THE EFFECTS OF CHAIN LENGTH ON THE INFRARED SPECTRA OF FATTY ACIDS AND METHYL ESTERS[1]

R. Norman Jones

The Division of Pure Chemistry, National Research Council, Ottawa, Canada

ABSTRACT

The infrared spectra of straight-chain fatty acids and their methyl esters have been measured over the range 1500–650 cm⁻¹ in carbon tetrachloride and carbon disulphide solution. The effects of the chain length on the peak intensities of the bands have been analyzed in relation to the group frequency assignments derived from comparative studies of deuterium-substituted methyl laurates.

INTRODUCTION

Comparison of the infrared spectrum of methyl laurate with the spectra of derivatives deuterated at specific sites (1) has shown that all of the 25 maxima and inflections between 3020 and 700 cm⁻¹ in the methyl laurate spectrum can be attributed to localized group vibrations. Twenty-one of these bands can be assigned, in good approximation, to one of four "characteristic zones", (*a*)–(*d*) of structure I, while the remaining four bands involve coupled modes extending over zones (*c*) and (*d*).
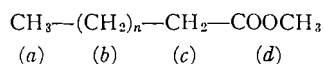
$$CH_3—(CH_2)_n—CH_2—COOCH_3$$
$$(a) \qquad (b) \qquad (c) \qquad (d)$$
$$I$$

If the group vibrations are strictly localized within the respective zones, it is easy to predict the effects of increasing the chain length. Bands associated with zones (*a*), (*c*), and (*d*) should be unaffected in position and intensity. For zone (*b*) the bands involving purely internal vibrations of each methylene group should intensify without wavenumber displacement, while for the modes that involve coupling between successive methylene groups, progressive wavenumber shifts may occur.

In order to examine these relationships, the spectra of the straight-chain methyl esters have been measured over the range $n = 0$ to $n = 15$ and the corresponding carboxylic acids (II) have been investigated between $n = 0$ and $n = 18$. The *n*-alkanes $(CH_3—(CH_2)_n—CH_3)$ have been studied previously from $n = 4$ to $n = 34$ under the same experimental conditions (2).
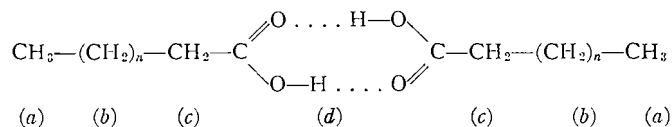
$$(a) \qquad (b) \qquad (c) \qquad (d) \qquad\qquad (c) \qquad (b) \qquad (a)$$
$$II$$

EXPERIMENTAL

The acids and esters were obtained from commercial sources. The lower-boiling esters were distilled at atmospheric pressure through a Todd column. Five percent of the third quarter of the distillate was collected, and the homogeneity was checked by vapor-phase chromatography. Propionic and butyric

acids were dried with anhydrous sodium sulphate and distilled at atmospheric pressure in the presence of potassium permanganate.

The spectra were measured from 1500 to 1300 cm^{-1} in carbon tetrachloride solution and from 1300 to 700 cm^{-1} in carbon disulphide solution on a Perkin–Elmer Model 112 spectrometer under conditions described previously (1, 2).

RESULTS

In the preceding paper, the bands and inflections in the spectrum of methyl laurate were designated alphabetically in order of decreasing wavenumber, and the same identification system will be used here. Since these measurements do not extend above 1500 cm^{-1} only bands H–Y are considered. Bands H–M, P–U, and Y are clearly recognizable in the spectra of all the esters. Bands N, O, V, W, and X, though observed in most of the ester spectra, are unsuitable for quantitative consideration, because of weakness, or for other reasons. They are noted in the last column of Table I but will not otherwise be discussed. The carboxylic acids are predominantly in the dimeric form (II); in their spectra, bands H, I, L, S, T, and Y can be unequivocally identified with their counterparts in the ester spectra. Other bands, common to the acids but not present in the ester spectra, are distinguished by lower case letters (bands a–f).

The positions and peak heights of the methyl ester and acid bands are listed in Tables I and II respectively. The ester bands can be identified by reference to Fig. 12 of the preceding paper. The acid bands are shown in the representative spectrum of lauric acid in Fig. 1.
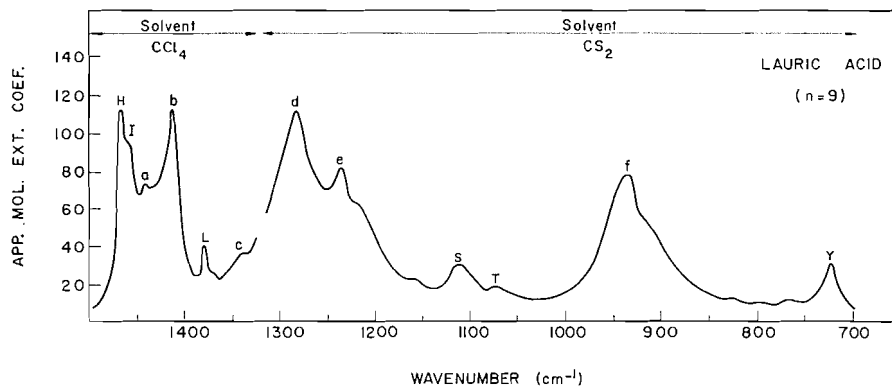

FIG. 1.

