundamental
300	~ 298 ~ 287			

\* Summation bands marked (1) are calculated from solution spectra.

## Vibrational spectra of methyl formate and deuterated analogs

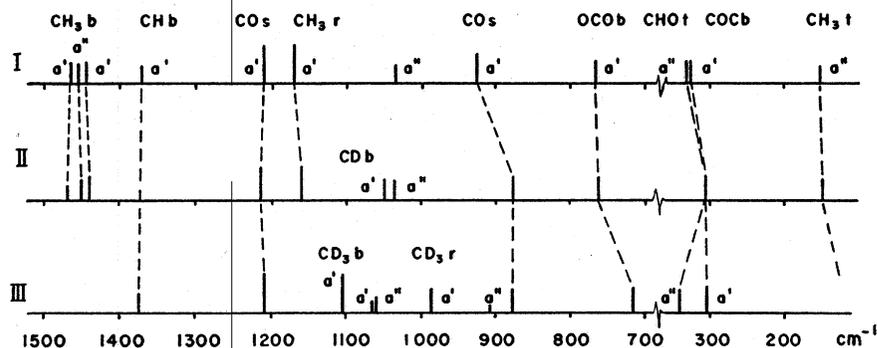


Fig. 3. Correlation of fundamental frequencies below  $1500\text{ cm}^{-1}$ .  
I,  $\text{HCOOCH}_3$ ; II,  $\text{DCOOCH}_3$ ; III,  $\text{HCOOCD}_3$ .

Table 3. Collected fundamentals

$\text{HCOOCH}_3$				$\text{DCOOCH}_3$			$\text{HCOOCD}_3$		
$\nu$	( $\text{cm}^{-1}$ )	Type	Approximate description*	( $\text{cm}^{-1}$ )	Type	$\nu/\nu'$	( $\text{cm}^{-1}$ )	Type	$\nu/\nu''$
$\nu_1$	3045	A	$\text{CH}_3(\text{CD}_3)$ a.s.	3041	A	1.00	2284	A	1.33
$\nu_2$	2969	AB	$\text{CH}_3(\text{CD}_3)$ s.s.	2967	A	1.00	2087	B	1.42
$\nu_3$	2943	AB	$\text{CH}(\text{CD})$ s.	2216	B	1.33	2931	AB	1.00
$\nu_4$	1754	AB	$\text{C}=\text{O}$ s.	(1732)†		(1.01)	1754	AB	1.00
$\nu_5$	1465	A	$\text{CH}_3(\text{CD}_3)$ a.b.	1468	A	1.00	1063	B?	1.38
$\nu_6$	1445	?	$\text{CH}_3(\text{CD}_3)$ s.b.	~1441	AB?	1.00	1102	A	1.31
$\nu_7$	1371	B	$\text{CH}(\text{CD})$ b.	1048	A	1.31	1368	B	1.00
$\nu_8$	1207	A	$\text{C}-\text{O}$ s.	1213	A	0.99	1210	A	1.00
$\nu_9$	1168	AB	$\text{CH}_3(\text{CD}_3)$ r.	1157	B	1.01	985	AB	1.19
$\nu_{10}$	925	B	$\text{C}-\text{O}$ s.	878	B	1.05	877	B	1.05
$\nu_{11}$	767	B	$\text{OCO}$ b.	762	B	1.01	714	B	1.07
$\nu_{12}$	325	A?	$\text{COC}$ b.	304	?	1.07	305	?	1.07
$a''$									
$\nu_{13}$	3012	C?	$\text{CH}_3(\text{CD}_3)$ a.s.	3007	(Q)	1.00	2258	(Q)	1.33
$\nu_{14}$	1454	(Q)	$\text{CH}_3(\text{CD}_3)$ a.b.	1447	(Q)	1.00	1060	(Q)	1.37
$\nu_{15}$	—		$\text{CH}_3(\text{CD}_3)$ r.	1033	(C)		—		
$\nu_{16}$	1032	C	$\text{CH}(\text{CD})$ b.	—			906	(Q)	
$\nu_{17}$	341§		skel. t.	(~300)			324‡		
$\nu_{18}$	130**		$\text{CH}_3(\text{CD}_3)$ t.	(130)††			—		

\* a.s., asym. str.; s.s., sym. str.; a.b., asym. bending; s.b., sym. bending; r., rocking; t., torsion.

† Estimated from resonance doublet.