DISCUSSION

In an initial analysis of the ϵ_{max}^{a} versus chain length relationships, the band intensities were plotted against n, as was done previously for the n-alkane spectra (2). For most of the bands approximately linear relationships were observed, except in a few cases for low values of n. Representative plots for bands S and Y of both the esters and acids are shown in Figs. 2 and 3. The diagrams for the other bands are not reproduced, but the slopes (α) and the zero abscissal intercepts (β) for a linear least-square fit through the points are reported in Table III together with the standard deviation (S). For the majority of the bands the distribution about the least-square fit appears random, except in a few cases where abnormal departures from linearity are noted for the shorter-chain compounds. In these instances the short-chain homologues were omitted in fitting the data. This is indicated under the column headed n' in Table III. The more significant

TABLE I

Band positions and intensities for methyl esters^a $(CH_3—(CH_2)_n—CH_2—COOCH_3)$

Chain length (n)	Band H (1467 cm⁻¹) ε_{max}	Band I (1458 cm⁻¹) ε_{max}	Band J (1436 cm⁻¹) ε_{max}	Band K (1419 cm⁻¹) ε_{max}	Band L ν_{max}	Band L ε_{max}	Band M (1362 cm⁻¹) ε_{max}	Band P ν_{max}	Band P ε_{max}
0	—^{c}	92	117	35^{e,i}	1382	26	118	—	—
3	71^d	72	127	33	1380	48	54	1244	140
4	73^d	75	131	33	1380	44	56	1234	102
5	77^d	81	126	34	1379	47	57	1250	98
6	90	87	130	34	1378	48	59	1248	105
7	97	98	133	35	1378	48	60	1244	105
9	113	107	136	36	1378	51	62	1245	97
13	145	125	144	36^e	1378	54	67	1244	98
15	164	143	149	36^e	1377	58	69	1244	95

Chain length (n)	Band Q ν_{max}	Band Q ε_{max}	Band R ν_{max}	Band R ε_{max}	Band S ν_{max}	Band S ε_{max}	Band U ν_{max}	Band U ε_{max}	Band V ν_{max}	Band V ε_{max}	Other bands^g
0	1198	245	1175	195	1086	72	1023	63	—	—	1328 (32); 1272 (50); 968 (16); 955 (8); 850 (37); 807 (20).
3	1192	120	1169	232	1100	64	1015	36	733	15	1350 (40); 1318 (48); 1287 (48); 1268 (52); 1217 (90); 1110 (60).
4	1198	112	1167	204	1102	66	1022	33	726	16	1318 (44); 1276 (60); 1256 (77); 976 (14); 934 (5); 918 (5); 745 ^{i} (6).
5	1198	132	1166	192	1105	67	1020	26	724	19	1318 (42); 1299^h (48); 1225 (92); 1118 (48); 992 (20); 763 (7).
6	1196	134	1165	176	1107	66	1020	27	721	21	1303^h (44); 1050 (19); 995 (20); 1098.
7	1198	138	1167	168	1110	63	1016	28	721	23	1064 (23); 898 (7); 864^j (11); 875^j (9); 836^h (8); 762 (8); 748 (6).
9	1196	137	1169	162	1112	64	1016	30	721	27	See reference 1. 835^h (13).
13	1196	138	1169	170	1115	58	1016	29	721	35	1300^k (55); 1090 ^{i} (25); 990; 877^l (12); 836^h (11); 762 (10).
15	1196	136	1168	171	1115	57	1015	31	721	41	1300^k (55); 1090 ^{i} (35); 990; 865^h (11); 835^h (10); 765 (9).

^{a}Bands H–M were measured in carbon tetrachloride solution and bands N–V in carbon disulphide. Unless otherwise indicated the band positions are listed in the column heading, and ε_{max} in the column.

^{b}1456 cm⁻¹.

^{c}Band H not observed.

^{d}Note that band H is weaker than band I.

^{e}1425 cm⁻¹.

^{f}Tentatively identified with band V of methyl laurate.

^{g}The band positions are given first followed by ε_{max} in parenthesis. Bands indicated in italics are superimposed on strong solvent absorption bands and their positions and intensities are less certain.

^{h}Tentatively identified with band W of methyl laurate.

^{i}Inflection.

^{j}Tentatively identified with band X of methyl laurate.

^{k}Tentatively identified with band O of methyl laurate.

^{l}Tentatively identified with band T of methyl laurate.

TABLE II

Band positions and intensities for carboxylic acids[a] (CH_3—$(CH_2)_n$—CH_2—COOH)

Chain length (n)	Band H (1466 cm⁻¹)	Band I (1458 cm⁻¹)	Band a (1440 cm⁻¹)	Band b		Band L		Band c (1336 cm⁻¹)	Band d	
				ν_{max}	ϵ^a_{max}	ν_{max}	ϵ^a_{max}		ν_{max}	ϵ^a_{max}
0	115[b]	—	—	1416	112	1385	45	38[i]	1284	83
1	54[c, d]	61[e]	60[i]	1415	109	1383	32	34[f]	1278	113
3	76[c]	63	65[i]	1415	112	1381	37	36	1288	103
4	77[c]	74	65[i]	1414	113	1381	38	36	1281	113
5	83	82	65[i]	1414	114	1380	39	36	1278	105
6	91	84	68[i]	1413	115	1380	39	36[i]	1284	116
7	97	88	68[i]	1413	112	1379	39	36[i]	1278	107
9	112	93	73	1413	113	1379	40	36[i]	1281	110
11	134	113	80	1412	114	1379	42	39	1282	113
13	146	116	83	1413	113	1379	42	39	1280	111
14	159	125	90	1412	114	1379	44	41[i]	1282	115
15	162	131	90	1413	114	1378	44	41	1280	117
16	169	140	92	1412	116	1379	44	41	1280	117
17	180	148	90	1412	117	1378	45	40[i]	1280	120
18	187	156	85	1412	116	1378	46	42	1280	116

TABLE II (*Concluded*)

Chain Length (n)	Band e ν_max	Band e ε_max	Band S ν_max	Band S ε_max	Band f (934±2 cm⁻¹)	Band Y ν_max	Band Y ε_max	Other bands^g
0	1235	192	1079	48	74^j	—	—	1425 (82); 1324 (42); 1134 (17); 994 (18); *849*^{k} (33); *808*^{k} (22).
1	1218	108	1091	31	77^j	749	13	1305^{i,n} (76); 1230^i (76); 1141 (18); 1078 (24); 1045^i (12); 890^i (30); *855*^{i} (15); 778 (25).
3	^{h}	—	1098	31	77	732	19	1308^{i,n} (65); 1262^l (83); 1243^l (86); 1212 (63); 1138 (16); 1075^i (22); *860*^{i} (20).
4	1235	89	1102	35	77	724	20	1295^{i,n} (90); 1205 (55); 1180^i (30); 1116 (27); *880*^{i} (30); *822* (17); 765 (10).
5	1230	86	1105	32	80	723	24	1296^{i,n} (90); 1202 (50); 1175^i (28); 790 (12).
6	1234	82	1108	36	80	721	26	1265^i (88); 1220^i (75); 1200^i (45); 1165^i (28); 1132 (20); 1050^{i,o} (15); *860*^{i} (15); *774* (12).
7	^{h}	—	1108	30	75	721	27	1245^l (76); 1227^l (69); 1212^i (62); 1198^i (37); 1163^i (24); 1060° (16); *860* (13); 762 (11); 738^{i,o} (14).
9	1235	81	1111	31	78	721	32	1300^{i,n} (85); 1260^i (80); 1220^i (62); 1160^i (22); 1070° (18); 765 (11); 740^{i,m} (12).
11	1234	80	1113^i	33	78	721	38	1080^{i,o} (20); *860* (16); *830* (14); 770 (12); 740^{i,m} (15).
13	1238	82	1115	32	79	721	42	1092° (26); *860*^{i} (24); 762 (14); 740^{i,m} (17).
14	1234	83	1115	33	81	721	43	1092° (26); *860*^{i} (18); 770 (13); 740^{i,m} (15).
15	1234	83	1115	32	81	721	45	1092^{i,o} (23); *870*^{i} (20); 740^{i,m} (15).
16	1234	83	1115	33	82	721	48	1092^{i,o} (27); *870*^{i} (20); 770^i (14); 740^{i,m} (18).
17	1235	84	1115	32	82	721	51	1095^{i,o} (27); *875*^{i} (25); 765^i (14); 735 ^{i,m} (18).
18	1233	83	1116	35	79	721	54	1095^{i,o} (32); 1060^i (20); 1022^i (18); *850*^{i} (17); 778 (12); 740^{i,m} (22).

^{a}Bands H–e were measured in carbon tetrachloride solutions and bands d–Y in carbon disulphide. Unless otherwise indicated, the band positions are listed in the column headings and ϵ^a_{max} in the column.

^{b}1463 cm⁻¹.

^{c}1468 cm⁻¹.

^{d}Note that band H is weaker than band I.

^{e}1460 cm⁻¹.

^{f}1340 cm⁻¹.

^{g}The band positions are given first followed by ϵ^a_{max} in parenthesis. Bands indicated in italics are superimposed on strong solvent absorption bands and their positions and intensities are less certain.

^{h}Anomalous; see section *Bands d and e*.

^{i}Inflection.

^{j}931 cm⁻¹.

^{k}One of these bands may be a methylene rock.

^{l}One of these bands may be the analogue of band *e*.

^{m}Tentatively identified with band X of methyl laurate.

^{n}Tentatively identified with band O of methyl laurate.

^{o}Tentatively identified with band T of methyl laurate (see section *Band T*).