‡ Solution value.

§ Solid solution in  $\text{N}_2$  matrix [12].

\*\* Ref. [13].

†† Estimated from combination frequency. (Q) Only Q branch observed.

### $a'$ fundamentals

Nine out of twelve  $a'$  fundamentals are assigned relatively easily for all three isotopic molecules on the basis of band contours and by comparing the spectra of  $\text{HCOOCH}_3$ ,  $\text{DCOOCH}_3$  and  $\text{HCOOCD}_3$ . These are:  $\text{CH}_3(\text{CD}_3)$  asym. str.,  $\text{CH}_3(\text{CD}_3)$  sym. str.,  $\text{CH}(\text{CD})$  str.,  $\text{C}=\text{O}$  str.,  $\text{CH}(\text{CD})$  bend.,  $\text{OHC}-\text{O}$  str.,  $\text{O}-\text{CH}_3(\text{O}-\text{CD}_3)$  str.,  $\text{OCO}$  bend. and  $\text{COC}$  bend. ( $\nu_1, \nu_2, \nu_3, \nu_4, \nu_7, \nu_8, \nu_{10}, \nu_{11}, \nu_{12}$  of  $\text{HCOOCH}_3$ ). Three of these modes—the two  $a'$   $\text{CD}_3$  stretching fundamentals of  $\text{HCOOCD}_3$  and the  $\text{C}=\text{O}$  stretching mode of  $\text{DCOOCH}_3$ —show Fermi resonance with primary combinations.

The strongest bands in the  $\text{CD}_3$  stretching region are taken to be essentially the  $a'$  fundamentals. The two extremely strong bands of  $\text{DCOOCH}_3$  with  $Q$  branches at 1751 and 1712  $\text{cm}^{-1}$  are assigned to the  $\text{C}=\text{O}$  stretching mode in resonance with the combination band  $1441 + 304$ .

$\text{CH}_3$  and  $\text{CD}_3$  bending modes ( $\nu_5$  and  $\nu_6$  of  $\text{HCOOCH}_3$ ) present some difficulties in both  $\text{DCOOCH}_3$  and  $\text{HCOOCD}_3$  because the two  $a'$  fundamentals and the  $a''$  fundamental overlap. In the vapor spectrum of  $\text{DCOOCH}_3$  a cluster of bands is observed around 1450  $\text{cm}^{-1}$ , probably involving two  $a'$  fundamentals, one  $a''$  fundamental and a combination band. The solution spectrum exhibits a strong band at 1431  $\text{cm}^{-1}$  with shoulders at ca. 1440 and 1460  $\text{cm}^{-1}$ . The highest vapor band, which seems to have a type- $A$  contour, is assigned to the  $a'$  asym.  $\text{CH}_3$  bending mode in analogy with  $\text{HCOOCH}_3$  [3]. The absorption maximum at 1441 and the shoulder at  $\sim 1431$   $\text{cm}^{-1}$  are assigned to the  $Q$ - and  $P$ -branches of the  $a'$  sym.  $\text{CH}_3$  bending mode. In gaseous  $\text{HCOOCD}_3$  a strong band with apparent  $PQR$  structure (1109, 1102, 1090  $\text{cm}^{-1}$ ) is assigned to the  $a'$  sym.  $\text{CD}_3$  bending mode, a weaker apparently type- $B$  band centering at 1063  $\text{cm}^{-1}$  (and overlapping with an  $a''$  mode) to the  $a'$  asym.  $\text{CD}_3$  bending mode. Corresponding solution bands are observed at 1086 and 1057  $\text{cm}^{-1}$ .

This leaves the in-plane methyl rocking modes. They are assigned to the very strong  $PQR$  band at 1168  $\text{cm}^{-1}$  in  $\text{HCOOCH}_3$ , the very strong doublet centering at 1157  $\text{cm}^{-1}$  in  $\text{DCOOCH}_3$  and the type- $AB$  band at 985  $\text{cm}^{-1}$  in  $\text{HCOOCD}_3$ . This mode has been previously assigned to a very weak solution band at  $\sim 1230$   $\text{cm}^{-1}$  for  $\text{HCOOCH}_3$  (not observed in the vapor spectrum or the Raman effect [8]), while the strong 1168  $\text{cm}^{-1}$  band was assigned to the  $a''$   $\text{CH}_3$  rock [3]. We suggest the alternate assignment for the following reasons:

(a) The 1168  $\text{cm}^{-1}$  band of  $\text{HCOOCH}_3$  has a  $P$ - $R$  separation of ca. 20  $\text{cm}^{-1}$  and a relatively weak  $Q$ -branch, thus resembling a type- $A$  or- $AB$  band more than a type- $C$  band (particularly if compared with the 1032  $\text{cm}^{-1}$   $a'$  fundamental).