TABLE III

Summary of linear relationships between band intensity and chain length
($\epsilon_{max}^a = \beta + n\alpha$ where $n' \leq n \leq n''$)

	α	β	Number of compounds m	Interpolation range		Standard deviation S	Figure of merit $\alpha/2s$
				n'	n''		
Band H (1468–1466 cm⁻¹)							
Alkanes[a]	7.74	40.3	15	6	34	2.21	1.75
Acids	7.88	44.4	12	4	18	2.10	1.87
Esters	8.17	40.1	5	6	15	0.94	4.35
Band J (1436 cm⁻¹)							
Esters	1.80	120.5	8	3	15	1.9	0.47
Band K (1419 cm⁻¹)							
Esters	0.28	32.5	8	3	15	0.56	0.25
Band b (1416–1412 cm⁻¹)							
Acids	0.20	111.9	15	3	18	1.06	0.095
Band L (1385–1378 cm⁻¹)							
Alkanes[a]	0.437	40.4	13	8	34	0.77	0.28
Acids	0.534	35.8	13	3	18	0.47	0.57
Esters	1.238	39.5	8	3	15	0.84	0.74
Band M (1362 cm⁻¹)							
Esters	1.220	51.05	8	3	15	0.40	1.53
Band d (1288–1278 cm⁻¹)							
Acids	0.72	104.9	13	3	18	3.35	0.11
Band P (1250–1244 cm⁻¹)							
Esters	−0.60	104.8	6	5	15	2.7	(−)0.11
Band e (1238–1230 cm⁻¹)							
Acids	−0.20	85.6	11	4	18	1.74	(−)0.058
Band Q (1198–1196 cm⁻¹)							
Esters	0.33	132.8	6	15	15	1.82	0.09
Band R (1169–1165 cm⁻¹)							
Esters	−0.083	170.2	5	6	15	4.5	(−)0.009
Band S (1116–1098 cm⁻¹)							
Acids	0.022	32.4	13	3	18	1.73	0.006
Esters	−0.78	69.2	8	3	15	1.52	(−)0.26
Band U (1020–1015 cm⁻¹)							
Esters	0.40	24.9	6	5	15	0.86	0.23
Band f (936–932 cm⁻¹)							
Acids	0.25	76.5	14	3	18	1.51	0.084
Band Y (732–721 cm⁻¹)							
Alkanes[a]	2.418	0.82	17	4	34	0.60	2.02
Acids	2.308	11.58	17	3	18	0.76	1.52
Esters	2.155	7.90	8	3	15	0.66	1.63

[a]Values for α and β for the n-alkanes differ slightly from the values reported in Table 5 of reference 2. They are based on more accurate analysis of the same data.

features of the ϵ_{max}^a versus n relationships for some of the individual bands will next be discussed, in relation to the zones with which they are associated.

Zone (a). The Terminal Methyl Group

Band L

Only band L near 1378 cm⁻¹ is uniquely identified with the terminal methyl group, and its assignment to the symmetrical C—H deformation is well established. The intensity increases slightly with the lengthening chain; the increment per methylene (α) is about 0.5 for n-alkanes and acids and about twice as large for the esters.

This increase in intensity is probably due to weak underlying absorption from zone (b), principally band ζ, which is observed at 1368 cm⁻¹ in the spectra of methyl laurates and n-dodecanes deuterated in the ω-methyl group. The effect of chain length on this

BAND S (Esters)

$\alpha = -0.78$
$\beta = 69.2$
$\epsilon \, max = 69.2 - 0.78n$

BAND S (Acids)

$\alpha = 0.022$
$\beta = 32.4$
$\epsilon \, max. = 32.4 + 0.022n$

BAND Y (Esters)

$\alpha = 2.155$
$\beta = 7.90$
$\epsilon = 7.90 + 2.155n$

BAND Y (Acids)

$\alpha = 2.308$
$\beta = 11.58$
$\epsilon = 11.58 + 2.29n$
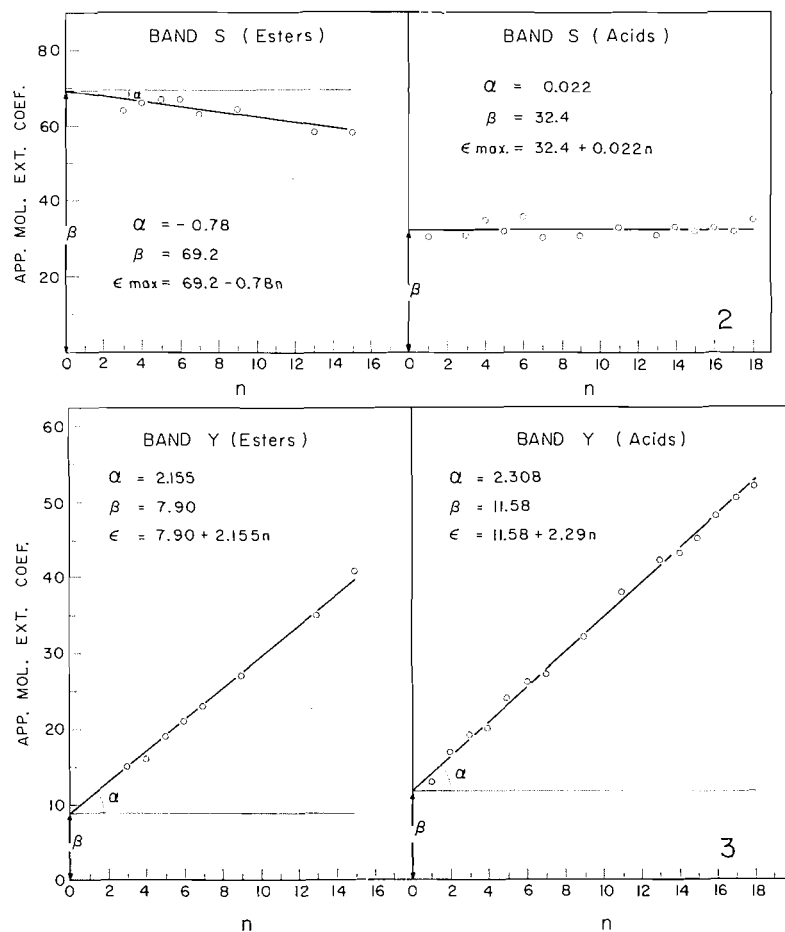
FIGS. 2 AND 3.