(b) The corresponding band of  $\text{DCOOCH}_3$  (1157  $\text{cm}^{-1}$ , very strong) is clearly of type  $B$ .

(c) The very high intensity of the 1168  $\text{cm}^{-1}$  band of  $\text{HCOOCH}_3$  and the 1157  $\text{cm}^{-1}$  band of  $\text{DCOOCH}_3$  strongly suggest  $a'$  assignment. Both  $a'$  and  $a''$   $\text{O}-\text{CH}_3$  (and  $\text{O}-\text{CD}_3$ ) rocking modes are weak in methanol and deuterated analogs [9]. The  $a''$   $\text{OCH}_3$  rocking fundamental is apparently also weak in methyl acetate [3]. In methyl formate it would be expected that the  $a'$ , but not the  $a''$  mode is substantially intensified by the proximity of the extremely strong  $a'$   $\text{C}-\text{O}$  stretching fundamental at 1207  $\text{cm}^{-1}$ . Assignment of the  $a'$   $\text{C}-\text{O}$  stretching fundamental is not affected, but by reassigning the  $a'$   $\text{CH}_3$  rock to a lower-frequency band,  $\nu_8$  (by conventional numbering) becomes the  $\text{C}-\text{O}$  stretching mode and  $\nu_9$ , the rocking mode, as indicated in Table 3.

#### $a''$ fundamentals

Four out of six  $a''$  fundamentals are expected to absorb in the investigated spectral region:  $a''$   $\text{CH}_3(\text{CD}_3)$  stretching,  $a''$   $\text{CH}_3(\text{CD}_3)$  bending,  $a''$   $\text{CH}_3(\text{CD}_3)$  rocking

[8] K. W. F. KOHLRAUSCH, *Ramanspectren*, Edwards, Ann Arbor (1945).

[9] M. FALK and E. WHALLEY, *J. Chem. Phys.* **34**, 1554 (1961).

and  $a''$  CH(CD) bending. The assignment of the  $\text{CH}_3$  and  $\text{CD}_3$  stretching modes ( $\nu_{13}$ ) is straightforward. The vapor bands corresponding to this mode in  $\text{DCOOCH}_3$  and  $\text{HCOOCD}_3$  exhibit a strong, sharp  $Q$ -branch, but no  $P$ - or  $R$ -branches could be detected. Although this is partially caused by overlapping with  $a'$  fundamentals, it must be concluded that the  $P$ - and  $R$ -branches of these fundamentals are very shallow. The  $a''$   $\text{CH}_3(\text{CD}_3)$  bending fundamentals are assigned to sharp bands at  $1447\text{ cm}^{-1}$  and  $1060\text{ cm}^{-1}$  in the vapor spectra of  $\text{DCOOCH}_3$  and  $\text{HCOOCD}_3$ , respectively.

The  $a''$   $\text{CH}_3(\text{CD}_3)$  rocking and  $a''$  CH(CD) bending modes are difficult to assign with reasonable confidence. Modes of this nature frequently give rise to very weak infrared bands in related molecules. Thus, the  $a''$  methyl rocking bands are very weak in methanol and deuterated analogs [9]. Similarly,  $a''$  CH and CD bending modes are very weak (or absent) in formic acids [1, 2] and acetaldehyde [10]. A similar situation appears to prevail in methyl formate and its deuterated analogs. In the region where the two modes are expected to absorb,  $\text{HCOOCH}_3$  shows only one band ( $1032\text{ cm}^{-1}$ ) which unmistakably has a type- $C$  contour;  $\text{DCOOCH}_3$  has one band at  $1033\text{ cm}^{-1}$  with a sharp  $Q$ -branch and very flat  $P$ - and  $R$ -branches;  $\text{HCOOCD}_3$  has an unassigned band with a very sharp  $Q$ -branch at  $906\text{ cm}^{-1}$  and apparently flat  $P$ ,  $R$  branches. The proximity of the  $1032$  and  $1033\text{ cm}^{-1}$  bands of  $\text{HCOOCH}_3$  and  $\text{DCOOCH}_3$  strongly suggests that both be associated with the methyl group. On the other hand, the corresponding solution band of  $\text{HCOOCH}_3$  ( $1021\text{ cm}^{-1}$ ) shows a concentration dependence suggesting involvement in weak hydrogen bonding and assignment to the CHO group [3]. The  $a''$  CH bending mode of  $\text{HCOOH}$  also absorbs at  $1033\text{ cm}^{-1}$  [1] (while that of  $\text{OHCCH}_3$  has been assigned to  $763\text{ cm}^{-1}$  [10]. No positive conclusions regarding  $\nu_{15}$  and  $\nu_{16}$  appear possible at present, except that the number of expected fundamentals appears to be higher than the number of bands with appreciable intensity. The assignment suggested for  $\nu_{15}$  and  $\nu_{16}$  in Table 3—which assumes mixed modes—must be regarded as tentative. EL SAYED [11] has recently pointed out that resonance interaction between two coinciding fundamental levels with the same symmetry could result in only one absorption band being observed, if the unperturbed fundamentals are of equal intensity. If the intensities of the unperturbed fundamentals differ greatly, two bands of comparable intensity would result (similarly to Fermi-type resonance between an overtone and a fundamental).  $\nu_{15}$  and  $\nu_{16}$  of  $\text{HCOOCH}_3$  appear to approach the first extreme,  $\nu_8$  and  $\nu_9$  the second one.

Two low-frequency torsional modes ( $\nu_{17}$  and  $\nu_{18}$ ) remain. MIYAZAWA [12] has shown by low-temperature studies that in  $\text{HCOOCH}_3$  the  $a'$  COC bending mode and  $a''$  skeletal torsional mode are both located close to  $300\text{ cm}^{-1}$ , although only one band is observed in the vapor and solution spectra [3].  $\text{DCOOCH}_3$  also shows only one band in the vapor state and in solution, but the solution spectrum of  $\text{HCOOCD}_3$  exhibits bands at  $300$  and  $324\text{ cm}^{-1}$ . The envelopes of the  $300\text{ cm}^{-1}$  region vapor bands of all three analogs have very odd contours, indicating overlapping modes. Assignment of  $\nu_{17}$  around  $300\text{ cm}^{-1}$  is in agreement with an estimated barrier of ca.  $10\text{ kcal/mole}$  [12]. The torsional methyl group mode of  $\text{HCOOCH}_3$  ( $\nu_{18}$ ) has been

[10] J. C. EVANS and H. J. BERNSTEIN, *Can. J. Chem.* **34**, 1083 (1956).

[11] M. A. EL-SAYED, *J. Chem. Phys.* **37**, 680 (1962).

[12] T. MIYAZAWA, *Bull. Chem. Soc., Japan* **34**, 691 (1961).

located by FATELEY and MILLER at  $130\text{ cm}^{-1}$  [13]. A weak, sharp combination band of  $\text{DCOOCH}_3$  at  $432\text{ cm}^{-1}$  suggests that the corresponding mode of the latter also absorbs around  $130\text{ cm}^{-1}$  ( $304 + 130 = 434$ ).

## SUMMARY AND DISCUSSION

All  $a'$  fundamentals of  $\text{HCOOCH}_3$ ,  $\text{DCOOCH}_3$  and  $\text{HCOOCD}_3$  have been assigned to observed bands on the basis of changes produced by deuteration, and band envelopes, which are in general agreement with prediction [7]. Earlier assignments for  $\text{HCOOCH}_3$  [3] are confirmed with the previously discussed modification. Even though the number of fundamentals is high, the assignments are, in a sense, not quite as difficult as in the case of some smaller molecules, such as deuterated methanols [9]. Due to the higher moments of inertia the vapor bands under moderate resolution assume a more easily discernible shape. Some  $a''$  fundamentals remain unassigned because of apparently low intensity or because they absorb below the investigated spectral region. The following product rule values were obtained for the  $a'$  fundamentals by using molecular parameters given by CURL [5]:

	Calc.	Obs.
$\text{DCOOCH}_3/\text{HCOOCH}_3$	0.518	0.499
$\text{HCOOCD}_3/\text{HCOOCH}_3$	0.196	0.202

Because one  $a''$  fundamental is missing in each molecule, no meaningful application of isotope rules to these modes appears at present possible.