underlying absorption is difficult to evaluate quantitatively, but it is apparent from Figs. 4 and 5 of reference 2 that it intensifies considerably in passing from n-tridecane ($n = 11$) to n-octacosane ($n = 26$). The intercept β must be interpreted cautiously; values of 40.4, 35.8, and 39.5 were obtained for the n-alkanes, acids, and esters respectively. Since there are two ω-methyl groups in the n-alkanes, the intrinsic intensity per methyl is about 20. The higher value for the acids and esters is probably due to overlap from the shoulders of neighboring bands. In the ester spectra there is obvious enhancement from the shoulder of band M at 1362 cm^{-1}. In the acid spectra there may be contributions from the wings of the strong bands at 1413 and 1281 cm^{-1}. The similarity of the β values of the three classes of homologues therefore appears to be fortuitous and suggests that the transfer of peak-intensity measurements from one class of homologue to another must be treated circumspectly, though significance can probably be attached to the α values.

For the acids, the peak frequency of band L is displaced progressively from 1385 cm^{-1} to 1378 cm^{-1} as the chain lengthens (Table II). This could be a true displacement resulting

from weak coupling with a skeletal mode,* though it could result from a superpositional displacement effect of the underlying zone (b) band at 1368 cm^{-1}. Similar displacements are noted for band L in the short-chain methyl esters. They were not observed in the n-alkane spectra, where chain lengths below $n = 4$ were not investigated.

Zone (b). The Polymethylene Chain

Bands S, T, X, and Y have been assigned to the polymethylene chain of methyl laurate, also the β component of band H. Band X is too weak and uncertainly located for quantitative consideration and is noted only in Tables I and II. The complex H/I band system is discussed in a later section, and we shall be concerned here only with bands S, T, and Y.

Band Y

It is well established that band Y is associated with the CH$_2$ out-of-plane rocking mode. The intensity behavior is very similar for the esters, acids, and n-alkanes, the α values being 2.418, 2.308, and 2.155 respectively. For the n-alkanes β is small (0.8); it is much larger for the esters and acids, indicating that there is underlying unresolved absorption in the spectra of these compounds. In butyric acid ($n = 1$) the band Y maximum is at 748 cm^{-1} and it shifts progressively to 721 cm^{-1} in pelargonic acid ($n = 6$) and the higher homologues. The ester band behaves similarly. It is commonly stated that this band reaches its constant position for a chain of four methylenes. The additional displacements for the —(CH$_2$)$_5$— and —(CH$_2$)$_6$— systems only amount to 2–3 cm^{-1}, but they are believed to be significant.

Band S

The position of this peak in the ester spectra shifts progressively from 1086 cm^{-1} for $n = 0$ to 1115 cm^{-1} for $n \geqslant 13$. Band S is also observed in the spectra of the acids. For a given chain length it occurs at the same position in both the ester and acid spectra, but the intensity for the acids is only about one half of that for the esters. In neither series of homologues is the intensity much affected by chain length (Fig. 2). In the n-alkanes the intensity is lower by a factor of 10 and the band is not clearly recognizable in the solution-phase spectra. For the acids of shorter chain length there is some suggestion of an alteration in the intensity of band S for odd and even values of n (Fig. 2). This has not been observed on any other band and may be spurious. The wavenumber shifts with chain length are consistent with the assignment to a predominantly C—C skeletal mode. In several of the lower members of both the acid and ester series band S exhibits pronounced asymmetry on the high-frequency side and in some compounds a second band is resolved (e.g. methyl caproate (Fig. 4)).