Table 3 suggests that  $\nu_1$  to  $\nu_8$ , and  $\nu_{13}$  and  $\nu_{14}$  could be approximately described as separable group vibrations, while lower frequency skeletal modes and methyl rocking modes are mixed. It is interesting in this connection to compare the frequencies assigned to internal methyl group modes (i.e. stretching and bending fundamentals of  $\text{CH}_3$  and  $\text{CD}_3$  groups) with frequencies calculated by KING and CRAWFORD [14, 15,] for a hypothetical standard molecule  $\text{Me}-\text{R}$  by using "representative values for group bond-lengths, bond-angles and force constants," and by taking R to be of infinite mass. By examining the terms in the vibrational equations and the group normal co-ordinates, and by applying the results to methyl halides and dimethyl acetylene, the authors conclude that all bending and stretching modes of  $\text{CH}_3$  and  $\text{CD}_3$  except the symmetric  $\text{CD}_3$  deformation (which is mixed with the  $\text{Me}-\text{R}$  stretch) are fairly insensitive to differences in the molecular framework, although small variations in group force constants (as defined by a relatively simple valence type force field) do occur. The establishment of such framework-independent modes is of obvious help in making assignments and, furthermore, permits additional factorization of the vibrational secular equation.

Table 4 compares the calculated standard frequencies [14, 15] with observed methyl group frequencies.

[13] W. G. FATELEY and F. A. MILLER, *Spectrochim. Acta* **17**, 857 (1961).

[14] W. T. KING and B. CRAWFORD, Jr., *J. Mol. Spectrosc.* **5**, 421 (1960).

[15] W. T. KING and B. CRAWFORD, Jr., *J. Mol. Spectrosc.* **8**, 58 (1962).

## Vibrational spectra of methyl formate and deuterated analogs

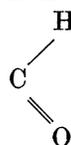
Table 4. Characteristic methyl group frequencies

Description	$\nu_0$ [14, 15]		Deviation (%)		
	R—CH <sub>3</sub>	R—CD <sub>3</sub>	HCOOCH <sub>3</sub>	DCOOCH <sub>3</sub>	HCOOCD <sub>3</sub>
Sym. str.	2932	2111	+1.3	+1.2	-1.2
Sym. bend.	1378	1066	+4.9	+4.6	+3.4
As. str.	3051	2275	{ -0.2*	{ -0.3	{ +0.4
			{ -1.3	{ -1.4	{ -0.7
As. bend.	1451	1039	{ +1.0	{ +1.2	{ +2.3
			{ +0.2	{ -0.3	{ +2.0

\* Upper value for  $a'$ , lower value for  $a''$  mode.

The deviations are generally remarkably small, the symmetric methyl deformation modes being a notable exception. The normal coordinates of the standard CH<sub>3</sub>—R molecule indicate that this mode is "internal" and that the frequency shift should be attributed mainly to changes in the group force constant covering this normal co-ordinate [14]. On this basis a group force constant  $H_\alpha + H_\beta + 2h_\beta = 1.08$  mdyn/Å (as compared to 0.99 for the standard molecule) can be calculated for the sym. methyl bending mode of HCOOCH<sub>3</sub> and DCOOCH<sub>3</sub>. The value of  $H_\beta$  and the symmetrical methyl group bending frequency are generally known to depend considerably on the nature (particularly the electronegativity) of the atom attached to the methyl group [15–17]. Other group force constants appear to be very close to the postulated values [14, 15].

Taking into account the loss of symmetry (as compared to Me—R), the considerable over-all number of fundamentals involving nearby bonds and absorbing close to the separable modes (particularly in HCOOCD<sub>3</sub>) and the possible variation of group force constants [14], the relatively good agreement in Table 4 appears somewhat surprising. If the six characteristic methyl group modes could indeed be factored out, the  $a'$  factor of the secular equation would involve eight and the  $a''$  four fundamentals. A qualitative preliminary investigation suggests that the


 group also exhibits separable modes which could conceivably be factored

from the secular equation. Caution, however, is evidently called for. Thus, for instance, the OD deformation mode of CD<sub>3</sub>OD contributes considerably to CD<sub>3</sub> deformation modes [18, 19] and it remains open to what extent the group vibration approach as defined [14] can be generalized, although the pattern observed in methyl formates appears by qualitative judgment to be favorable for such treatment.

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