Band T

This weaker band was identified in the methyl laurate spectrum with a skeletal mode that Sheppard designated "the 1060 series" (4). In the ester spectra it is only resolved over the narrow range of chain length from $n = 6$ to $n = 9$, and is most prominent for $n = 7$. It shifts progressively from 1050 cm^{-1} for $n = 6$ to merge into the low-frequency shoulder of band S for $n \geqslant 13$. In the spectra of the acids it can be distinguished

Although the symmetrical C—H deformation mode of the methyl group is commonly regarded as an internal vibration, very simple calculations show that appreciable axial motion of the carbon atom is involved, and this must produce some perturbation at the next carbon atom. For the XY$_3$ molecule of C_{3v} symmetry Herzberg observes (3) that the motion of the X atom amounts to $3m_Y/m_X.S_2.\sin \beta$, where m_X and m_Y are the masses of the X and Y atoms, β is the angle between the XY bond and the symmetry axis, and S_2 the symmetry co-ordinate. From this it follows that the linear displacement of the carbon atom of the methyl group, in the absence of any coupling with the rest of the chain, would amount to about 8% of the displacement of each hydrogen atom.
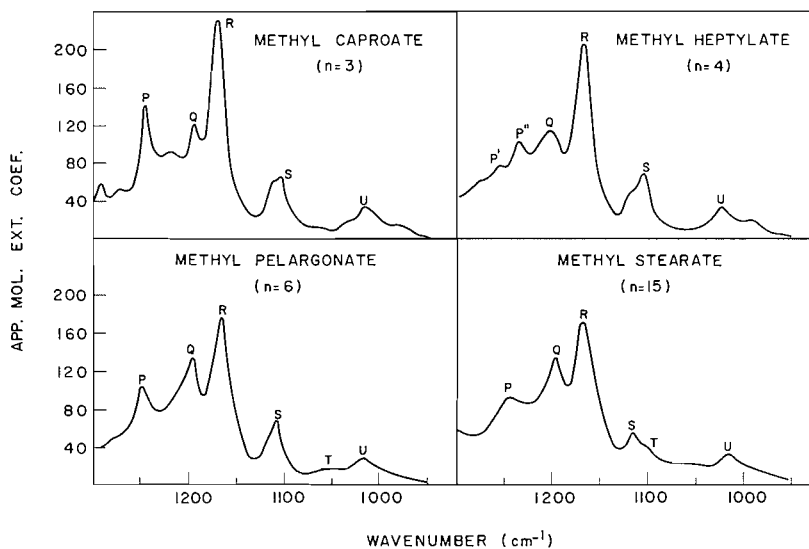
FIG. 4.

as an inflection for $n = 6$, 11, 15–18 and is resolved for $n = 7$, 9, 13, 14. Its position is similar for the esters and acids of the same chain length.

In both the acid and ester spectra there are other weaker inflections in the regions of bands S and T. Presumably these are derived from complex underlying absorption associated with skeletal modes of various subunits of the chain in trans–trans, trans–gauche, and gauche–gauche conformations. These show significant variation from compound to compound.

Zone (c). The α-Methylene Group

On the basis of the selective deuteration of methyl laurate, band K at 1419 cm^{-1} and band M at 1362 cm^{-1} have been assigned respectively to the scissoring and wagging modes of the α-methylene group.

Band K

In the ester spectra band K has an almost constant intensity ($\alpha = 0.2$); it lies on the shoulder of the strong band J, which is also insensitive to chain length. Band K has no obvious counterpart in the spectra of the acids.

Band M

For band M $\alpha = 1.17$ and it is therefore more affected by chain length than is band K. This is almost certainly due to its superposition on the methylene chain absorption (bands ζ, η) and indeed the intensification effect is very similar to that of the neighboring band L, for which $\alpha = 1.24$. The corresponding band in the spectra of the acids has not been positively identified. The acids do possess a band at 1336 cm^{-1} (band c) which might be associated with this mode.

Zone (d). The Carbomethoxy Group

Band J

This band, which has been assigned to the carbomethoxy group, shows a small intensity increment with chain length ($\alpha = 1.80$); this can be reasonably attributed to the overlap

effect of the wings of bands H, I, and ϵ. The general appearance of the band is similar in all the ester spectra and there is no significant wavenumber displacement.

Bands Involving Multiple Zones

There are two types of bands involving more than one zone. One is typified by the H/I band system for which three components are recognized (bands β, γ, and δ), associated respectively with zones (b), (a), and (d). The deuterium-substitution studies on methyl laurate lead to the conclusion that the overlap is a simple additive one. The second type of multiple zone absorption is illustrated by the P, Q, R, and U bands of methyl laurate, where there can be no doubt that strongly coupled vibrations involving the participation of the atoms of both zones (c) and (d) are involved.

Bands H and I

In the H/I band system band H is dominant in the spectra of the long-chain homologues of the acids, esters, and n-alkanes. For all three classes of compound the ϵ_{max}^{a}/n plot for band H is linear with $\alpha = 8$ for esters and alkanes in which $n \geqslant 6$ and for acids in which $n \geqslant 4$. For all three homologous series the intercept β is ~ 40.

For the short-chain compounds, the components of the H/I doublet are separately resolved. Band I becomes more prominent as the chain length diminishes, and the contour changes are qualitatively in accord with the postulated contributions from three component bands associated respectively with the scissoring mode of the chain methylene group (band β), the asymmetrical C—H bending mode of the ω-methyl group (band γ), and the asymmetrical C—H bending mode of the carbomethoxy group (band δ). Band β contributes predominantly to band H and bands γ and δ to band I, though the distinction is not a sharp one. If the carbomethoxy group has the planar conformation III there should be an additional band due to the a', a'' degeneracy

$$\begin{array}{c} \quad\quad O \\ \quad\quad \parallel \\ -C \\ \quad \backslash_{O} \diagup CH_3 \end{array}$$

III
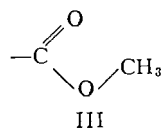
splitting of the asymmetrical C—H deformation mode. Wilmshurst (5) has assigned the a' vibration of methyl acetate to a weak band at 1469 cm^{-1} and the a'' vibration to a stronger band at 1450 cm^{-1}. There is no indication of this second band in the spectra considered here, but the a' band could be making an undetected contribution to band H. There is evidence from the C—H stretching region of the methyl laurate spectrum that the carbomethoxy group exists wholly or predominantly in conformation III and it is difficult to see why this should not hold also for the other homologues.

Bands P, Q, R, and U

These bands involve coupled vibrations extending through the (c) and (d) zones. They are observed with little change in position or intensity in the esters for which $n \geqslant 5$. For methyl heptylate ($n = 4$) band P is replaced by a doublet at 1255 and 1234 cm^{-1}, whereas for methyl caproate ($n = 3$) band P occurs at the normal position but with enhanced intensity. Band Q is "normal" at all chain lengths. The position of band R is unchanged at all chain lengths but it is significantly more intense for $n = 3$ and $n = 4$. The weaker band U is little affected. These bands are shown in Fig. 4. The spectrum of methyl propionate ($n = 0$) has bands at 1223, 1198, and 1175 cm^{-1} which may correspond with the P, Q, and R bands.

From the perturbations in the contours of the P, Q, and R bands of the lower homologues, it can be reasoned that zone (b) as well as zones (c) and (d) exercises some influence on these bands, particularly on band P. If this is so the perturbation effect of the polymethylene chain becomes constant when the number of methylene groups exceeds five. The effect could result from coupling with a skeletal mode of the chain, or it could be due to a steric effect influencing the conformation of the (c) and (d) zone structure. It would obviously be of interest to investigate the effect of temperature on these band contours for the short-chain esters. For methyl laurate temperature variation from 30° C to −70° C has no pronounced effect on the P, Q, R band contour.*

Other Bands Specific to the Carboxylic Acid Group

Bands a–f of the acids (Fig. 1) have no counterparts in the ester spectra.

Band a

This weak band appears as an inflection in the spectra of the short-chain acids and is resolved for $n \geqslant 9$. It might be identified with the scissoring vibration of the α-methylene group, since it is absent from the spectrum of $CH_3.(CH_2)_9.CD_2.COOH$.

Band b

This band, which occurs near 1416 cm^{-1}, exhibits an almost constant intensity. Sinclair, McKay, Myers, and Jones (6) assigned it erroneously to the α-methylene scissoring mode, but later Hadži and Sheppard (7) showed it to be associated with the carboxylic acid dimer group and assigned it to a mode in which C—O stretching vibrations are coupled with an O—H in plane deformation. In the acids substituted in the a-methylene group (e.g. isobutyric acid, α-bromostearic acid) it is displaced to 1430–1420 cm^{-1}.

Band c

This band appears as a weakly resolved peak or inflection near 1336 cm^{-1} and has been tentatively identified with the α-methylene wag (see section *Band M*).

Bands d and e

The prominent P, Q, R triplet of the ester spectra is replaced by the d and e doublet in the spectra of the acids. These are probably "C—O stretching" bands of the dimer ring system coupled with O—H in-plane deformations (cf. band b) (7). The intensity of band d is reasonably constant for all chain lengths except $n = 0$, but the position of the peak wanders between 1278 and 1288 cm^{-1} in an unsystematic fashion for the short-chain compounds; for $n \geqslant 9$ it remains steady at 1281 ± 1 cm^{-1}. The weaker band e is more variable in position, though it also becomes stabilized for $n \geqslant 9$. A distinct anomaly is observed for caproic acid $(n = 3)$, where band e is replaced by a doublet at 1262 and 1242 cm^{-1}. Capric acid $(n = 7)$ also shows a splitting of the absorption in the neighborhood of band e.

The shorter-chain acids show numerous other weakly resolved peaks and inflections in the region of the d and e bands. These are noted in the last column of Table II. They modulate the contour of the band envelope in a manner that is characteristic for each acid. This region of the acid spectra calls for more detailed examination under high resolution. In the solid phase these compounds exhibit well-defined progressions of equally spaced bands which are commonly attributed to coupled wagging or twisting vibrations of the methylene chain units. These vibrations may also be the cause of the fine structure in the liquid-phase spectra, though the uniform spacing is not apparent.

Band f

This characteristically broad band is well known in the spectra of carboxylic acids and has been assigned by Davies and Sutherland (8) to an out-of-plane deformation mode of the carboxylic acid dimer ring. The intensity is remarkably constant ($\alpha = 0.27$), consistent with its localization in zone (d). It exhibits a pronounced asymmetry on the low-frequency side.

CONCLUDING REMARKS

Over the range n' to n'', where linear correlations between ϵ_{max}^{a} and n appear to hold, the α values effectively distinguish the bands associated with the internal modes of the zone (b) bands, for which $\alpha = 2$–8, from the other types of bands which give much lower values of α. The zone (b) bands associated with skeletal modes also show low α values, but are distinguished by progressive frequency displacements. An exception must be made for the small frequency displacement of band L associated with zone (a). Most of the bands associated with zones (a), (c), and (d) do exhibit some intensification with increasing chain length, but this can be reasonably attributed to overlap effects from the shoulders of zone (b) bands. In the course of this intensity analysis no serious anomalies were observed that are inconsistent with the commonly accepted group frequency assignments for these bands, as reported in the earlier literature and substantiated by the measurements on the deuterium-substituted methyl laurates.

In column 7 of Table III the standard deviation (S) is reported, where

[1]
$$S = \sqrt{\frac{\sum(\epsilon_{obs} - \epsilon_{calc})^2}{m}},$$

in which ϵ_{obs} is the experimentally observed absorption maximum, ϵ_{calc} the value obtained from the least-square fit, and m the number of compounds measured. Statistical considerations suggest that random errors in excess of $2S$ are improbable. The quantity $\alpha/2S$, shown in the final column of Table III, is therefore a convenient measure of the significance of the peak intensity as a criterion of chain length.

In the experimental section the absolute precision of the peak-intensity measurements was not discussed. In the present state of infrared spectrophotometry, it is not possible to evaluate quantitatively the experimental errors affecting absolute peak-intensity measurements. Since the measurements discussed here were made prior to the availability of commercial grating spectrometers, they do not represent the highest standards of photometric accuracy now obtainable with these new instruments. The spectral slit width employed was in the range 1–2 cm⁻¹, and although the majority of the bands are broad, we have preferred to express the intensities in "apparent" and not "absolute" units. Several laboratories are currently concerned with the determination of absolute standards for infrared band intensity measurements. When these data are available it will be of considerable interest to reinvestigate some of these acid and ester bands on a high-resolution grating spectrometer, accurately calibrated with respect to the absolute intensity. We would anticipate that the systematic errors associated with the finite slit function will principally affect the β values and that the increments per methylene will be less sensitive to this variable.

In this and the preceding paper we have dealt in considerable detail with the quantitative analysis of the infrared spectra of a family of compounds of a degree of complexity intermediate between the simple molecules susceptible to a rigid treatment by the methods of vibrational theory, on the one hand, and the large molecules of predominant

biological interest on the other. There are obvious difficulties in attempting to extend to such molecules the techniques of vibrational analysis applicable to small ones. While those concerned with the theory of molecular vibrations are well aware of this difficulty, organic chemists are naturally reluctant to accept the thesis that much of the absorption that they observed in the spectra of complex molecules must be dismissed as of empirical significance only. This creates a strong temptation to overextend the group frequency concept. The breakdown of the spectrum into sets of bands associated with more or less clearly differentiated subunits of molecular structure makes possible an analysis of complex spectra on a zonal basis without the necessity of invoking precise vibrational mechanisms.

In these solution-phase studies of homologous series we have been dealing with systems in which complex conformational equilibria are present, due to the flexibility of the polymethylene chain. The molecular spectroscopist can eliminate this by going to the crystalline state, and most of the literature dealing with the vibrational analysis of the polymethylene chain is restricted to solid-phase studies. The organic chemist seeking information about the contribution of polymethylene chain structure to the spectra of more complex molecules will not always be in a position to lay out the chain in a crystal of known s-trans chain configuration. Furthermore, if bulky cyclic groups are also present there can be no assurance that information derived from the analysis of the crystalline polymethylene chain system of simple hydrocarbons will be transferable to the very different packing system in more complex structures. Although the spectra of the liquid–phase polymethylene systems are less informative, the information they do convey is more widely applicable. This problem is currently being investigated with a series of long-chain steroid esters.

ACKNOWLEDGMENTS

REFERENCES

1. R. N. JONES.   Can. J. Chem. This issue.
2. R. N. JONES.   Spectrochim. Acta, 9, 235 (1957).
3. G. HERZBERG.   Infrared and Raman spectra of polyatomic molecules. Van Nostrand Co. Inc., New York. 1945. p. 155.
4. J. K. BROWN, N. SHEPPARD, and D. M. SIMPSON.   Phil. Trans. Roy. Soc. London, Ser. A, 247, 35 (1954).
5. J. K. WILMSHURST.   J. Mol. Spectroscopy, 1, 201 (1957).
6. R. G. SINCLAIR, A. F. McKAY, G. S. MYERS, and R. N. JONES.   J. Am. Chem. Soc. 74, 2578 (1952).
7. D. HADŽI and N. SHEPPARD.   Proc. Roy. Soc. (London), A, 216, 247 (1953).
8. M. DAVIES and G. B. B. M. SUTHERLAND.   J. Chem. Phys. 6, 755 (1938).